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# Environmental impacts of large-scale adoptions of hydrogen as energy carrier: a scenario-based life cycle assessment

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## Abstract

The world is according to the International Panel on Climate Change (IPCC) facing a severe threat in terms of climate change, and the use of fossil fuels for transportation and electricity production is a major contributor of greenhouse gas (GHG) emissions. The use of hydrogen is foreseen to reduce GHG emissions by means of substituting fossil fuel in transportation as well as increase energy security in electricity production by means of using hydrogen as temporary storage of energy. The latter will reduce some of the drawbacks of electricity produced from renewable energy as compared to that of fossil energy, thus being a potentially important factor in the transfer from a fossil to a renewable energy system.

In my thesis, I have compared GHG emissions from a selection of what I believe are the most relevant hydrogen production methods as for today and towards 2050 by means of conducting life cycle assessments. Then, I have estimated a technical potential for hydrogen production in 2050, based on available biomass as hydrogen source in the form of waste, short rotational crops and residues from agriculture, forestry and farming. Last, I conduct a life cycle assessment of the hydrogen semi-truck Nikola One, to found the basis of presenting a scenario implying full substitution of fossil by hydrogen fuel for road freight transport in Europe towards 2050 – also taking into account an expected growth in the volume of freight transportation and an assumption of a radical improvement in the average GHG emissions from European electricity production.

The thesis starts by presenting a factor 10 variation in life cycle assessment values for GHG emissions per produced unit (kg) of hydrogen for the following production methods shown in the table. For the proton exchange membrane water electrolyzer, 85% of the emissions was due to the use of electricity – which was attributed the current European electricity mix factor for GHG emissions – leaving 15% for production of the electrolyzer. For the remaining methods, that are based on biomass as hydrogen source, the average distribution of GHG emissions are 25% from the use of short rotational woody crops, and forestry residues as biomass feedstock, 29% from the use of fossil gas as energy source for heat and steam, 38% from the use of electricity, and the remaining 8% for other sources.

I chose to use the EU Reference Scenario for 2050 as a background for constructing my scenario on hydrogen production and implementation of hydrogen in road freight transport. To assess

the potential for GHG emission reduction towards 2050 from producing hydrogen, I assume that the production methods that use fossil gas for heating will convert to biomass. Furthermore, I assume that a 37% reduction in the average GHG emission per kWh from European electricity production. Thus, the expected GHG emissions in 2050 per unit (kg) of production is calculated to be as shown in the table. Still there is a factor 10 variation in GHG emission between the lowest and highest-ranking production method, and the lowest and highest-ranking methods are still the same (biogas steam reforming, and proton exchange membrane water electrolyze respectively). Gasification has however changed its order of rank from the third highest currently to the second lowest in 2050.

Production method	Emissions (kg CO <sub>2</sub> -eq/kg H <sub>2</sub> )		Reduction up to 2050
	Current	Expected 2050	
Biogas steam reforming	3,9	2,8	28 %
Gasification	10,8	3,7	66 %
Dark fermentation and photo fermentation	8,0	5,5	31 %
Dark fermentation and microbial electrolysis cell	13,2	8,9	33 %
Proton exchange membrane water electrolyzer	40,0	27,0	33 %

In order to stipulate the available hydrogen production capacity for Europe in 2050, I assume that it mainly will consist of hydrogen from biomass due to its low GHG emissions. In order to achieve a sufficient system delivering capacity of hydrogen, I assume that water electrolysis for hydrogen production in 2050 can use 1% of the anticipated available capacity of electricity from solar, wind, and hydropower to produce hydrogen. My calculations show that by using all the technical biomass capacity, in form of waste, short rotational crops and residues from agriculture, forestry, and farming - a total of 92.9 megatons of hydrogen can be produced per year, given my choice of a European mix of hydrogen production methods in 2050, consisting of biogas steam reforming, gasification and dark fermentation together with photo fermentation. The total yearly hydrogen production from water electrolysis is estimated to be 0.3 megatons, resulting in a European average GHG emission per unit (kg) of produced hydrogen to be 4 kg CO<sub>2</sub>-eq in 2050; which is 67% lower than the current dominating hydrogen production method of steam methane reforming of fossil gas.

I estimate that 21 megatons of hydrogen are needed in order to allow a full transition to hydrogen fuel in European road freight transport by 2050, also allowing for a 57% increase in the total volume of road freight transportation up to 2050. Thus, 23% of the estimated total annual European production of hydrogen in 2050 would be assigned to road freight transportation. In order to assess the potential GHG mitigation potential for a freight transport fleet fueled by hydrogen, I have conducted a life cycle assessment of the hydrogen truck Nikola One. The results, still assuming an average emission of 4 kg CO<sub>2</sub>-eq per unit (kg) produced hydrogen, show that there is a large potential for reducing GHG emissions from road freight transportation; namely 45% compared to current emission level, and 54% compared to a scenario for 2050 with 100% fossil fuels and 57% increase in transport volume.

My thesis shows that there is a theoretical large potential for large-scale hydrogen production from biomass in Europe towards 2050 and that hydrogen, in theory, can supply fuel for the entire road freight transport fleet – thus allowing for a substantial decrease in GHG emissions from road freight transportation by 2050. Which level of GHG emissions to be achieved in 2050 is dependent on the choices made regarding the method for producing hydrogen, the extent of fossil gas to still be in use, and the European energy mix for producing electricity.

## Samandrag

Verda står ifølge FN sitt klimapanel overfor eit alvorleg trugsmål når det gjeld klimaendringar, og bruken av fossile brenslar for transport og elektrisitetsproduksjon er ein stor kjelde til utslepp av klimagassar. Bruken av hydrogen kan redusere utsleppa av drivhusgassar direkte gjennom å erstatte fossilt brensel i transport, og indirekte ved å auke leveringstryggleiken i elproduksjon gjennom å bruke hydrogen som midlertidig lagring av energi. Dette vil igjen redusere ein viktig ulempe ved elektrisitet får fornybar samanlikna med fossil energi, og dermed vere ein potensielt viktig faktor i omstillinga frå eit fossilt til eit fornybart energisystem.

Avhandlinga startar med å presentere ein faktor 10 forskjell i livsløp utslepp av klimagassar per produsert eining (kg) hydrogen for i alt fem produksjonsmetodar, jf. tabellen under. For utslepp av klimagassar knytt til bruk av elektrisitet har eg nytta gjennomsnitt for Europeisk elproduksjon. For metoden «PEMWE» kjem 85% av utsleppa frå bruken av elektrisitet og 15% frå produksjon av elektrolysen. For dei andre metodane, som er basert på biomasse som hydrogenkjelde, er gjennomsnittleg fordeling av klimagassutsleppa som følgjer: 25% frå bruk av energiskog som biomasse, 29% frå bruk av fossilt gass til varme og damp, 38% frå bruken av elektrisitet, og 8% til oppvarming frå andre kjelder.

Metode for hydrogenproduksjon	Utslepp av klimagassar (kg CO <sub>2</sub> -ekvivalentar/kg H <sub>2</sub> )		Reduksjon 2050
	I dag	2050	
Biogass damp-reformering	3,9	2,8	28 %
Gassifisering	10,8	3,7	66 %
Mørk fermentering med fotofermentering	8,0	5,5	31 %
Mørk fermentering med mikrobiell elektrolysecelle	13,2	8,9	33 %
Protonutveksling membran vann elektrolyse (PEMWE)	40,0	27,0	33 %

Eg har valt å bruke EU sitt energi-referansescenario for 2050 som bakgrunn for mitt eige scenario for produksjon og bruk av hydrogen i godstransport på veg. For å vurdere potensialet for reduksjon av klimagassutslepp fram mot 2050, føreset eg at produksjonsmetodane som bruker fossilt gass til oppvarming blir konvertert til biomasse. Vidare føreset eg 37% reduksjon



i gjennomsnittleg utslepp av klimagassar per kWh frå europeisk elektrisitetsproduksjon. Tabellen over viser forventa utvikling fram mot 2050. Framleis er det ein faktor 10 forskjell mellom produksjonsmetoden med lågast og høgast utslepp, og metodane med lågast (biogass-damp-reforming) og høgast (PEMWE) er dei sama. Gassifisering har er endra frå å vere den metoden med det tredje høgaste relative utsleppet i dag til det nest lågaste i 2050.

Eg føreset at i 2050 vil hydrogen i hovudsak bli produsert med biomasse som hydrogenkjelde fordi det inneber låge utslepp av drivhusgassar. Vidare føreset eg at elektrolyse av vatn til hydrogenproduksjon kan bruke 1% av den forventa tilgjengelege Europeiske kapasiteten når det gjeld elektrisitet frå sol, vind og vasskraft. Om ein så nyttar all teknisk tilgjengeleg kapasitet for biomasse frå matavfall, energiskog, og rester frå jordbruk, skogbruk og fiskeoppdrett, kan det produserast 92,9 megatonn hydrogen i Europa per år i 2050, gitt at hydrogenet blir produsert ved hjelp av metodane biogass damp-reforming, gassifisering, og mørk fermentering med med fotofermentering. Det samla årlege potensialet for hydrogenproduksjonen frå elektrolyse av vatn er rekna til å vere 0,3 megatonn, noko som samla sett gjev eit gjennomsnittleg europeisk utslepp av klimagassar per kg produsert hydrogen på 4 kg CO<sub>2</sub>-ekvivalantar i 2050. Dette er 67% lågare enn dagens produksjon, som i hovudsak skjer gjennom reformering av fossil gass.

Mine utrekningar viser at det er naudsynt med 21 megatonn hydrogen for fult ut å erstatte fossil drivstoff i europeisk godstransport innan 2050, der det også er tatt omsyn til ei forventa auke på 57% i volumet av godstransport på veg i same periode. Dette inneber at godstransport på veg legg beslag på 23% av den samla estimerte kapasiteten i Europeiske hydrogenproduksjon i 2050. For å rekne ut kva dette inneber i reduksjon av klimagassutslepp for godstransport på veg har eg gjennomført ein livssyklusvurdering av hydrogenbilen «Nikola One» og nytta desse tala for all godstransport på veg i 2050. Resultatet viser eit teknisk potensiale på 45% reduksjon samanlikna med dagens utslepp, og 54% om ein føreset 57% auke i transportvolumet fram mot 2050.

Avhandlinga viser at det er eit stort teoretisk potensiale for auke i hydrogenproduksjon frå biomasse i Europa frem til 2050, og at hydrogen i teorien kan levere drivstoff til heile godstransportflåten i Europa – noko som i tilfelle gjev eit teoretisk potensiale for om lag ein halvering av utsleppa frå godstransport på veg i Europa fram mot 2050. Kva utsleppsreduksjonar som er moglege å oppnå i praksis er mellom anna avhengig av val av

dominerande metode for å produksjon av hydrogen, bruken av fossilt gass, og den europeiske energimixen for å produsere elektrisitet.

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## List of abbreviations

<b>2DS</b>	Two Degree Target	<b>ICE</b>	Internal Combustion Engine
<b>AD</b>	Anaerobic Digestion	<b>IPCC</b>	Intergovernmental Panel on Climate Change
<b>AEM</b>	Anion Exchange Membranes	<b>LCI</b>	Life Cycle Inventory
<b>AWE</b>	Alkaline Water Electrolysis/Electrolyzer	<b>LCIA</b>	Life Cycle Impact Assessment
<b>BDL</b>	Biomass Derived Liquid	<b>LHV</b>	Lower Heating Value
<b>BPP</b>	Bipolar Plates	<b>LTS</b>	Low Temperature Shift
<b>BSR</b>	Biomass Steam Reforming	<b>MEC</b>	Microbial Electrolysis Cell
<b>CC</b>	Current Collector	<b>MPL</b>	Micro-Porous Layer
<b>CCS</b>	Carbon Capture and Storage	<b>MSW</b>	Municipal Solid Waste
<b>CEM</b>	Cation Exchange membranes	<b>OER</b>	Oxygen Evolution Reaction
<b>CIG</b>	Char Indirect Gasifier	<b>PEMWE</b>	Proton Exchange Membrane Water Electrolysis/Electrolyzer
<b>CSL</b>	Corn Steep Liquor	<b>PF</b>	Photo Fermentation
<b>DAP</b>	Diammonium Phosphate	<b>PGM</b>	Platinum Group Metals
<b>DC</b>	Direct Current	<b>PSA</b>	Pressure Swing Adsorption
<b>DF</b>	Dark Fermentation	<b>RE</b>	Renewable Energy
<b>FBBG</b>	Fluidized Bed Bubbling Gasifier	<b>RES</b>	Renewable Energy Sources
<b>FBC</b>	Fluidized bed combustor	<b>RoW</b>	Rest of the World
<b>FC</b>	Fuel Cell	<b>SMR</b>	Steam Methane Reforming
<b>FCEV</b>	Fuel Cell Electrical Vehicle	<b>SPA</b>	Structural Path Analysis
<b>GHG</b>	Greenhouse Gas	<b>SPE</b>	Solid Polymer Electrolyte
<b>GIG</b>	Gas Indirect Gasifier	<b>SRWC</b>	Short Rotational Woody Crops
<b>H<sub>2</sub></b>	Hydrogen Gas	<b>STH</b>	Solar To Hydrogen
<b>HER</b>	Hydrogen Evolution Reaction	<b>VAF</b>	Volatile Fatty Acids
<b>HRS</b>	Hydrogen Refueling Station	<b>VRE</b>	Variable Renewable Energy
<b>HTS</b>	High Temperature Shift	<b>WGSR</b>	Water-Gas Shift Reaction
<b>HTSE</b>	High Temperature Steam Electrolysis		



# 1 Introduction

Man-made global warming is one of the most severe issues of our time, and is mainly due to the emissions of anthropogenic fossil CO<sub>2</sub> to the atmosphere. This is because we rely on fossil fuels as an energy source for nearly all our activities, from producing electricity and heating houses, industrial processes, to transportation. Transport alone is responsible for 14% of our global greenhouse gas emissions, and the richest 10% of the people on Earth are responsible for 80% of motorized passenger-kilometers (IPCC, 2014). It is predicted that in a business as usual scenario the emissions from transport will nearly double in 2050. To be able to reduce the greenhouse gas (GHG) emissions from the transport sector, a conversion from fossil fuels to energy carriers made from renewable energy is suggested by the IPCC, in addition to achieve a modal shift in transportation and even travel less (IPCC, 2014). The main categories of alternative energy carriers to be used in transportation are electricity, bio fuels and hydrogen.

Hydrogen has a specific energy of 122 MJ per kg, which is about 2.5 times as much as fossil fuels (Hosseini & Wahid, 2016). When used as a fuel, it has no other direct emissions than water, resulting in no local pollution. With the use of fuel cells, a vehicle fueled by hydrogen has the same advantages as an electric vehicle, with instant torque, regenerative braking and low noise. Furthermore, challenges related to time for battery charging and driving range anxiety can be ignored.

Hydrogen also has advantages that fit well with the global goal of transition from fossil to renewable energy. The so-called variable renewable energy sources, such as wind and solar, are as the name implies, variable. Hydrogen can be used to store the energy and use it directly for transportation, or transform it back to electricity again when needed. This will on a national basis strengthen the energy security of a country, making it less dependent on energy or effect import.

Today, 96% of the global supply of hydrogen comes from gasification and steam reforming of various fossil fuels, where steam reforming of natural gas is the most widely used - with a GHG emission of 12.2 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> (Spath & Mann, 2000). For hydrogen to be an alternative fuel for transportation, a shift from fossil to a climate friendly hydrogen production must take place. The two alternatives are to use biomass as feedstock instead of fossil fuels, or to separate

water through electrolysis by means of renewable energy. For this thesis, a set of anticipated climate friendly hydrogen productions methods have been compared, namely, gasification, dark fermentation, photo fermentation, microbial electrolysis cell, and proton exchange membrane water electrolysis. For the processes that use biomass as hydrogen source, I have chosen two sources: short rotational woody crops, and forestry residues.

Biogas steam reforming and gasification of biomass uses the same hydrogen production methods as for the case of fossil fuels, but replaces the fossil hydrogen-feedstock with biomass. They both have the potential for large as well as small-scale production, while a main difference lies in that gasification use raw biomass, whereas steam reforming uses biogas or bio-oil. The use of bio-oil or biogas can reduce the amount of transportation needed, due to higher energy density compared to that of raw biomass.

Dark fermentation is a process that uses fermentation bacteria to convert glucose and other sugars to hydrogen, thus having the advantage of low energy intensity and the use of biomass residues as hydrogen. Dark fermentation produces an effluent that contains volatile fatty acids (VAF). VAF can be used as feedstock for both photo fermentation, which uses sunlight to fuel the process, and microbial electrolysis cell, which uses electricity to extract the hydrogen out from the effluent.

Electrolysis of water by applying electricity is currently the main technique for producing hydrogen. Electrolysis of water can be done in two ways: Alkaline water electrolyzer (AWE), or with a proton exchange membrane water electrolyzer (PEMWE). AWE is currently the dominating electrolysis method, and has been used in industrial scale for decades (Carmo, Fritz, Mergel, & Stolten, 2013). One of the problems with AWE is that it cannot handle fluctuations in energy input, and therefore is unfit in combination with variable renewable energy such as wind power. The alternative - the PEMWE- has two major advantages compared to AWE, by being able to handle a varying electricity input, and delivering hydrogen with a higher purity (Carmo et al., 2013).

Together with my supervisors we have decided that the focus of this thesis is climate change impacts of large-scale adoptions of hydrogen as energy carrier. The first research question of my thesis is thus: **What is the potential for climate friendly hydrogen production in Europe**

**towards 2050?** Hydrogen is used in different processes and for different purposes. I have chosen to study the use of hydrogen in road freight transport because the sector today is dependent on fossil fuels. For passenger cars, converting to an electrical drivetrain with energy supplied from a battery is a good option for mitigating GHG emissions (Ellingsen, Singh, & Strømman, 2016). For road freight transport the issues with a large battery and a long charging time might be too hard to overcome. Thus, my second research question is: **What is the GHG mitigation potential by using hydrogen as fuel for road freight transport in Europe in 2050?**

To answer the two research questions, these steps have been taken:

1. Quantify emissions on a per kg H<sub>2</sub> produced for a set of production methods that has a potential for future large-scale hydrogen production.
2. Do a scenario based analysis on key aspects of the hydrogen production towards 2050 to identify the GHG mitigation potential of each of the selected hydrogen production methods.
3. Do a coarse calculation of the available production capacity for the different production methods based on available biomass and electricity for electrolysis
4. Calculate the GHG emissions for a European hydrogen mix for 2050, consisting of the different production methods analyzed, their specific emission and their production capacity potential
5. Assess the GHG mitigation potential applying the anticipated European hydrogen mix of 2050 as fuel for road freight transport

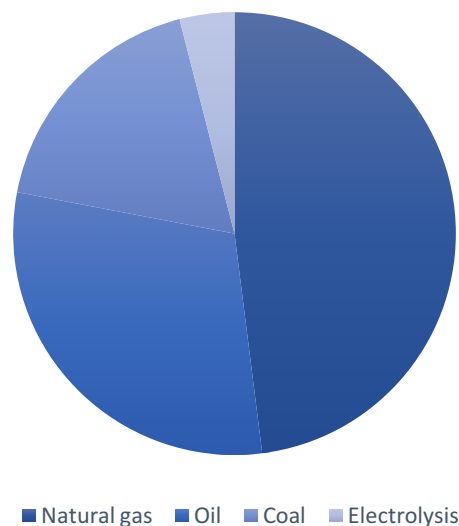
I will apply a life cycle assessment (LCA) perspective for quantifying GHG emissions, thus including GHG emissions through the whole lifecycle of a given system. The assessment will be done on the basis of a functional unit of **1 kg H<sub>2</sub>** produced applying a well-to-door system boundary, i.e. to include emissions from energy extraction and until hydrogen is produced in the factory. The functional unit is chosen to be able to compare different hydrogen production methods that vary in size and technology. The initial LCA will be done for today's technology, and then do a scenario based analysis of the potential for climate friendly hydrogen production towards 2050. As means of quantifying the result of a large-scale hydrogen production, I will compare road freight transportation fueled on hydrogen and on fossil fuels per **1 tonne-kilometre**. In LCA terms this is a well-to-wheel perspective.

## 2 Background: Hydrogen production and application

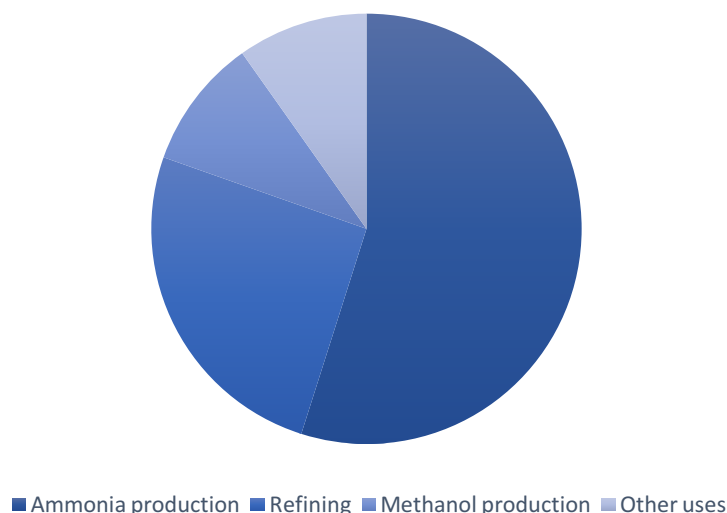
In this chapter I will present an overview over today's production of hydrogen from fossil fuels, water electrolysis, and the emerging alternative of hydrogen from biomass. Then I will briefly review the potential role of hydrogen as an energy carrier in future low-carbon economies.

### 2.1 Hydrogen production today

Hydrogen can principally be produced from two different feedstocks: water or materials with a high content of hydrocarbons. The hydrocarbon rich materials can either be from fossil sources or renewable biomass and the process energy for all the different production methods can be both fossil and renewable. Today hydrogen is mainly produced from and by fossil energy, where steam methane reforming of natural gas is the most common method. Hydrogen from fossil energy represents 96% of the total global production, and the remaining 4% is from electrolysis of water by means of electricity, with unknown distribution of energy sources (Zakkour & Cook, 2010). In 2008 total of 50 megatons was produced, where 55 % of the hydrogen is used for production of ammonia, to be used in fertilizers, while the rest is used in petro chemistry and for production of other chemical products (Zakkour & Cook, 2010). Figure 1 shows the distribution between production methods for hydrogen and Figure 2 displays the major consumers of hydrogen 2008. It has not been possible to obtain newer data, but it is assumed that the share amongst both production feedstock and consumption haven't changed much since.



**FIGURE 1 – GLOBAL HYDROGEN PRODUCTION IN 2008 (ZAKKOUR & COOK, 2010)**



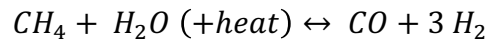
**FIGURE 2 – GLOBAL HYDROGEN CONSUMPTION IN 2008 (ZAKKOUR & COOK, 2010)**

## 2.2 Hydrogen from fossil fuels

Today most of the world's hydrogen is produced from fossil fuels. The two main techniques for hydrogen production are steam methane reforming and gasification. The following section is a short overview of these techniques and their characteristics.

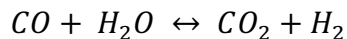
### 2.2.1 Steam methane reforming

Steam methane reforming (SMR) of natural gas is the leading method for producing  $H_2$  today and produces 48% of the hydrogen worldwide (Lipman, 2004). The GHG-emissions per kg  $H_2$  produced throughout the lifecycle is 12.2 kg (Spath & Mann, 2000). The technique is mature and well known (Spath & Mann, 2000), and consists of four main steps: desulfurization, catalytic reforming, CO conversion and gas separation (Pant & Gupta, 2009). The gas is pre-treated with a desulfurizer to remove sulfur. This is done by adding  $H_2$ , to create  $H_2S$ .  $H_2S$  is then removed with a zinc oxide (ZnO) bed. The reason for removing the sulfur is so that it doesn't deactivate the catalyst used in the reactor where the reforming takes place (Kalamaras & Efstathiou, 2013). The gas is then heated by heat exchangers. In the catalytic reforming, hot gas is mixed with hot steam, at 700-1000°C in a reactor with a pressure of 3-25 bar, where a syngas is produced in the presence of a metal based catalyst, normally nickel (Jaber, Naterer, & Dincer, 2010). The chemical reaction of steam reforming, shown in Formula 1, is an endothermic reaction, meaning that it will need heat to react (Susmozas, Iribarren, & Dufour, 2013).



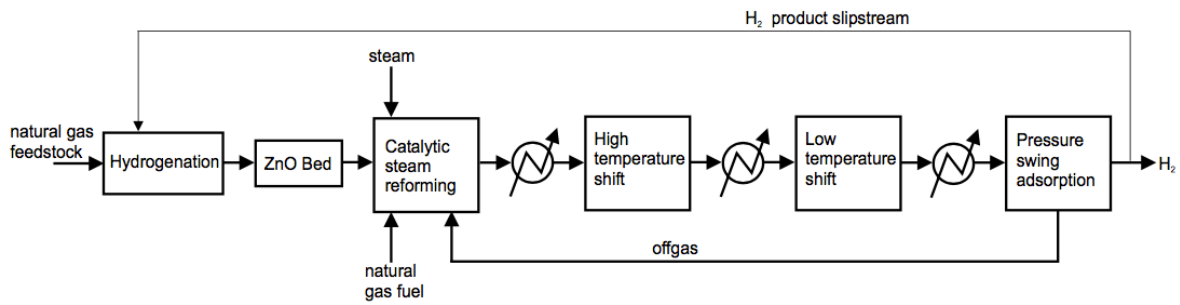
**FORMULA 1 – THE CHEMICAL REACTION OF STEAM METHANE REFORMING**

The syngas, which is the product of the steam reforming, consists mainly of H<sub>2</sub> and CO (Susmozas et al., 2013). To increase the total yield of hydrogen, carbon monoxide (CO) can be used for water-gas shift reaction (WGSR). WGSR is a reversible and exothermic chemical reaction, shown in Formula 2, which reacts CO and water vapor to hydrogen and CO<sub>2</sub>, assisted by a catalyst (Newsome, 1980). The WGSR is divided into two reactions, the high temperature shift (HTS) reaction, which takes place between 320-450 °C and the low temperature shift (LTS) reaction, between 200-250°C (Newsome, 1980). The HTS usually uses a catalyst that consists of 74.2% iron(III) oxide (Fe<sub>2</sub>O<sub>3</sub>), 10% chromium(III) oxide (Cr<sub>2</sub>O<sub>3</sub>) and 0.2% magnesium oxide (MgO), with remaining percentage attributed to volatile components. The LTS catalyst is made of 33% Copper(II) oxide (CuO), 34-53% zinc oxide (ZnO) and 15-33% aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) (Newsome, 1980).



**FORMULA 2 – THE WATER-GAS SHIFT REACTION**

The gas is finally purified through Pressure Swing Adsorption (PSA). The PSA is a cyclic process, where one takes advantage of a gas affinity for a certain catalyst. Since different species of gasses have affinity for different catalysts, and will react at different pressures, it is possible to clean the gas with the PSA. In the start of a cycle, the gas is pressurized. The higher the pressure, the more will a specific gas react and be adsorbed by the catalyst. The gas that leaves the PSA only consist of species that did not react with the specific catalysts. Afterwards, a regeneration of the bed is done by a pressure swing operation (Riboldi & Bolland, 2015). The pressure is reduced inside the column to extract the off-gas, so that the adsorbent can be used again (Sircar, 2002). The off-gas from the PSA can be used to heat the reactor, often combined with fossil gas. A by-product of steam methane reforming is high pressure steam that can be sold or used for other purposes (Boyano, Blanco-Marigorta, Morosuk, & Tsatsaronis, 2011; Spath & Mann, 2000).



**FIGURE 3 – FLOWCHART OF STEAM METHANE REFORMING (SPATH & MANN, 2000)**

Hydrogen production through steam reforming usually uses fossil gas as hydrogen source, but can also use ethanol, propane and gasoline. In a climate perspective, the use of fossil gas, is a lesser of two evils in this case, since the CO<sub>2</sub> emissions are directly linked to the H:C ratio for the hydrogen source. This is why using ethanol, propane, gasoline or other fossil fuels have higher emission than fossil gas. Sse Table 1 for H:C ratio for different hydrogen sources.

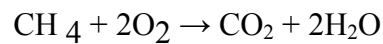
**TABLE 1 – HYDROGEN TO CARBON RATIO FOR FOSSIL AND BIOLOGICAL HYDROGEN SOURCES**

<b>Fuel</b>	<b>Hydrogen / carbon - ratio</b>
Methane	2.0
Gasoline	1.1
Crude oil	1.1
Municipal solid waste	0.8
Biomass	0.7
Coal	0.4

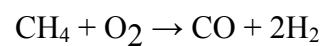
### 2.2.2 Gasification

Gasification of hydrocarbons is, together with steam reforming, a mature technology which today mainly is used to convert fossil fuels to hydrogen, ammonia and other chemicals (Demirbas, 2006). The process of gasification is divided into three different parts of: partial oxidation, water-gas shift reaction and purification.

Gasification is combustion with a limited amount of oxygen. The reaction is then not a full combustion (Formula 3), but rather a partial oxidation (Formula 4). The result is a gas that consist of CO, H<sub>2</sub> (and N<sub>2</sub> if air is used instead of oxygen). The partial oxidation is achieved by heating the hydrogen source up to 500 – 1400 °C, while controlling the oxygen level and in some cases adding steam (Ciferno & Marano, 2002). Formula 5 shows the result of adding water vapor, which increases the yield of hydrogen.



**FORMULA 3 – FULL OXIDATION OF METHANE (KALAMARAS & EFSTATHIOU, 2013)**



**FORMULA 4 – PARTIAL OXIDATION OF METHANE WITH OXYGEN (KALAMARAS & EFSTATHIOU, 2013)**



**FORMULA 5 – PARTIAL OXIDATION OF METHANE WITH WATER VAPOR (KALAMARAS & EFSTATHIOU, 2013)**

There are three main categories for gasifiers: fixed bed gasifiers, fluidized bed gasifiers and indirect gasifiers (Iribarren, Susmozas, Petrakopoulou, & Dufour, 2014). Fixed bed gasifiers can either be updraft/countercurrent or downdraft/concurrent. In updraft, which is the most mature and simple, biomass moves down the gasifier, while the gasifying agent moves upwards (Ciferno & Marano, 2002). Updraft gasifiers can handle a high moist content (up to 60%), but produces large amounts of tar, thus demanding extensive cleaning (Zhang, Xu, & Champagne, 2010). In downdraft gasifiers, the biomass and gasifying agent both moves downward. The process has low tar production, which leads to lower cleaning demand, but cannot handle moist content above 20%, and have low thermal efficiency, because gas leaves the system with a temperature of 900-1000 deg.



Fluidized bed gasifiers use a bed of inert material, such as sand and alumina, to distribute heat better, and increasing the fluid-dynamic. It is done by injecting the feedstock into the bed from below at high speed. If the speed is equal to the minimum fluidization velocity, the bed and feedstock will act like a fluid together, and the gasifier is a bubbling gasifier (FBBG). If the speed is higher than minimum fluidization speed, some of the bed will be transported together with the gas and need to be filtered out with a cyclone, and circulated back to the bed. This is called a circulating fluidized bed gasifier (CFBG) (Belgiorno, De Feo, Della Rocca, & Napoli, 2003).

Fluidized gasifiers can handle a wide range of biomass particle sizes (Ciferno & Marano, 2002) and CFBR also produce hydrogen with little tar and unconverted carbon. They are thus suitable for large-scale production, even though the BFBR have a higher heat exchange efficiency. By using steam instead of air as gasifying agent, the hydrogen yield can be increased further. But the technique is by (Corella, Toledo, & Molina, 2008) seen as too expensive due to high energy intensity, and indirect gasification is proposed as an alternative (Iribarren et al., 2014).

Indirect gasification can be carried out in two types of reactors: gas indirect gasifiers (GIG) or char indirect gasifiers (CIG). They both have a separate unit for delivering heat by combustion and uses pure steam as gasifying agent. For the GIG, some of the gas is combusted in a separate burner, which feeds a fluidized bed with hot steam to increase H<sub>2</sub> content. Alternatively, CIG use the char, which is separated out with the bed material from the cyclone, as fuel in a fluidized bed combustor (FBC). By burning the char in the FBC, the bed material gets heated up and circulated back to the gasifier (Belgiorno et al., 2003). CIG has the highest conversion rates and gas yields according to (Belgiorno et al., 2003).

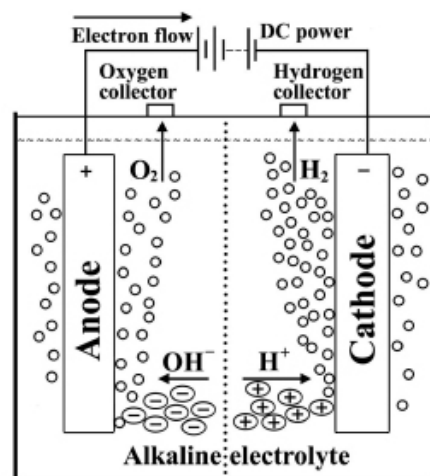
### 2.3 Hydrogen from water

For hydrogen to be an energy carrier to mitigate climate change for the transport sector, the emissions of CO<sub>2</sub> have to be reduced, compared to emissions from steam reforming of fossil gas, which today is 11.9 kg CO<sub>2</sub>-eq per kg hydrogen produced (Spath & Mann, 2000). One option then is to produce the hydrogen by means of water electrolysis. Water electrolysis is an electrochemical process where you use electricity to split water into hydrogen and oxygen (Smolinka, Ojong, & Lickert, 2016), and has been known for over 200 years (Kreuter & Hofmann, 1998). Today there are three pathways for water splitting: alkaline water electrolysis,

proton exchange membrane water electrolyzer and high temperature steam electrolysis (HTSE). For the sake of limiting the scope of this work, and because HTSE is at a non-commercial stage of development, HTSE is excluded in this work. The following two subsections introduce alkaline water electrolysis, and proton exchange membrane water electrolyzer, respectively.

### 2.3.1 Alkaline water electrolysis

The alkaline water electrolysis (AWE) is the most used electrolysis today and have production systems in the megawatt range (Ursua, Gandia, & Sanchis, 2012). The principle of alkaline electrolysis is to apply a voltage over two electrodes submerged in a liquid containing water and an alkaline electrolyte. The two electrodes are isolated from each other by a diaphragm that will let hydroxide ions and water through, but separate the hydrogen and oxygen gas – cf Figure 4 below (Carmo et al., 2013). In a life cycle perspective, the emissions from alkaline water electrolysis can vary due to the emissions from the electricity consumption. Aall (2016) did a comparison between different energy mixes for alkaline water electrolysis based on data from Burkhardt et al., 2016. It showed that the emission could range from 1.92 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> with electricity generated from wind power, and up to 33.3 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> for electrolysis using European electricity mix of 0.492 kg H<sub>2</sub> per kWh (Aall, 2016).



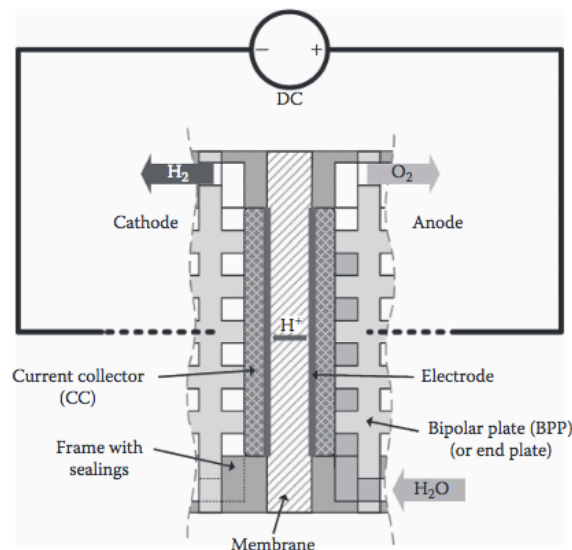
**FIGURE 4 – ALKALINE WATER ELECTROLYSIS (SANTOS, SEQUEIRA, & FIGUEIREDO, 2013)**

### 2.3.2 Proton exchange membrane water electrolysis

The first proton exchange membrane water electrolyzer (PEMWE) was created by General Electric in 1966 (Russell, Nuttall, & Fickett, 1973), and was made for use in space-crafts and

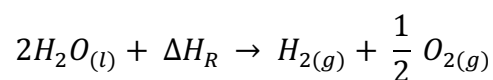
submarines (Grigoriev, Porembsky, & Fateev, 2006). Today PEMWE are primarily used to produce high quality hydrogen for hydrogen welding, metallurgy and fuel cells. PEMWE has also, in combination with photo voltaic (PV), reached a solar-to-hydrogen (STH) efficiency of 30%. This is the highest demonstrated STH percentage for any test system (Jia et al., 2016). This is promising for lowering the price of hydrogen, where STH ratio is seen as an important factor for lowering costs (Bonke, Wiechen, MacFarlane, & Spiccia, 2015).

The PEMWE cell is made up by a membrane, and an electrode, a current collector, and a bipolar plate on each side. Each side is connected to the direct current (DC) source. The cells can be placed next to another, linked together with the bipolar plate, and therefore be electrically connected, while chemically separated. Several PEMWE cells together forms a PEM stack (Smolinka et al., 2016).



**FIGURE 5 – A SIMPLIFIED DESIGN OF A SINGLE CELL IN A PROTON EXCHANGE MEMBRANE WATER ELECTROLYZER STACK (SMOLINKA ET AL., 2016)**

The PEMWE produces hydrogen by splitting water ( $H_2O$ ) into hydrogen and oxygen according to Formula 6.



**FORMULA 6 – WATER SPLITTING WITH ELECTROLYSIS (SMOLINKA ET AL., 2016)**

Two molecules of water and the thermodynamic energy needed to split the water molecules becomes a molecule of hydrogen gas and half a molecule of oxygen gas.

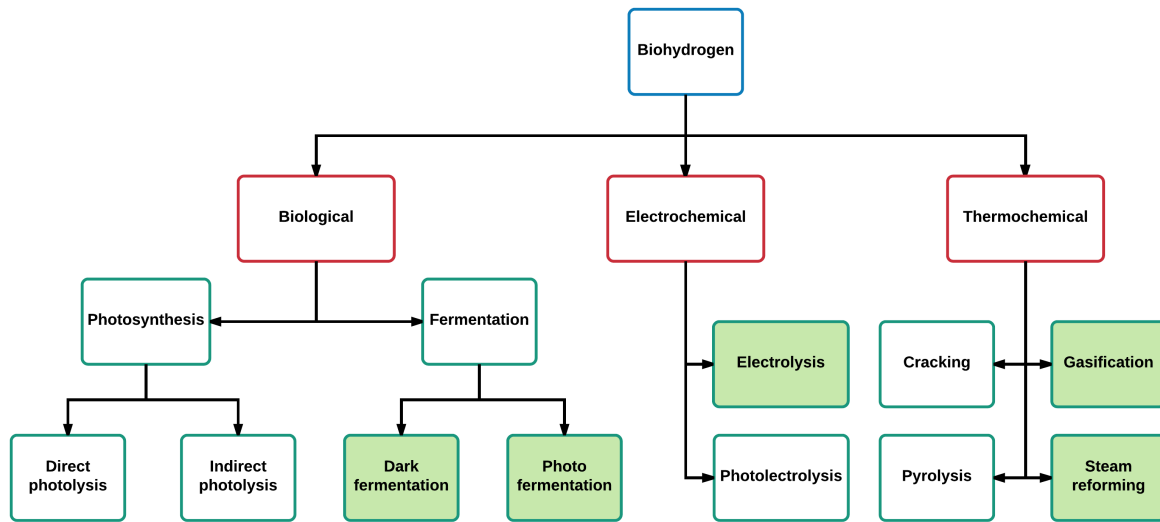
Hydrogen is made with a PEMWE by ejecting water into the anode side of the electrolyzer. The bipolar plates will lead the water to the current collector, also called the gas diffusion layer, which it will diffuse through. This is possible since the current collector is made of a porous material, normally a titanium mesh of sintered titanium. The water splits into oxygen, protons and electrons, at the catalyst layer, due to the applied voltage at the current collector. The voltage must be above 1.482V, which is the thermo-neutral voltage at which water will split. The protons will go through the membrane, while the electrons will be forced to go around, via the current collector and the separator plates. The oxygen gas will be transported out of the cell, through the current collector and the bipolar plate. The electrons and the protons will react at the cathode side of the cell and form hydrogen gas. The hydrogen gas then leaves the cell through the cathode current collector and the bipolar plate (Barbir, 2005; Carmo et al., 2013).

Research on PEMWE is currently focused on reducing the amount of noble metals, to reduce the investment cost (Kongstein, CEA, & Ødegård, 2010). The production efficiency is also tried to be improved by optimizing the oxygen evolution reaction at the anode, which today is the main reason for the overpotential (Aricò et al., 2013), where overpotential is the increase in voltage. At high currents the ohmic resistance in the membrane will also contribute to losses, and reduced efficiency (Aricò et al., 2013). Recent technological break-throughs has also made it possible to scale up the PEMWE and making it useful for creating hydrogen at an industry scale. There is to my knowledge not done a LCA of a PEMWE before this thesis.

## 2.4 Hydrogen from biomass

Biomass accounted for about 10,2% (50,3 EJ) of the worlds primary energy demand in 2008, and is seen as having a large climate mitigation potential, with an estimated capacity of between 100 and 300 EJ in 2050 (Edenhofer et al., 2011). There are several ways of turning some of this biomass into hydrogen (Figure 6). The three main categories creating hydrogen from biomass are thermochemical, electrochemical and biological hydrogen production (Ni, Leung, Leung, & Sumathy, 2006). Gasification, steam reforming, pyrolysis and cracking are the four different thermochemical processes. Direct biophotolysis, indirect biophotolysis, dark fermentation (DF) and photo fermentation (PF) are the four main processes for biological hydrogen production. In addition, microbial electrolysis cell (MEC) is an electrochemical process, which takes advantage of the residues from dark fermentation. Figure 6 shows the different hydrogen

production pathways for both hydrogen from biomass and from water electrolysis. The methods marked in green are studied in this thesis.



**FIGURE 6 – THE MAIN ALTERNATIVE METHODS FOR H<sub>2</sub> PRODUCTION FROM ENERGY SOURCES (A. SINGH ET AL., 2015)**

Liquefying biomass through pyrolysis can produce hydrogen, but the main product is pyrolysis oil. Direct and indirect biophotolysis uses algae to produce hydrogen instead of oxygen through photosynthesis, where indirect biophotolysis has another process of dark fermentation in addition (Ni et al., 2006). These H<sub>2</sub> production techniques are only on a research level, with little data available for a LCA, and will not be discussed further. In addition to the purely biomass based hydrogen production techniques, microbial electrolysis cell (MEC), which is an electrolysis that can be used on effluent from dark fermentation, is included in this thesis.

There are four main categories of biomass feedstocks for hydrogen production. (1) Energy crops: herbaceous energy crops, woody energy crops, industrial crops, agricultural crops and aquatic crops. (2) Agricultural residues and waste: crop waste and animal waste. (3) Forestry waste and residues: mill wood waste, logging residues, trees and shrub residues. (4) Industrial and municipal wastes: municipal solid waste (MSW), sewage sludge and industry waste. (Ni et al., 2006). Out of these, the focus in this thesis will be on energy crops, specifically short rotational woody crops (SRWC) and forestry residues.

Due to the general characteristics of biomass (Table 2), in particular the low hydrogen content, compared to fossil fuels (approximately 6% vs 25% for methane), and a high content of oxygen

(40%) the yield for bioH<sub>2</sub> is not as high as for conventional H<sub>2</sub> production from fossil energy for the thermochemical processes. For the chemical processes, the ideal substrate is glucose, but it is too expensive. Several feedstocks such as agricultural residues, food waste and lignocellulosic biomass have a relatively high content of carbohydrates (Turner et al., 2008). For lignocellulosic material, the carbohydrates are extracted from the cellulose and hemicellulose, while the amount of lignin is an inhibitor for carbohydrate extraction.

**TABLE 2 – MATERIAL COMPOSITION AND HYDROGEN AND OXYGEN CONTENT FOR LIGNOCELLULOSIC BIOMASS (SAWATDEENARUNAT, SURENDRA, TAKARA, OECHSNER, & KHANAL, 2015) (TURNER ET AL., 2008)**

<b>Material</b>	<b>Amount</b>
Hydrogen content	6 %
Oxygen content	40 %
Cellulose	35 – 50 %
Hemicellulose	20 – 35 %
Lignin	10 – 25%

#### 2.4.1 Thermochemical hydrogen production

There are several technologies for producing hydrogen through a thermochemical process. Singh et al. classifies gasification, steam reforming, cracking and pyrolysis as thermochemical processes. They all use heat to extract the hydrogen from the feedstock, and the processes are well known for their low cost and high efficiency (Hosseini & Wahid, 2016). As elaborated in “Hydrogen from fossil fuels” gasification and steam methane reforming have been used for several decades to produce hydrogen from a fossil feedstock. But with small or no change in process and design, one can produce hydrogen from a biogenic feedstock (Kalinci, Hepbasli, & Dincer, 2009). Pyrolysis is closely related to gasification, but the reaction takes place without oxygen, while gasification controls the amount of oxygen to reach a partial oxidation. In this thesis, the focus is on steam reforming and gasification as thermochemical processes, and the rest will not be elaborated further.

### *Biogas Steam Reforming*

Steam reforming of biomass derived liquids (BDL) or biogas are similar to steam reforming of fossil gas (Wulf & Kaltschmitt, 2013), with the same process steps as methane steam reforming, explained in subsection Steam methane reforming. BDL is reacted with steam at high temperatures. In presence of a catalyst, syngas is created, containing hydrogen and carbon monoxide gas. The carbon monoxide is further mixed with steam in a water-gas shift reaction to create hydrogen and carbon dioxide gas. The gas is then purified in a PSA, with pure hydrogen as the result.

The advantage with biogas steam reformation is that the carbon dioxide emissions occurring in the steam reforming are biogenic, and therefore this process has a potential for lower greenhouse gas emissions (Wulf & Kaltschmitt, 2013).

Biogas steam reforming (BSR) can be used for several feedstocks, as long as it is possible to produce either biogas or bio-oil from it (Wulf & Kaltschmitt, 2013). This makes the BSR versatile, but it also sets a quality demand for the feedstock, since its not all types of biomass that is economically profitable to convert to bio-oil/gas. The process of refining the feedstock also means that there have to be at least one more process, which in addition to adding cost to the hydrogen, also contributes to higher emissions. The fact that you have to convert biomass to oil or gas, has the advantage that the need for transport decreases, due to higher energy density. This can be important for a centralized production facility. BSR has also been suggested for more small scale decentralized production (Marquevich, Sonnemann, Castells, & Montané, 2002).

The fuel for biogas steam reforming can be both gas and oil and made in several ways (Marquevich et al., 2002). Two of them: gasification and pyrolysis, can also be used for creating hydrogen, and will thus be excluded as pretreatment for the biomass in this study. Another way us anaerobic digestion, which has been assessed as one of the best ways of creating biogas in respect to energy and the environment (Fehrenbach et al., 2008). Anaerobic digestion uses microorganisms to ferment the organic substrate into biogas.

### *Gasification*

Gasification of coal is a known and mature technology and it has been demonstrated that it was fully transferable to wood, with just small changes (Hauserman, 1997). The process is therefore the same as described in the subsection Gasification, with a three-step process of gasification, water-gas shift reaction and purification.

The main advantage for gasification, opposed to steam reforming, is that there is no need for pretreatment. The only criteria is that the biomass must have a moist content of < 35% to use a conventional gasifier (Demirbaş, 2002). If the moist content is above, supercritical water gasification is a possible option (Ni et al., 2006). Gasification has another advantage in the potential for scaling the system after the demand. It has been reported lignocellulosic biomass gasification plants with a hydrogen production capacity from 14.5 kg H<sub>2</sub> per hour and up to 6500 kg H<sub>2</sub> per hour (Iribarren et al., 2014; Kalinci, Hepbasli, & Dincer, 2012).

The downside of gasification, when comparing to steam reformation, is that the price per amount of H<sub>2</sub> produced is about three times higher (Spath, Lane, Mann, & Amos, 2000), and the hydrogen yield is lower (Balat, 2008). It has by others been said to be “the most promising economic route for the conversation of syngas to transportation fuels” (Turner et al., 2008). The main limitations for commercialization of gasification is the high logistic costs of the gasification plants, and the removal of tars from the hydrogen, to reach high quality gas. (Kalamaras & Efstathiou, 2013)

#### 2.4.2 Biochemical hydrogen production

The route of biochemical hydrogen production is a collection of processes for taking hydrogen out of the biomass with the use of bacteria, algae, supported by heat, sunlight and electricity (A. Singh et al., 2015). The main techniques are dark fermentation and photo fermentation, which uses fermentative microorganisms, supported by heat and sunlight respectively (A. Singh et al., 2015). Algae can also be forced to produce hydrogen, instead of oxygen, through photosynthesis given the right conditions (Peden et al., 2013). In the cross section between biochemical hydrogen production, and electrochemical hydrogen production there is also a technique called microbial electrolysis cell, which uses the liquid leftovers from dark fermentation to lower voltage level needed to split water (A. Singh et al., 2015). All production pathways mentioned have been categorized as early development (Q. Dai, 2016).



### *Dark fermentation*

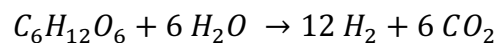
Dark fermentation (DF) one of the most promising pathways for biohydrogen, due to its low energy intensity, and the use of residues (Das & Veziroğlu, 2001; Nandi & Sengupta, 1998) and is being said to be “one of the promising hydrogen production methods, which can ensure the future of sustainable hydrogen economy” (Hosseini & Wahid, 2016). It is also one of the most common production methods for biochemical hydrogen production today (A. Singh et al., 2015). DF uses heterotrophic bacteria to ferment carbohydrates under anaerobic conditions into H<sub>2</sub> gas, volatile fatty acids (VFAs) and CO<sub>2</sub> (Argun & Kargi, 2011).

One of the advantages for dark fermentation, is that it can use a wide range of feedstocks, like food industry-, municipal-, and agricultural waste (Hosseini & Wahid, 2016). In addition to more conventional feedstock as lignocellulosic biomass from crops and wood (Turner et al., 2008). The effluent from dark fermentation can also be used as source for hydrogen through photo fermentation or microbial electrolysis cell (Q. Dai, 2016). This is due to the high content of volatile fatty acids, which is the product of fermentation of sugars (Asadi, Alavijeh, & Zilouei, 2017). The major drawback with dark fermentation is the low yield of H<sub>2</sub>, even for fermentation of the most basic sugars (Zheng et al., 2009).

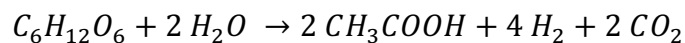
Dark fermentation is divided into three parts: pretreatment, dark fermentation and gas cleaning (Q. Dai, 2016). Pretreatment is aimed to create a hydrolysate with a high content of monosaccharides. For this thesis, out of the several pretreatment methods for dark fermentation, the process of hydrolysis and enzyme treatment as pretreatment for lignocellulosic biomass has been chosen as the most relevant. The pretreatment aims to break down the matrix of polymeric compounds including cellulose, hemicellulose, and lignin. This is done in three steps. First the mass is heated to 80<sup>o</sup>C with dilute sodium hydroxide (NaOH), to create a deacetylation (remove an acetyl group). Secondly its heated to 160<sup>o</sup>C together with dilute sulfuric acid. The last step is an enzymatic hydrolysis, where the biomass is diluted and added enzymes like cellulase to decompose cellulose and other polysaccharides down to monosaccharides. The process is feed by small amounts of corn steep liquor (CSL) and diammonium phosphate (DAP) (Davis et al., 2015). The hydrolysate is then added to the reactor for dark fermentation.

In dark fermentation hydrogen is produced by anaerobic bacteria, grown in the dark on a carbohydrate rich hydrolysate. The technique takes the process of adiabatic digestion, which consists of hydrolysis, acidogenesis, acetogenesis and methanogens, and excludes the last process, which produced methane. The first part, the hydrolysis, is done in the pretreatment. The hydrolysate from the hydrolysis is then mixed with microbes which transform sugars to Volatile fatty acids (VFA), through acidogenesis, and microbes which transform VFA into acetate, CO<sub>2</sub> and H<sub>2</sub> through acetogenesis (Hallenbeck & Benemann, 2002). The process is supported by ammonia to keep the pH-level at optimum (Q. Dai, 2016).

The maximum potential yield of oxidation of glucose is 12 moles of H<sub>2</sub>, per mole of glucose (link chemical formula of glucose), but with acetic acid fermentation, which is used for DF, the theoretical maximum is 4 moles. The actual yield is between 1 and 2,5 moles per mole of glucose (A. Singh et al., 2015).



**FORMULA 7 – THEORETICAL HYDROGEN YIELD FROM GLUCOSE THROUGH FERMENTATION (ARGUN & KARGI, 2011)**



**FORMULA 8 – DARK FERMENTATION OF GLUCOSE (ARGUN & KARGI, 2011)**

The last part of hydrogen production from dark fermentation is the purification/cleaning of the gas. To get a clean hydrogen gas, which qualifies for use in a fuel cell it has to be purified, and the preferred method of today is the pressure swing adsorption (PSA). PSA is also used for all the other systems in this thesis, which is not based on electrolysis, and explained in the subsection Steam methane reforming.

Even with a relative low yield for dark fermentation, it is one of the most promising production pathways for biochemical hydrogen (Kraemer & Bagley, 2007). The reason is that the restudies from dark fermentation can be used as input for both photo fermentation (PF) and microbial electrolysis cell (MEC). By combining DF and PF a yield of 12 moles of H<sub>2</sub> per mole of glucose can in theory be reached (Basak & Das, 2007). A study has reached a yield of 5.374 moles of H<sub>2</sub> per mole of glucose (B.-F. Liu et al., 2010).

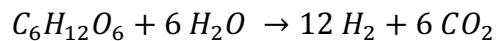
There has been research on dark fermentation since the 1980s, but there is still no large scale dark fermentation plants commercially operative. This is mainly due to low stability of the DF and low energy efficiency of the process (Tapia-Venegas et al., 2015). Low stability is here referred to as the need for maintenance of the production (Kyazze et al., 2006). This stability issue is caused by having mixed cultures, meaning having both the acidogenesis, acetogenesis at the same place (Kyazze et al., 2006). But having the mixed cultures also makes it possible to have lower quality feedstock, and less need for sterile conditions, which is demanding to satisfy (Tapia-Venegas et al., 2015).

On a research level glucose and other monosaccharides have been used as feedstock, but the cost is high and might triple the hydrogen cost if used in large scale production (Hay, Wu, & Juan, 2013) The last years it has been observed a changeover to use waste and wastewater, for waste management, that also has a commercial value (Boboescu et al., 2014). Tapia-Venegas et al. showed in (Tapia-Venegas et al., 2015) that the yield from industrial waste can vary between 0.46 to 23.97 mmol H<sub>2</sub> per g COD, depending on concentration and conditions for operation. Also household waste has been used for dark fermentation, with reported higher yields with increased temperature (D.-H. Kim, Kim, & Shin, 2009). Lignocellulosic biomass is also attractive for DF, with high content of glucose and xylose, both monosaccharides, but the demand for pretreatment to be able to use the sugar is a big challenge (Turner et al., 2008).

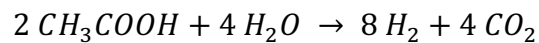
### *Photo fermentation*

Photo fermentation uses bacteria of the type photosynthetic non-sulfur (PNS) photosynthetic bacteria. These can grow as photoheterotrophs, photoautotrophs or chemoheterotrophs (Basak & Das, 2007). Photoheterotrophs harvest energy from sunlight, and carbon from organic sources, photoautotrophs (plants) harvest energy from sunlight and carbon from CO<sub>2</sub>, while chemoheterotrophs (animals) harvest energy from oxidizing inorganic chemicals, and carbon from organic sources (Basak & Das, 2007). To create hydrogen from organic compounds the PSN bacteria must grow under photoheterotrophic conditions, meaning with sunlight and organic carbon source, but also in anaerobic conditions (Redwood, Paterson-Beedle, & Macaskie, 2009). The reason for anaerobic conditions is that the bacteria are not able to split water alone, but under anaerobic conditions the bacteria can use simple organic acids as electron

donors. These electrons are transported to the nitrogenase by ferredoxin using energy in the form of ATP. When nitrogen is not present this nitrogenase enzyme can reduce proton into hydrogen gas again using extra energy in the form of ATP (Akkerman, Janssen, Rocha, & Wijffels, 2002). The fermentation takes place in a photobioreactor, where the design is optimized to expose the bacteria to as much light as possible. The most used photobioreactor today is the tubular photobioreactor, which is a tube constructed by glass or polymers.



**FORMULA 9 – CHEMICAL REACTION FOR DARK FERMENTATION AND PHOTO FERMENTATION, WITH GLUCOSE AS FEEDSTOCK (ARGUN & KARGI, 2011)**



**FORMULA 10 – PHOTO FERMENTATION OF ACETIC ACID (ARGUN & KARGI, 2011)**

In contrast to dark fermentation (DF), Photo fermentation (PF) must have strict control of the environmental condition, to have an efficient H<sub>2</sub> production. (Argun & Kargi, 2011), where pH should be between 6.8 and 7.5 with temperature between 31 and 36°C (Basak & Das, 2007). The effluent from DF (Kapdan & Kargi, 2006), containing volatile fatty acids (VFA), in addition to monosaccharides are possible carbon sources (Argun & Kargi, 2011). These again can be produced by for example lignocellulosic biomass.

The main issues for photo fermentation are the lack of preferred carbon sources, and the issue of non-uniform light distribution through the fermentation broth (Basak & Das, 2007). The light issue is the most important factor for reduction in production rate (Argun & Kargi, 2011).

#### *Photo fermentation and Dark fermentation*

By combining dark fermentation and photo fermentation, either sequentially or combined, the yield from H<sub>2</sub> production can be increased (Afsar et al., 2011). The theoretical maximum is 12 moles, per mole of glucose (Basak & Das, 2007), but not even results at 8 mol H<sub>2</sub> per mol, which is said to be the economically supportable level, has been reached (Argun & Kargi, 2010). An issue with combined fermentation is that the PNS bacteria, which goal is to ferment VFAs from DF, starts ferment the glucose. Once PNS adapts to ferment glucose it's a long process for adapting PNS back to ferment VFA (Argun & Kargi, 2010). This problem can be

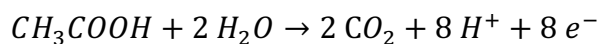
avoided by lowering the carbon concentration and remove some of the VFA. Yield from combined DF and PF at 7.1 mol H<sub>2</sub> per mol glucose has been reported. Alternatively, sequential fermentation has the issue of pretreatment for both processes, and doubling of infrastructure.

### 2.4.3 Electrochemical hydrogen production

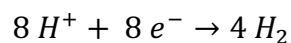
#### *Microbial electrolysis cell*

Microbial electrolysis cell (MEC) is another alternative to photo fermentation for oxidizing the effluent of dark fermentation is to produce hydrogen by applying external energy through electrolysis. The difference between regular electrolysis is that by using effluent water from dark fermentation, instead of pure water, the required voltage needed to create hydrogen is reduced (Manish & Banerjee, 2008).

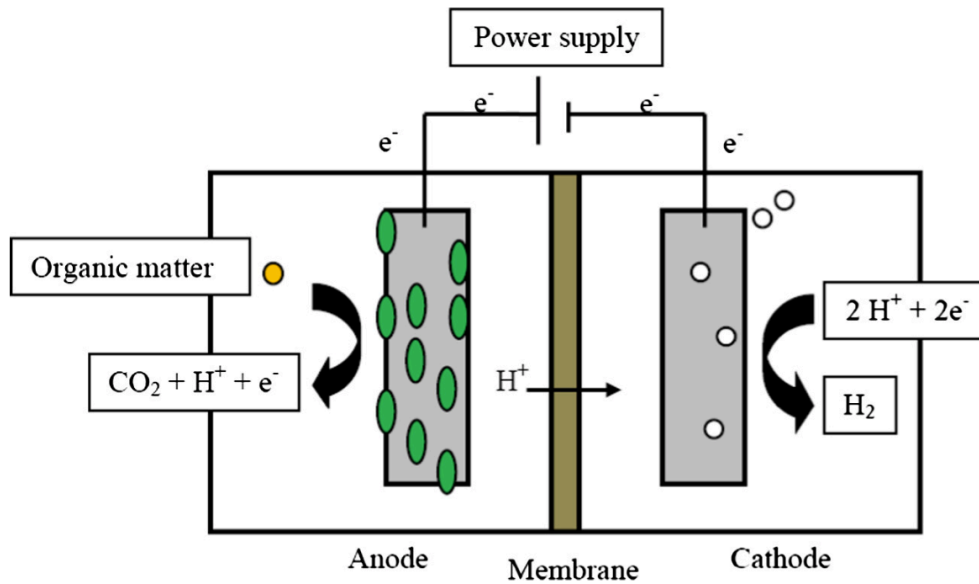
MEC was discovered in 2005 by Penn State University and Wageningen University in the Netherlands separately. In MEC bacteria is electrochemically activated to oxidize organic matter, generating electrons, protons and carbon dioxide. The electrons get transported to the anode, while protons stay in the solution. The electrons travel, with help from external voltage, from anode to cathode via a copper wire, where they together with protons create hydrogen gas. The needed applied voltage must be minimum 0.2V, and is normally in the interval between 0.2 and 0.8 V (H. Liu, Grot, & Logan, 2005). The applied voltage to split water in a regular electrolysis is normally 1.23-1.8 V (Kadier et al., 2016).



**FORMULA 11 – REACTION AT ANODE FOR MICROBIAL ELECTROLYSIS CELL**



**FORMULA 12 – REACTION AT CATHODE FOR MICROBIAL ELECTROLYSIS CELL**



**FIGURE 7 – SCHEMATIC OF TYPICAL TWO CHAMBER MICROBIAL ELECTROLYSIS CELL CONSTRUCTION AND OPERATION (KADIER ET AL., 2016)**

The main components in a MEC is the anode, cathode and the membrane. The anode can be made of different sorts of carbon or graphite. The Cathode, where the hydrogen evolution reaction (HER) happens, could have been made of carbon as well, but that would lead to slow reactions and a high overpotential. By using platinum as catalyst, the overpotential is reduced. Using platinum has many disadvantages, including high cost and a high environmental damage from mining and extraction (Logan et al., 2008). A lot of effort is put into finding an alternative to platinum cathode and it has been discovered that the HER can be catalyzed by bacteria instead of an inorganic metal catalyst. Research has still to show how to develop this biocathode (Rozendal, Jeremiassen, Hamelers, & Buisman, 2007). Membranes can be cation exchange membranes (CEM) made of Nafion 117, the same that is used for proton exchange membrane water electrolyzer or anion exchange membranes (AEM) (Logan et al., 2008). An issue with the CEM membrane is that there over time will be more protons at the anode, than at cathode, due to the fact that other cation species ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$ ) in wastewater transport electrons. This results in a pH increase at the cathode and decrease at anode. This again leads to a voltage loss (Logan et al., 2008). Alternatively, the use of AEM has shown potential, by being able to transport negative charged chemical buffers through the membrane. These transported chemicals work as a buffer for the pH (J. R. Kim, Cheng, Oh, & Logan, 2007).

MEC can be used as wastewater treatment with the function of producing hydrogen, reduce solids production, which lower sludge handling cost, and reduce odor (Logan et al., 2008). This has been tested out once, but was not seen as efficient enough to compete with today's wastewater treatment methods (Ditzig, Liu, & Logan, 2007).

Research on if MEC works well directly with cellulose from lignocellulosic biomass alone, shows a low yield, and need further research (Logan et al., 2008). But it is well known that MEC works with VFAs from the effluent after DF (Logan et al., 2008).

## 2.5 Hydrogen in the future

In this subsection, I will present the key findings from the International Energy Agency (IEA) report – Technology Roadmap, Hydrogen and Fuel Cells on how hydrogen will be produced, what it will be used for, when hydrogen will be used in large-scale and what will be the potential mitigation of GHG emissions. In the report biomass is classified as renewable energy.

Hydrogen can be produced from any primary energy source, through either water electrolysis or thermochemical processes, as discussed previously in this chapter. Körner, Tam, Bennett, and Gagné (2015) predicts that a large share of the hydrogen will be produced by variable renewable energy. This will both create hydrogen with a low emission and be a key part of stabilizing a future energy system with variable production.

Körner et al. (2015) further predicts that the use of hydrogen, generated from electricity can be utilized in four different ways. Firstly, as power-to-power. Körner et al. (2015) reports that variable renewable energy (VRE) might have a share of above 40% as a part of the goal of preventing global warming above 2°C. Electrolyzers can be used to produce hydrogen when VRE is at its peak, and temporarily be stored under pressure. Then hydrogen can be converted back to electricity through a fuel cell when renewable production is low or demand is high.

Secondly, hydrogen can be used as power-to-fuel, meaning that electricity is converted to hydrogen, to then be used as fuel for fuel cell electrical vehicle (FCEV). Thirdly, a power-to-gas, pathway is when the generated hydrogen is blended into fossil gas, or to create synthetic methane. By blending hydrogen into fossil gas or creating synthetic methane one can simplify transport, which otherwise is demanding for clean hydrogen, due to its volatile nature. The

fourth use of hydrogen by Körner et al. (2015) is to use it as power-to-feedstock, by using the hydrogen as feedstock for industrial processes by for example the refining industry.

In addition to creating hydrogen from electricity, which in principle can origin from any primary energy source, Körner et al. (2015) presents an option of co-producing hydrogen together with electricity from coal with CCS, specifically in China.

As fuel for transport, hydrogen is predicted to be responsible for 14% of the overall annual transport emission reductions in USA, EU and Japan, according to the changes that have to be made to switch from the 6DS to 2DS trajectory (Körner et al., 2015). The 6DS is the trajectory scenario towards 6°C global warming at the end of this century and 2DS is the trajectory scenario towards 2°C global warming at the end of this century (IPCC, 2014), and is what is popularly called the “Two degree target”. The cumulative contribution to emission reduction from the transport sector in 2050 is estimated to be between 7% for USA, and up to 10% for Japan, and in total be 3 gigaton CO<sub>2</sub>-eq for USA, EU and Japan (Körner et al., 2015).

For this scenario to become a reality drastic changes have to be made. One of the main challenges is the need for infrastructure. It is estimated that for each FCEV sold from today and towards 2050, between USD 900 and USD 1 900 will have to be spent on hydrogen infrastructure development, depending on region.



### 3 Materials and methods

In this chapter I will present the method of life cycle assessment (LCA), do a system description and describe how the inventory was created. Data for a scenario analysis of the LCA will also be presented.

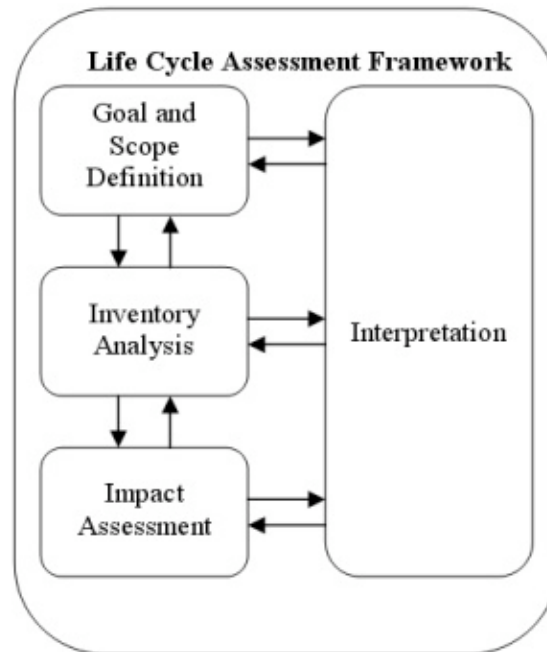
#### 3.1 Method description

For this thesis, I have chosen to do a LCA, together with a scenario analysis. In this chapter, the method of life cycle assessment will be presented together with a short description of the scenario analysis.

##### 1.1.1 Life cycle assessment

LCA is a method to quantify environmental impacts over the lifetime of a product or a system, to then to compare the results with other similar products and systems. The results will give an understanding of which product or system to choose, or where to act to improve the output of a given product or system, and is a useful tool for private and public decision makers (Standard, 2006).

ISO 14040 “Environmental management – Life cycle assessment – Principles and framework” is a set of generic guidelines on how to perform an LCA. The standard divides an LCA into four parts: Goal and scope definition, life cycle inventory (LCI), life cycle impact assessment (LCIA) and interpretation. In the first part the goal and scope for the project must be defined, and this includes to specify the system boundaries and a necessary level of detail. In the inventory part, relevant data for inputs and outputs to the system in question should be gathered and systemized, and must be detailed enough to meet the goals of the study. The third part involves calculations of the impacts based on the inventory done. Finally, results from the LCIA and possibly also the LCI are analyzed in light of the goal and scope of the assessment, and also alternatively presented to a decision maker.



**FIGURE 8 – STAGES OF A LCA**

### *Arda*

To make the LCA calculations easier, one can use a program for the calculation. At Industrial ecology, NTNU the program Arda has been developed based on Matlab for this purpose. In addition to the regular calculations of impacts, Arda also lets you perform a structural path analysis (SPA). The SPA tracks down the major emission contributors for a given material or process in the system.

### *Ecoinvent*

LCA is a data intensive assessment tool, and to be able to deliver robust results, the background data has to be detailed and transparent. Researchers at Eidgenössische Technische Hochschule (ETH) Zürich created in 2000 the database Ecoinvent to update and harmonize data for LCI and to improve the background data for LCAs (Frischknecht et al., 2005). For this assessment Ecoinvent 3.2 has been used.

### *ReCiPe*

To better be able to assess the impacts from a given system, through an LCA, a characterization model can be used. ReCiPe is such a model, and creates a recipe for how to add up and link the

different emissions to impact categories. For this thesis, climate change is the only impact category that is being studied, and ReCiPe 2008, version 1.11. is used.

### 1.1.2 Scenario analysis

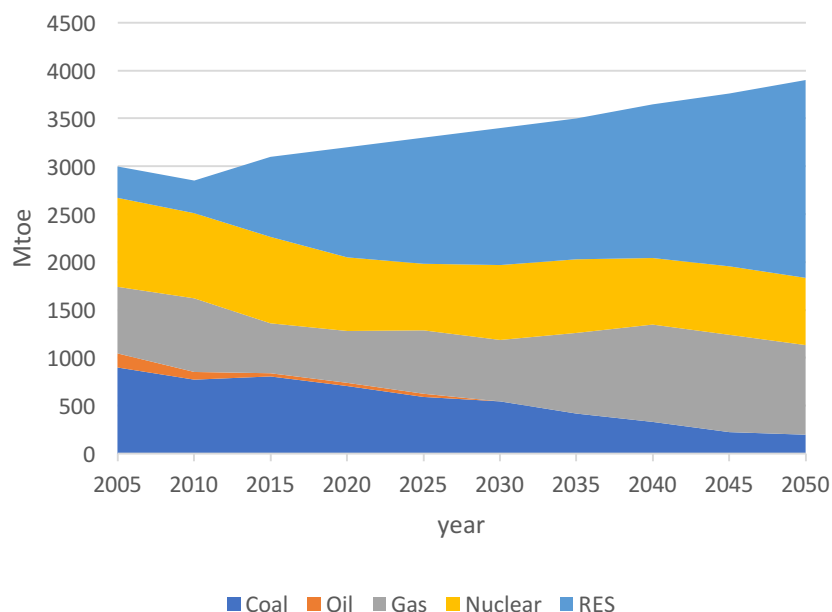
To be able to assess the impacts of hydrogen production for Europe in 2050 I have done a scenario analysis. By finding relevant scenarios for the European electricity mix, and assuming a use of biomass as heat source, instead of fossil gas for the hydrogen processes that need heat and steam, an estimate on the impacts per unit hydrogen can be calculated. By using scenarios for the potential for biomass production in Europe by 2050 an estimate on total hydrogen production from biomass can be calculated.

## 3.2 2050 scenario for Europe

In this chapter, three aspects that have a potential to change the GHG emissions per kg hydrogen produced will be presented and their potential change towards 2050 will be discussed.

### 1.1.3 Electricity

To predict the electricity mix for Europe in 2050 I use EUs own reference scenario – Energy, transport and greenhouse gas (GHG) emissions - Trends to 2050 (Capros et al., 2016). Capros et al. (2016) is based on EUs and the Member States projected development towards 2050, together with global trends and energy and climate policies adopted by EU and Member States. Legally binding 2020 targets are included. Politically agreed, but not legally adopted targets for 2030 is not included. The main results for Capros et al. (2016) is that the dependency for fossil fuel will decrease, due to more use of renewable energy sources (RES), and an increase in energy efficiency. This will result in a large change in electricity mix. The reference scenario predicts that the total GHG emissions will by 2050 be down 48% in respect to 1990 levels (Capros et al., 2016). Figure 9 shows the absolute electricity mix for Europe towards 2050.



**FIGURE 9 – EU POWER GENERATION BY FUEL TOWARDS 2050 (CAPROS ET AL., 2016)**

Data from the EU Reference Scenario is used to find out how much the electricity emission will go down per kWh from 2015 towards 2050. The emission per kWh from Ecoinvent processes with Germany as origin country is shown in Table 3. CCS is not included, and no calculations on emission reduction per kWh from the different electricity sources.

**TABLE 3 - EMISSION PER KWH AND ELECTRICITY MIX FOR 2015 AND 2050 (FRISCHKNECHT ET AL., 2005)\***

Electricity source	[g CO <sub>2</sub> -eq/kWh]	2015	2050
Solids	1056	26 %	5 %
Oil	879	1 %	0 %
Gas	766	17 %	24 %
Nuclear	11	29 %	18 %
RES	64	27 %	53 %

\*Renewable energy (RES) is assumed to be equal parts hydro, wind and solar

The result, when computing the average GHG emission from the electricity mix for 2015 and 2050 is 434 g CO<sub>2</sub>-eq per kWh, and 273 g CO<sub>2</sub>-eq per kWh, respectively. The emission from 2015 do not match the Ecoinvent process of average generated electricity in Europe (492 g CO<sub>2</sub>-eq/kWh), but it is close. The percentage decrease in emissions from the calculated values

is at 37%. It is thus assumed that the emissions from the European electricity mix will decrease with 37% towards 2050, with the initial value of 492 g CO<sub>2</sub>-eq per kWh.

#### 1.1.4 Heat and steam

Heat and steam are important inputs to the hydrogen production methods that use biomass as hydrogen source. Today, most of the steam and heat come from the burning of fossil fuels, while for the 2050 scenario I assume that the hydrogen production processes use biomass instead as some hydrogen production methods already do today.

#### 1.1.5 Ammonia

Fertilizers, based on ammonia, is used for growing short rotational woody crops, and ammonia is used in dark fermentation. Ammonia is today made through the Haber-Bosch process, which fixates nitrogen from the air, by applying voltage and hydrogen (Jennings, 2013). The hydrogen used today for this process is mainly from steam reforming of fossil gas. There might thus be a potential reduction in emissions from the use of ammonia by 2050, if hydrogen is used at a large scale for freight transport and for ammonia production. The potential for emission reduction from ammonia, through the use of hydrogen from biomass will be discussed in the chapter Results and discussion.

### 3.3 Study scope and key data and assumptions

This thesis aims to measure the greenhouse gas (GHG) emissions related to the production of hydrogen from five different production methods. These are (1) biogas steam reforming, (2) gasification, (3) dark fermentation together with photo fermentation, (4) dark fermentation together with microbial electrolysis cell, and (5) proton exchange membrane water electrolysis. All systems, except proton exchange membrane water electrolysis use biomass as hydrogen source. And all the systems that use biomass has the need for pretreatment of biomass, except gasification. To be able to evaluate and compare the different hydrogen production techniques, the life cycle inventories for the systems have to be defined in a consistent manner. This is done by setting a consistent system boundary that is equal for all production methods. This includes to use a common assumption about not looking at end of life and recycling, a consistent selection of Ecoinvent processes (including common Ecoinvent processes for electricity and heat supply) and the use of a single analytic framework of Ecoinvent and recipe. The studies used to create the inventories for the hydrogen production methods with biomass as hydrogen

source have mainly been chosen from Valente, Iribarren, and Dufour (2016), which contains a list over most of the LCAs done on hydrogen production from 1998 and up to 2016.

The core system contains the biomass feedstock, pretreatment and hydrogen production for all systems which use biomass. For the proton exchange membrane water electrolysis (PEMWE) the core system only consists of the hydrogen production. Additionally, a hydrogen truck, based on Nikola One will be used to compare the different hydrogen alternatives against other fuels for transportation.

I have chosen to use short rotational woody crops (SRWC) and forest residues from forest industry in Scandinavia as biomass feedstock. Steam reforming of biogas needs pretreatment in the form of anaerobic digestion (AD) to convert biomass to biogas and dark fermentation needs hydrolysis and enzyme treatment as pretreatment for the biomass. All systems are to some extent dependent on electricity to complete the production of hydrogen, and all except PEMWE use steam or heat in the process of producing hydrogen. On the basis of the research question for this thesis, the most effort in precise modeling will be put into parameters concerning greenhouse gas emissions.

#### 1.1.6 Hydrogen production

Steam reformation of biogas and bio-derived liquids has been chosen since it is a mature technology, which most of the hydrogen today is produced with, but with a fossil feedstock. The emissions of today's system, with fossil gas as feedstock, mostly occur from the CO<sub>2</sub> released in the reformation (Spath & Mann, 2000), and there is thus potential to reduce these emissions by using biomass as feedstock, with biogenic emissions. Gasification is together with steam reforming a mature technology used to create hydrogen from fossil fuels. The same technique can be used on biomass, and has the advantage of tackling biomass with high moist content. Another technology which is mature is the proton exchange membrane water electrolyzer (PEMWE). It has been chosen on the basis of its ability to produce high quality hydrogen, with a variable load, which makes it an interesting alternative as support to wind parks, and to even out load in the grid. Dark fermentation is chosen as the main biochemical hydrogen process due to its ability to produce hydrogen by the help of little more than bacteria's. The effluent from dark fermentation can also be used for hydrogen production through either photo fermentation or microbial electrolysis cell (MEC). Photo fermentation and

MEC have been chosen as two alternatives to couple with dark fermentation, where photo fermentation is mainly dependent on sunlight, and MEC can operate as long as electricity is applied.

The aim has not been to try to create highly detailed inventories for each of the hydrogen production methods, but rather to gather a wide range of data for each method, to be able to calculate and predict the variety of emissions today and in the future. This is especially important for the non-commercial techniques, which have a wide span of reported inputs and outputs. While for gasification and steam reforming, which are both mature and well known, the focus has been more on comparing if there is a change in process and inputs from a fossil to a biomass feedstock.

### 3.4 Life cycle inventory for biomass feedstock

As biomass feedstock for all the studied bio-hydrogen production methods in this thesis, short rotational woody crops (SRWC) and residues from forestry have been chosen. The inventory for SRWC and residues are based on Gibon, Arvesen, and Hertwich (2017). The data set available from Gibon et al. (2017) is for electricity generation from biomass with a combined heat and power. The biomass inventories from Gibon et al. (2017) are again based on data from A. Singh et al. (2015). The inventory consists of data on diesel, fertilizer, chemicals and irrigation inputs to woody bioenergy crops, as well as land use and direct field emissions of CO<sub>2</sub>, pesticides, nitrogen and phosphorus compounds and have been established by A. Arvesen (2016). Forest residues inventory is based on B. Singh, Guest, Bright, and Strømman (2014). Only data concerning the production and treatment of the biomass from Gibon et al. (2017) was used, and then adjusted from Ecoinvent 2.1 to 3.2. with equivalent processes.

To be able to use the data set from Gibon et al. (2017) some assumptions had to be made. The output value for the dataset from Gibon et al. (2017) was per MJ, while most of the studied systems use kg biomass as unit. For some of the biomass feedstocks, data on energy content could be found. For biomass with no data on energy content it was assumed that the calorific value was 19.3 MJ per kg dry mass, meaning 0 % moist. I have calculated the average value based on calorific values from known biomasses. When the calorific value is known, the lower heating value, meaning the energy that is left after evaporating water and other substances, can be calculated. The lower heating value of the mass with a given moistness is calculated with

the Formula 13.  $H_i$  is the lower heating value (LHV) for biomass  $i$ ,  $H_{i0}$  is the calorific value for biomass  $i$  with a water content of 0%.  $W$  is the water content, ranging from 0 to 100.

$$H_i = \frac{H_{i0} * (100 - w) - 2.44 * w}{100}$$

**FORMULA 13 – LOWER HEATING VALUE AS FUNCTION OF MOISTNESS. SOURCE (KRAJNC, 2015)**

For dark fermentation a conversion from kg biomass and energy content, to percentage usable sugar had to be made, since sugars are the feedstock of dark fermentation. To estimate how much biomass to use for dark fermentation, calculations from De Vrije, De Haas, Tan, Keijsers, and Claassen (2002) has been used. De Vrije et al. (2002) calculated that the conversion rate from lignocellulosic biomass of usable sugars is 33%, thus it is needed 18.2 kg of short rotational woody crops or forestry residues to produce 1 kg of hydrogen from dark fermentation and photo fermentation (De Vrije et al., 2002). For this study, it is assumed the same conversion rate for dark fermentation in combination with microbial electrolysis cell is the same as for dark fermentation in combination with photo fermentation.

### 3.5 Life cycle inventory for biogas steam reforming

Today, steam reforming is mainly used to create hydrogen from fossil gas, and hence the available data on steam reforming is mainly for methane steam reforming. It is though possible to use the same inventory for biogas, since the only main difference is that the methane is biogenic instead of fossil (Wulf & Kaltschmitt, 2013). To build a good inventory it has been focused on being able to have process data on all steps of the steam reforming, including data on construction of the plants.

Three out of eight data sets use biogas for steam reformation, while the rest is for fossil gas. They are all fairly new, with six of them from 2012 to 2016. The production capacity varies from 4.75 kg  $H_2$  per hour and up to 5627 kg  $H_2$  per hour and the electricity consumption goes from 0.17 kWh to 3.93 kWh. The use of fossil gas for heating varies from non, up to 19.3 MJ per kg  $H_2$ .



The main elements of the biogas steam reforming system are the hydrogen source, the pretreatment of the biomass, including infrastructure for pretreatment, and the steam reforming process with infrastructure, electricity use and heat use.

### *Pretreatment*

Steam reforming can use both gasses and liquids as feedstock for hydrogen production. The gasses and liquids can be produced in several ways, including: pyrolysis, gasification and anaerobic digestion (Potts & Martin, 2009). Since gasification is a process that is being evaluated by itself in this study, and therefore probably would increase emissions by combining it with BSR, it has not been chosen as pretreatment. Pyrolysis is also a process quite similar to gasification, with the difference being that oxygen is a part of gasification, while pyrolysis is without – see the subsection on Thermochemical hydrogen production for more detail. On the basis of pyrolysis being similar to gasification it has not been chosen as pretreatment. Anaerobic digestion, which is a fermentation of biomass, have been chosen because it is said to have a low impact per produced unit of gas (Appels et al., 2011) and the data availability is good, with a process for an anaerobic digestion plant in Ecoinvent. For process flows for anaerobic digestion Sawatdeenarunat et al. (2015) have been used as source.

Factors for methane production from lignocellulosic biomass include the mix between cellulose, hemicellulose and lignin and C/N-ratio, where content of lignin is the most important (Gunaseelan, 2007). Precise data on bio-methane potential from softwood have not been possible to obtain. Instead the content of cellulose, hemicellulose and lignin have been compared to a list of other lignocellulosic biomass and their methane yield through anaerobic digestion. See Appendix 1 for table on yield. The content of softwood is reported to be 33-42% cellulose, 21-40% hemicellulose and 27-32% lignin. None of the biomasses from Sawatdeenarunat et al. (2015) matches those values, but wheat straw is close, with 38.2% cellulose, 21.2% hemicellulose and 23.4% lignin. The yield from wheat is calculated to be 0.3745 Nm<sup>3</sup> CH<sub>4</sub> per kg wheat. The average yield from ten different lignocellulosic biomasses is 0.339 Nm<sup>3</sup> CH<sub>4</sub> per kg biomass. Since the content of lignin is higher in softwood than in wheat, a value below 0.3745 Nm<sup>3</sup> CH<sub>4</sub> per kg and the average from all ten biomasses is therefore used as basis for calculating the amount of biomass needed. Calculations show that it is needed 3.8 kg of softwood biomass to produce 1 kg of biogas from anaerobic digestion.

### *Biomass feedstock*

For the creation of the biomass feedstock inventory, six datasets, with a total of seven production pathways is available, since Q. Dai (2016) have data on two. Q. Dai (2016) use pyrolysis oil from lignocellulosic biomass, Susmozas et al. (2013), Wulf and Kaltschmitt (2013), and Lombardi, Carnevale, and Corti (2011) use fossil gas. Wulf, Thormann, and Kaltschmitt (2017) use bio-methane and Markevich et al. (2002) use Soybean-, Rapeseed-, and Palm oil. These feedstocks are not automatically comparable, and vary from 2.75 kg biomass per kg H<sub>2</sub> to 10.73 kg biomass per kg H<sub>2</sub>. All of the feedstocks have been through various sorts of pretreatments, also making the comparison harder. Anaerobic digestion, which is used in Wulf and Kaltschmitt (2013) has been chosen as pretreatment. Since the product of anaerobic digestion is bio gas, bio gas and fossil gas is chosen as background for feedstock consumption for biogas steam reforming, since they are basically the same gas, but with different origin. The four values for gas consumption per kg H<sub>2</sub> produced have similar values, and the average of these have been used for further calculations. It is assumed that there is a need for 4.06 kg of bio gas to produce one kg of hydrogen gas from steam reforming.

### *Electricity*

There are four different sources that report the electricity consumption for in total six biogas steam reforming systems. Q. Dai (2016) have two systems, but assume the same electricity consumption for both. These two inputs are thus assessed as one. The same goes for Wulf and Kaltschmitt (2012) and Wulf and Kaltschmitt (2013), that uses the same data source for electricity, and thus is counted as one. Only Q. Dai (2016) specifically mentions for what processed the electricity is used for, where 3 kWh is used before the cleaning process in the pressure swing adsorption (PSA), then adjusted by 20% for an assumed loss of H<sub>2</sub> in production, and assumed electricity consumption in PSA to be 0.175 kWh, all on a per kg H<sub>2</sub> basis. The rest of the systems do not mention the details of the electricity use, or if there is any on-site production of electricity, and thus have to be assumed that are correct values, even though they vary from 0.17 kWh (Wulf & Kaltschmitt, 2013) to 3.93 kWh (Q. Dai, 2016). The average of 2.17 kWh per kg H<sub>2</sub> from biogas steam reformation.

### *Heat*

Only three out of eight data sources used to construct the inventory use external heat to supply the steam reforming and the water shift gas reaction (WSGR). The rest uses some of the feedstock as energy source to heat up the steam. Q. Dai (2016) use 19.3 MJ fossil gas for the reformer, but due to a in situ carbon dioxide capture, there is no need for the WSGR (Q. Dai, 2016). Susmozas et al. (2013) have a consumption of 8.12 MJ, but supplies some of the demanded heat from the PSA off-gas, which is burned together with fossil gas. Marquevich et al. (2002) use 15.6 MJ of fossil gas per kg H<sub>2</sub>, with no use of off-gas or other sources. The average value of these three is 14.34 MJ, but since Marquevich et al. (2002) is the only source that is reporting a use of only fossil gas that matches the constructed system for this thesis, the value of 15.6 MJ is chosen for fossil gas consumption.

**TABLE 4 – KEY INVENTORY PARAMETERS PER KG H<sub>2</sub> FOR BIOGAS STEAM REFORMING**

<b>Process</b>	<b>Amount</b>	<b>Unit</b>
Biomass to pretreatment	3.80	kg
Biogas to steam reforming	4.06	Kg
Electricity	2.17	kWh
Fossil gas	15.6	MJ

### *Material inputs*

Process materials for the different catalysts in biogas steam reforming process, except the steam reformation itself, are all based on Strømman and Hertwich (2004), which did a hybrid LCA of hydrogen production using a autothermal reformer. Hybrid LCA is a LCA with background data from economic flows through input output analysis (Strømman & Hertwich, 2004). The autothermal reformer uses the same processes before and after the reforming of the gas, and is thus used. For the pretreatment, three different processes are being used. These are hydrogenation, desulphurization and pre-reforming, and they are used to remove Sulphur and other substances that is not favorable for the reformation. For operation of the steam reformer Nickel(II) oxide, based on Susmozas et al. (2013) is used. The water gas shift reaction catalysts

are divided in high temperature shift catalysts and low temperature shift catalyst, and all materials for the different catalyst can be found in Appendix 1.

### *Construction*

The construction of the biogas steam reforming plant is based on three different studies. M. Granovskii, I. Dincer, and M. Rosen (2006), Lombardi et al. (2011) and Boyano et al. (2011) all have a high data resolution and the average of the three inventories is used. Table 5

**TABLE 5 – CONSTRUCTION MATERIAL PER KG H<sub>2</sub> FOR BIOGAS STEAM REFORMATION (BOYANO ET AL., 2011; M. GRANOVSKII ET AL., 2006; LOMBARDI ET AL., 2011)**

<b>Material</b>	<b>Amount</b>	<b>Unit</b>
Concrete	1,15E-02	kg
Steel	3,00E-03	kg
Aluminum	2,17E-05	kg
Iron	3,20E-05	kg
Steel high alloy	1,44E-04	kg
Steel low alloy	8,77E-05	kg
Alumina	6,04E-07	kg
Cast iron	2,00E-04	kg
Nickel	4,55E-08	kg

### *Direct emissions*

Susmozas et al. (2013) only have biogenic CO<sub>2</sub> as direct emission, Wulf and Kaltschmitt (2012) also have emission on methane, while Lombardi et al. (2011) have data on CO, NO<sub>x</sub> and PM in addition to biogenic CO<sub>2</sub>. The modeling of emissions from biogas steam reforming is done by including all the mentioned emissions to be sure to all is covered. For CO<sub>2</sub> emissions, the average value is calculated, since very little variation in the values. The methane is not modeled as an emission, since Wulf and Kaltschmitt (2012) states the methane can go into the process again as fuel for steam, and thus be converted to a biogenic CO<sub>2</sub> emission. Table 6 shows the emissions per kg hydrogen produced.

**TABLE 6 – EMISSIONS PER KG HYDROGEN PRODUCED FROM BIOGAS STEAM REFORMING**

<b>Emissions</b>	<b>Amount</b>	<b>Unit</b>
Biogenic CO <sub>2</sub>	9,14E+00	kg
CO	7,98E-05	kg
NO <sub>x</sub>	8,98E-04	kg
PM	2,20E-05	kg

### 3.6 Life cycle inventory for biomass gasification

The data available on gasification is mainly for gasification of coal or other fossil fuels. For this study, the focus has been to obtain data for gasification of biomass. All nine of the sources used to construct the inventory are gasification for biomass, published between 2012 and 2014. The production capacity varies from 2.4 kg H<sub>2</sub> per hour (Bartolozzi, Rizzi, & Frey, 2013) and up to 6500 kg H<sub>2</sub> per hour (Iribarren et al., 2014). Electricity consumption spans from 0.036 kWh per kg H<sub>2</sub> (Iribarren et al., 2014) to 19.08 kWh per kg H<sub>2</sub> (Wulf & Kaltschmitt, 2013).

#### *Biomass feedstock*

To measure how much biomass is needed to produce 1 kg of hydrogen, seven data sources have been evaluated. For short rotational woody crops and forestry residues, used as biomass in this thesis, the energy content is known and given in MJ. Thus, calculating needed energy from the biomass for all the seven systems have been done by converting mass to energy content. All sources report the amount of biomass needed in kg, except Wulf and Kaltschmitt (2012) which report that the gasification need 164 MJ from the biomass. To be able to calculate the same parameter for the other six data sources, the humidity of the biomass has to be known. Then the lower heating value (LHV) of each biomass can be calculated. By using Formula 13, the lower heating value, given a specific humidity, can be calculated. The formula is an approximation, but through tests against a table over LHV and moisture of different lignocellulosic biomasses it had an average error of only 7%. By calculations of the energy content for each of the different biomasses, an average value of 229.19 MJ is obtained and used further for calculations. In Appendix 1, a table over the content of carbon, hydrogen, oxygen and the calorific value/higher

heating value for the different lignocellulosic biomasses used for this study. The values have been used as basis for the calculations shown in Table 7.

**TABLE 7 – BIOMASS DEMAND TO CREATE 1 KG OF H<sub>2</sub> THROUGH GASIFICATION**

<b>Source</b>	<b>Biomass</b>	<b>Amount [kg]</b>	<b>Humidity [%]</b>	<b>LHV<sup>b</sup> [MJ/kg]</b>	<b>Energy [MJ]</b>
Iribarren et al. (2014)	Poplar	25.5	50	8.38	214.00
Wulf et al., 2013	Willow	17.2	30	12.71	218.58
Weinberg et al., 2013	Poplar	12.5	15 <sup>a</sup>	15.95	199.20
Susmozas et al., 2013	Poplar	36.3	50	8.38	304.03
Moreno et al., 2013	Avg <sup>c</sup>	13.6	15 <sup>a</sup>	14.87	201.87
Wulf et al., 2012	Wood	10.3	15 <sup>a</sup>	15.95	164.00
Bartolozzi et al., 2013	Poplar	16.7	20	14.87	247.87
<b>Average values</b>		<b>18.86</b>	<b>0.28</b>	<b>13.66</b>	<b>229.19</b>

<sup>a</sup> Assume humidity of 15%

<sup>b</sup> Calculated with Formula 13

<sup>c</sup> Average of pine, eucalyptus, almond pruning and vine pruning

### *Electricity*

From the data sets, there are six different values for electricity consumption per kg of H<sub>2</sub> produced. Four of the values are between 2.3 kWh and 4.3 kWh, while Iribarren et al. (2014) is at 0.42 kWh, and Wulf and Kaltschmitt (2013) is at 19.1 kWh. The reported value from Iribarren et al. (2014) is due to the fact that they produce their own electricity together with hydrogen, and hence have a low external electricity demand. Wulf and Kaltschmitt (2013) has data based on Hofbauer et al. (2002). The data from Hofbauer et al. (2002) is not possible to access, but Wulf et al. (2017) have also based the inventory of Hofbauer et al. (2002) for a fast internal circulating fluidized bed gasifier. The electricity consumption was then at 4.1 kWh, with all the other values of capacity, demand for operating materials and so on being the same. It is thus assumed that the value of 19.1 kWh is not representative for the electricity consumption for gasification. The electricity consumption is hence calculated as an average of the other four sources, plus the reported consumption by Wulf et al. (2017) at 4.1 kWh. The electricity demand for the production of 1 kg of H<sub>2</sub> is after calculation 3.41 kWh.

### *Heat*

For six out of nine systems, heat is supplied by burning some of the biomass. Of the remaining three, Iribarren et al. (2014) uses small amounts (5.5 MJ/kg H<sub>2</sub>) of fossil gas to complement the burned off-gas from the PSA, while there is no data for Bartolozzi et al. (2013). The only system that only uses fossil gas for heating is Moreno and Dufour (2013), which reports to use 135.2 MJ fossil gas per kg H<sub>2</sub> produced. This value has thus been chosen for fossil gas consumption for gasification of biomass.

### *Material input*

The inventory for gasification is based on Weinberg and Kaltschmitt (2013), except data on sodium hydroxide, which is based on Bartolozzi et al. (2013). For the following water-gas shift reaction (WGSR), which is divided into high temperature shift (HTS) reaction and low temperature shift (LTS) reaction, the catalyst data is based on Strømman and Hertwich (2004). For the gasifier of the type steam fluidized, olivine is used as a bed material (Koppatz et al., 2009). Olivine does not exist in Ecoinvent and there has not been found an alternative. Table 8 shows the inventory for the process materials for the gasification and cleaning.

**TABLE 8 – INVENTORY FOR PROCESS MATERIALS FOR THE GASIFICATION AND CLEANING OF BIOMASS**

<b>Material</b>	<b>Value</b>	<b>Unit</b>	<b>Process</b>
Magnesium oxide	5,89E-04	kg	Unknown
Activated charcoal	5,51E-03	kg	Gas cleaning
Calcium carbonate	1,20E-01	kg	Gasification
Monoethanolamine	1,84E-03	kg	Gas cleaning
Sodium hydroxide	1,13E-02	kg	Unknown
Sulphuric acid	2,75E-03	kg	Gasification
Olivine	4,02E-01	kg	Gasification
Zinc oxide	2,75E-03	kg	Gas cleaning
Iron(III) oxide	2,79E-04	kg	HTS
Chromium(III) oxide	3,22E-05	kg	HTS
Copper(II) oxide	5,69E-06	kg	HTS
Aluminum oxide	1,45E-07	kg	LTS
Zinc oxide	2,19E-04	kg	LTS
Copper(II) oxide	3,60E-04	kg	LTS

*Construction*

The only source for construction inventory is Kalinci et al. (2012), but there are construction inventory for both a downdraft gasifier and a circulating fluidized gasifier, thus converging two out of three possible main configurations of gasifiers. The values have been modified to fit the system, but they are based on M. Granovskii, I. Dincer, and M. A. Rosen (2006), which again base the data on Spath and Mann (2000). The paper from Spath and Mann (2000) is a LCA of hydrogen production from steam reforming. The inventory for the gasification plant is shown in Table 9.

**TABLE 9 – INVENTORY PER KG H<sub>2</sub> FOR THE GASIFICATION PLANT**

<b>Material</b>	<b>Amount</b>	<b>Unit</b>
Concrete	1,66E-02	kg
Steel	5,30E-03	kg
Aluminum	4,35E-05	kg
Iron	6,48E-05	kg



### *Direct emissions*

Four sources have information on direct emissions (Table 10) from two out of three gasifier configurations. From the table, its observable that there are large variations in the emissions, both in species and amounts. To be able to evaluate the importance of the different emissions, a worst-case scenario will be applied, and the highest values will be used for the inventory for all except methane (CH<sub>4</sub>). Moreno and Dufour (2013) is the only source that have a methane emission. This emission is the non-converted methane after gasification and purification, and is in the base case of the study assumed being a direct emission. This is normally not the case, while instead the gas is looped back into the system and used for heat, which is also done in Moreno and Dufour (2013), in the second scenario. The emission of methane is thus not included in the emission inventory, but assumed to be reused.

**TABLE 10 – DIRECT EMISSIONS FROM GASIFICATION FROM FOUR DIFFERENT DATA SOURCES AND THE CALCULATED AVERAGE VALUES**

<b>Source</b>	<b>Gasifier</b>	<b>CO<sub>2</sub></b>	<b>CO</b>	<b>CH<sub>4</sub></b>	<b>N<sub>2</sub>O</b>	<b>NH<sub>3</sub></b>	<b>Unit</b>
Iribarren et al. (2014)	Indirect	1,67E+01			3,48E-04	1,04E-03	kg
Susmozas et al. (2013)	Indirect	3,28E+01			1,01E-02		kg
Moreno and Dufour (2013)	Fixed	1,89E+01	1,74E-01	9,29E-02			kg
Bartolozzi et al. (2013)	Unknown	2,30E+01	1,20E-05		6,25E-03		kg
Used values		3,28E+01	1,74E-01		1,01E-02	1,04E-03	kg

3.7 Life cycle inventory for dark fermentation and photo fermentation of biomass  
The data sources available for this thesis have not made it possible to create an inventory for each of the different bio-hydrogen processes, and thus dark fermentation and photo fermentation will be presented together, as they are in literature, and the same will be done for dark fermentation and microbial electrolysis cell (MEC). The biomass feedstock is only calculated for the combined systems, since it is assumed that photo fermentation and MEC both convert the effluent from dark fermentation to hydrogen. A general observation is that there are large variations for the different input variables for the biochemical processes since the techniques are not fully developed at an economic scale, but are still on a research level and small scale.

### *Biomass feedstock*

Dark fermentation converts glucose to hydrogen (Argun & Kargi, 2011), and the biomass used as feedstock must thus be in usable glucose equivalents. The different data sources on dark fermentation and photo fermentation have different input variables for biomass feedstock and an effort has been made to convert the different feedstocks into usable glucose equivalents.

Djomo, Humbert, and Dagnija (2008) use potato peels, and reports both how much biomass and how much glucose is needed to create 1 kg hydrogen from potato peels. Djomo and Blumberga (2011) have three different cases with (1) steam potato peels, (2) sweet sorghum and (3) wheat straw. Djomo and Blumberga (2011) do not present data on available glucose for the different biomasses, and conversion rates have to be obtained from other sources. For wheat straw, Yu, Zheng, Dorgan, and Chen (2011) concludes with a conversion rate from wheat straw to glucose of 24%, and Thanapimmetha, Vuttibunchon, Saisriyoot, and Srinophakun (2011) calculates a conversion rate of 33.5% for sweet sorghum. For the first case, steam potato peels, no data have been obtained. Manish and Banerjee (2008) use sugarcane as feedstock and have a sucrose output of 10,45% from sugarcane. In Appendix 1 a detailed table over the different feedstocks and their glucose yield. The average amount of glucose needed for dark fermentation is 6 kg, with a span from 3.1 kg to 9.7 kg. With a calculated lower heating value of 16.3 MJ per kg biomass for short rotational woody crops, and forestry residues, the equivalent biomass energy needed is 196.7 MJ.

### *Pretreatment*

The pretreatment of the biomass has the objective of delignification, meaning to remove lignin, and break down cellulose and hemicellulose to monosaccharides through the process of enzyme treatment and hydrolysis (Saratale, Chen, Lo, Saratale, & Chang, 2008). The pretreatment is needed because lignocellulosic biomass do not contain easily fermentable sugars, but rather cellulose and hemicellulose, kept together with lignin (Ntaikou, Antonopoulou, & Lyberatos, 2010). Sodium hydroxide (NaOH) is reported to be used for pretreatment for potato peels, sweet sorghum and wheat straw by Djomo and Blumberga (2011). The only other source on pretreatment is PI, Dai, Han, and Wang (2016), which is not for dark fermentation and photo fermentation, but rather dark fermentation and MEC. The fact that it uses MEC instead of photo fermentation as the second stage has nothing to do with the pretreatment, since the

pretreatments function is only to make the glucose in the biomass available for dark fermentation. For NaOH, an average has been used, while for the rest, PI et al. (2016) is the only source. The inventory values can be found in Table 11.

**TABLE 11 – PROCESS MATERIAL INVENTORY FOR PRETREATMENT PF BIOMASS FOR DARK FERMENTATION**

<b>Material</b>	<b>Abbreviation</b>	<b>Value</b>	<b>Unit</b>
Sodium hydroxide	NaOH	0,44	kg
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	0,21	kg
Calcium stearoyl lactylate	CSL	0,01	kg
Diammonium phosphate	DAP	0,01	kg

### *Electricity*

Three different sources, with a total of five process pathways where available for calculation of electricity consumption for the fermentation. Djomo et al. (2008) uses an electricity consumption of 1.42 kWh for fermentation and also includes 0.47 kWh for pretreatment. These data are again based on data from Claassen et al. (2004), but the only available data from the paper is the cost of electricity, and the values for electricity consumption is thus uncertain. For fermentation Manish and Banerjee (2008) use 3.82 kWh for fermentation, while a electricity consumption of between 9.3 and 9.4 kWh is used in Djomo and Blumberga (2011) for potato peels, sweet sorghum and wheat straw. Djomo and Blumberga (2011) also states that data is based on pilot plant. None of the values for electricity use can be neglected, even though the difference amongst them is relatively large. An average of 6.68 kWh is thus chosen.

### *Steam*

Both Djomo and Blumberga (2011) and Q. Dai (2016) have data on steam consumption for pretreatment. Both Djomo and Blumberga (2011) is reporting a consumption of 27.8 to 28.3 MJ steam per kg hydrogen and bases the values on Markowski et al. (2010), with no further elaboration. Q. Dai (2016) which uses MEC in combination with dark fermentation, instead of photo fermentation have a steam consumption of 22.9 MJ. The average value of 26.8 MJ steam per kg H<sub>2</sub> produced is chosen.

### *Process materials*

The only material input for dark fermentation is ammonia, which is used to keep the pH level constant (Q. Dai, 2016). Manish and Banerjee (2008) use 0.12 kg and Q. Dai (2016) uses 0.10 kg ammonia. The average of 0.11 is used in the inventory for this thesis.

### *Construction*

Djomo and Blumberga (2011) is the only source with information on the infrastructure of the fermentation, with a bioreactor of 95 m<sup>3</sup> for dark fermentation, and a photo reactor of 300 m<sup>3</sup>. Inventory data for a 10 m<sup>3</sup> bioreactor have been obtained from Ioannou-Ttofa, Foteinis, Chatzisyneon, and Fatta-Kassinis (2016), and scaled linearly to match the bioreactor of 95 m<sup>3</sup>, see Table 12 for details.

**TABLE 12 – INVENTORY PER KG H<sub>2</sub> FOR A 95M<sup>3</sup> BIOREACTOR BASED ON (IOANNOU-TTOFA ET AL., 2016)**

<b>Materials</b>	<b>Value</b>	<b>Unit</b>
Stainless steel	8,99E-05	kg
Cast iron	9,64E-06	kg
Aluminium alloy	6,51E-06	kg
Membrane high grade EPDM	2,07E-06	kg
PVC	2,07E-06	kg
Chlorinated polyethylene	3,10E-05	kg
Polysulphone	3,10E-07	kg
UPVC PE	1,94E-06	kg

I have not been able to find inventory for a photobioreactor for the photo fermentation, but Bosma et al. (2014) gives the specifications for a tubular photobioreactor, which is the most used today. The reactor pipe has an outer diameter of 0.05m, inner diameter of 0.046m. To be able to contain 300m<sup>3</sup> it has to be 180 000 m of pipe. By using polyethylene with a density of 946 kg per m<sup>3</sup> the total demand for polyethylene is 51.5 tons. Divided by the total production of 90 000 tons of H<sub>2</sub> through the lifetime, a total of 5,60E-04 kg polyethylene per kg H<sub>2</sub> is needed. The pumps and other parts of the photobioreactor has not been modeled.

## Direct emissions

The only direct emission from dark fermentation and photo fermentation is biogenic carbon dioxide, see Formula 9 in Chapter 2, subsection Photo fermentation. Djomo et al. (2008) reports an emission of 11.3 kg CO<sub>2</sub>, Manish and Banerjee (2008) has an emission of 13 kg CO<sub>2</sub> and the three processes from Djomo and Blumberga (2011) Djomo et al., 2011 have an emission of 11 kg CO<sub>2</sub>. The average of 11.5 kg is used for this inventory.

### 3.8 Life cycle inventory for dark fermentation and microbial electrolysis cell of biomass

Since dark fermentation is the first process in this inventory, data on biomass required and inventory on pretreatment, including heat demand, is assumed to be the same as for dark fermentation followed by photo fermentation. The materials used in the process of fermenting is also only ammonia for dark fermentation, and nothing for MEC.

#### *Electricity*

The only source that has data on electricity consumption for dark fermentation and MEC separately is PI et al. (2016), which states that dark fermentation uses 2.28 kWh, while MEC uses 15 kWh per kg H<sub>2</sub> produced (PI et al., 2016). This matches well with the calculated average electricity consumption 6.68 kWh for both dark fermentation and photo fermentation. Photo fermentation might have a higher electricity consumption than dark fermentation due to the use of pumps to circulate the masses through the pipes for sunlight exposure. The value of 15 kWh of electricity consumption for MEC is reasonable, since MEC is an electrolysis with a high electricity demand, but still lower than the alkaline water electrolysis of 68 kWh or PEM water electrolysis of 72 kWh per kg H<sub>2</sub>.

#### *Construction*

For the MEC inventory two sources are available. Manish and Banerjee (2008) only gives data on the platinum loading for the cathode catalyst, while Foley, Rozendal, Hertle, Lant, and Rabaey (2010) present data for the entire MEC. The data does not report the use of platinum for the cathode, only carbon, which is unusual, due to the fact that MEC normally contains platinum. For the inventory platinum will thus be included as an extra input, to be able to cover a normal material for MEC. The membrane used by Foley et al. is a cation exchange membrane.

The inventory for this was not available and the use of the same membrane that is used for PEMWE – Nafion 117 – is assumed to be a good approximation. The data in Nafion 117 is elaborated in subsection Life cycle inventory of proton exchange membrane water electrolysis. Inventory for dark fermentation has been described in subsection Life cycle inventory for dark fermentation and photo fermentation of biomass.

**TABLE 13 – MATERIALS PER KG H<sub>2</sub> FOR MICROBIAL ELECTROLYSIS CELL CONSTRUCTION**

<b>Part</b>	<b>Material</b>	<b>Value</b>	<b>Unit</b>
Cathode	Platinum	2,30E-07	kg
Cathode	Carbon fiber	1,50E-03	kg
Anode	Carbon fiber	2,25E-03	kg
Membrane	Nafion	1,50E-02	kg
Contractor	Stainless steel	4,41E-03	kg
Mesh	Stainless steel	5,89E-03	kg
Brushes	Stainless steel	3,28E-03	kg
Top disc	PVC	1,56E-03	kg
Bottom disc	PVC	1,56E-03	kg
Bottom distributor	Stainless steel	1,95E-03	kg
Top distributor	Stainless steel	1,95E-03	kg
Piping	PVC	1,99E-04	kg
Enclosure	PVC	2,59E-02	kg

#### *Direct emissions*

Djomo et al. (2008) reports a biogenic carbon dioxide emission of 12.39 kg per kg H<sub>2</sub> produced. This matches well with data on dark fermentation in combination with photo fermentation.

### 3.9 Life cycle inventory of proton exchange membrane water electrolysis

To my knowledge there has never before been conducted a life cycle assessment (LCA) of a proton exchange membrane water electrolyzer (PEMWE). It was thus not possible to use data

from other LCAs of PEMWE, but instead I based the inventory Smolinka (2014), a confidential cost breakdown analysis of large scale PEMWE. For this thesis, I am only allowed to use material. Since the target for the study by Smolinka (2014) was to analyze costs, only the materials driving the cost of the PEMWE is included. These materials are also the main components of the PEMWE stack. The parts that are included; membrane, anode- and cathode catalyst, current collector, bipolar plates and the pressure plate. To verify the material combination from Smolinka (2014), they were cross checked with data from Carmo et al. (2013), which confirmed that the materials where right. I have not been able to verify the amount used for the different materials. The inventory supplied from Smolinka et al. for a stack of 216 kW is displayed in Table 14.

**TABLE 14 - INVENTORY FOR A PROTON EXCHANGE MEMBRANE WATER ELECTROLYZER STACK OF 216 KW (SMOLINKA, 2014)**

<b>Part</b>	<b>Material</b>	<b>Unit</b>	<b>Value</b>
Membrane	Nafion 117	kg	4.6
Anode catalyst	Iridium	kg	8.5
Cathode catalyst	Carbon	kg	3.6
	Platinum	kg	2,4
Current collector	Carbon paper	kg	819.0
	Titanium	kg	4992.0
Bipolar plates	Titanium	kg	8663.0
	Tantalum	kg	10.0
Pressure plate	Stainless steel	kg	23565.0

The report did not contain data on lifetime for the stack or power consumption. An estimate on lifetime was chosen to be 40 000 hours. This is based on data from Sheridan, Thomassen, Mokkelbost, and Lind (2010), where lifetime normally varies from 20 000 hours to 40 000 hours. Siemens is reporting a lifetime of over 80 000 hours for their PEMWE: SILYZER 200 (Siemens, 2015).

#### *Membrane*

From Smolinka (2014) the amount of Nafion 117 as a membrane is given. From Vasquez Correa (2013) the same membrane is used with also the added energy use and use of other

materials. I assume a linear relationship between the main component in the membrane, the membrane itself, and the rest of the required materials and energy. By scaling up these values by the factor of Nafion from (Smolinka, 2014) per kW divided by Nafion from (Vasquez Correa, 2013) per kW. All elements were available in the Ecoinvent database, and therefore needed no further adjustments.

**TABLE 15 – INVENTORY FOR A PROTON EXCHANGE MEMBRANE (PEM) FOR A PEM WATER ELECTROLYZER OF 216 KWH (VASQUEZ CORREA, 2013)**

<b>Material</b>	<b>Value</b>	<b>Unit</b>
Nafion 117	4,6	kg
e-PTFE	0,3	kg
De-ionised water	20,6	kg
1-Propanol	11,3	kg
Ethanol	0,7	kg
Mixed Ethers and Other VOCs	0,4	kg
Energy for Membrane Production	19,0	kWh

#### *Anode catalyst*

From Smolinka (2014) the anode material is iridium (IV) oxide with the chemical formula  $\text{IrO}_2$ . Iridium oxide does not exist in the database Ecoinvent. An alternative to use iridium (Ir) is to use platinum (Pt) (Nuss & Eckelman, 2014). Platinum and iridium are mined together with other metals in South Africa, Canada and Russia (Nuss & Eckelman, 2014) and therefore platinum is a good proxy. Nuss and Eckelman (2014) reports that there is a slight difference in the amount of  $\text{CO}_2$ -eq emitted per kg, where iridium emits 8 860 kg  $\text{CO}_2$ -eq per kg Ir and platinum 12 500 kg  $\text{CO}_2$ -eq per kg Pt. To be able to calculate the emissions from iridium, the weight of iridium has then been adjusted down with the factor of 0.71, which is the weighting between emissions of  $\text{CO}_2$ -eq from iridium and platinum.

#### *Cathode catalyst*

The cathode catalyst is activated carbon supported platinum – Pt/C (Smolinka, 2014). The weighting between them is 40 wt% platinum on carbon, meaning that 40% of the total weight is platinum and the rest is carbon. Ecoinvent 3.3 has activated carbon in its database, but Arda only works with Ecoinvent 3.2. The inputs to activated carbon, found in Ecoinvent 3.3 was therefore manually modeled directly in Arda to construct activated carbon.



### *Current collector*

The current collectors have an anode of sintered titanium, and the cathode is made of carbon paper (Smolinka, 2014). The modeling of titanium is straight forward, but for the carbon paper adjustments must be done. The thickness of the cathode is 2 mm and 1,54 mm of it is a carbon paper with micro-porous layer (MPL) and the rest is without MPL. Mass density of carbon paper with MPL is 0.6 g per cm<sup>3</sup> and without MPL 0.45 g per cm<sup>3</sup> (FUELCELLSETC, 2013). Carbon fiber reinforced plastic does not exist in Ecoinvent, so glass fiber reinforced plastic is used as a proxy on the basis of advice from co-supervisor Anders Arvesen, researcher at Industrial Ecology, NTNU.

### *Bipolar plates*

From Smolinka (2014) it is given that the bipolar plates are made of titanium, coated with tantalum. Both has been calculated in Ecoinvent and need no further approximations.

### *Pressure plate*

The pressure plate is made from stainless steel and was assumed to be a global mix of stainless steel. Stainless steel exists as a process in Ecoinvent.

### *Electricity*

The reported energy consumption for a PEMWE varies from 50.1 kWh per kg H<sub>2</sub> to 83.4 kWh per kg H<sub>2</sub> (Carmo et al., 2013). For further calculations 72 kWh per kg of hydrogen produced is chosen. An upper high value has been chosen for reported energy consumption since this assessment is generic. The results will thus not be a worst case, but still put a lot of emphasis in the electricity.

## 3.10 Life cycle inventory of a hydrogen semi-truck

The company Nikola has launched a hydrogen fueled semi-truck called Nikola One. This will be the world's first hydrogen truck with a range that can match existing fossil based trucks. Key parameters for Nikola One is listed in Table 16. To assess how hydrogen from the different production techniques perform on the basis of GHG emissions for freight transport, an inventory for a hydrogen semi-truck based on the data from Nikola One has been created. A hydrogen truck is, in the same way as a hydrogen car, the same as the electrical version, but

with a smaller battery, a fuel cell and a hydrogen tank. The truck, including the electrical systems, electrical engines and battery is based on Raabe (2017), a yet unpublished master thesis on electrical semi-trucks. The hydrogen fuel cell and associated balance of plant is based on Windsheimers (2016) a unpublished project thesis on fuel cell vehicles. The biggest difference between the Nikola One, and a regular semi-truck is the assumption of lifetime. Where a regular semi-truck has a lifetime of 500 000 km, Nikola One is said to have a lifetime of at least 1 600 000 km.

**TABLE 16 – SPECIFICATIONS OF A NIKOLA ONE HYDROGEN FUELED SEMI-TRUCK FOR FREIGHT TRANSPORTATION**

<b>Nikola One</b>	<b>Value</b>	<b>Unit</b>
Vehicle weight	15	ton
Payload	36	ton
Hydrogen fuel consumption	0.046	kg/km
Engine	745	kW
Battery	320	kWh
Fuel cell	300	kW
Lifetime	1 600 000	km

## 4 Results and discussion

In the first part of the results I will discuss emissions of greenhouse gasses (GHG) per kg of hydrogen produced on a well-to-gate perspective, analyzing the present situation. Biogas steam reforming, gasification of biomass, dark fermentation and photo, dark fermentation and microbial electrolysis cell and proton exchange membrane water electrolysis will be compared against the two current best practice systems for producing hydrogen. These are steam methane reforming and alkaline water electrolysis.

For the 2050-scenario, the effect of an electricity mix in Europe with lower GHG emissions per kWh and the possibility for technological evolvement with respect to the use of biomass instead of fossil gas for heat and steam will be discussed. Then I will calculate an estimate on the potential for how much hydrogen can be produced on a yearly basis from both biomass, and water electrolysis. The result will sum up to a suggestion for a hydrogen production mix for Europe, with a calculated average GHG emission per kg hydrogen produced.

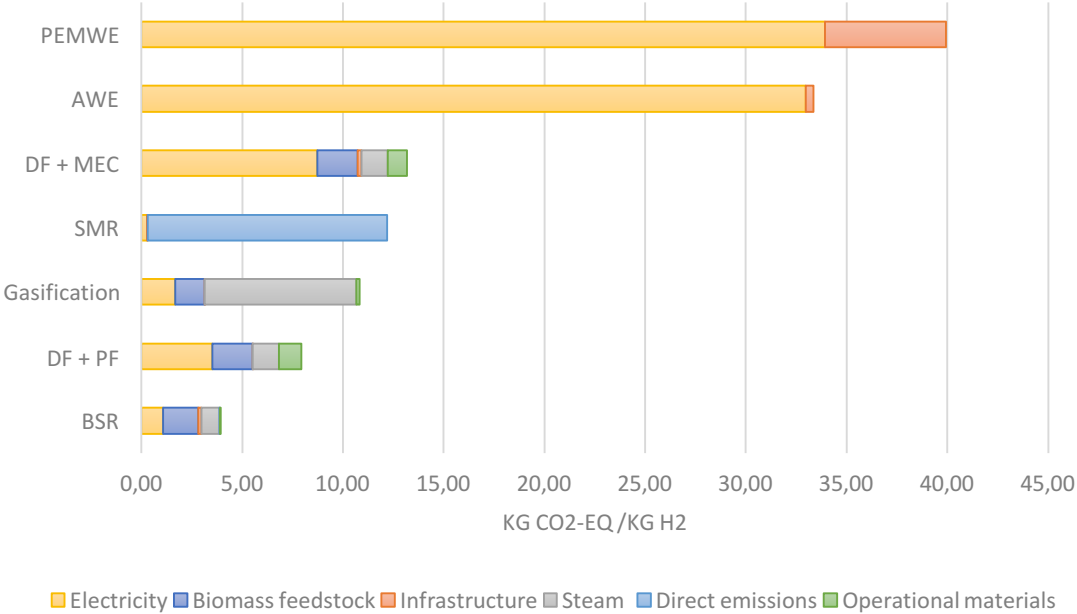
To assess the effect of using the hydrogen, I have chosen road freight as a case. I will assess how well the different hydrogen production alternatives perform on GHG emissions, against fossil fueled semi-trucks for road freight transportation, when using results from the scenario analysis. I will do this by using a generically modeled LCA of the hydrogen semi-truck Nikola One, and use the calculated hydrogen as fuel.

In the last part, I will discuss the uncertainties in the model, calculations and assumptions present in the thesis; and then finish off by discussing future research needs regarding climate friendly production and application of hydrogen for Europe towards 2050.

### 4.1 Climate change

Figure 10 shows the difference between different production methods in GHG emissions per kg hydrogen. Biogas steam reforming is by far the production method with the lowest emission, with 3.9 kg CO<sub>2</sub>-eq per kg H<sub>2</sub>. The combination of dark fermentation (DF) and photo fermentation (PF) follows with an emission of 7.95 kg CO<sub>2</sub>-eq per kg H<sub>2</sub>. Gasification of biomass is just below the reference system of steam methane reformation (SMR), with an emission of 10.82 kg CO<sub>2</sub>-eq per kg H<sub>2</sub>. Just above SMR dark fermentation in combination with

microbial electrolysis cell (MEC) emits 13.18 kg CO<sub>2</sub>-eq per kg H<sub>2</sub>. Both of the two electrolysis methods are far above the rest of the production methods with 33.3 and 40 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> for alkaline water electrolyzer (AWE) and proton exchange membrane water electrolyzer (PEMWE) respectively. In the coming paragraphs, I will discuss the benchmark processes SMR and AWE, before I do a more detailed analysis of all the different production systems, and the biomass feedstock used.



**FIGURE 10 - EMISSIONS OF GHG FOR PROTON EXCHANGE MEMBRANE WATER ELECTROLYZER (PEMWE), ALKALINE WATER ELECTROLYZER (AWE), DARK FERMENTATION AND MICROBIAL ELECTROLYSIS CELL (DF + MEC), STEAM METHANE REFORMING (SMR), GASIFICATION, DARK FERMENTATION + PHOTO FERMENTATION (DF + PF) AND BIOGAS STEAM REFORMING (BSR)**

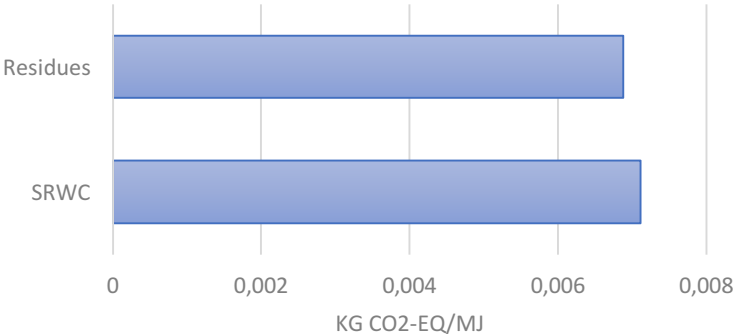
Steam methane reforming (SMR) and alkaline water electrolysis (AWE) are both used as benchmark values. SMR is the leading technology for hydrogen production today, with an emission of 12 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> (Spath & Mann, 2000). The emissions occur during the production of fossil gas and in the production of hydrogen in the steam methane reformer, due to the reforming of fossil gas, which produces CO<sub>2</sub> together with H<sub>2</sub>. Details about SMR can be found in Chapter 2 – subsection Steam methane reforming.

Alkaline water electrolysis (AWE) is the leading non-fossil hydrogen method today. The GHG emissions can potentially be relatively low, given a clean energy mix, but with the European

energy mix (0.429 kg CO<sub>2</sub>-eq/kWh), the emissions are quite high. This is due to an energy demand of 67 kWh/kg H<sub>2</sub>, for separating water into hydrogen and oxygen. Details about AWE can be found in Chapter 2 – subsection Alkaline water electrolysis.

4.1.1 Biomass feedstock

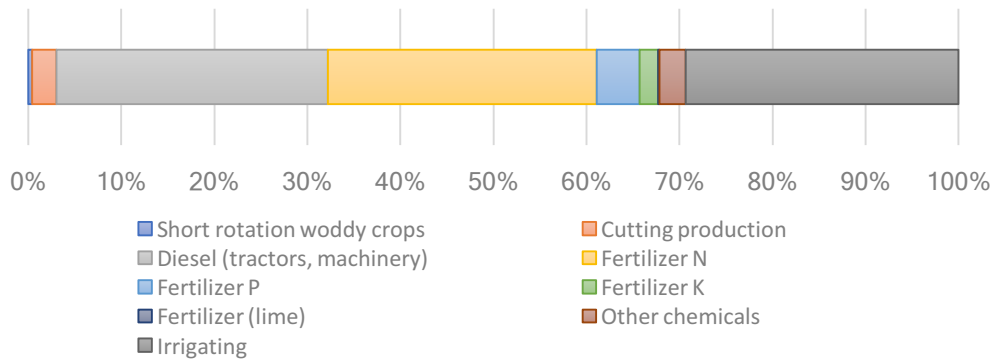
For this assessment, both short rotational woody crops (SRWC) and residues from forestry have been used as feedstock. SRWC and residues have a fairly similar level of GHG emission, i.e. 7.1 g CO<sub>2</sub>-eq per MJ biomass and 6.9 g CO<sub>2</sub>-eq per MJ biomass respectively. Their emissions do on the other hand not originate from the same processes.



**FIGURE 11 – GHG EMISSIONS PER MJ FOR SHORT ROTATIONAL WOODY CROPS (SRWC) AND FORESTRY RESIDUES**

*Short rotational woody crops*

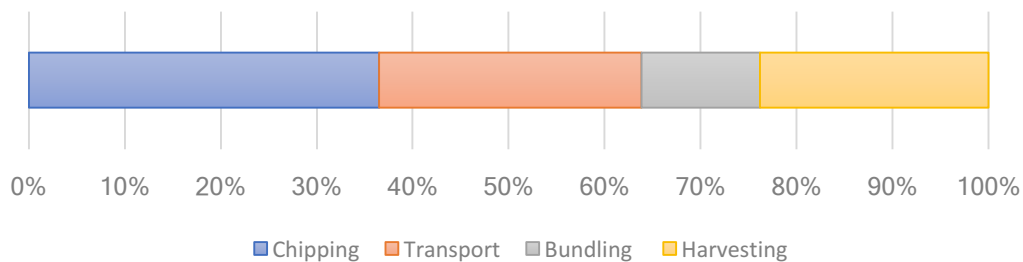
Figure 12 shows that the main contributors of GHG emissions for short rotational woody crops are from combustion of diesel, the use of nitrogen based fertilizers like ammonia (NH<sub>3</sub>), and irrigation. While the combustion of diesel has a direct link to climate change, due to the release of CO<sub>2</sub> in combustion, irrigation and nitrogen fertilizers have an indirect link. The main component of nitrogen based fertilizers ammonia are made through the Haber-Bosch method, which fixates nitrogen from the air, together with hydrogen gas. As mentioned in the background chapter, the hydrogen produced today mainly originates from steam reformation of fossil gas, or gasification of other heavier fossil fuels. The hydrogen production is thus responsible for most of the emissions from fertilizer production. The indirect GHG emissions related to irrigation is due to the use of electricity for pumping the water. An electricity mix with a high percentage of fossil energy will imply that GHG emissions will also be high.



**FIGURE 12 – SHARE OF GHG EMISSIONS FOR SHORT ROTATIONAL WOODY CROPS**

### *Forestry residues*

The emissions of greenhouse gasses from residues from forestry shown in Figure 13 is related to transport, bundling and harvesting. Emission transports are due to the combustion of fossil fuels for the truck. The emissions from bundling and harvesting are because of the combustion of fossil fuels for machine operation.

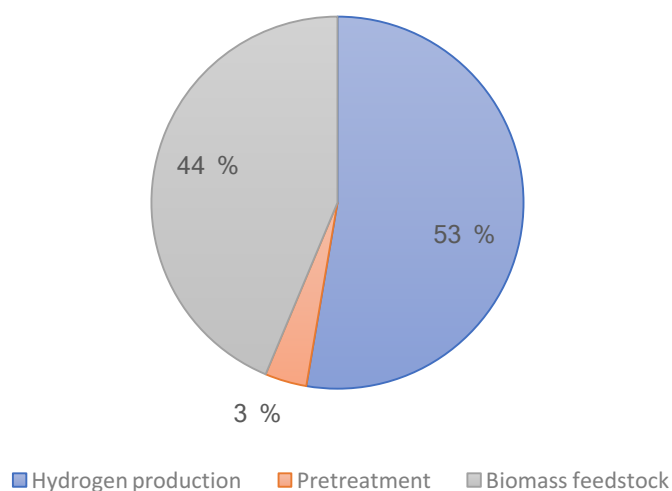


**FIGURE 13 – SHARE OF GHG EMISSIONS FOR FOREST RESIDUES**

For further discussion, I assume that the biomass feedstock will consist of 50% SRWC and 50% residues from forestry.

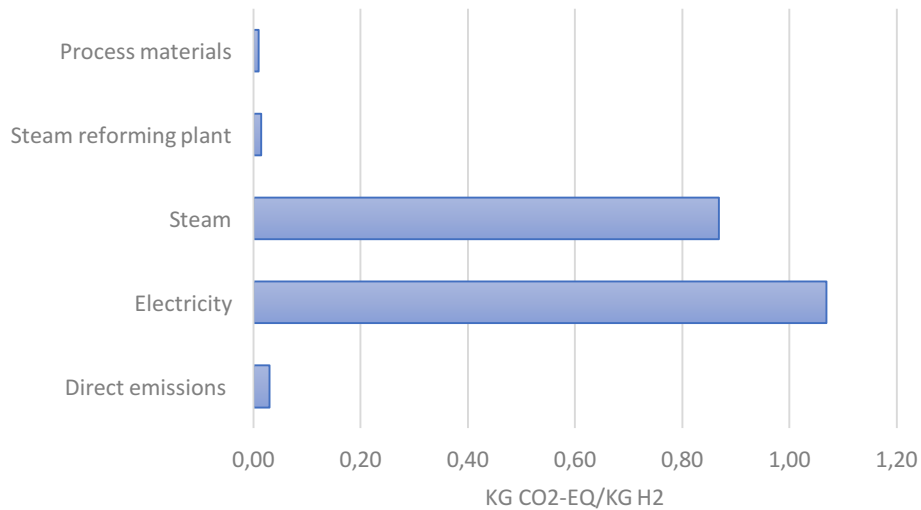
#### 4.1.2 Biogas steam reforming

Figure 14 shows emissions per kg H<sub>2</sub> produced for biogas steam reforming. The process responsible for the largest contribution of GHG emission is the hydrogen production, constituting 53% of the total emissions. Emissions from the biomass feedstock (in this case 50% SRWC and 50% forestry residues) constitutes 44% of the emissions, while the pretreatment, which is anaerobic digestion, merely make up 3% of the total emissions.



**FIGURE 14 – GHG EMISSION DISTRIBUTION FOR BIOGAS STEAM REFORMING**

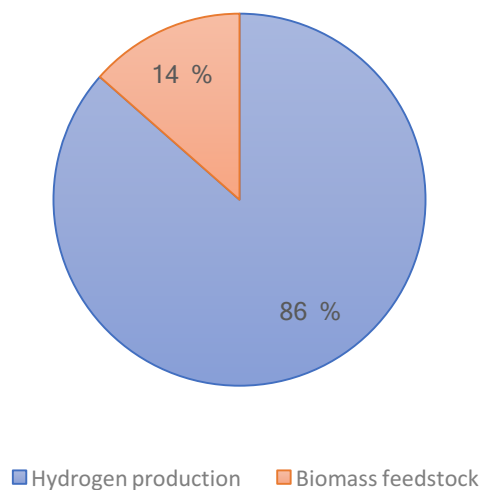
The feedstock emissions have been discussed above in the subsection Biomass feedstock and is therefore excluded from further explanation. Figure 15 shows the details of the constitution of GHG emissions relating to the production of hydrogen. The two main contributors are the use of steam and electricity, with a contribution of 44% and 54% respectively. The steam production uses fossil gas as feedstock, and the electricity use is assumed to be a European energy mix, with an emission of 0.492 kg CO<sub>2</sub>-eq per kWh. Only three out of eight data sources for biogas steam reforming (BSR) used fossil gas as heat source, while the rest used the off-gas from the Pressure Swing Adsorption process together with biomass to supply the heat. There is thus a large potential in reducing the emissions from the use of steam in BRS.



**FIGURE 15 - PRODUCTION RELATED GHG-EMISSIONS FROM STEAM REFORMING OF BIOGAS**

#### 4.1.3 Gasification

Figure 16 shows the partial contribution to the emissions of 10.84 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> from gasification of biomass. Emissions from the feedstock is responsible for 14%, while the gasification process is responsible for 86% of the emissions. There is no pre-treatment needed for gasification.

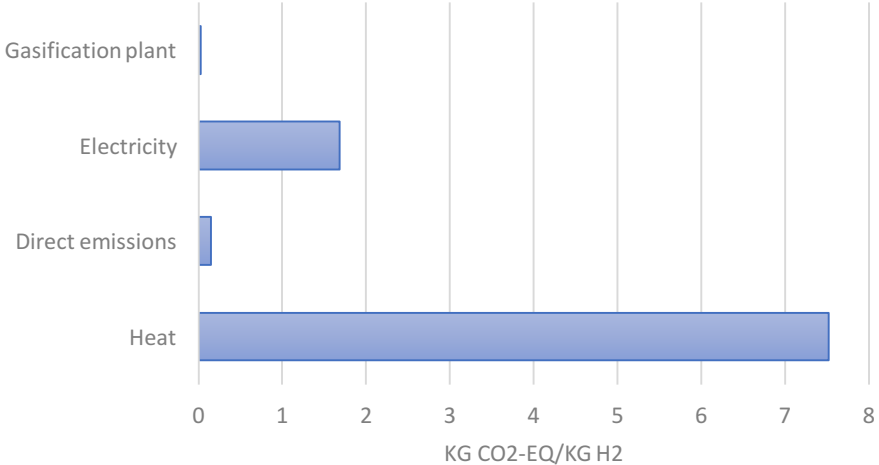


**FIGURE 16 – GHG-EMISSION DISTRIBUTION FOR GASIFICATION OF BIOMASS**

Figure 17 shows the GHG emissions by the different parts of the gasification process. The two main sources are related to the use of heat and electricity. As for all systems, a European energy



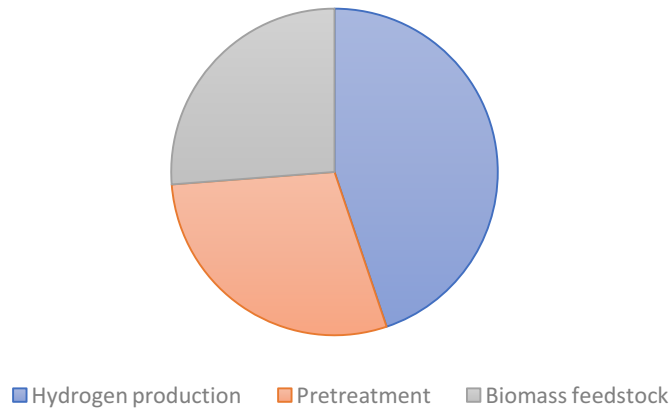
mix is used for the electricity, whereas fossil gas is assumed to be the energy source for producing heat, all of which results in high levels of GHG emissions. Only three out of nine systems used to create the inventory for gasification use an external source of heat in the form of fossil gas. The rest of the systems use off-gas from the PSA, and in some situations in addition to biomass from the feedstock, to supply heat and steam. This implies a large potential for reduction of GHG emissions, since producing heat alone accounts for as much as 69% of the total GHG emissions from gasification of biomass.



**FIGURE 17 – GHG-EMISSIONS FROM GASIFICATION OF BIOMASS**

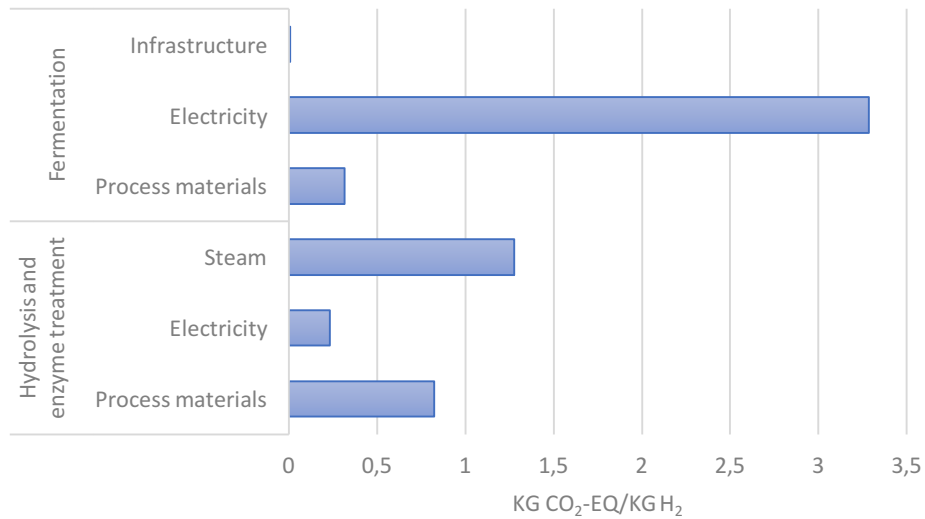
4.1.4 Dark fermentation and photo fermentation

Figure 18 shows the contribution of GHG-emission from biomass feedstock, pretreatment of feedstock and the hydrogen production through dark fermentation and photo fermentation. The process accounting for the highest share of emissions is the fermentation (45%), while pretreatment is responsible for 29%. For hydrolysis and enzyme treatment as pretreatment and fermentation Figure 19 shows a detailed disaggregation. As for the biomass, with a contribution of 26%, the emissions are discussed in the subsection on Biomass feedstock.



**FIGURE 18 – GHG-EMISSION DISTRIBUTION FOR DARK- AND PHOTO FERMENTATION, INCLUDING PRETREATMENT AND BIOMASS FEEDSTOCK**

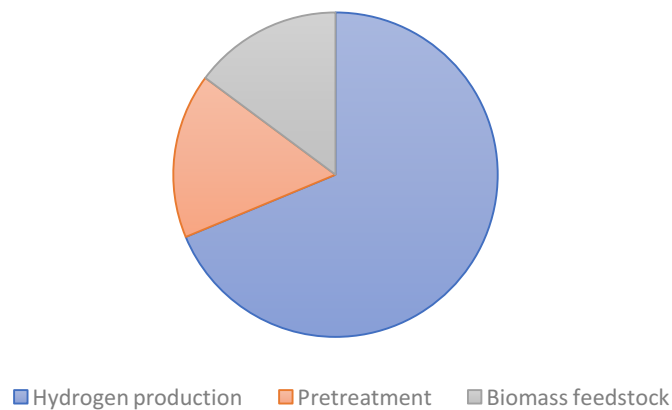
Figure 19 shows that the electricity-use is the main contributor of GHG emissions in the process of hydrolysis, enzyme treatment and fermentation of biomass, where only 7% occurs in the pretreatment, while the remaining 93% is from the fermentation. The use of electricity is not specified in the available data sources on dark fermentation and photo fermentation, but is assumed to be used for the purposes of running electrical machines and pumps. The steam from pretreatment, which has the second highest emission in total, is used to heat up the biomass for the enzyme treatment as described in chapter 3 – subsection Life cycle inventory for dark fermentation and photo fermentation of biomass. The high emission is due to the use of fossil gas as energy for heat production. Emissions related to the use of materials for pretreatment is caused by the use of sodium hydroxide and glucose. The emissions related to sodium hydroxide is caused by the electrolytic process of production, which involves a high energy demand. The emissions related to glucose also stems from production, but by use of fossil fueled machinery - like tractors. The last major contributor to GHG emissions is related to the use of ammonia. Use of ammonia involves, as explained in the subsection Biomass feedstock, high emissions of CO<sub>2</sub> due to the use of fossil gas as source of hydrogen for the Haber Bosch method.



**FIGURE 19 – GHG-EMISSIONS FROM PRETREATMENT AND FERMENTATION OF BIOMASS**

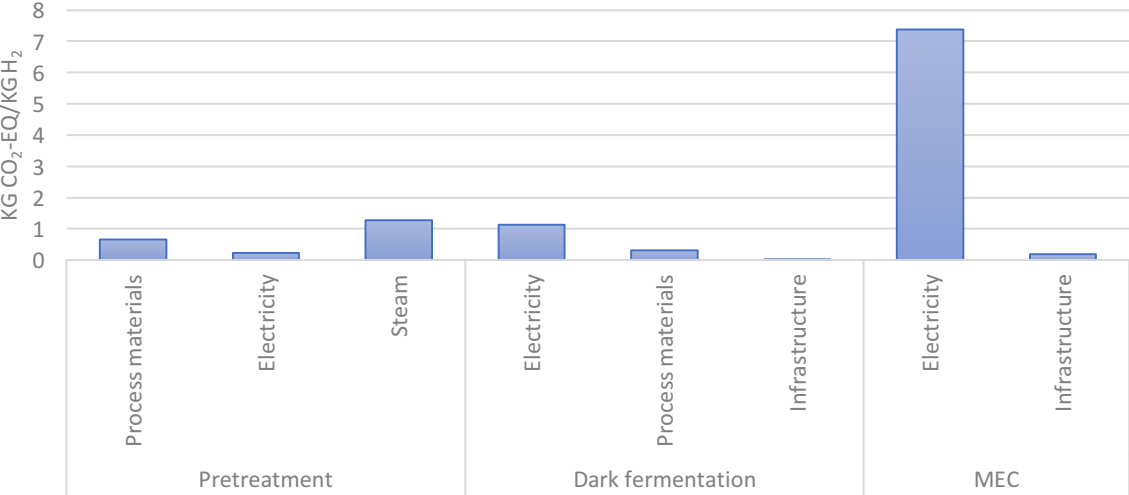
#### 4.1.5 Dark fermentation and microbial electrolysis cell

Figure 20 shows the distribution of GHG emissions between the processes of biomass feedstock, the pretreatment of the feedstock and the hydrogen production itself. The main share of emissions, with a cut of 69%, is from the hydrogen production. Biomass feedstock accounts for 15 %, while pretreatment accounts for 16% of the total emissions.



**FIGURE 20 – GHG-EMISSION DISTRIBUTION FOR DARK FERMENTATION AND MICROBIAL ELECTROLYSIS CELL (MEC) OF BIOMASS**

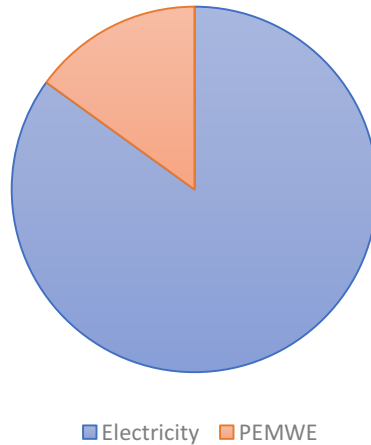
Figure 21 shows a disaggregated presentation of emissions from hydrogen production and pretreatment. The by far largest contributor of GHG-emissions is the electricity-use for the microbial electrolysis cell, accounting for 7.4 kg CO<sub>2</sub>-eq per kg H<sub>2</sub>, which is 56 percent of the total emissions. The emission is due to the high consumption of electricity (15 kWh/kg H<sub>2</sub>) and the emissions from electricity production in Europe (0.492 kg CO<sub>2</sub>eq/kWh). The second largest source of GHG emission is related to the use of steam heated up by means of using fossil gas. The process materials for hydrolysis and enzyme pretreatment is the same in value and type as for dark fermentation and photo fermentation. The only process material involved in dark fermentation is ammonia (for more detail information see the subsection about Dark fermentation and photo fermentation).



**FIGURE 21 – PROCESS EMISSIONS FROM DARK FERMENTATION AND MICROBIAL ELECTROLYSIS CELL (MEC) OF BIOMASS**

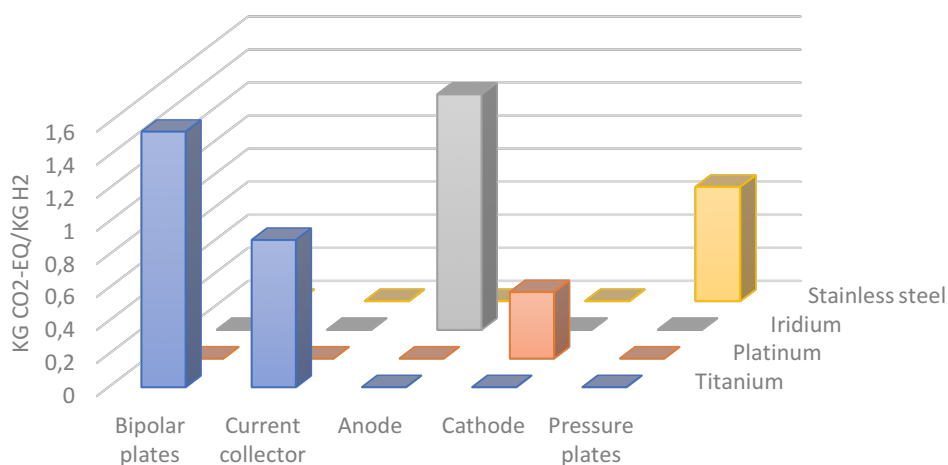
4.1.6 Proton exchange membrane water electrolyzer

The total GHG-emissions for producing 1 kg of hydrogen by means of proton exchange water electrolysis (PEMWE) was calculated to be 40 kg CO<sub>2</sub>-eq. Figure 22 shows that 85 % of these emissions are related to electricity-use. The remaining 15% are indirect emissions relating to the components used in the electrolyzer. Even though its only 15% of the total contribution, the absolute emission is 6 kg CO<sub>2</sub>-eq per kg H<sub>2</sub>, which is more than the entire contribution from BRS.



**FIGURE 22 – SHARE OF GHG-EMISSIONS FOR HYDROGEN PRODUCTION THROUGH PROTON EXCHANGE MEMBRANE WATER ELECTROLYSIS**

Figure 23 shows how the different materials in the main components of the PEM stack contribute to climate change. The Nafion 117 membrane, which is a part of the stack, has been excluded from further analysis, since the contribution to climate change is close to negligible, even though it is the part of the PEM stack that has the most detailed data. The emissions from bipolar plates and current collector occur due to a large use of titanium, in which titanium constitutes for 33 % of the total impacts from the system. The anode due to the use of iridium (19%), cathode from platinum (5.4%) and pressure plates from stainless steel (9.2%). The next step is to analyze why these materials have such a big impact on the PEMWE.



**FIGURE 23 – GHG EMISSIONS FROM THE DIFFERENT PARTS AND MATERIALS OF THE PROTON EXCHANGE MEMBRANE WATER ELECTROLYZER**

### *Platinum and iridium*

As reported in the system description about anode and cathode catalyst, both platinum and iridium are mined in Russia, South Africa and Canada. This is confirmed in the structural path analysis, which points at electricity for mining in South Africa, mining operation in Russia and South Africa in addition to combustion of diesel in South Africa, as the main contributors to the GHG emissions.

### *Titanium*

Both the bipolar plates and the current collectors are made of titanium. As for platinum and iridium, it is not known where the titanium originated, and therefore assumed a global market. The SPA shows high emissions due to the global production of titanium tetrachloride, which again has high emissions due to electricity use. Titanium is today produced in China (45%), Russia (20%), Japan (18%), Kazakhstan (12%) and Ukraine (5%) (USGS, 2014). This can explain the high emissions from electricity consumption since these countries are supplied mainly with fossil fuels. Emissions from the production of titanium tetrachloride is due to the fact that reduction to titanium tetrachloride is done by using chlorine and coke (Clark, 2015). The reduction of titanium tetrachloride with coke, results in the creation of carbon monoxide and carbon dioxide (Clark, 2015).

### *Stainless steel*

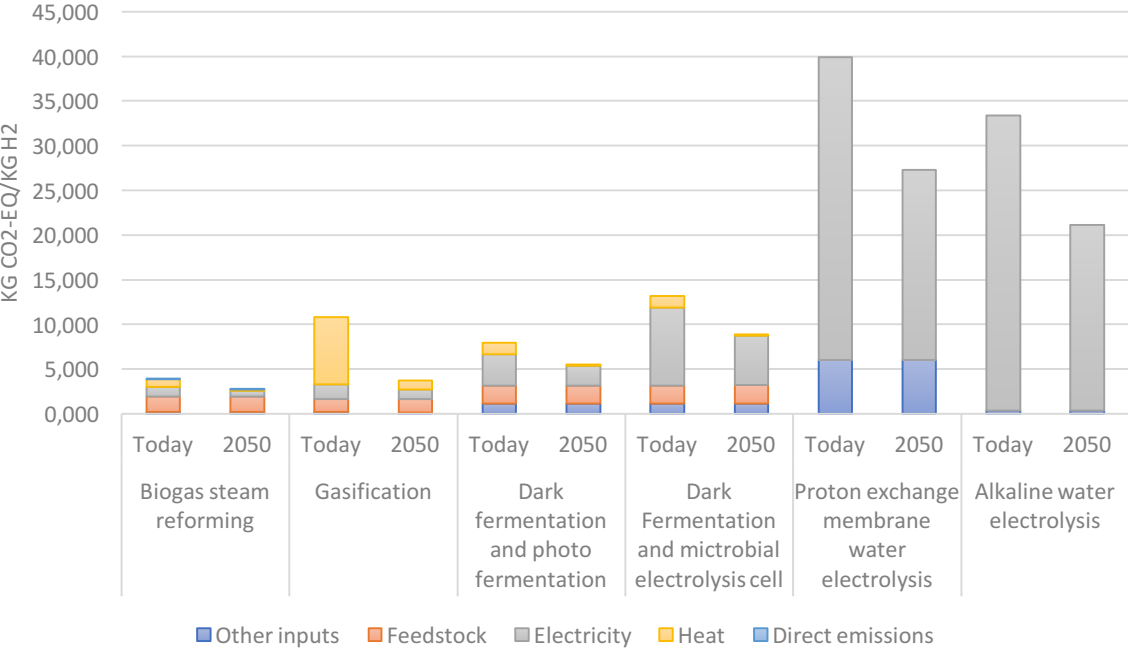
The construction that holds the PEM together, the pressure plates, are made of stainless steel. Like titanium most steel is produced in China (50%), but the total production is globally distributed, and produced in over 37 countries (WSA, 2016). The SPA shows that the impacts are coming from the steel production (RoW) and ferronickel production (GLO). In Ecoinvent, ferronickel is needed to produce nickel for use as an alloying element in steel, in particular stainless steel. The chosen steel production mix is according to Ecoinvent the average European consumption mix, which represent the average world production mix (Ecoinvent, 2015). Steel production is like other metal production; it is energy demanding and needs coke. Electricity is the main contributor to GHG emissions through production from coal, and the second largest is from coke (Burchart-Korol, 2013). Ferronickel, which is an important ingredient in stainless steel (Bartzas & Komnitsas, 2015), needs coke or coal as a reductant (Swinbourne, 2014) and electricity as energy. Since there is a global demand for steel, the production of ferronickel is

also supplied with electricity from fossil fuels, and have direct emissions of CO<sub>2</sub> from the use of coke and coal.

## 4.2 Scenario for 2050

### 4.2.1 Electricity mix and heat source

For 2050 it is assumed that all the processes that involves the use of heat and steam can use biomass as energy source instead of fossil gas, as several processes do today. By using EUs Reference Scenario (Capros et al., 2016) I have assumed a reduction of 37% in GHG-emissions per kWh for the European electricity mix compared with the current emission level. Details on the calculation behind this assumption can be found in Chapter 3 – Materials and methods. Figure 24 shows the result of using biomass as energy source for heat, and a European electricity mix with a 37% GHG-emission reduction per kWh compared to current emissions level.



**FIGURE 24 – A 2050-SCENARIO FOR GHG-EMISSIONS PER UNIT HYDROGEN FOR THE ASSESSED PRODUCTION METHODS**

As seen in Figure 24, every hydrogen production method is expected to have a lower impact per produced kg of hydrogen in 2050 compared to current emissions as a result of assuming a cleaner electricity mix and the use of biomass as heat source instead of fossil gas. Biogas steam

reforming is also in 2050 the production method with the lowest impact (2.7 kg CO<sub>2</sub>-eq), with gasification (4.3 kg CO<sub>2</sub>-eq) and combined dark- and photo fermentation (5.5 kg CO<sub>2</sub>-eq) following right after. Dark fermentation together with MEC has just passed steam methane reforming, with an emission of 8.8 kg CO<sub>2</sub>-eq per kg H<sub>2</sub>. Both PEM water electrolysis and alkaline water electrolysis still have high emissions due to the use of electricity from the European electricity mix, and are still about double the emissions compared to that of steam methane reforming. What is not included for the electrolyzers is an assumption of lower energy use per kWh for both PEMWE and AWE and reduction in emissions from the construction of the PEMWE for 2050. The internal ranking between the different processes does not change, except for the case of gasification, which pass in order dark fermentation in combination with photo fermentation. A detailed overview of absolute and relative changes is shown in Table 17.

**TABLE 17 – ESTIMATED IMPROVEMENTS IN GHG EMISSIONS FOR THE DIFFERENT PRODUCTION METHODS BY 2050 AS COMPARED TO 2015**

	<b>BSR</b>	<b>Gasification</b>	<b>DF + PF</b>	<b>DF + MEC</b>	<b>PEMWE</b>	<b>AWE</b>	<b>Unit</b>
Relative reduction	32 %	54 %	30 %	32 %	32 %	37 %	percent
Absolute reduction	1,3	5,9	2,4	4,3	12,6	12,2	kg CO <sub>2</sub> -eq
Emission in 2050	2,6	4,9	5,5	8,9	27,3	21,1	kg CO <sub>2</sub> -eq

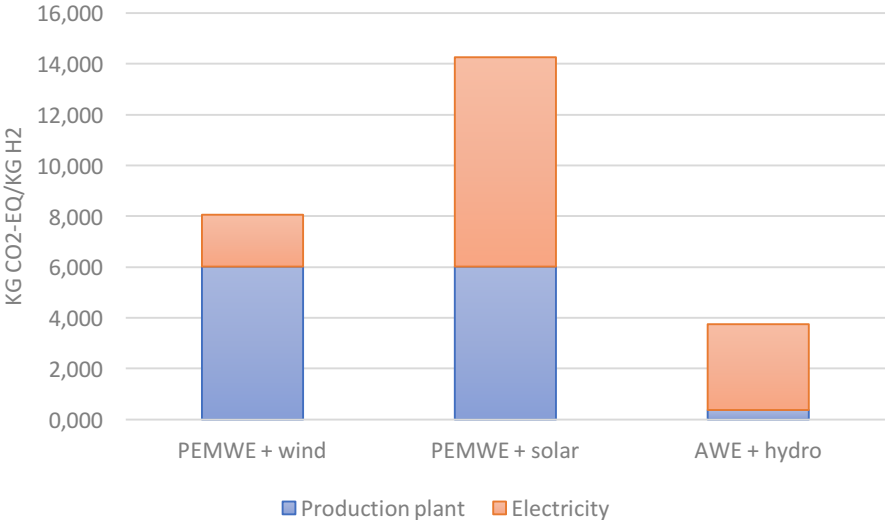
Figure 24 illustrates that neither alkaline nor PEM water electrolysis is an alternative that will contribute substantially to GHG mitigation, due to the high share of emissions that stems from electricity-use (78% and 98% respectively) and the GHG emission factor for European electricity production assumed in the applied EU energy scenario. An alternative to using the water electrolyzers to produce hydrogen directly off the European grid, is to use them specifically with renewable energy. The argument for why this is a good idea is that one of the drawback with most renewable energy is that it is hard to store, and the need for energy storage will become more important in the future.

Unlike the other systems studied in this thesis, the electrolysis is not dependent on biomass for the production of hydrogen. This makes it easier to have a production facility for hydrogen together with the electricity generation. The electrolyzers can then take advantage of some of the drawbacks with renewable power.



Wind power production has the disadvantage of being susceptible to large variations in the delivery of power. For economic reasons the energy transfer capacity from the wind farm to the grid is often below the maximum production capacity. There will thus be incidents when production is higher than the transfer capacity, and wind mills have to reduce production or in worst case be shut down temporarily (IER, 2016). By matching the wind farm with an PEM water electrolyzer, one can instead of shutting down wind mills rather use the excess electricity to produce hydrogen. This is possible with a PEM water electrolyzer, which can vary the load quickly to match the electricity production of the mills, unlike alkaline water electrolyzer (Aricò et al., 2013; Carmo et al., 2013). PEM water electrolyzer can also be supplied by electricity from photovoltaics as described in Jia et al. (2016). Alkaline water electrolyzer on the other hand, is best used with hydro power (Smolinka, Garche, Hebling, & Ehret, 2012).

Figure 25 shows PEM water electrolyzer supplied with solar and wind and alkaline water electrolysis supplied with hydro-electricity production. Both PEMWE supplied with wind electricity and AWE supplied with hydroelectricity do have emissions below the threshold of 12.2 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> which is the emissions from steam methane reforming. But only AWE supplied with solar PV is at the emission level close to biogas steam reforming, gasification and fermentation.



**FIGURE 25 – GHG EMISSIONS FROM PROTON EXCHANGE MEMBRANE WATER ELECTROLYSIS (PEMWE) AND ALKALINE WATER ELECTROLYSIS (AWE) WITH ELECTRICITY GENERATED FROM WIND-, SOLAR-, AND HYDRO POWER**

#### 4.2.2 Ammonia

Several of the processes included in this study involves the use of ammonia. For the case of short rotational woody crops ammonia is used through fertilizers, and for the case of dark fermentation it is used to keep the pH-level of the fermentation stable. As explained in the subsection Biomass feedstock, the main input to ammonia production is hydrogen, and secondly the electricity. By assuming that there will be a large-scale hydrogen production in Europe, bio-hydrogen or hydrogen from renewable water electrolysis can be used as feedstock and an emission reduction can be accomplished. This will again have a positive feedback on the emissions per kg hydrogen produced.

The combination of dark- and photo fermentation is currently the most ammonia intense production method, with an emission of 0.32 kg CO<sub>2</sub>-eq from dark fermentation and 0.61 kg CO<sub>2</sub>-eq from the use of nitrogen based fertilizer. Ahlgren et al. (2008) have compared regular ammonium nitrate fertilizer production with fossil gas with the alternative of using straw and short rotational crops (willow) as hydrogen source (Ahlgren et al., 2008). The result was an overall GHG emission reduction of 70% and 78% for willow and straw respectively. Applying these results to the use of ammonia and fertilizer for dark fermentation, a reduction of 0.65 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> can in theory be accomplished, resulting in an overall reduction of 12%; while for the case of biogas steam reforming, with a nitrogen based fertilizer use with an emission of 0.52 kg CO<sub>2</sub>-eq per kg H<sub>2</sub>, a reduction of 14% can be accomplished.

#### 4.2.3 Hydrogen production capacity for Europe

I have in this thesis calculated the GHG-emissions per kg H<sub>2</sub> for several production methods, both with the use of biomass, and with the use of water electrolysis. To estimate how much bio-hydrogen can be produced in Europe by 2050 I have chosen to look at the potential for (1) dedicated bio-energy crops, (2) the combination of agricultural residues, animal manures and municipal solid waste (MSW), and (3) biomass residues from forestry. To estimate hydrogen production from electrolysis, I have chosen to couple PEM water with off-shore and on-shore wind power, and photovoltaics, as discussed in Jia et al. (2016). Alkaline water electrolysis is assumed to be used together with hydro power as augmented in the above chapter.

Today, global bio-energy accounts for approximately 10% of the humanity’s primary energy, with a total figure of 50 EJ per year (Haberl, Beringer, Bhattacharya, Erb, & Hoogwijk, 2010). By means of reviewing current estimates for bio-energy for the world towards 2050, Haberl et al. provides an estimate of 24 EJ per year as a technical potential for Europe for the three biomasses discussed in the previous paragraph. The technical potential, meaning how much biomass is available if all available biomass is used. The report discusses the technical potential for biomass globally with disaggregation down to Western Europe and Central plus East Europe. For the energy crops a conservative estimate is used due to the competing nature of energy crops versus crops for animal and human food (Haberl et al., 2010). The technical potential for biomass from dedicated bio-energy crops, agricultural residues, animal manures, municipal solid waste and biomass residues from forestry for Europe in 2050 is shown in Table 18.

**TABLE 18 - TECHNICAL POTENTIAL FOR BIOMASS IN EUROPE FOR 2050 (HABERL ET AL., 2010)**

	<b>Energy crops</b>	<b>Crop residues</b>	<b>Municipal solid waste</b>	<b>Animal manures</b>	<b>Forest residues</b>	<b>Unit</b>
West Europe	5	3	1	3	6	EJ/yr
Central + East Europe	2	1	0	1	2	EJ/yr
Total in Europe	7	4	1	4	8	EJ/yr
Share	29 %	17 %	4 %	17 %	33 %	

The chosen hydrogen production techniques for converting the biomass potential in Table 18 are biogas steam reforming, gasification and dark- and photo fermentation, hereby abbreviated as fermentation. Dark fermentation together with MEC has been excluded due to the high emission in comparison to dark- and photo fermentation, while serving the same function. Both gasification and biogas steam reforming is included since gasification works well on moist biomass, while biogas steam reforming enables for more efficient transport. Table 19 shows the biomass requirement for hydrogen production, and the associated emissions of greenhouse gasses.

**TABLE 19 - DATA ON BIOMASS REQUIREMENT AND EMISSIONS FROM BIO-HYDROGEN PRODUCTION**

	<b>Steam reforming</b>	<b>Fermentation</b>	<b>Gasification</b>	<b>Unit</b>
Biomass energy per kg H <sub>2</sub> <sup>a)</sup>	261	308	231	MJ/kg
Emission <sup>b)</sup>	2,67	5,25	5,55	kg CO <sub>2</sub> /kg H <sub>2</sub>

<sup>a)</sup> adjusted for LHV of 18.5 MJ instead of used 19.32 MJ

<sup>b)</sup> using 50% SRWC and 50% forestry residues as biomass feedstock

When assessing which hydrogen production method to use on which biomass feedstock there is only one feedstock that is method specific, namely, animal manure, which can only be produced with fermentation Guo, Trably, Latrille, Carrère, and Steyer (2010). In principle, this means that one can use the manure in an anaerobic digestion, which is nearly the same process as dark fermentation, and then use the resulting biogas for steam reforming. In this thesis, it is though assumed that fermentation is used to produce hydrogen from animal manure. Gasification is chosen for municipal solid waste and forest residues, due to the probability for high moist content. Biogas steam reforming is assumed to use the rest of the biomass. The technical potential for bio-hydrogen following the technical potential for biomass for 2050, using the above-mentioned production methods, is 92.9 megaton hydrogen per year.

To look at the potential for hydrogen production through electrolysis of hydrogen with renewable energy, EUs Reference Scenario is used to look at the available generated renewable electricity for 2050. It is assumed a total of 3900 TWh net electricity, with a 11% share from solar, 25% from wind and 11% from hydro, shown in Table 20.

**TABLE 20 – SHARE OF ELECTRICITY GENERATION IN 2050 FOR EUROPE**

	<b>Solar PV</b>	<b>Wind</b>	<b>Hydro</b>	<b>Unit</b>
Share of electricity generation	11	25	11	%
Absolute generation	429	975	429	TWh/yr

When assessing the technical potential to produce hydrogen by means of electrolysis of water supplied with renewable energy, the question is not how much electricity that is available for hydrogen production, but rather how much one is willing to use, and if there is a potential for

using electricity that is not used for other purposes. It is thus assumed that PEM water electrolysis is used to generate hydrogen from surplus electricity from wind power, and assumed to exploit 1% extra electricity. PEM water electrolysis together with solar PV is used as explained in discussed in Jia et al., 2016. This method is not assumed to be done in a large scale, but instead work as smaller fuel stations to cover the entire road network. It is also assumed that this is 1% of the total solar PV production. Hydro power is used together with alkaline water electrolyzer to constantly produce hydrogen by using a lesser amount of available capacity, and is assumed to be 1%. The resulting yearly production capacity of 93.9 megaton hydrogen for Europe is displayed in Table 21, assuming that the entire available biomass is used for hydrogen production, and that 1% of generated electricity from solar, wind and hydro is used for hydrogen production. The resulting average emission for hydrogen produced in Europe by 2050 is 4 kg CO<sub>2</sub>-eq per kg H<sub>2</sub>.

**TABLE 21 – YEARLY HYDROGEN PRODUCTION POTENTIAL FOR EUROPE IN 2050**

	<b>BSR</b>	<b>Gasification</b>	<b>Fermentation</b>	<b>PEMWE</b>	<b>AWE</b>	<b>Unit</b>
Production potential	42,10	37,81	12,99	0,20	0,06	M t/yr
Share of production	45,2 %	40,6 %	13,9 %	0,2 %	0,1 %	%

#### 4.2.4 Hydrogen as fuel for road freight transportation

There are four ways of transportation, namely, on road, in air, by sea or rails, and you can either transport goods or people. Both transportation by sea and rails usually have low emissions today, making it not that interesting to study, and air transportation by hydrogen is not a viable option today. That leaves me with road transportation. In the decision between personal transportation and freight transportation I choose freight. For private cars, the alternative of using electric cars with battery is calculated to have a good potential for GHG emission reduction (Ellingsen et al., 2016). While for freight transport the use of battery weight and charging might pose as a real issue. Road freight transport is also the freight transport with the highest emission per tkm if you exclude airplanes (Simonsen, 2010). It also exists in all European countries and the technology is emerging through Nikola One, a fuel cell semi-truck, and others.

#### 4.2.5 Life cycle assessment of Nikola One

To assess the potential GHG emission reduction of freight transport I have completed a life cycle assessment the fuel-cell semi-truck Nikola One. The Nikola One will in few years be one of the first hydrogen driven semi-truck in the world, but have already data available to do a coarse LCA. The LCA have been done by using LCA results from the work of two fellow students at the master's degree programme Industrial Ecology at NTNU Norway, namely, Windsheimers (2016) and Raabe (2017). To assess the potential emission reduction the Nikola One is compared to a semi-truck with a payload above 11 tons based on Simonsen (2010). For the infrastructure, I assume that is the same for both the hydrogen and fossil fuel system.

**TABLE 22 – LIFE CYCLE GHG EMISSIONS PER TKM FOR FREIGHT TRANSPORT FUELED WITH HYDROGEN AND DIESEL**

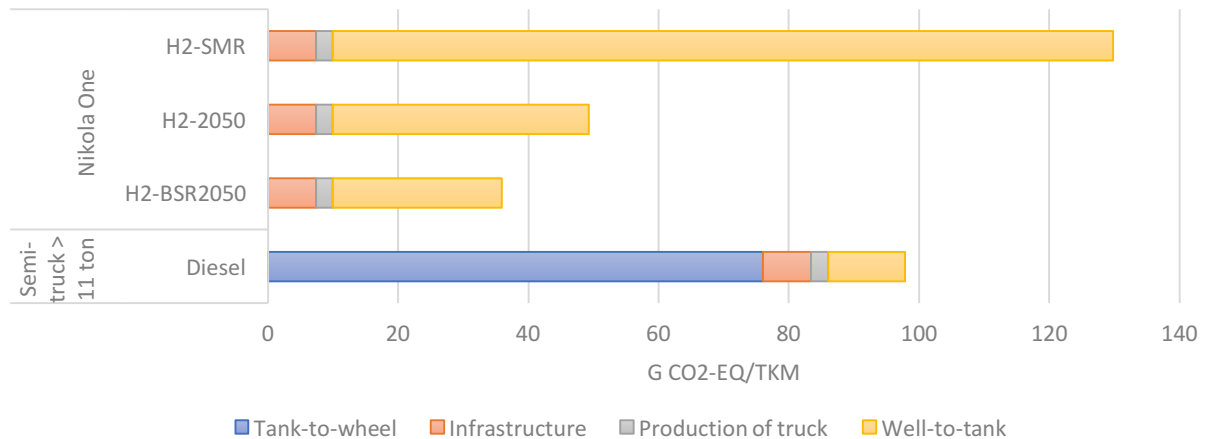
<b>Fuel</b>	<b>Tank-to-wheel</b>	<b>Infrastructure</b>	<b>Production</b>	<b>Well-to-tank</b>	<b>Sum</b>	<b>Unit</b>
H <sub>2</sub> -2050 <sup>a)</sup>	0,00	7,38	2,59	39,30	49,27	g CO <sub>2</sub> eq/tkm
H <sub>2</sub> -BSR <sup>b)</sup>	0,00	7,38	2,59	25,94	35,91	g CO <sub>2</sub> eq/tkm
H <sub>2</sub> -SMR <sup>c)</sup>	0,00	7,38	2,59	119,85	129,81	g CO <sub>2</sub> eq/tkm
Diesel <sup>d)</sup>	76,00	7,38	2,69	11,81	97,88	g CO <sub>2</sub> eq/tkm

<sup>a)</sup> The calculated hydrogen mix for 2050 (4 kg CO<sub>2</sub>-eq/kg H<sub>2</sub>)

<sup>b)</sup> Hydrogen from biogas steam reformation for 2050 (2.8 kg CO<sub>2</sub>-eq/kg H<sub>2</sub>)

<sup>c)</sup> Hydrogen from methane steam reforming today (12.2 kg CO<sub>2</sub>-eq/kg H<sub>2</sub>)

Figure 26 shows graphically the results from Table 22. The emissions on a tkm basis can be reduced with 51% compared to a regular fossil semi-truck of today, given the average European emission of 4 kg CO<sub>2</sub>-eq per kg H<sub>2</sub>. A best-case scenario of hydrogen from biogas steam reforming for 2050 (2.8 kg CO<sub>2</sub>-eq/kg H<sub>2</sub>) and worst-case methane steam reforming today (12.2 kg CO<sub>2</sub>-eq/kg H<sub>2</sub>) is shown as well.



**FIGURE 26 – GHG-EMISSIONS FOR NIKOLA ONE FUELED BY HYDROGEN FROM STEAM METHANE REFORMING (H<sub>2</sub>-SMR), BIOGAS STEAM REFORMING IN 2050 (H<sub>2</sub>-BSR2050), THE HYDROGEN MIX OF 2050 (H<sub>2</sub>-2050) AND A SEMI-TRUCK FUELED BY DIESEL**

#### 4.2.6 Hydrogen production capacity of 2050

Today the road freight transport is at 1 768 billion tkm a year (Eurostat, 2016), and Capros et al. (2016) estimate a 57% increase in road freight transport by 2050. Capros et al. (2016) also predicts a reduction in specific fuel consumption by 23%. Given these data, I calculated a yearly consumption of 21 megatons of hydrogen, if the entire road freight transport fleet were to switch to hydrogen. By reference, this is 23% of the estimated hydrogen production capacity of Europe by 2050. I thus assume that Europe has the capacity to cover the entire demand for hydrogen used as fuel for road freight transport. Key data can be seen in Table 22.

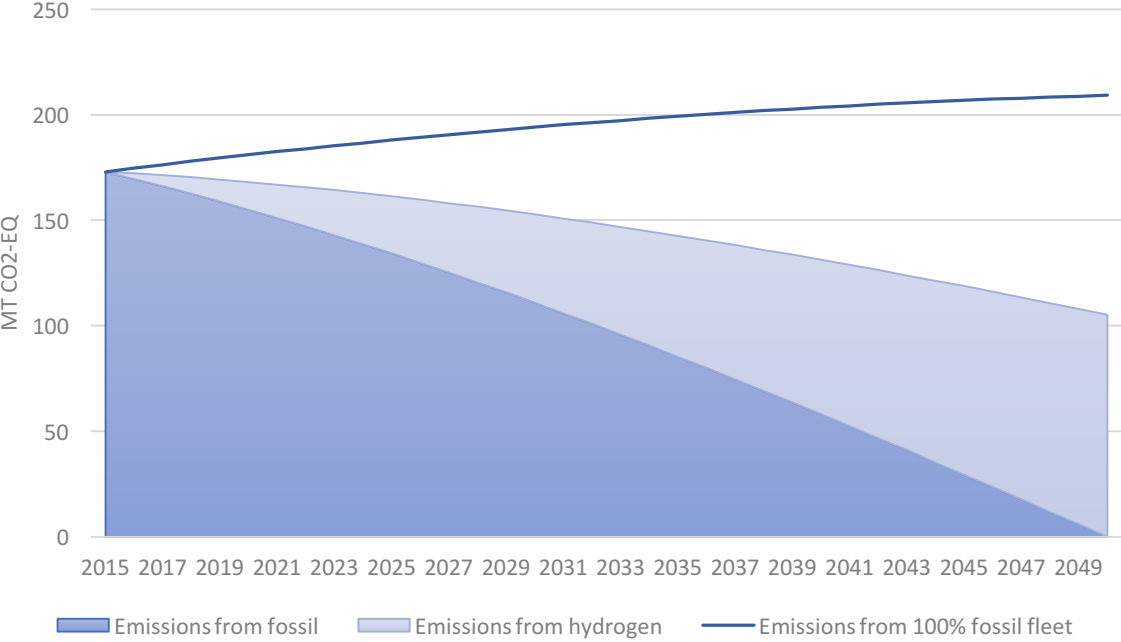
**TABLE 23 - FREIGHT TRANSPORT ON ROAD IN EUROPE BY 2050**

Data	Value	Unit
Freight road transport in Europe - 2015 <sup>a)</sup>	1 768 908 000 000	t*km/year
Estimated freight road transport in Europe – 2050	2 775 620 000 000	t*km/year
Hydrogen consumption for a Nikola One - 2050 <sup>b)</sup>	7.6	g H <sub>2</sub> /tkm
Hydrogen to cover freight road transport in Europe - 2050	21 000 000 000	kg H <sub>2</sub> /year
Hydrogen production capacity for Europe - 2050	93 200 000 000	kg H <sub>2</sub> /year

<sup>a)</sup> (Eurostat, 2016)

<sup>b)</sup> Assume 23% hydrogen consumption reduction by 2050 (Capros et al., 2016)

Figure 27 shows the potential for GHG emission reduction in Europe towards 2050, by gradually increasing the share of hydrogen fueled semi-trucks for freight transport. The blue line represents the emission pathway if the road freight transport fleet keep using fossil fuels. The dark area displays the emissions from the fossil part of the fleet, while the light area represents the emissions from hydrogen fueled transports towards 2050, with a gradual increase in the share of hydrogen trucks. For all trajectories, it is assumed a gradual increase in fuel efficiency towards 23% in 2050, and a gradual increase in tonne-kilometre (tkm) towards 57% in 2050. Emissions from fossil freight transport is based on data for emissions per tkm from Simonsen (2010), and then multiplied with the demand for tkm in Europe. Compared to today, there is a reduction of 45% in GHG emissions per year, by using hydrogen as fuel for freight transport. The percentage reduction, compared to a scenario with no hydrogen fueled transport is at 54%.



**FIGURE 27 – GHG EMISSION EVOLVEMENT FOR ROAD FREIGHT TRANSPORT TOWARDS 2050, WITH A GRADUALLY INCREASE OF HYDROGEN SEMI-TRUCKS**

### 4.3 Uncertainties in the calculations

I have not done a quantitative sensitivity analysis to investigate uncertainties, like a Monte Carlo simulation, for this thesis. Instead a more qualitative analysis of uncertainties is performed in this section. First, I present a list of all the key inputs to the inventory, and then discussing them in short. A more thorough discussion for the different parts of the inventory is



made in chapter 3 - Materials and methods. Then a short discussion on the parts that has not been included in the inventory follows. At last a discussion on the uncertainties around the scenario analysis of 2050 is presented.

For the inventory, I have chosen to grade the different materials and processes on both uncertainty and consequence. The scale is in this order: little, some, much. The uncertainties evaluations are made based on available data, data quality, grade of relevance and age. For the consequence evaluation use of electricity and heat, is generally seen as having potentially much consequences. Transport, biomass use, and process materials as some consequence and construction as little consequence.

#### 4.3.1 Inventory

Inventory includes both the values used in the inventory, and the process of LCA, with its databases and calculations.

##### *LCA framework*

- **Ecoinvent database.** The Ecoinvent database is the most commonly used database for life cycle assessments. The data used in this study is assumed to be on a European level, with little detail.
  - Uncertainty: little/some
  - Consequence: some
- **ReCiPe.** ReCiPe is used to allocate emissions to different impact categories. For this study, the only impact category used is climate change, which is well represented in ReCiPe.
  - Uncertainty: little
  - Consequence: some

##### *Biomass Feedstock*

- **Inventory data** obtained from Gibon et al. (2017). It is not accounted for potential land use change related emissions or the difference in timing between the emissions of CO<sub>2</sub> and its uptake in Gibon et al. (2017). The entire data set is converted from Ecoinvent 2.2 to 3.2. with similar processes, and thus low uncertainty.
  - Uncertainty: little

- Consequence: much
- **Formula on LHV.** Obtained from The Wood Fuels Handbook by Krajnc (2015)
  - Uncertainty: little
  - Consequence: some

#### *Anaerobic digestion as pretreatment for BSR*

- **Process data.** Based on Sawatdeenarunat et al. (2015)
  - Uncertainty: little
  - Consequence: little
- **Anaerobic digestion plant.** Input from Ecoinvent.
  - Uncertainty: little
  - Consequence: little
- **Methane yield from biomass.** Methane yield on the basis of lignin, cellulose and hemicellulose content from lignocellulosic biomass is given Sawatdeenarunat et al. (2015). None of the used biomass feedstocks I used were represented in the table, but wheat straw had values close to the once in the table.
  - Uncertainty: some
  - Consequence: some

#### *Biogas steam reforming*

- **Production plant.** Based on M. Granovskii et al. (2006), Lombardi et al. (2011) and Boyano et al. (2011), with similar values for inputs. M. Granovskii et al. (2006) bases the entire production plant inventory on Spath and Mann (2000), while Lombardi et al. (2011) bases some of the inventory on Spath and Mann (2000), which can explain some of the similar values.
  - Uncertainty: some
  - Consequence: little
- **Biogas.** Based on the three data sources that use fossil gas, namely, Susmozas et al. (2013), Wulf and Kaltschmitt (2013) and Lombardi et al. (2011), and Wulf and Kaltschmitt (2013) that uses biomethane. The reported values have low variation.
  - Uncertainty: little
  - Consequence: much

- **Electricity.** Low detail on what processes that use electricity. Large percentage variation on electricity use. Also, high variation on what electricity mix that is chosen.
  - Uncertainty: some/much
  - Consequence: much
- **Fossil gas.** Only three out of eight data sources use fossil gas for steam, the rest uses biomass and biogas. The values are varying, due to different uses of the gas, and not enough data detail. The numbers are still coherent with another, given the different uses of the gas. Sources: Susmozas et al. (2013) Markevich et al. (2002) and Q. Dai (2016).
  - Uncertainty: some
  - Consequence: much
- **Process materials.** Susmozas et al. (2013) is used as source for the steam reforming itself, while Strømman and Hertwich (2004) is used for the other needed processes for steam reforming. Strømman and Hertwich (2004) do not model a steam reforming facility, while instead a autothermal reforming facility, which have the same processes before and after the reforming, as steam reforming.
  - Uncertainty: little
  - Consequence: little
- **Direct emissions.** Only one source for each of the emissions, except for biogenic carbon dioxide, which Susmozas et al. (2013), Lombardi et al. (2011) and Wulf and Kaltschmitt (2012) all report data.
  - Uncertainty: some
  - Consequence: little

### *Biomass gasification*

- **Production plant.** The only data source available, Kalinci et al. (2012), uses a secondary source, Mikhail Granovskii et al. (2006), which again base the calculation on an adjusted inventory of a methane steam reformer from Spath and Mann (2000).
  - Uncertainty: some
  - Consequences: little
- **Biomass.** Data availability is good, but six out of seven reported values from the data sources had to be converted from kg biomass to MJ biomass. The conversion is a source of error. Then an average of the calculated amount of MJ biomass was used, which also is a source of error.

- Uncertainty: some
- Consequence: some
- **Electricity.** Four of the six reported values for electricity consumption was close to each other. The two outliers have been argued that can be ignored for the calculation of electricity consumption.
  - Uncertainty: little
  - Consequence: much
- **Fossil gas.** Only one out of nine data sources have specific data on use of fossil gas for heating. Six sources use biomass, one uses fossil gas as a supplement and the last has no data on the use of gas. The result is that the fossil gas use of Moreno and Dufour (2013) is used.
  - Uncertainty: some
  - Consequence: much
- **Process materials.** The inventory is based on Weinberg and Kaltschmitt (2013), Bartolozzi et al. (2013) and Strømman and Hertwich (2004). All the inputs except sodium hydroxide have only one data source. Olivine has not been found in Ecoinvent, but is not assumed to have a major contribution.
  - Uncertainty: some
  - Consequence: little
- **Direct emissions.** Four sources on emissions, and the most severe emissions assumed to be biogenic, but the sources both report different species and emission. It is also assumed that the methane emission can be excluded from the emission inventory, and instead be used as heat source.
  - Uncertainty: some
  - Consequence: some

#### *Dark fermentation and photo fermentation*

- **Production plant.** Only Djomo et al. (2008) as source for the size of the bioreactor and the photoreactor. None of sources had data on construction of the reactors. Inventory of a smaller bioreactor from Ioannou-Ttofa et al. (2016) had to be scaled to fit the bioreactor in Djomo et al. (2008). For the photoreactor the plastic pipes used in Bosma et al. (2014) was scaled to fit Djomo et al. (2008). The rest of the photoreactor has not been modeled.

- Uncertainty: some
  - Consequence: little
- **Biomass.** To do calculations on biomass, all biomass had to be adjusted to the amount of available glucose for each biomass. The conversion rates were from two different sources and the total glucose content in the biomass was calculated, with values varying from 3.14 to 9.73. It is not expected that these values would be equal, but the span might lead to potential errors, since biomass has a fair share of the emissions.
  - Uncertainty: some
  - Consequence: some
- **Electricity.** The three different data sources Djomo et al. (2008), Manish and Banerjee (2008) and Djomo and Blumberga (2011) are used. They range from 1.42 kWh up to 9.3 kWh, without being able to explain the variety. This leads to uncertainty, and electricity has as stated much potential for consequence.
  - Uncertainty: some/much
  - Consequence: much
- **Fossil gas.** The two sources Djomo and Blumberga (2011) and Q. Dai (2016) report similar consumption, and the average is used.
  - Uncertainty: little
  - Consequence: much
- **Process materials.** Only ammonia as input. I use the average of two sources.
  - Uncertainty: little
  - Consequence: some
- **Direct emissions.** Three sources of biogenic CO<sub>2</sub>, with similar values. The average has been used.
  - Uncertainty: little
  - Consequence: little
- **Pretreatment.** Three sources for pretreatment: Ntaikou et al. (2010), Djomo and Blumberga (2011) PI et al. (2016). Only NaOH is reported by all sources. The rest of the materials are based on PI et al. (2016).
  - Uncertainty: some
  - Consequence: little

### *Dark fermentation and microbial electrolysis cell*

- **Production plant.** Two sources available for construction of microbial electrolysis cell. Foley et al. (2010) gives data on the entire cell and stack, while Manish and Banerjee (2008) only gives data on platinum. Data on dark fermentation is assumed to be the same as reported in dark fermentation and photo fermentation.
  - Uncertainty: some
  - Consequence: little
- **Biomass.** I assume the same as for dark fermentation and photo fermentation.
  - Uncertainty: some
  - Consequence: some
- **Electricity.** I only use PI et al. (2016) as source for electricity for dark fermentation and MEC. The value seems reasonable.
  - Uncertainty: some
  - Consequence: much
- **Fossil gas.** I assume the same consumption of fossil gas as for dark fermentation and photo fermentation.
  - Uncertainty: little
  - Consequence: much
- **Process materials.** No process data except ammonia for dark fermentation. I assume the same values as for dark fermentation and photo fermentation.
  - Uncertainty: little
  - Consequence: some
- **Direct emissions.** As for dark fermentation and photo fermentation, its only biogenic carbon dioxide emissions. I have only Djomo et al. (2008) as source.
  - Uncertainty: some
  - Consequence: little
- **Pretreatment.** I assume the same as for dark fermentation and photo fermentation.
  - Uncertainty: some
  - Consequence: little

### *Proton exchange membrane water electrolyzer*

- **Production plant.** All the data is based on Smolinka et al. (2016). It is only data for the most cost intensive materials for the stack. These materials are assumed to be the ones with the most impacts, but still leads to a uncertainty due to data availability.

- Uncertainty: some
- Consequence: much
- **Electricity.** The reported energy consumption for a PEMWE varies from 50.1 kWh/kg H<sub>2</sub> to 83.4 kWh/kg H<sub>2</sub> (Carmo et al., 2013). For calculations 72 kWh per kg of hydrogen produced is chosen. An upper high value has been chosen for reported energy consumption since this assessment is generic. The results will therefore not be a worst case, but still put a lot of emphasis in the electricity.
  - Uncertainty: little
  - Consequence: much

Table 24 visualizes the different uncertainties multiplied with the consequence. Electricity is clearly the common parameter with the largest potential for wrong emission values. Both electricity and fossil gas gets high values due to a potentially high consequence.

**TABLE 24 – VISUALIZATION OF UNCERTAINTY MULTIPLIED CONSEQUENCE FOR THE INVENTORY DATA**

	<b>Production plant</b>	<b>Biom ass</b>	<b>Electri city</b>	<b>Fossil gas</b>	<b>Process materials</b>	<b>Direct emissions</b>	<b>Pretreat ment</b>
BSR	1	3	7,5	6	1	2	2,25
Gasification	2	4	3	6	2	4	
DF + PF	2	4	7,5	3	2	1	
DF + MEC	2	4	6	3	2	2	2
PEMWE	6		3				

*Excluded inventory data*

- **Transport.** Transport is usually a part of the inventory with a potential for high impact. For this study transport data has been hard to find, and thus excluded.
  - Consequence: some
- **End of life.** Data on end of life has not been able to acquire for this thesis. The consequence for the studied impact category of climate change is not expected to be much, but for other impact categories it can be of greater concern.
  - Consequence: little

#### 4.3.2 Scenario analysis

- **Electricity mix.** The electricity for 2050 is based on Capros et al. (2016) – EU Reference Scenario. The goals for the electricity mix is quite ambitious, but it is based on what the different countries of EU think themselves. Capros et al. (2016) does not give a number on the how much the emissions will go down per kWh, which is what is needed for this thesis. Instead a, electricity generation mix is shown in Chapter 3 – Methods and materials, 2050 scenario for Europe. To go from the mix, to an emission per kWh, I had to use emission data for the different electricity sources, to match with the estimated generation. I used Ecoinvent-processes from Germany to represent all the different electricity sources. These numbers are valid for today, but for a future scenario they might be too high. For example, is the value for solar PV at over 114 g CO<sub>2</sub>-eq per kWh, while we already have data from de Wild-Scholten (2013), saying that the emissions can be as low as 15.8 g CO<sub>2</sub>-eq per kWh in a life cycle perspective. From the LCA its seen that the use of electricity is one of the largest emissions factors for several of the hydrogen production methods. The uncertainty connected to the emissions from the electricity mix is thus a substantial factor for the total emissions from hydrogen. Since the goal of this assessment is not to precisely calculate the GHG emissions of 2050, but rather to give an estimate on the potential the use of electricity mix data from Capros et al. (2016) is good enough for this thesis.
- **Technical potential for biomass.** As source for the technical potential Haberl et al. (2010) is used. The paper evaluates other research on technical potential for different parts of the world, and calculates a new proposal on the basis of these. By showing estimates for both West Europe, and East and South Europe, it's evident that the data detail is good enough for this thesis. Haberl et al. (2010) also states that the estimates for short rotational crops, which can in theory compete with animal and human food, are conservative, to be sure to only use land and resources that is not used by any else. For the residues and waste estimates are not being that conservative, but rather showing the potential. For hydrogen production, or any other use, it is not possible to say that the estimated potential of 24 EJ per year is actually economically usable, but since that is not a part of the task it is not an issue. And since the need for hydrogen to road freight transportation only would need 23% of the technical potential is might actually be possible.



- **Increased fuel efficiency.** Capros et al. (2016) assumes an increased fuel efficiency of 23% for Europe in 2050 in EU Reference Scenario. I have assumed the same efficiency increase for hydrogen based transportation. To assume this factor for hydrogen as well might not be such a bad assumption, since the focus on fuel cells has increased, and that one improves fuel efficiency over time in general.
- **Transport demand.** The estimated increase in transport demand is based on Capros et al. (2016). Even though the demand factor will change the absolute emissions in the scenario for 2050, it would probably not influence a decision making on the basis of this thesis. This is because the relative differences between the fossil emission pathway versus the shifting towards hydrogen will be the same, independent of the transport demand.
- **GHG emission intensity for freight transport.** By basing the entire calculation of emissions from fossil road freight transportation on Simonsen (2010) the possibility for not representing the entire fleet is present. But since I only use data on the road freight transport with the lowest emission by using a semi-truck with a payload capacity above 11 tons, the emissions might be in the lower part of the scale. This means that the actual potential might be even better.
- **Nikola One.** The LCA of the Nikola One was not done in the proper way, as a LCA should be done. Instead of gathering inventory from different sources and put them together, I have rather borrowed results from the project thesis of Max Windsheimer and the master thesis of Erlend Brenna Raabe. I supplied them with data on the Nikola One, shown in Table 16, Chapter 3 – subsection Life cycle inventory of a hydrogen semi-truck. They did the calculations with their own data, and scaled according to the specs of Nikola One. Another factor that might affect these results is that Nikola reports a lifetime of 1 600 000 km and a freight capacity of 36 tons. These numbers have not yet been tested, and for my calculations I assumed that all of the 36 tons of payload was used at all times during the lifetime. I did not do calculation on needed infrastructure for the hydrogen system, besides the production of the hydrogen. I assume that the biggest fraction is due to fuel production, but storage and transport of hydrogen might also have big impacts due to the volatile nature of hydrogen.

## 5 Conclusion

Hydrogen has been proposed as a way of mitigating climate change by using it as fuel for transportation. The use of hydrogen has no other direct emission than water, but the production of hydrogen today is 96% fossil, thus resulting in a high amount of GHG-emissions. I have studied five potentially climate friendly hydrogen production methods by means of applying a life cycle assessment, and conducted a scenario analysis.

The *first* research question of this thesis is: **What is the potential for climate friendly hydrogen production in Europe towards 2050?** My initial calculations show that several of the hydrogen production methods have the potential of attaining a lower emission per kg H<sub>2</sub>, than the leading methods of today (12.2 kg CO<sub>2</sub>-eq/kg H<sub>2</sub>). The most promising production methods of hydrogen from biomass: biogas steam reforming, gasification, and dark- and photo fermentation also have an average of 39% emission reduction potential towards 2050. This is due to an anticipated future situation with lower emissions from the European electricity mix in combination with a technical shift from using fossil gas to biomass as energy source for heat and steam producing in the process of producing hydrogen. By using the most promising methods of hydrogen production, in combination with an assumption of maximum availability of biomass for producing hydrogen, a yearly production of 93 200 000 tons hydrogen can be achieved with an average emission of 4 kg CO<sub>2</sub>-eq per kg was calculated.

The *second* research question is: **What is the GHG mitigation potential by using hydrogen as fuel for road freight transport in Europe in 2050?** By applying hydrogen with an average emission of 4 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> as fuel for road freight transportation, and by using a Nikola One semi-truck, life cycle results show a potential of 50 % reduction in GHG-emissions on a 1 tonne-kilometre basis compared to the standards of today of 100g CO<sub>2</sub>-eq per tkm. By converting the entire EU truck fleet to run on hydrogen, and assume a 57% increase in tonne-kilometre demand from 2015 towards 2050, the estimated theoretical emission reduction in relative terms a 45% decrease in GHG emissions compared to today, and a 54% GHG reduction compared to a scenario with only fossil fuels in 2050.

### 5.1 Hydrogen from biomass

Out of the four hydrogen production methods that use biomass as hydrogen source, biogas steam reformation, gasification and dark fermentation in combination with photo fermentation gives the most promising results in a 2050 perspective, with emissions of 2.6, 4.9 and 5.5 kg CO<sub>2</sub>-eq respectively – as compared to 2015 emission figures of 3.9, 10.8 and 7.9 kg CO<sub>2</sub>-eq respectively, all of which are per kg hydrogen. Dark fermentation together with microbial electrolysis cell has an emission of 8.9 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> in 2050, which is not much better than steam methane reforming of fossil gas today.

### 5.2 Hydrogen from water electrolysis

Proton exchange membrane water electrolysis (PEMWE) has an emission of 40 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> given today's European electricity mix, and 27.3 kg CO<sub>2</sub>-eq with a European electricity mix of 2050. This makes the production methods less relevant, since they cannot produce hydrogen with sufficiently low emissions. To reduce the emissions, PEMWE can be supplied with renewable energy. Hydrogen produced with electricity from wind energy has an emission of 8 kg CO<sub>2</sub>-eq. This is quite high, compared to biogas steam reforming (2.8 kg CO<sub>2</sub>-eq). The reason for still considering PEMWE for hydrogen production is that it is, opposed to alkaline water electrolyzer (AWE), able to handle a variable load and can thus take advantage of electricity from a wind power plant with variable output, and work as an energy battery. AWE can on the other hand be used supplied with electricity from hydro power, resulting in an emission of 3.9 kg CO<sub>2</sub>-eq per kg H<sub>2</sub>.

### 5.3 The hydrogen production mix of 2050

A technical estimate for 2050 of the available biomass from short rotational woody crops, and different sorts of biomass residues shows that the technical potential for hydrogen from biomass is 92 900 000 tons of hydrogen per year. This calculation is, among other preconditions, based on the assumption that 1% of electricity from solar PV, hydropower and wind power in Europe will be used as distributed hydrogen production through water electrolysis, as an alternative in places where bio-hydrogen is hard to produce, or too far away to transport. The total potential for environmental friendly hydrogen production in Europe per year is then calculated to be 93 200 000 tons. This figure is based on the assumption that the share of hydrogen from biomass is close to 100%, leaving only 0,3% to water electrolysis. This European hydrogen production mix has an average emission of 4 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> for 2050.

## 5.1 The 2050 potential for GHG emission mitigation in road freight transport

I have chosen to illustrate the partial application of hydrogen as a means for mitigating climate change by analysing the potential mitigation potential of shifting from fossil to hydrogen fuel in road freight transportation. This is done by comparing a theoretical full substitution of the current composition of trucks by a standardised hydrogen truck - the Nikola One – and assumed that the whole fleet is fueled by my estimates for 2050 European hydrogen hydrogen-mix (4 kg CO<sub>2</sub>-eq). The calculations show an emission reduction potential of 51% per tonne-kilometre compared to a 2015 version of a fossil fueled semi-truck. To convert by 2050 the entire European road freight transport fleet over to hydrogen would imply a yearly production of 21 000 000 tons hydrogen, also taking into account an assumed 57% increase in tonne-kilometer per year by 2050 compared with 2015. This is 23% of the technical potential for bio-hydrogen production per year, meaning that a full conversion is technically possible concerning fuel production.

## 5.2 Final remarks and further research

As I have presented in this thesis, there is a large potential for climate friendly hydrogen production, and there is a large potential for achieving large GHG emission cuts in freight transportation by shifting from fossil to hydrogen. However, the extent that this potential is realized is dependent on the choice of method for producing hydrogen, the achieved level of GHG emission reduction per kWh of electricity used to produce hydrogen, and finally a conversion from using fossil gas, to using biomass as energy source for heat and steam. The technical potential for biomass is large enough to at least cover the fuel consumption of road freight transport. With the help of strategically placed water electrolyzers, both PEMWE and AWE, using renewable energy, a complete hydrogen fuel system can be developed. By using this system for road freight transport, there is a potential for GHG emission reduction, compared to freight transport of today.

To improve the quality of the results from this thesis, more detailed data on inventory have to be acquired, including transportation and end-of-life, and uncertainties around the use of fossil gas and electricity have to be reduced. Other impact categories than climate change should also be studied to get a better foundation for decision making. For production methods, specially PEMWE has to be studied more in detail, since the data availability is not sufficient as is. An

assessment in the potential improvements for PEM, concerning both material use and electricity use is also advised. An assessment of potential electricity use in the future for alkaline water electrolysis should also be done. To better be able to assess the effect of hydrogen fuel for freight transport, a more detailed LCA of the Nikola One and other fuel cell semi-trucks should be conducted.

For further research, more production methods, like the use of algae or high temperature electrolysis, and other pretreatment alternatives for steam reforming and dark fermentation, have to be included. The variety of biomass feedstocks have to be tested against the different production methods, to find the optimal one. And hydrogen must be tried to use as fuel for freight and personal transport at sea. The use of climate friendly hydrogen for ammonia and fertilizer production should also be further assessed. The potential for negative emissions through carbon capture and storage should also be investigated.

## References

A. Arvesen, G. L., M. Pehl, A.H. Strømman, E.G. Hertwich. (2016). Approaches and data for combining life cycle assessment and integrated assessment modelling (Version In preparation).

Afsar, N., Özgür, E., Gürkan, M., Akköse, S., Yücel, M., Gündüz, U., & Eroglu, I. (2011). Hydrogen productivity of photosynthetic bacteria on dark fermenter effluent of potato steam peels hydrolysate. *International Journal of Hydrogen Energy*, 36(1), 432-438.

Ahlgren, S., Baky, A., Bernesson, S., Nordberg, Å., Norén, O., & Hansson, P.-A. (2008). Ammonium nitrate fertiliser production based on biomass–environmental effects from a life cycle perspective. *Bioresource technology*, 99(17), 8034-8041.

Akkerman, I., Janssen, M., Rocha, J., & Wijffels, R. H. (2002). Photobiological hydrogen production: photochemical efficiency and bioreactor design. *International Journal of Hydrogen Energy*, 27(11), 1195-1208.

Appels, L., Lauwers, J., Degève, J., Helsen, L., Lievens, B., Willems, K., . . . Dewil, R. (2011). Anaerobic digestion in global bio-energy production: potential and research challenges. *Renewable and Sustainable Energy Reviews*, 15(9), 4295-4301.

Argun, H., & Kargi, F. (2010). Bio-hydrogen production from ground wheat starch by continuous combined fermentation using annular-hybrid bioreactor. *International Journal of Hydrogen Energy*, 35(12), 6170-6178.

Argun, H., & Kargi, F. (2011). Bio-hydrogen production by different operational modes of dark and photo-fermentation: an overview. *International Journal of Hydrogen Energy*, 36(13), 7443-7459.

Aricò, A., Siracusano, S., Briguglio, N., Baglio, V., Di Blasi, A., & Antonucci, V. (2013). Polymer electrolyte membrane water electrolysis: status of technologies and potential applications in combination with renewable power sources. *Journal of Applied Electrochemistry*, 43(2), 107-118.

Asadi, N., Alavijeh, M. K., & Zilouei, H. (2017). Development of a mathematical methodology to investigate biohydrogen production from regional and national agricultural

crop residues: A case study of Iran. *International Journal of Hydrogen Energy*, 42(4), 1989-2007.

Balat, M. (2008). Possible methods for hydrogen production. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 31(1), 39-50.

Barbir, F. (2005). PEM electrolysis for production of hydrogen from renewable energy sources. *Solar Energy*, 78(5), 661-669. doi:<http://dx.doi.org/10.1016/j.solener.2004.09.003>

Bartolozzi, I., Rizzi, F., & Frey, M. (2013). Comparison between hydrogen and electric vehicles by life cycle assessment: a case study in Tuscany, Italy. *Applied Energy*, 101, 103-111.

Bartzas, G., & Komnitsas, K. (2015). Life cycle assessment of ferronickel production in Greece. *Resources, Conservation and Recycling*, 105, Part A, 113-122. doi:<http://dx.doi.org/10.1016/j.resconrec.2015.10.016>

Basak, N., & Das, D. (2007). The prospect of purple non-sulfur (PNS) photosynthetic bacteria for hydrogen production: the present state of the art. *World Journal of Microbiology and Biotechnology*, 23(1), 31-42.

Belgiorno, V., De Feo, G., Della Rocca, C., & Napoli, R. (2003). Energy from gasification of solid wastes. *Waste management*, 23(1), 1-15.

Bilanzdija, N., Voca, N., Kricka, T., Matin, A., & Jurisic, V. (2012). Energy potential of fruit tree pruned biomass in Croatia. *Spanish Journal of Agricultural Research*, 10(2), 292-298.

Boboescu, I. Z., Ilie, M., Gherman, V. D., Mirel, I., Pap, B., Negrea, A., . . . Maróti, G. (2014). Revealing the factors influencing a fermentative biohydrogen production process using industrial wastewater as fermentation substrate. *Biotechnology for biofuels*, 7(1), 139.

Bonke, S. A., Wiechen, M., MacFarlane, D. R., & Spiccia, L. (2015). Renewable fuels from concentrated solar power: towards practical artificial photosynthesis. *Energy & Environmental Science*, 8(9), 2791-2796.

Bosma, R., de Vree, J., Slegers, P., Janssen, M., Wijffels, R., & Barbosa, M. (2014). Design and construction of the microalgal pilot facility AlgaePARC. *Algal Research*, 6, 160-169.

- Boyano, A., Blanco-Marigorta, A. M., Morosuk, T., & Tsatsaronis, G. (2011). Exergoenvironmental analysis of a steam methane reforming process for hydrogen production. *Energy*, 36(4), 2202-2214. doi:10.1016/j.energy.2010.05.020
- Brito, P. S., Oliveira, A. S., & Rodrigues, L. F. (2014). Energy valorization of solid vines pruning by thermal gasification in a pilot plant. *Waste and Biomass Valorization*, 5(2), 181-187.
- Burchart-Korol, D. (2013). Life cycle assessment of steel production in Poland: a case study. *Journal of Cleaner Production*, 54, 235-243.  
doi:<http://dx.doi.org/10.1016/j.jclepro.2013.04.031>
- Capros, P., De Vita, A., Tasios, N., Siskos, P., Kannavou, M., Petropoulos, A., . . . Nakos, C. (2016). EU Reference Scenario 2016-Energy, transport and GHG emissions Trends to 2050.
- Carmo, M., Fritz, D. L., Mergel, J., & Stolten, D. (2013). A comprehensive review on PEM water electrolysis. *International Journal of Hydrogen Energy*, 38(12), 4901-4934.
- Ciferno, J. P., & Marano, J. J. (2002). Benchmarking biomass gasification technologies for fuels, chemicals and hydrogen production. *US Department of Energy. National Energy Technology Laboratory*.
- Clark, J. (2015, July 2016). Titanium. Retrieved from <http://www.chemguide.co.uk/inorganic/extraction/titanium.html>
- Claassen, P., Budde, M., Van Noorden, G., Hoekema, S., Hazewinkel, J., Van Groenestijn, J., & De Vrije, G. (2004). *Biological hydrogen production from agro-food-by-products*. Paper presented at the Total food: exploiting co-products, Norwich, UK, 25-28 April, 2004.
- Corella, J., Toledo, J.-M., & Molina, G. (2008). Biomass gasification with pure steam in fluidised bed: 12 variables that affect the effectiveness of the biomass gasifier. *International Journal of Oil, Gas and Coal Technology*, 1(1-2), 194-207.
- Cuiping, L., Chuangzhi, W., & Haitao, H. (2004). Chemical elemental characteristics of biomass fuels in China. *Biomass and bioenergy*, 27(2), 119-130.
- Das, D., & Veziroğlu, T. N. (2001). Hydrogen production by biological processes: a survey of literature. *International Journal of Hydrogen Energy*, 26(1), 13-28.



- Davis, R., Tao, L., Scarlata, C., Tan, E., Ross, J., Lukas, J., & Sexton, D. (2015). Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons: Dilute-Acid and Enzymatic. *National Renewable Energy Laboratory*.
- De Vrije, T., De Haas, G., Tan, G., Keijsers, E., & Claassen, P. (2002). Pretreatment of Miscanthus for hydrogen production by *Thermotoga elfii*. *International Journal of Hydrogen Energy*, 27(11), 1381-1390.
- de Wild-Scholten, M. M. (2013). Energy payback time and carbon footprint of commercial photovoltaic systems. *Solar Energy Materials and Solar Cells*, 119, 296-305.
- Demirbaş, A. (2002). Hydrogen production from biomass by the gasification process. *Energy Sources*, 24(1), 59-68.
- Demirbas, M. F. (2006). Hydrogen from various biomass species via pyrolysis and steam gasification processes. *Energy Sources, Part A*, 28(3), 245-252.
- Ditzig, J., Liu, H., & Logan, B. E. (2007). Production of hydrogen from domestic wastewater using a bioelectrochemically assisted microbial reactor (BEAMR). *International Journal of Hydrogen Energy*, 32(13), 2296-2304.
- Djomo, S. N., & Blumberga, D. (2011). Comparative life cycle assessment of three biohydrogen pathways. *Bioresour Technol*, 102(3), 2684-2694.  
doi:10.1016/j.biortech.2010.10.139
- Djomo, S. N., Humbert, S., & Dagnija, B. (2008). Life cycle assessment of hydrogen produced from potato steam peels. *International Journal of Hydrogen Energy*, 33(12), 3067-3072. doi:10.1016/j.ijhydene.2008.02.006
- Ecoinvent. (2015). Steel production. Retrieved from <https://v32.ecoquery.ecoinvent.org/Details/LCI/b79b4b52-eafc-4d32-8d50-77cef7391a31/dd7f13f5-0658-489c-a19c-f2ff8a00bdd9>
- Edenhofer, O., Pichs-Madruga, R., Sokona, Y., Seyboth, K., Kadner, S., Zwickel, T., . . . von Stechow, C. (2011). *Renewable energy sources and climate change mitigation: Special report of the intergovernmental panel on climate change*: Cambridge University Press.

Ellingsen, L. A.-W., Singh, B., & Strømman, A. H. (2016). The size and range effect: lifecycle greenhouse gas emissions of electric vehicles. *Environmental Research Letters*, *11*(5), 054010.

Eurostat. (2016, October 2016). Road freight transport statistics. Retrieved from [http://ec.europa.eu/eurostat/statistics-explained/index.php/Road\\_freight\\_transport\\_statistics\\_-\\_Main\\_statistical\\_findings](http://ec.europa.eu/eurostat/statistics-explained/index.php/Road_freight_transport_statistics_-_Main_statistical_findings)

Fehrenbach, H., Giegrich, J., Reinhardt, G., Sayer, U., Gretz, M., Lanje, K., & Schmitz, J. (2008). Kriterien einer nachhaltigen Bioenergienutzung im globalen Maßstab. *UBA-Forschungsbericht*, *206*, 41-112.

Foley, J. M., Rozendal, R. A., Hertle, C. K., Lant, P. A., & Rabaey, K. (2010). Life cycle assessment of high-rate anaerobic treatment, microbial fuel cells, and microbial electrolysis cells. *Environmental science & technology*, *44*(9), 3629-3637.

Frischknecht, R., Jungbluth, N., Althaus, H.-J., Doka, G., Dones, R., Heck, T., . . . Spielmann, M. (2005). The ecoinvent Database: Overview and Methodological Framework (7 pp). *The International Journal of Life Cycle Assessment*, *10*(1), 3-9. doi:10.1065/lca2004.10.181.1

FUELCELLSETC. (2013). What is the Difference Between Carbon Paper and Carbon Cloth Based Gas Diffusion Layers (GDL)? Retrieved from <http://fuelcellsetc.com/2013/03/comparing-gas-diffusion-layers-gdl/>

Gibon, T., Arvesen, A., & Hertwich, E. G. (2017). Life cycle assessment demonstrates environmental co-benefits and trade-offs of low-carbon electricity supply options. *Renewable and Sustainable Energy Reviews*, *76*, 1283-1290.

Granovskii, M., Dincer, I., & Rosen, M. (2006). Life cycle assessment of hydrogen fuel cell and gasoline vehicles. *International Journal of Hydrogen Energy*, *31*(3), 337-352. doi:10.1016/j.ijhydene.2005.10.004

Granovskii, M., Dincer, I., & Rosen, M. A. (2006). Life cycle assessment of hydrogen fuel cell and gasoline vehicles. *International Journal of Hydrogen Energy*, *31*(3), 337-352.

- Grigoriev, S. A., Poremsky, V. I., & Fateev, V. N. (2006). Pure hydrogen production by PEM electrolysis for hydrogen energy. *International Journal of Hydrogen Energy*, 31(2), 171-175. doi:<http://dx.doi.org/10.1016/j.ijhydene.2005.04.038>
- Gunaseelan, V. N. (2007). Regression models of ultimate methane yields of fruits and vegetable solid wastes, sorghum and napiergrass on chemical composition. *Bioresource technology*, 98(6), 1270-1277.
- Guo, X. M., Trably, E., Latrille, E., Carrère, H., & Steyer, J.-P. (2010). Hydrogen production from agricultural waste by dark fermentation: A review. *International Journal of Hydrogen Energy*, 35(19), 10660-10673. doi:10.1016/j.ijhydene.2010.03.008
- Haberl, H., Beringer, T., Bhattacharya, S. C., Erb, K.-H., & Hoogwijk, M. (2010). The global technical potential of bio-energy in 2050 considering sustainability constraints. *Current Opinion in Environmental Sustainability*, 2(5), 394-403.
- Hallenbeck, P. C., & Benemann, J. R. (2002). Biological hydrogen production; fundamentals and limiting processes. *International Journal of Hydrogen Energy*, 27(11), 1185-1193.
- Hauserman, W. B. (1997). Relating catalytic coal or biomass gasification mechanisms to plant capital cost components. *International Journal of Hydrogen Energy*, 22(4), 409-414.
- Hay, J. X. W., Wu, T. Y., & Juan, J. C. (2013). Biohydrogen production through photo fermentation or dark fermentation using waste as a substrate: overview, economics, and future prospects of hydrogen usage. *Biofuels, Bioproducts and Biorefining*, 7(3), 334-352.
- Hofbauer, H., Rauch, R., Löffler, G., Kaiser, S., Fercher, E., & Tremmel, H. (2002). *Six years experience with the FICFB-gasification process*: na.
- Hosseini, S. E., & Wahid, M. A. (2016). Hydrogen production from renewable and sustainable energy resources: Promising green energy carrier for clean development. *Renewable and Sustainable Energy Reviews*, 57, 850-866. doi:10.1016/j.rser.2015.12.112
- IER, I. f. e. r. (2016). Lessons from Sweden and Germany. Retrieved from <http://instituteforenergyresearch.org/analysis/lessons-sweden-germany>

Ioannou-Ttofa, L., Foteinis, S., Chatzisyneon, E., & Fatta-Kassinou, D. (2016). The environmental footprint of a membrane bioreactor treatment process through Life Cycle Analysis. *Sci Total Environ*, 568, 306-318. doi:10.1016/j.scitotenv.2016.06.032

IPCC. (2014). Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Edenhofer, O., R. Pichs-Madruga, Y. Sokona, E. Farahani, S. Kadner, K. Seyboth, A. Adler, I. Baum, S. Brunner, P. Eickemeier, B. Kriemann, J. Savolainen, S. Schlömer, C. von Stechow, T. Zwickel and J.C. Minx (eds.)]. *Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA*.

Iribarren, D., Susmozas, A., Petrakopoulou, F., & Dufour, J. (2014). Environmental and exergetic evaluation of hydrogen production via lignocellulosic biomass gasification. *Journal of Cleaner Production*, 69, 165-175. doi:10.1016/j.jclepro.2014.01.068

Jaber, O., Naterer, G., & Dincer, I. (2010). Natural gas usage as a heat source for integrated SMR and thermochemical hydrogen production technologies. *International Journal of Hydrogen Energy*, 35(16), 8569-8579.

Jennings, J. R. (2013). *Catalytic ammonia synthesis: fundamentals and practice*: Springer Science & Business Media.

Jia, J., Seitz, L. C., Benck, J. D., Huo, Y., Chen, Y., Ng, J. W. D., . . . Jaramillo, T. F. (2016). Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%. *Nature Communications*, 7.

Kadier, A., Simayi, Y., Abdeslahian, P., Azman, N. F., Chandrasekhar, K., & Kalil, M. S. (2016). A comprehensive review of microbial electrolysis cells (MEC) reactor designs and configurations for sustainable hydrogen gas production. *Alexandria Engineering Journal*, 55(1), 427-443. doi:10.1016/j.aej.2015.10.008

Kalamaras, C. M., & Efstathiou, A. M. (2013). Conference Paper Hydrogen Production Technologies: Current State and Future Developments.

Kalinci, Y., Hepbasli, A., & Dincer, I. (2009). Biomass-based hydrogen production: a review and analysis. *International Journal of Hydrogen Energy*, 34(21), 8799-8817.

- Kalinci, Y., Hepbasli, A., & Dincer, I. (2012). Life cycle assessment of hydrogen production from biomass gasification systems. *International Journal of Hydrogen Energy*, 37(19), 14026-14039. doi:10.1016/j.ijhydene.2012.06.015
- Kapdan, I. K., & Kargi, F. (2006). Bio-hydrogen production from waste materials. *Enzyme and Microbial Technology*, 38(5), 569-582.
- Kim, D.-H., Kim, S.-H., & Shin, H.-S. (2009). Hydrogen fermentation of food waste without inoculum addition. *Enzyme and Microbial Technology*, 45(3), 181-187.
- Kim, J. R., Cheng, S., Oh, S.-E., & Logan, B. E. (2007). Power generation using different cation, anion, and ultrafiltration membranes in microbial fuel cells. *Environmental science & technology*, 41(3), 1004-1009.
- Kongstein, O. E., CEA, N. G., & Ødegård, A. (2010). «NEXPEL Project» Next-generation PEM electrolyzer for sustainable hydrogen production WP5 “Porous current collectors and materials for bipolar plate” Bibliographic review.
- Koppatz, S., Pfeifer, C., Rauch, R., Hofbauer, H., Marquard-Moellenstedt, T., & Specht, M. (2009). H<sub>2</sub> rich product gas by steam gasification of biomass with in situ CO<sub>2</sub> absorption in a dual fluidized bed system of 8 MW fuel input. *Fuel Processing Technology*, 90(7), 914-921.
- Kraemer, J. T., & Bagley, D. M. (2007). Improving the yield from fermentative hydrogen production. *Biotechnology letters*, 29(5), 685-695.
- Krajnc, N. (2015). *Wood Fuels Handbook*: FAO.
- Kreuter, W., & Hofmann, H. (1998). Electrolysis: the important energy transformer in a world of sustainable energy. *International Journal of Hydrogen Energy*, 23(8), 661-666.
- Kyazze, G., Martinez-Perez, N., Dinsdale, R., Premier, G., Hawkes, F., Guwy, A. J., & Hawkes, D. (2006). Influence of substrate concentration on the stability and yield of continuous biohydrogen production. *Biotechnology and bioengineering*, 93(5), 971-979.
- Körner, A., Tam, C., Bennett, S., & Gagné, J. (2015). Technology roadmap-hydrogen and fuel cells. *International Energy Agency (IEA)*.

Lipman, T. E. (2004). *What will power the hydrogen economy? Present and future sources of hydrogen energy*. Retrieved from

Liu, B.-F., Ren, N.-Q., Xie, G.-J., Ding, J., Guo, W.-Q., & Xing, D.-F. (2010). Enhanced bio-hydrogen production by the combination of dark-and photo-fermentation in batch culture. *Bioresource technology*, *101*(14), 5325-5329.

Liu, H., Grot, S., & Logan, B. E. (2005). Electrochemically assisted microbial production of hydrogen from acetate. *Environmental science & technology*, *39*(11), 4317-4320.

Logan, B. E., Call, D., Cheng, S., Hamelers, H. V., Sleutels, T. H., Jeremiasse, A. W., & Rozendal, R. A. (2008). Microbial electrolysis cells for high yield hydrogen gas production from organic matter. *Environmental science & technology*, *42*(23), 8630-8640.

Lombardi, L., Carnevale, E., & Corti, A. (2011). Life cycle assessment of different hypotheses of hydrogen production for vehicle fuel cells fuelling. *Int J Energy Environ Eng*, *2*, 63-78.

Manish, S., & Banerjee, R. (2008). Comparison of biohydrogen production processes. *International Journal of Hydrogen Energy*, *33*(1), 279-286.

Markowski, M., Urbaniec, K., Budek, A., Trafczyński, M., Wukovits, W., Friedl, A., . . . Zacchi, G. (2010). Estimation of energy demand of fermentation-based hydrogen production. *Journal of Cleaner Production*, *18*, S81-S87.

Marquevich, M., Sonnemann, G. W., Castells, F., & Montané, D. (2002). Life cycle inventory analysis of hydrogen production by the steam-reforming process: comparison between vegetable oils and fossil fuels as feedstock. *Green Chemistry*, *4*(5), 414-423.

McKendry, P. (2002). Energy production from biomass (part 1): overview of biomass. *Bioresource technology*, *83*(1), 37-46.

Moreno, J., & Dufour, J. (2013). Life cycle assessment of hydrogen production from biomass gasification. Evaluation of different Spanish feedstocks. *International Journal of Hydrogen Energy*, *38*(18), 7616-7622.

Nandi, R., & Sengupta, S. (1998). Microbial production of hydrogen: an overview. *Critical reviews in microbiology*, *24*(1), 61-84.

- Newsome, D. S. (1980). The water-gas shift reaction. *Catalysis Reviews Science and Engineering*, 21(2), 275-318.
- Ni, M., Leung, D. Y. C., Leung, M. K. H., & Sumathy, K. (2006). An overview of hydrogen production from biomass. *Fuel Processing Technology*, 87(5), 461-472.  
doi:10.1016/j.fuproc.2005.11.003
- Ntaikou, I., Antonopoulou, G., & Lyberatos, G. (2010). Biohydrogen production from biomass and wastes via dark fermentation: a review. *Waste and Biomass Valorization*, 1(1), 21-39.
- Nuss, P., & Eckelman, M. J. (2014). Life cycle assessment of metals: A scientific synthesis. *PLoS One*, 9(7), e101298.
- Pant, K., & Gupta, R. B. (2009). Fundamentals and use of hydrogen as a fuel. *Hydrogen fuel: production, transport, and storage*, 3-32.
- Peden, E. A., Boehm, M., Mulder, D. W., Davis, R., Old, W. M., King, P. W., . . . Dubini, A. (2013). Identification of global ferredoxin interaction networks in *Chlamydomonas reinhardtii*. *Journal of Biological Chemistry*, 288(49), 35192-35209.
- PI, A. E., Dai, Q., Han, J., & Wang, M. (2016). Life Cycle Analysis of Emerging Hydrogen Production Technologies.
- Potts, L. G., & Martin, D. J. (2009). ANAEROBIC DIGESTION, GASIFICATION, AND PYROLYSIS. *Waste Management and Minimisation*, ed. Sollars, Cheeseman, Smith and Blakey, *Encyclopedia of Life Support Systems*, 194-294.
- Q. Dai, A. E., J. Kelly, J. Han, and M. Wang. (2016). Life Cycle Analysis of Hydrogen Production from Nonfossil Sources.pdf.
- Redwood, M. D., Paterson-Beedle, M., & Macaskie, L. E. (2009). Integrating dark and light bio-hydrogen production strategies: towards the hydrogen economy. *Reviews in Environmental Science and Bio/Technology*, 8(2), 149.
- Riboldi, L., & Bolland, O. (2015). Evaluating Pressure Swing Adsorption as a CO<sub>2</sub> separation technique in coal-fired power plants. *International Journal of Greenhouse Gas Control*, 39, 1-16. doi:<https://doi.org/10.1016/j.ijggc.2015.02.001>

Rozendal, R. A., Jeremiasse, A. W., Hamelers, H. V., & Buisman, C. J. (2007). Hydrogen production with a microbial biocathode. *Environmental science & technology*, 42(2), 629-634.

Russell, J., Nuttall, L., & Fickett, A. (1973). Hydrogen generation by solid polymer electrolyte water electrolysis. *American Chemical Society Division of Fuel Chemistry Preprints*, 18(3), 24e40.

Raabe, E. B. (2017). *Life cycle assessment of Electrification of Heavy Duty Vehicles*. (MSc Masters thesis ).

Santos, D. M. F., Sequeira, C. A. C., & Figueiredo, J. L. (2013). Hydrogen production by alkaline water electrolysis. *Química Nova*, 36, 1176-1193.

Saratale, G. D., Chen, S.-D., Lo, Y.-C., Saratale, R. G., & Chang, J.-S. (2008). Outlook of biohydrogen production from lignocellulosic feedstock using dark fermentation—a review.

Sawatdeenarunat, C., Surendra, K., Takara, D., Oechsner, H., & Khanal, S. K. (2015). Anaerobic digestion of lignocellulosic biomass: Challenges and opportunities. *Bioresource technology*, 178, 178-186.

Sheridan, E., Thomassen, M., Mokkelbost, T., & Lind, A. (2010). *The development of a supported Iridium catalyst for oxygen evolution in PEM electrolyzers*. Paper presented at the 61st Annual Meeting of the International Society of Electrochemistry. International Society of Electrochemistry, Nice.

Siemens. (2015). SILYZER 200 (PEM electrolysis system) Retrieved from [https://www.industry.siemens.com/topics/global/en/pem-electrolyzer/silyzer/Documents/silyzer-200-en\\_v1.3\\_InternetVersion.pdf](https://www.industry.siemens.com/topics/global/en/pem-electrolyzer/silyzer/Documents/silyzer-200-en_v1.3_InternetVersion.pdf)

Simonsen, M. (2010). Transport, energi og miljø. *Sogndal, Norway: Vestlandsforskning*.

Singh, A., Sevda, S., Abu Reesh, I., Vanbroekhoven, K., Rathore, D., & Pant, D. (2015). Biohydrogen Production from Lignocellulosic Biomass: Technology and Sustainability. *Energies*, 8(12), 13062-13080. doi:10.3390/en81112357



Singh, B., Guest, G., Bright, R. M., & Strømman, A. H. (2014). Life Cycle Assessment of Electric and Fuel Cell Vehicle Transport Based on Forest Biomass. *Journal of Industrial Ecology*, 18(2), 176-186. doi:10.1111/jiec.12098

Sircar, S. (2002). Pressure swing adsorption. *Industrial & engineering chemistry research*, 41(6), 1389-1392.

Smolinka, T. (2014). *Cost break down for key components of the stack*. Retrieved from

Smolinka, T., Garche, J., Hebling, C., & Ehret, O. (2012). *Overview on water electrolysis for hydrogen production and storage*. Paper presented at the International Symposium on Water Electrolysis and Hydrogen as Part of the Future Renewable Energy System, Copenhagen, Denmark, May.

Smolinka, T., Ojong, E. T., & Lickert, T. (2016). Fundamentals of PEM Water Electrolysis. *PEM Electrolysis for Hydrogen Production: Principles and Applications*, 11.

Spath, P. L., Lane, J. M., Mann, M. K., & Amos, W. (2000). Update of hydrogen from biomass-determination of the delivered cost of hydrogen. *Milestone Report for the US department of Energy's Hydrogen Program*.

Spath, P. L., & Mann, M. K. (2000). *Life cycle assessment of hydrogen production via natural gas steam reforming*: National Renewable Energy Laboratory Golden, CO.

Standard, I. (2006). Environmental management-Life cycle assessment-Principles and framework: ISO.

Strømman, A. H., & Hertwich, E. (2004). Hybrid life cycle assessment of large scale hydrogen production facilities.

Susmozas, A., Iribarren, D., & Dufour, J. (2013). Life-cycle performance of indirect biomass gasification as a green alternative to steam methane reforming for hydrogen production. *International Journal of Hydrogen Energy*, 38(24), 9961-9972. doi:10.1016/j.ijhydene.2013.06.012

Swinbourne, D. (2014). Understanding ferronickel smelting from laterites through computational thermodynamics modelling. *Mineral Processing and Extractive Metallurgy*, 123(3), 127-140.

Tapia-Venegas, E., Ramirez-Morales, J. E., Silva-Illanes, F., Toledo-Alarcón, J., Paillet, F., Escudie, R., . . . Marone, A. (2015). Biohydrogen production by dark fermentation: scaling-up and technologies integration for a sustainable system. *Reviews in Environmental Science and Bio/Technology*, 14(4), 761-785.

Thanapimmetha, A., Vuttibunchon, K., Saisriyoot, M., & Srinophakun, P. (2011). *Chemical and microbial hydrolysis of sweet sorghum bagasse for ethanol production*. Paper presented at the World Renewable Energy Congress-Sweden; 8-13 May; 2011; Linköping; Sweden.

Turner, J., Sverdrup, G., Mann, M. K., Maness, P. C., Kroposki, B., Ghirardi, M., . . . Blake, D. (2008). Renewable hydrogen production. *International Journal of Energy Research*, 32(5), 379-407.

Ursua, A., Gandia, L. M., & Sanchis, P. (2012). Hydrogen production from water electrolysis: current status and future trends. *Proceedings of the IEEE*, 100(2), 410-426.

USGS, U. S. G. S. (2014). TITANIUM AND TITANIUM DIOXIDE. *Mineral Commodity Summaries*. Retrieved from <https://minerals.usgs.gov/minerals/pubs/commodity/titanium/mcs-2014-titan.pdf>

Valente, A., Iribarren, D., & Dufour, J. (2016). Life cycle assessment of hydrogen energy systems: a review of methodological choices. *The International Journal of Life Cycle Assessment*, 1-18.

Vasquez Correa, L. F. (2013). Life Cycle Assessment of Hydrogen Fuel Cell Vehicles.

Weinberg, J., & Kaltschmitt, M. (2013). Life cycle assessment of mobility options using wood based fuels--comparison of selected environmental effects and costs. *Bioresour Technol*, 150, 420-428. doi:10.1016/j.biortech.2013.08.093

Windsheimers, M. (2016). *Life-Cycle Assessment of Fuel Cell Vehicles* Project thesis Industrial ecology NTNU.

WSA, W. S. A. (2016). Steel Statistical Yearbook

Wulf, C., & Kaltschmitt, M. (2012). Life cycle assessment of hydrogen supply chain with special attention on hydrogen refuelling stations. *International Journal of Hydrogen Energy*, 37(21), 16711-16721. doi:10.1016/j.ijhydene.2012.03.028

Wulf, C., & Kaltschmitt, M. (2013). Life cycle assessment of biohydrogen production as a transportation fuel in Germany. *Bioresour Technol*, *150*, 466-475.

doi:10.1016/j.biortech.2013.08.127

Wulf, C., Thormann, L., & Kaltschmitt, M. (2017). Comparative Environmental Life Cycle Assessment of Biohydrogen Production from Biomass Resources *Biohydrogen Production: Sustainability of Current Technology and Future Perspective* (pp. 269-289): Springer.

Yu, X., Zheng, Y., Dorgan, K. M., & Chen, S. (2011). Oil production by oleaginous yeasts using the hydrolysate from pretreatment of wheat straw with dilute sulfuric acid. *Bioresource technology*, *102*(10), 6134-6140.

Zakkour, P., & Cook, G. (2010). CCS Roadmap for Industry: High-purity CO<sub>2</sub> sources. *Sectoral Assessment-Final Draft Report. Global Technology Roadmap for CCS in Industry*.

Zhang, L., Xu, C. C., & Champagne, P. (2010). Overview of recent advances in thermo-chemical conversion of biomass. *Energy Conversion and Management*, *51*(5), 969-982.

Zheng, H., O'Sullivan, K., Mereddy, R., Zeng, R. J., Duke, M., & Clarke, W. (2009). *Production of bio-hydrogen using a membrane anaerobic reactor: limitations due to diffusion*. Paper presented at the Environmental Research Event 2009.

Aall, Ø. K. A., Anders; Aall, Carlo; Strømman, Anders. (2016). *Life cycle assessment of hydrogen production with a PEM electrolyzer*. Project thesis Industrial Ecology NTNU.

## Appendix 1 – Methods and materials

**TABLE 1 – METHANE YIELD THROUGH ANAEROBIC DIGESTION FROM DIFFERENT BIOMASSES**

<b>Biomass</b>	<b>Min</b>	<b>Max</b>	<b>Avg</b>	<b>Unit</b>
Sugar beet	387	408	397,5	Nm <sup>3</sup> CH <sub>4</sub> /ton VS
Fodder beet	398	424	411	Nm <sup>3</sup> CH <sub>4</sub> /ton VS
Maize	291	338	314,5	Nm <sup>3</sup> CH <sub>4</sub> /ton VS
Wheat	351	378	364,5	Nm <sup>3</sup> CH <sub>4</sub> /ton VS
Triticale	319	335	327	Nm <sup>3</sup> CH <sub>4</sub> /ton VS
Sorghum	286	319	302,5	Nm <sup>3</sup> CH <sub>4</sub> /ton VS
Grass	286	324	305	Nm <sup>3</sup> CH <sub>4</sub> /ton VS
Red clover	297	347	322	Nm <sup>3</sup> CH <sub>4</sub> /ton VS
Sunflower	231	297	264	Nm <sup>3</sup> CH <sub>4</sub> /ton VS
Wheat grain	371	398	384,5	Nm <sup>3</sup> CH <sub>4</sub> /ton VS
Avg	321,7	356,8	339,25	Nm <sup>3</sup> CH <sub>4</sub> /ton VS

**TABLE 2 – OPERATIONAL CATALYST MATERIAL FOR HYDROGENATOR AS PRETREATMENT FOR BIOGAS STEAM REFORMING**

<b>Materials</b>	<b>Chemical formula</b>	<b>Amount</b>	<b>Unit</b>
Aluminium oxide	Al <sub>2</sub> O <sub>3</sub>	9,6E-05	kg / kg H <sub>2</sub>
Nickel(II) oxide	NiO	4,7E-06	kg / kg H <sub>2</sub>
Molybdenum trioxide	MoO <sub>3</sub>	1,7E-05	kg / kg H <sub>2</sub>

**TABLE 3 – OPERATIONAL CATALYST MATERIAL FOR DESULPHURIZATION AS PRETREATMENT FOR BIOGAS STEAM REFORMING**

<b>Materials</b>	<b>Chemical formula</b>	<b>Amount</b>	<b>Unit</b>
Aluminium oxide	Al <sub>2</sub> O <sub>3</sub>	1,17E-05	kg / kg H <sub>2</sub>
Zinc oxide	ZnO	1,56E-04	kg / kg H <sub>2</sub>

**TABLE 4 – OPERATIONAL CATALYST MATERIAL FOR THE PREREFORMER AS PRETREATMENT FOR BIOGAS STEAM REFORMING**

<b>Materials</b>	<b>Chemical formula</b>	<b>Amount</b>	<b>Unit</b>
Aluminium oxide	Al <sub>2</sub> O <sub>3</sub>	1,45E-07	kg / kg H <sub>2</sub>
Nickel(II) oxide	NiO	1,38E-04	kg / kg H <sub>2</sub>
Silicon dioxide	SiO <sub>2</sub>	1,15E-05	kg / kg H <sub>2</sub>
Chromium(III) oxide	Cr <sub>2</sub> O <sub>3</sub>	4,11E-06	kg / kg H <sub>2</sub>
Calium oxide	CaO	2,14E-05	kg / kg H <sub>2</sub>

**TABLE 5 – OPERATIONAL CATALYST MATERIAL FOR THE HIGH TEMPERATURE SHIFT FOR BIOGAS STEAM REFORMING**

<b>Materials</b>	<b>Chemical formula</b>	<b>Amount</b>	<b>Unit</b>
Iron(III) oxide	Fe <sub>2</sub> O <sub>3</sub>	2,79E-04	kg / kg H <sub>2</sub>
Chromium(III) oxide	Cr <sub>2</sub> O <sub>3</sub>	3,22E-05	kg / kg H <sub>2</sub>
Copper(II) oxide	CuO	5,69E-06	kg / kg H <sub>2</sub>

**TABLE 6 – OPERATIONAL CATALYST MATERIAL FOR THE LOW TEMPERATURE SHIFT FOR BIOGAS STEAM REFORMING**

<b>Materials</b>	<b>Chemical formula</b>	<b>Amount</b>	<b>Unit</b>
Aluminium oxide	Al <sub>2</sub> O <sub>3</sub>	1,45E-07	kg / kg H <sub>2</sub>
Zinc oxide	ZnO	2,19E-04	kg / kg H <sub>2</sub>
Copper(II) oxide	CuO	3,60E-04	kg / kg H <sub>2</sub>

**TABLE 7 - ULTIMATE ANALYSIS OF LIGNOCELLULOSIC BIOMASS AND CALCULATED HHV (BILANZDIJA, VOCA, KRICKA, MATIN, & JURISIC, 2012; BRITO, OLIVEIRA, & RODRIGUES, 2014; CUIPING, CHUANGZHI, & HAITAO, 2004; MCKENDRY, 2002)**

<b>Content</b>	<b>Willow</b>	<b>Poplar</b>	<b>Pine</b>	<b>Eucalyptus</b>	<b>Almond pruning</b>	<b>Vine pruning</b>	<b>Wood<sup>a</sup></b>	<b>Unit</b>
Carbon	46,79	47,46	49,41	50,15	49,28	46,64	47,46 <sup>b</sup>	%
Hydrogen	7,1	6,74	7,67	7,45	6,51	5,55	6,74 <sup>b</sup>	%
Oxygen	40,6	44,5	42,19	39,64	43,34	47,02	44,5 <sup>b</sup>	%
HHV	19,58	19,66	20,85	20,85	20,03	18,65	19,66	MJ/kg

<sup>a</sup> Not specified species

<sup>b</sup> Average wood

**TABLE 8 – GLUCOSE YIELD FOR DIFFERENT FEEDSTOCKS FOR DARK FERMENTATION**

	<b>Manish and Djomo et al. (2008)      Banerjee (2008)      Djomo and Blumberga (2011)</b>						<b>Unit</b>
	Potato peels	Sugarcane	Potato peels	Sweet sorghum	Wheat straw		
	Feedstock						
Fresh weight	-	93,09	80,20	-	-		
Dry weight	14,04	-	-	11,93	13,20		Kg
Conversion rate	-	10,45 %	-	33,49 %	23,80 %		-
Glucose	7,02	9,73	-	4,00	3,14		Kg

## Appendix 2 – Results and discussion

**TABLE 25 – TECHNICAL POTENTIAL FOR HYDROGEN PRODUCTION FROM BIOMASS**

<b>Method</b>	<b>BSR</b>	<b>BSR</b>	<b>Fermentati on</b>	<b>Fermentatio n</b>	<b>Gasificati on</b>	<b>Unit</b>
H <sub>2</sub> source	Energy crops	Crop residues	MSW	Animal manure	Forrest residues	-
Energy source	Energy crops	Crop residues	MSW	Animal manure	Forrest residues	-
Technical capacity	2,68E+10	1,53E+10	3,25E+09	1,30E+10	3,46E+10	Kg H <sub>2</sub>
Emission	2,67	2,67	5,25	5,25	5,55	Kg CO <sub>2</sub> - eq/kg H <sub>2</sub>

**TABLE 26 –POTENTIAL FOR HYDROGEN PRODUCTION WITH ELECTROLYSIS FROM RENEWABLE ENERGY**

<b>Method</b>	<b>PEMWE</b>	<b>PEMWE</b>	<b>AWE</b>	<b>Unit</b>
H <sub>2</sub> source	Water	Water	Water	-
Energy source	Solar	Wind	Hydro	-
Potential	5,96E+07	1,35E+08	6,31E+07	Kg H <sub>2</sub>
Emission	14,24	8,06	3,76	Kg CO <sub>2</sub> -eq/kg H <sub>2</sub>