

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
Faculty of Technology
Degree Programme in Energy Technology

Master's Thesis

Antti Holopainen

**CARBON SOURCES FOR POWER-TO-GAS APPLICATIONS IN
THE FINNISH ENERGY SYSTEM**

Examiner: Professor Timo Hyppänen

Supervisor: Associate Professor Tero Tynjälä

ABSTRACT

Lappeenranta University of Technology
Faculty of Technology
Degree Programme in Energy Technology

Antti Holopainen

Carbon sources for Power-to-Gas applications in the Finnish energy system

Master's Thesis

2015

80 pages, 30 figures, 17 tables

Examiners : Professor Timo Hyppänen
Associate Professor Tero Tynjälä

Keywords: Power-to-Gas, CCS, methanation, biogenic carbon sources.

This thesis is done as a part of the NEOCARBON project. The aim of NEOCARBON project is to study a fully renewable energy system utilizing Power-to-Gas or Power-to-Liquid technology for energy storage. Power-to-Gas consists of two main operations: Hydrogen production via electrolysis and methane production via methanation. Methanation requires carbon dioxide and hydrogen as a raw material. This thesis studies the potential carbon dioxide sources within Finland. The different sources are ranked using the cost and energy penalty of the carbon capture, carbon biogenicity and compatibility with Power-to-Gas. It can be concluded that in Finland there exists enough CO₂ point sources to provide national PtG system with sufficient amounts of carbon. Pulp and paper industry is single largest producer of biogenic CO₂ in Finland. It is possible to obtain single unit capable of grid balancing operations and energy transformations via Power-to-Gas and Gas-to-Power by coupling biogas plants with biomethanation and CHP units.

TIIVISTELMÄ

Lappeenrannan Teknillinen Yliopisto

Teknillinen tiedekunta

Energiatekniikan koulutusohjelma

Antti Holopainen

Hiililähteet Power-to-Gas sovelluksiin Suomalaisessa energiajärjestelmässä.

Diplomityö

2015

80 sivua, 30 kuvaa, 17 taulukkoa

Työn tarkastajat: Professori Timo Hyppänen
 Tutkijaopettaja Tero Tynjälä

Hakusanat: Power-to-Gas, CCS, metanointi, bioperäinen hiili.

Keywords: Power-to-Gas, CCS, methanation, biogenic carbon.

Tämä diplomityö tehdään osaksi NEOCARBON projektia. NEOCARBON tutkii Power-to-Gas ja Power-to-Liquid teknologiaa energian varastointimuotona 100% uusiutuvassa energiajärjestelmässä. Power-to-Gas koostuu kahdesta päävaiheesta: vedyn tuotanto elektrolyysillä ja metaanin tuotanto metanoinnilla. Metanointi vaatii hiilidioksidia ja vetyä raaka-aineeksi. Tämän diplomityön tarkoitus on kartoittaa soveltuvia hiilidioksidilähteitä Suomessa. Eri lähteitä on arvioitu hiilidioksidin talteenoton kustannusten ja energiankulutuksen, hiilen bioperäisyyden ja Power-to-Gas yhteensopivuuden mukaan. Voidaan todeta että Suomessa on riittävä CO₂ tuotantopotentiaali kansallisen PtG järjestelmän toimintaan. Paperiteollisuus on suurin yksittäinen biogeenisen CO₂ päästöjen lähde. Yhdistämällä biometanointi biokaasulaitoksiin ja yhdistetyn lämmön ja sähkön tuotantoon voidaan saavuttaa yksikkö joka kykenee Power-to-Gas ja Gas-to-Power energianmuunnoksiin ja sähköverkon tasapainottamiseen.

ACKNOWLEDGEMENTS

This thesis has been done at the Lappeenranta University of Technology as a part of the NEOCARBON research. The study has been an interesting chance to obtain knowledge of different energy storage methods and future technologies under development to integrate renewable energy into today's energy systems.

I'd like to thank my supervisor Tero Tynjälä for his instructions and Michael Child for providing me the scenario data for 2050 100% renewable Finland. I'd also like to thank Eero Inkeri for sharing his ideas and thoughts on the research.

Lastly I wish to thank all the friends and mates I've met at LUT during my studies here. Without you lot, I wouldn't have enjoyed my stay as well as I did.

Antti Holopainen

July 2015

Lappeenranta, Finland

TABLE OF CONTENTS

1	INTRODUCTION	5
1.1	INCENTIVES	5
1.2	OBJECTIVES OF THE THESIS	5
1.3	STRUCTURE OF THE THESIS	6
2	ENERGY STORAGE SYSTEMS	7
2.1	STATE-OF-THE-ART ENERGY STORAGE.....	7
2.2	PTG TECHNOLOGY	11
2.2.1	<i>Electrolysis</i>	<i>12</i>
2.2.2	<i>Chemical methanation.....</i>	<i>16</i>
3	CO₂-CAPTURE FOR PTG	19
3.1	STATE OF THE ART CCS TECHNOLOGIES	20
3.1.1	<i>Post-combustion capture technologies.....</i>	<i>21</i>
3.1.2	<i>Oxyfuel.....</i>	<i>24</i>
3.1.3	<i>Pre-combustion technologies</i>	<i>27</i>
3.2	POTENTIAL CO ₂ SOURCES	28
3.2.1	<i>Power plants.....</i>	<i>29</i>
3.2.2	<i>Byproduct CO₂.....</i>	<i>31</i>
3.2.3	<i>Atmospheric CO₂</i>	<i>42</i>
3.3	ENERGY PENALTY AND CAPTURE COST OF CCS.....	42
3.4	EFFECT OF CCS ON PTG EFFICIENCY	44
3.5	100% RENEWABLE FINLAND 2050	45
4	CO₂ AVAILABILITY IN FINLAND	49
4.1	BIOGAS	51
4.1.1	<i>Low utilization case: Existing biogas plants.....</i>	<i>55</i>
4.1.2	<i>Medium utilization case: W-fuel report biogas plants.....</i>	<i>58</i>
4.1.3	<i>High utilization case: Theoretical maximum.....</i>	<i>59</i>
4.2	LARGE SCALE POINT SOURCES	59
4.2.1	<i>Power plants.....</i>	<i>61</i>
4.2.2	<i>Steel industry</i>	<i>62</i>
4.2.3	<i>Cement and lime production.....</i>	<i>62</i>
4.2.4	<i>Pulp and Paper industry.....</i>	<i>63</i>
4.2.5	<i>Refineries.....</i>	<i>64</i>
4.2.6	<i>Petrochemical industry</i>	<i>65</i>
4.2.7	<i>Bioethanol production.....</i>	<i>65</i>

5	RESULTS AND DISCUSSION	67
6	CONCLUSIONS	71
	LÄHTEET	72
	APPENDIX	

NOMENCLATURE

Latin alphabet

dG_r	Standard Gibbs free energy of reaction	kJ/mol
dH_{298}	Standard enthalpy of reaction	kJ/mol
e	Specific energy consumption	MJ/kg
LHV	Lower heating value	MJ/kg
HHV	Higher heating value	MJ/kg
q_v	Volumetric flow	m ³ /s
V	Volume	m ³

Greek alphabet

η	Efficiency
--------	------------

Abbreviations

ASU	Air separation unit
BEV	Battery electric vehicle
BF	Blast furnace
BP	Bridging power
CAES	Compressed air energy storage
CCS	Carbon capture and storage
CHP	Combined heat and power
CLC	Chemical looping combustion
DH	District heating
GtP	Gas-to-Power
EM	Energy management
FTR	Fired tubular reformer
HEB	High energy battery
IGCC	Integrated gasification combined cycle
MFR	Methane formation rate
Mtoe	Million tonnes of oil equivalent
NGCC	Natural gas combined cycle
OCM	Oxygen conducting membrane
PEM	Proton exchange membrane

PtG	Power-to-Gas
PtL	Power-to-Liquid
PHS	Pumped hydro storage
PQ	Power quality
PV	Photovoltaics
SMES	Superconducting magnetic energy storage
SMR	Steam methane reforming
SNG	Synthetic natural gas
SOEC	Solid oxide electrolysis
TGRBF	Top gas recycling blast furnace
WGSMR	Water-gas shift membrane reactor

1 INTRODUCTION

Reduction of greenhouse gas emissions has become major issue for the energy sector due to the global warming. Renewable options for fossil-based fuels are promoted globally and in Germany especially the *energiewende* has resulted in rapid growth of installed solar and wind power capacity. As the share of renewables in the energy system increases the effect of their weaknesses are emphasized, namely the natural intermittency of solar and wind. To reach a fully renewable energy system some form of energy storage and grid balancing operations are required. PtG (Power-to-Gas) offers one such alternative, with storage capacities far beyond of other energy storage systems. Besides the energy storage, the PtG has the added value of producing hydrogen and methane which are both extremely valuable raw materials for industry.

Implementation of PtG requires steady supply of carbon dioxide for methanation reaction. Different carbon sources have their unique carbon concentrations, impurities and production rates. The required carbon separation technologies also affect the end-product carbon quality and the capture cost and energy penalty. All of these must be taken into account when choosing the suitable source for PtG integration.

1.1 Incentives

This thesis is part of the NEOCARBON research project conducted by Lappeenranta University of Technology, VTT and University of Turku. NEOCARBON focuses on research of the PtG energy storage system from the Finnish perspective. Different ways to integrate PtG with Finnish industry and energy sector are studied. The thesis focuses on the specific application of Power-to-SNG in the energy sector and excludes other conversion processes and applications, such as Power-to-Hydrogen and Power-to-Liquids (PtL) and their use for traffic fuel production.

1.2 Objectives of the thesis

Objective of this thesis is to map different carbon dioxide sources for PtG applications. Different industrial sources are examined alongside the necessary CO₂ capture technologies. Suitability of different sources and extraction methods is evaluated.

1.3 Structure of the Thesis

In chapter two the state-of-the-art energy storage systems are briefly discussed before the main introduction into PtG technology. Different options for electrolysis and methanation are introduced. Chapter three reviews available carbon capture technologies and the main emitters of CO₂. In chapter four the amount of available carbon in Finland from various sources is estimated. Chapter five summarizes the results and discusses the options for carbon sources. Chapter six has the conclusions.

2 ENERGY STORAGE SYSTEMS

In 2011, the European Commission published a roadmap for moving to a competitive low carbon economy in 2050. The European Council reconfirmed in February 2011 the EU objective of reducing greenhouse gas emissions 80-95% by 2050 compared to 1990 level. Reaching this objective will require almost complete decarbonization of the energy sector and as such the share of low carbon technologies in electricity production is estimated to reach nearly 100% in 2050. (EU commission 2011).

Decarbonization of energy sector requires significant increase in renewable energy production and there is considerable global potential in the use of solar and wind power. However, increasing the share of solar and wind emphasizes the problems associated with the technologies, such as the natural intermittency of the electricity production. This leads to system balancing and capacity availability problems within the energy system. On top of this, increase in renewable production does not directly help with decarbonization of transport or industrial sectors which are currently heavily relying on fossil fuels. (Varone, Ferrari 2015).

Overcoming the problems caused by the strong fluctuations characteristic to renewable technologies will require new technological innovations. Power grid expansion, load management, short term and long term energy storage are few of the technologies proposed to compensate for the shortcomings of renewables. (Reiter, Lindorfer 2015). Grid expansion and improved load management will not be sufficient to successfully integrate intermittent renewable power production into the energy system. Energy storage systems are required. The currently available energy storage technologies range from technologically mature and sound systems, such as pumped hydro storage and batteries, to more experimental systems such as flywheels and capacitors. (Lehner et al. 2014)

2.1 State-of-the-art energy storage

The different electrical storage technologies can be roughly divided into categories according to the medium of storage: mechanical energy, chemical energy, electrical energy and thermal energy. Another way is to sort the technologies according to discharge time of the storage. Storage systems with discharge time of seconds to minutes are used for power quality (PQ), systems with discharge time between minutes to an hour provide bridging

power (BP) and systems with discharge time over an hour provide energy management (EM). (Akinyele, Rayudu 2014)

Power quality providing energy storage systems include capacitors, flywheels and superconducting magnetic energy storage. Capacitors are one of the few ways for direct storage of electricity. They can store electricity at very high rate, yet are limited by the low energy density of the system. Capacitors suffer from high self-discharge losses and short discharge time which make capacitors poor for anything but short term storage. New electrochemical capacitors are under development which offer considerable improvements on energy density, but even then their energy density is lower when compared to traditional lead-acid batteries. (Akinyele, Rayudu 2014)

Flywheels provide short term energy storage and can typically reach high efficiencies of 90-95 %. However, the technology suffers from very high self-discharge and frictional losses and are not suitable for long-term storage. (Akinyele, Rayudu 2014)

In superconducting magnetic energy storage (SMES) direct current is fed into superconducting coil and the energy is stored in the generated magnetic field. SMES can provide high efficiency of 98% with high charging and discharging rates. However, short discharge duration, high cost and environmental concerns of the magnetic fields limit the application of SMES. (Akinyele, Rayudu 2014)

Bridging power energy storages provide quick response time of seconds or minutes with discharge time up to an hour. Traditional lead-acid and lithium-ion batteries fall under the category of BP-systems. Such rechargeable batteries offer fast response to load changes for short term storage operation, yet suffer from energy discharging and high costs when used for long-term storage. It should also be noted that disposed batteries contain toxic materials and as such have negative impact on environment. (Akinyele, Rayudu 2014)

Energy management storage systems offer continuous discharge power for several hours and can store the energy for several months. Such systems include compressed-air energy storage, pumped hydro storage, thermal energy storage and high-energy batteries. (Akinyele, Rayudu 2014)

Pumped hydro storage (PHS) is one of the most mature technologies. In PHS water is pumped into a reservoir at elevated altitudes and later released through water turbines to generate power. The storage can operate with relatively high efficiency of 70-85 %. The downside is that the capacity of pumped hydro storage is limited and construction of new

storage facilities is not well accepted by the public due to the impact the construction has on the landscape. (Lehner et al. 2014)

Compressed air energy storage (CAES) is a technology where energy is stored by compressing air into a tank and then releasing it through a turbine. Main drawback is the small amount of energy stored per volume and hence the large size of storage facilities with higher energy storage capacity. Further limitations to the implementation of this technology include high costs and low efficiency if heat is not utilized from the process. (Lehner et al. 2014)

Thermal energy storages can be divided to low-temperature storages and high temperature storages, depending on the operating temperature. Low-temperature processes operate either by cooling, or freezing, water or involve the use of cryogen in the process. High-temperature process utilizes molten salt to store solar energy, however the process limited to thermal solar collectors and is not suitable for storing energy from other sources. (Akinyele, Rayudu 2014)

High energy batteries (HEB) include several different battery types which in general have increased energy density over traditional lead-acid battery. The best commercially available technology (NaS) can offer up to four times the power and energy density of a lead-acid battery. Other restrictions to large scale implementation depend heavily on particular technology. (Akinyele, Rayudu 2014)

When large quantities of energy need to be stored for extensive periods of time the storage capacity and energy density become critical parameters for energy storage. Chemical energy carriers have high energy densities which make different chemical energy storage systems well suited for long-term energy storage. (Lehner et al. 2014). There are numerous different options for the chemical energy carriers, such as methanol, dimethyl ether and methane (Varone, Ferrari 2015). From the figure 1 it can be seen that hydrogen and methane, which are products of PtG chemical storage system, have very high energy density when compared to different battery technologies, CAES and PHS. (Lehner et al. 2014). Methanol, which is one of the potential end products of Power-to-Liquid (PtL), has even higher energy density when compared to gaseous chemical energy carriers.

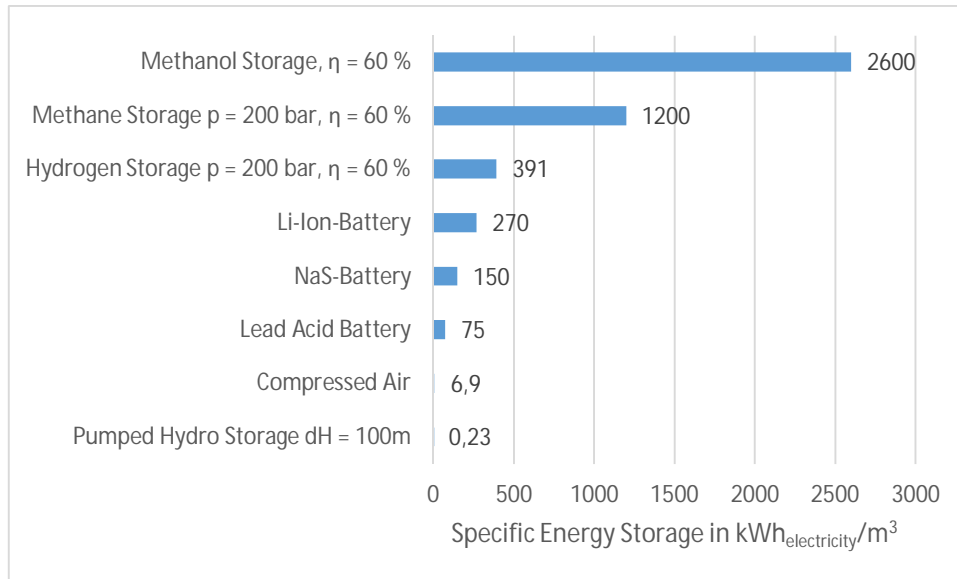


Figure 1. Different energy storage systems by energy density. (Lehner et al. 2014).

In the table 1 are listed the different storage technologies with their respective efficiencies, capacities and time scales. When a large scale energy storage in the gigawatt-range is needed for a period of days to months, PHS and PtG technologies stand out as the technologies of choice. (Lehner et al. 2014).

Table 1. Different storage technologies with efficiency, capacity rating and time scale. (Lehner et al. 2014).

Technology	Efficiency	Capacity Rating [MW]	Time scale
Pumped hydro	70-85 %	1 - 5,000	Hours - months
Li-Ion battery pack	80-90 %	0.1 - 50	Minutes - days
Lead acid battery	70-80 %	0.05 - 40	Minutes - days
Power-to-Gas	30-75 %	0.01 - 1,000	Minutes - months
Compressed air	70-75 %	50 - 300	Hours - months
Vanadium redox battery	65-85 %	0.2 - 10	Hours - months
Sodium sulphur battery	75-85 %	0.05 - 34	Seconds - hours
Nickel cadmium battery	65-75 %	45	Minutes - days
Flywheel	85-95 %	0.1 - 20	Seconds - minutes

The products of PtG system, hydrogen and methane, benefit from their role as raw material in various industrial applications as well as a fuel for mobility sector. Methane also benefits from existing natural gas (NG) distribution and storage infrastructure and technologies that utilize NG for power generation. Hydrogen can also be injected into NG infrastructure in low concentrations (less than 2%). However, each conversion step brings

an additional efficiency loss to the process and the total PtG efficiency from electricity to gas is between 50 to 75 %. (Lehner et al. 2014)

In the next subchapters the thesis will go through the PtG technology as well as technologies included in the concept: electrolysis and methanation. Because of the integral part CO₂-sources play in the PtG cycle, this thesis will go through the most carbon intensive industries and the state of the art CCS techniques. PtL systems, despite their promise, are excluded from the scope of this thesis.

2.2 PtG technology

Conversion of electricity into chemical energy carriers through Power-to-Gas (PtG) provides an option for storage of excess renewable energy production. PtG produces hydrogen through process called electrolysis where water is split into hydrogen and oxygen by direct current. Hydrogen can then be further upgraded into synthetic natural gas (SNG) through process of methanation. (Varone, Ferrari 2015). In the methanation hydrogen is combined with carbon dioxide in a chemical or biological reactor. This hydrogen upgrade to SNG creates a demand for a CO₂-source which can meet the availability and quality requirements of the methanation process as well as provide sufficient quantities of CO₂ for large scale storage of renewable energy. Potential CO₂-sources include wide range of industries and traditional power plants as well as smaller scale point sources such as biogas producing fermentation plants and bioethanol plants. (Reiter, Lindorfer 2015)

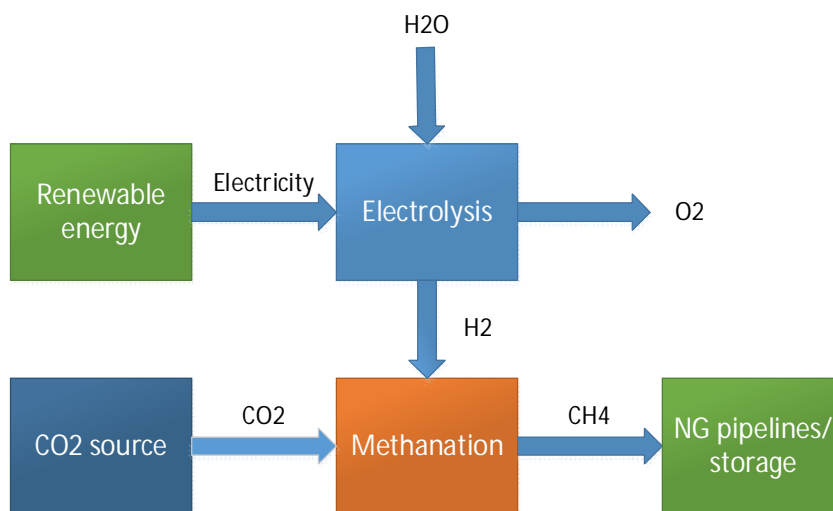


Figure 2. PtG in a nutshell.

2.2.1 Electrolysis

Electrolysis is the process of dissociation of water into its components, hydrogen and oxygen using electrical current (Harrison, Levene 2008). Electrolysis is the first fundamental step in PtG system which connects the electrical energy sources to chemical energy storage. 55 million metric tons of hydrogen is produced annually for wide range of industrial applications (Lehner et al. 2014). Roughly 50 % of hydrogen consumed is produced from natural gas with steam methane reforming (SMR) which is well established and mature technology. Currently the electrolytic production of hydrogen is not economically competitive when compared to SMR. The hydrogen production via electrolysis is driven by electricity, thus, electricity price has major impact on electrolyzer economics. (Harrison, Levene 2008).

There are two electrolyzer technologies which are currently available at commercial scale; alkaline electrolysis and proton exchange membrane (PEM). Other promising technologies such as solid oxide electrolysis are in development. (Harrison, Levene 2008.)

The electrolysis system efficiency is defined as the higher heating value of hydrogen divided by the energy consumed by the electrolysis system per kilogram of hydrogen produced. The definition is presented in equation (1)

$$\eta_{\text{electrolyzer}} = \frac{HHV_{H_2}}{\frac{\left(\frac{P_{el,in}}{\eta_{PS}}\right) + P_{el,aux}}{m_{H_2}}} \quad (1)$$

Where

$\eta_{\text{electrolyzer}}$	is the electrolyzer efficiency
HHV_{H_2}	is the higher heating value of hydrogen
$P_{el,in}$	is the electricity consumed by electrolyzer
η_{PS}	is the efficiency of the power system
$P_{el,aux}$	is the electricity consumed by auxiliary devices
m_{H_2}	is the mass of produced hydrogen

Alkaline electrolysis is the most established electrolyzer technology to date. In alkaline technology two metallic electrodes are set in an aqueous solution of KOH or NaOH. The electrodes are separated with a cell separator which is made out of porous and electrolyte impregnated material. The construction can be seen in the figure 3.

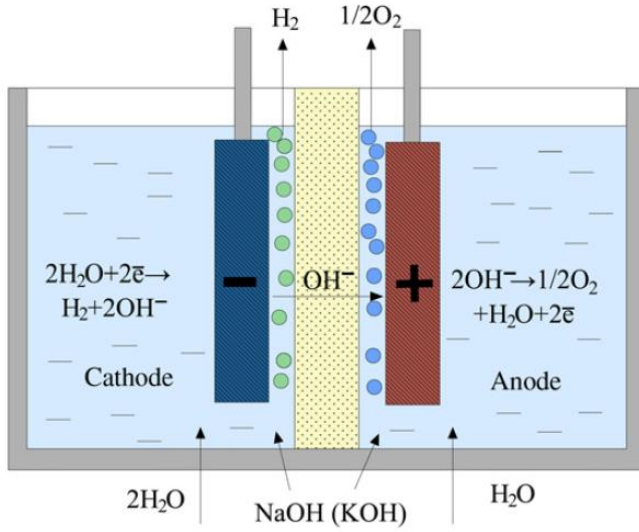


Figure 3. Construction of basic alkaline electrolyzer.

On the cathode side water is reduced according to reaction equation (2)



The hydroxyl passes through the cell separator to cathode, where it is oxidized according to reaction equation (3)



Alkaline water electrolysis is available in industrial applications in the megawatt-range and single electrolyzers can produce up to 670 Nm³/h. Operational temperatures are between 80-90°C and the efficiency is between 60-80%. Pressurized operation is achievable up to 30 bar. The current alkaline electrolyzer technologies cannot operate at very low current densities which impedes the part load operation and is a problem when operated in conjunction with renewable energy sources. (Gandía et al. 2013).

In proton-exchange membrane water electrolysis the two electrodes are pressed on the opposite sides of proton-conducting polymer electrolyte and the construction is immersed in pure water. The proton-conducting polymer serves also as a cell separator. Construction of PEM electrolyzer can be seen in figure 4.

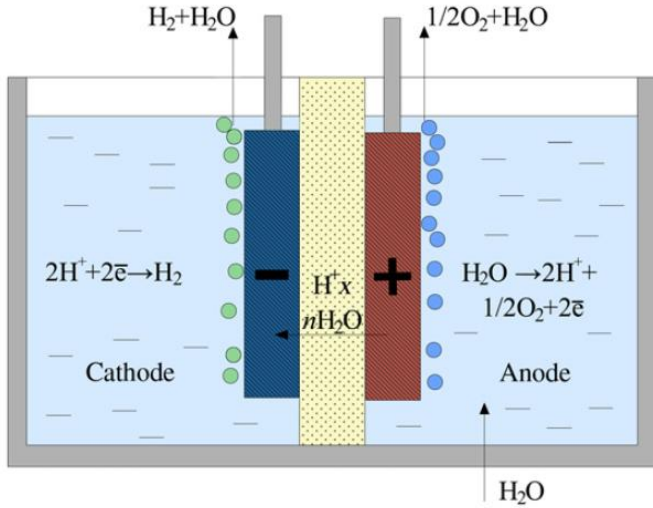


Figure 4. PEM electrolyzer.

Oxygen is produced at the anode side based on the reaction equation (4)



The hydrogen ions (protons) are transferred through the proton-conducting polymer to the cathode, where hydrogen is formed according to reaction equation (5)



PEM electrolyzers are considered the safest and most efficient technology for water electrolysis. Efficiency of 82% is achievable with best current technology (Carmo et al. 2013). Commercial operators provide electrolyzers operating at 280 bars with hydrogen production rate of 26 m³/h, and pressurized operation up to 700 bar is believed possible. The critical component in PEM electrolyzer operation is the ion-exchange membrane. The membrane and the catalysts used at anode and cathode have to withstand highly acidic conditions. This increases the capital costs for not only the proton-exchange membrane and the catalysts but also for the other cell components. For this reason PEM electrolysis is very expensive technology. On the other hand PEM can operate in highly dynamic conditions, load change from 0 to 100% can be achieved in less than 50ms which makes PEM very attractive technology for renewable energy storage. (Gandía et al. 2013).

Solid oxide electrolysis (SOEC) is a high-temperature water electrolysis technology. The cell separator is made of oxide-ion conducting ceramic material which acts as an electrolyte. The construction of SOEC electrolyzer is presented in figure 5.

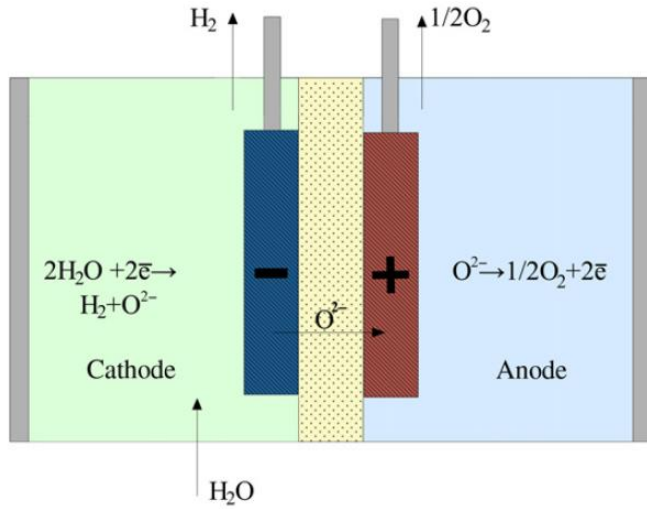
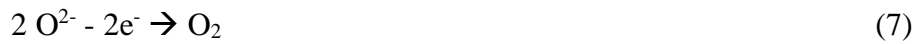


Figure 5. Construction of SOEC electrolyzer.

Water molecules are reduced at the cathode according to reaction equation (6)



The oxygen ions are transferred to the anode through the ceramic cell separator, where oxygen is formed according to reaction equation (7)



Typical operational temperature for SOEC is between 800-1000°C. Research projects on SOEC have been able to reach efficiencies close to 100%. Another point of interest is the possibility of co-electrolysis of water and CO₂ to produce syngas (CO + H₂) which is of great commercial interest in the production of synthetic fuels. The high operating temperature also results in fully reversible electrochemical processes which enables the SOEC to operate either as a fuel cell or as an electrolysis cell. (Gandía et al. 2013). The fuel cell operation provides the ability to convert Gas-to-Power (GtP) which increases the overall system flexibility in electricity grid load management.

Issues with the technology include aggressive degradation of performance with increased operating hours. Corrosion at anode due to oxygen evolution is one example of the problems associated with the technology. The material degradation issues have to be resolved before practical applications can be considered. (Gandía et al. 2013).

2.2.2 Chemical methanation

Methanation is the second process step in PtG system. Methanation systems can be divided into two different processes; the chemical and biological methanation (Lehner et al. 2014). The mechanisms involved in chemical methanation will be presented first.

The chemical methanation process, also known as Sabatier reaction, is the process of converting CO₂ or CO into methane. The process involves a reaction with H₂ and use of a metal catalyst, typically nickel or ruthenium. The chemical reactions are shown below:



The reaction is highly exothermic and typically takes place between 250 °C and 400 °C. (Hoekman et al. 2010). Thermodynamically it can be concluded that methanation profits from low temperature and high pressure conditions (Kopyscinski et al. 2010)

Lower temperatures favor the Sabatier reaction while at higher temperatures the opposite reaction becomes more dominant. Steam methane reforming, which is the opposite of Sabatier reaction, is commercially operated around 800-1000 °C to produce H₂. (Hoekman et al. 2010)

Majority of commercially operated methanation reactors are either fixed bed or fluidized bed reactors. Fixed beds were originally designed to purify small amounts of CO from hydrogen rich gases in ammonia plants. The small amount of CO compared to the heat capacity of the flowing gas meant that the heat produced by the reaction was not a problem. For methane production with high volumes of CO₂ or CO the heat of reaction becomes an issue and the beds must be cooled. Otherwise the temperatures inside the bed increase to levels where catalyst destruction becomes an issue and methane production is limited due to approaching of the chemical equilibrium. The main processes that have been proven suitable

for methane production are either series of adiabatic fixed bed reactors with gas recycling and cooling or fluidized bed reactors. (Kopyscinski et al. 2010)

Fluidized bed reactor is suitable for large scale operation of heterogeneously catalyzed and highly exothermal reactions. High gas velocities and mixing of solids (catalysts) promote near-uniform temperature profile which makes controlling the reaction easier. Heat and mass transfer is more efficient when compared to fixed beds and the catalyst is easier to replace and recycle. The main drawback is the higher attrition of the catalyst and the bed itself. (Kopyscinski et al. 2010)

Another proposed reactor concept that is in a research phase is the three phase methanation (3PM) utilized in a slurry bubble column. In the 3PM the catalyst with a diameter of $<100\mu\text{m}$ is suspended in an inert liquid. The gas is fed into the slurry where it reacts, releasing the heat into the fluid. The fluid makes it easier to control the catalyst temperature and to dissipate heat from the process. Large heat capacity of the fluid can help to balance fluctuations in the methanation process which is another advantage in PtG applications. (Götz et al. 2014).

The disadvantage of using chemical methanation for PtG is the catalyst intolerance for catalyst poisons such as Sulphur and Sulphur containing molecules. In order to utilize CO_2 with trace amounts of impurities the flue gas would have to be cleaned first, which increases process investment costs. Depending on the reactor design the chemical methanation has a recommended minimum load value. For fixed bed reactors minimum load of 40% is reported and for 3PM reactors 10-20%. However with improved reactor design the minimum loading could be further decreased. The catalyst can react quickly to dynamic load changes and the limitations to process dynamics are related to process control issues instead of the chemistry of the process. (Götz et al. 2014).

2.2.2.1 Biological methanation

Biological methanation, also called as methanogenesis, is the process where micro-organisms serve as a methane producing bio-catalyst. These methanogenic bacteria belong to the domain of Archaea and are known to operate through the following reaction paths: Acetoclastic methanogenesis



And hydrogenotrophic methanogenesis



Biological methanation is most well-known in biogas production processes where methane is produced from decomposing biomass. (Lehner et al. 2014). The process of anaerobic digestion of biomass involves numerous different micro-organisms and proceeds in four stages with methanation as the final step in the whole process. Some of the bacteria participate in multiple reactions while some perform only one reaction. Disruption of any one stage will lead to disruption of entire process. (Burkhardt, Busch 2013).

The anaerobic digesters are used as a standard technology for various applications including treatment of waste residues such as sewage sludge, waste water, livestock manure, organic industrial waste and municipal solid waste. (Seadi et al. 2008)

Two different ways to implement biological methanation in PtG have been proposed: In situ hydrogen injection into digesters in biogas plants or the use of external reactor. Direct injection of hydrogen into anaerobic digesters benefits from low investment costs, but is limited by the CO_2 production rate of the digester. Bioreactors on the other hand can be designed to employ a desired microbial culture to utilize pure CO_2 and H_2 . The bioreactors can also utilize alternative CO_2 sources besides biogas. For all designs the mass transfer limitation between gas and liquid phases is the rate limiting step. (Götz et al. 2014)

Advantage of methanogenesis is that it takes place at low temperatures (40-70°C) and at atmospheric pressure thus simplifying the process. The main disadvantage of the process is the mass transfer limitation between gaseous and liquid phases due to the sub-par solubility of hydrogen to water. This will have limiting effect on hydrogen injection rate. (Götz et al. 2014). It should be taken into account that the living organisms involved in biological methanation are sensitive to changes in the process conditions such as temperature, pH, level of nutrients and organic loading rate. Mishandling of the process parameters could lead to the destruction of the microbial culture. (Mao et al. 2015).

Efficiency of the methanation reaction in both chemical and biological process route is limited by the Sabatier reaction to a maximum of 80% (Benjaminsson et al. 2013). How well each methanation reactor achieves this maximum efficiency is dependent on the reactor design.

3 CO₂-CAPTURE FOR PTG

The methanation process of PtG creates a demand for reliable CO₂-source which can meet the quality standards required by the methanation technology and can produce CO₂ in large quantities during times of excess renewable electricity production. (Reiter, Lindorfer 2015).

To identify suitable CO₂ sources for PtG applications some form of criteria must be established for comparison of different sources. The methanation process itself sets certain limitations to the gas purity which must be met. In context of climate change it is important to know whether the CO₂ is of biogenic or fossil origin. Lastly, specific costs of the technology and energy consumption per kg of CO₂ produced will decide whether the technology is economically feasible or not. (Reiter, Lindorfer 2015).

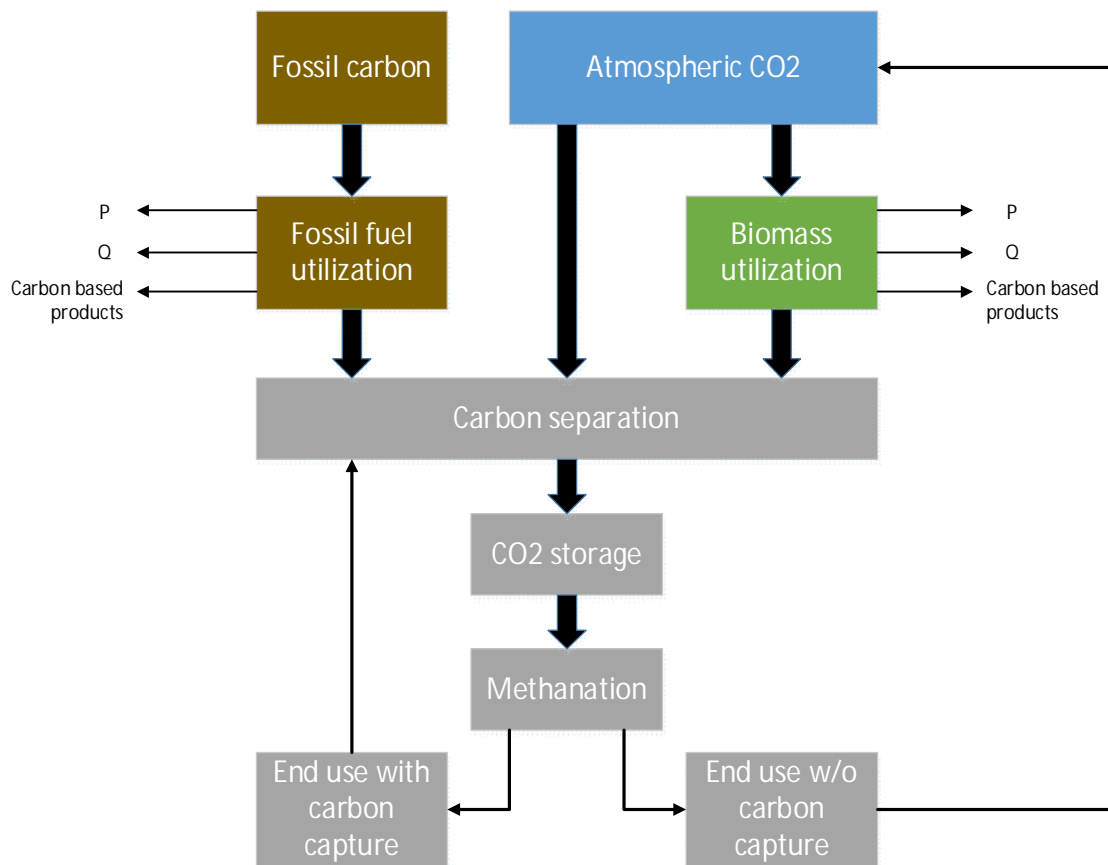


Figure 6. Source carbon circulation related to the PtG process.

Catalysts employed in typical Sabatier reactors are prone to deactivation due to existence of different catalyst poisons and impurities in the feed gas. The most harmful trace substances include SO₂, H₂S, particles, tar, N₂ and NH₃. List of the critical requirements for

CO₂ feed gas can be seen in table 2. (Reiter, Lindorfer 2015). For further information about catalyst deactivation, refer to Bartholomew 2001.

Table 2. CO₂ quality requirements for chemical methanation input.

Component	Unit	Methanation input	CO ₂ stream
H ₂	vol.%	35 - 80	-
CO ₂	vol.%	0 - 30	0 - 100
CO	vol.%	0 - 25	0 - 100
CH ₄	vol.%	0 - 10	0 - 50
N ₂	vol.%	<3	<15
O ₂	vol.%	n.s.	n.s.
H ₂ O	vol.%	0 - 10	0 - 50
Particles	mg/m ³	<0.5	<2.5
Tar	mg/m ³	<0.1	<0.5
Na, K	mg/m ³	<1	<5
NH ₃ , HCN	mg/m ³	<0.8	<4
H ₂ S	mg/m ³	<0.4	<2
Nox	mg/m ³	n.s.	n.s.
Sox	mg/m ³	n.s.	n.s.
Halogens	mg/m ³	<0.06	<0.3

The bacteria employed in biological methanation are more tolerant of the typical impurities found in methanation feed gases. The bacteria show high tolerance especially to sulphur, ammonia and oxygen. (Götz et al. 2014). CO₂ stream quality is affected by the CO₂ source as well as the carbon capture technology (Reiter, Lindorfer 2015). For this reason it is useful to explore different carbon separation technologies in the following chapter.

3.1 State of the art CCS technologies

CO₂- capture technologies can be divided into several subcategories: Post-combustion, Oxy-fuel combustion and Pre-combustion. Post-combustion technologies separate the CO₂ from flue gas flow after the combustion of fuel. Oxy-fuel combustion technologies burn the fuel in oxygen-filled environment, thus producing concentrated CO₂ stream which is ready for capture. Pre-combustion systems process the fuel in a gasification reactor, producing a stream of syngas which is then further processed in water-gas shift reactor to produce a mixture of CO₂ and H₂. The CO₂ is then captured with chemical solvent and H₂ is used as fuel. (Metz et al. 2005).

Carbon separation technologies can be further divided by the method of separation. Technical maturity of these systems vary from commercial applications to laboratory

scale processes. In figure 7 are listed the most notable carbon separation technologies. While large scale implementation of CCS has yet to take place, CO₂ separation in energy production has been studied extensively in various CCS studies and projects. (Rubin et al. 2012).

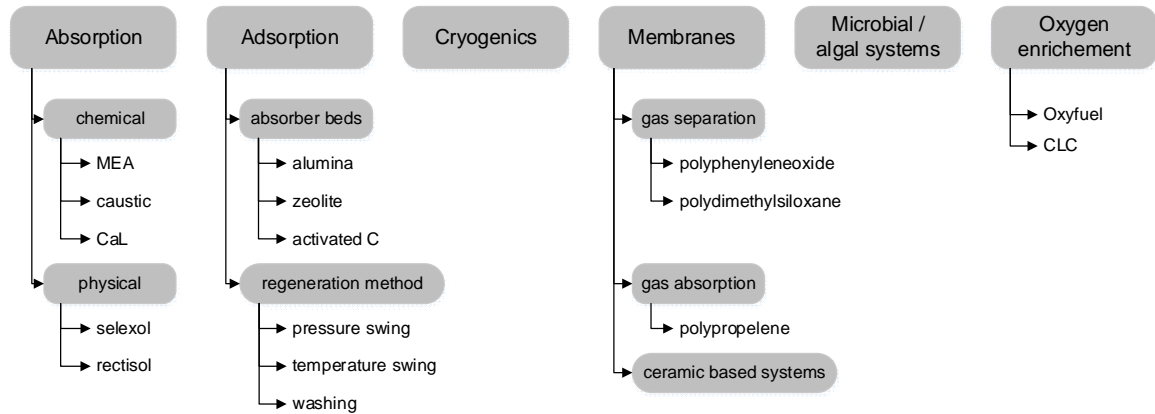


Figure 7. Overview of different CO₂ separation technologies.

Most carbon separation techniques require substantial amounts of energy and thus cause significant energy penalty, incurring increased costs for the operation of CO₂ producing plant. (Rubin et al. 2012).

3.1.1 Post-combustion capture technologies

Even though carbon separation technologies have not yet been extensively applied to full scale power plants, some of the post combustion technologies have been commercially available for decades. The main application so far has been to remove trace amounts of CO₂ from gas streams other than combustion products. These technologies have been used in wide range of industries, ranging from natural gas production to food and beverage industry. (Rubin et al. 2012)

3.1.1.1 Chemical solvents

The chemical solvents are technologically the most advanced and mature technology (Metz et al. 2005). Chemical solvents refer to flue gas scrubbing technologies with various organic solvents, usually including amines. In solvent scrubbing the CO₂ rich flue gas is sprayed with aqueous solution of amine-rich solvent in an absorber column. The solvent is then collected and transferred to a stripper column where it is heated to release the captured

CO₂. The resulting CO₂ stream is then dried and compressed. Typically solvent scrubbing can capture 85-90% of the feed-in flue gas. One of the advantages of solvent scrubbing is the ability to remove CO₂ even from flue gas streams with low partial pressure (3kPa – 15kPa) of CO₂. Negative properties of amines include high regeneration heat required and corrosivity. (Rubin et al. 2012). The amine solvent is also prone to react with other acidic gas components besides CO₂, such as NO_x and SO_x. Reaction with these impurities will lead to the formation of heat stable salts which decrease the absorption capacity of the solvent. Removal of these components is required to prevent excessive solvent deactivation. (Metz et al. 2005).

3.1.1.2 Membrane separation

Membranes refer to permeable material which can selectively remove CO₂ from other components in the flue gas. Basically the membrane acts as a filter in the flue gas stream, capturing CO₂ while allowing other components to pass through. (Rubin et al. 2012). The flow across the membrane is typically driven by pressure gradient over the membrane, thus higher pressure flue gas streams are preferred for membrane separation (Metz et al. 2005). Membrane technologies have been used since 1980 for gas purification in commercial processes (Rubin et al. 2012). By now membrane technology can be considered technically mature and it has some advantages over solvent scrubbing technologies, such as lower capital cost and lower energy consumption. However the membrane technology requires flue gas with high CO₂ concentration and at lower concentrations the solvent scrubbing technology proves more effective. To increase the membrane CO₂ capture efficiency at lower partial pressures its selectivity needs to be improved. (Metz et al. 2005).

3.1.1.3 Pressure / temperature swing adsorption

The term “pressure / temperature swing adsorption” refers to the method of sorbent regeneration. There are two main methods for adsorbent regeneration; either by reducing the operating pressure (pressure swing) or increasing operating temperature (temperature swing). The actual working capacity of an adsorbent is determined by the difference in adsorption and regeneration conditions. (Abanades et al 2015).

Pressure swing adsorption has been commercially operated for purification of syngas in steam methane reforming. Process occurs in two phases; adsorption and desorption. In adsorption phase the CO₂ is captured in a bed reactor containing solid sorbents like activated

carbon, alumina or zeolites. In desorption phase the operational pressure is decreased, prompting the release of the captured CO_2 from the sorbent. The characteristics of pressure swing adsorption is that it does not selectively capture only CO_2 but also other impurities from the flue gas. For this reason it has been preferred method for hydrogen purification. (Metz et al. 2005).

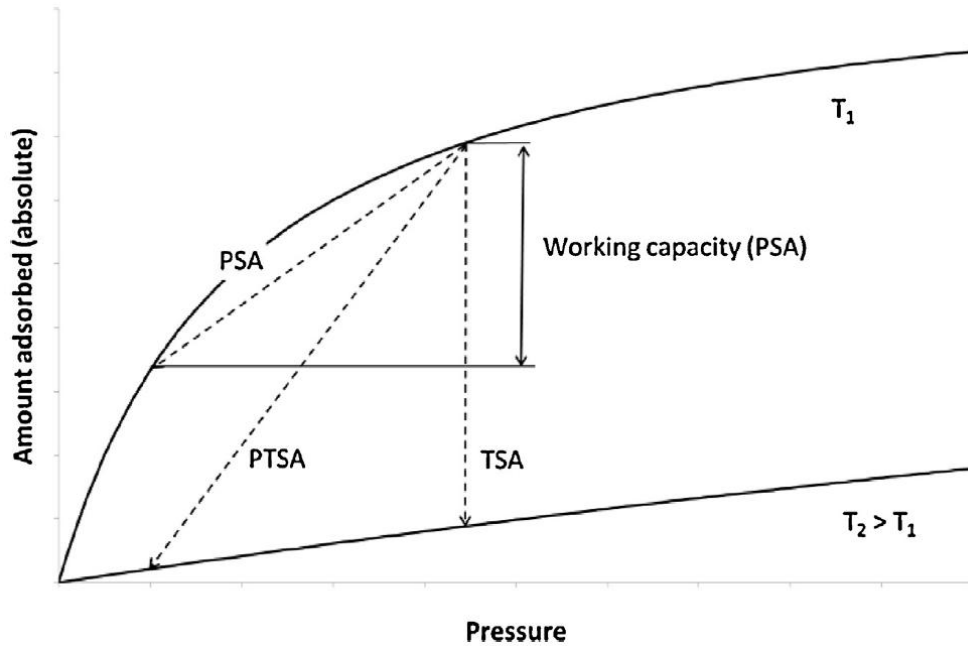


Figure 8. Adsorption isotherms at different temperatures and working capacity. (Abanades et al 2015).

3.1.1.4 Calcium looping cycle

Calcium looping cycle employs solid sorbents instead of liquid ones. The preferred solid sorbent is calcium oxide (CaO), which is used in a separate carbonator reactor to capture the CO_2 from flue gases. The formed calcium carbonate (CaCO_3) is then looped to a calciner where the reverse reaction takes place. Releasing the CO_2 from the carbonate requires heat and this is provided by burning fuel in pure-oxygen environment, thus producing concentrated stream of CO_2 . The CaO formed in the calciner is then looped back to the carbonator reactor. (Rubin et al. 2012). The CaO can react with both SO_2 and H_2S , forming either CaSO_4 or CaS and causing loss in absorbent efficiency. The advantages of calcium looping cycle include its lower energy consumption in relation to amine-based solvent scrubbing, the utilization of cheap sorbent which is available in great abundance and the synergy with cement industry as the cement industry can utilize spent sorbent as a raw material. (Dean et al. 2011).

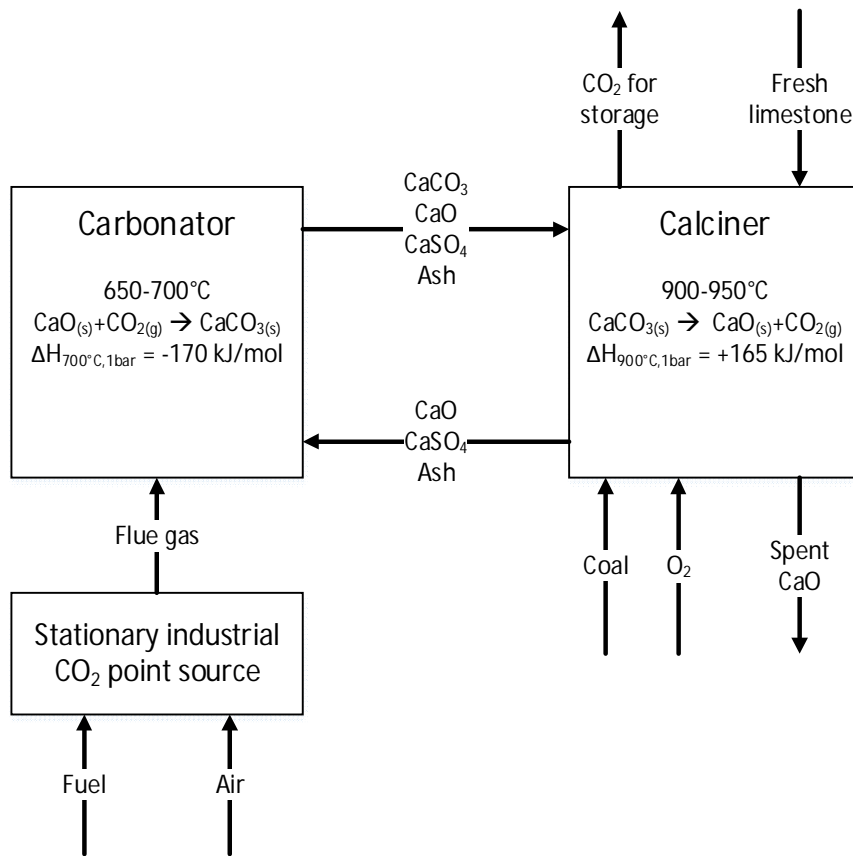


Figure 9. Calcium looping cycle. (Dean et al. 2011).

In the last decade the technology has evolved from few lab scale experiments to pilot testing in the MW range. This advance is largely attributed to similarity of some key components (calciner, carbonator) with existing combustion technologies which utilize circulating fluidized beds. There are some engineering challenges which need to be overcome before full scale commercial operation becomes practical, such as increasing the sorbent resistance to physical attrition, process cost reduction and efficiency increase. (Abanades et al 2015).

3.1.2 Oxyfuel

Oxyfuel, or oxy-combustion, refers to the combustion of fuel in a high-oxygen environment devoid of nitrogen. This is achieved by using air separation unit (ASU) to remove nitrogen from combustion air. Pure oxygen, with concentration above 95 vol%, is then fed to the boiler for combustion. The flue gases in Oxyfuel combustion include high concentrations of CO₂ and smaller amounts of H₂O with the possibility of some leak-in nitrogen. Because of a very high adiabatic combustion temperature in pure-oxygen

conditions, some of the flue gas must be recycled to moderate the flame temperature. (Scheffknecht et al. 2011)

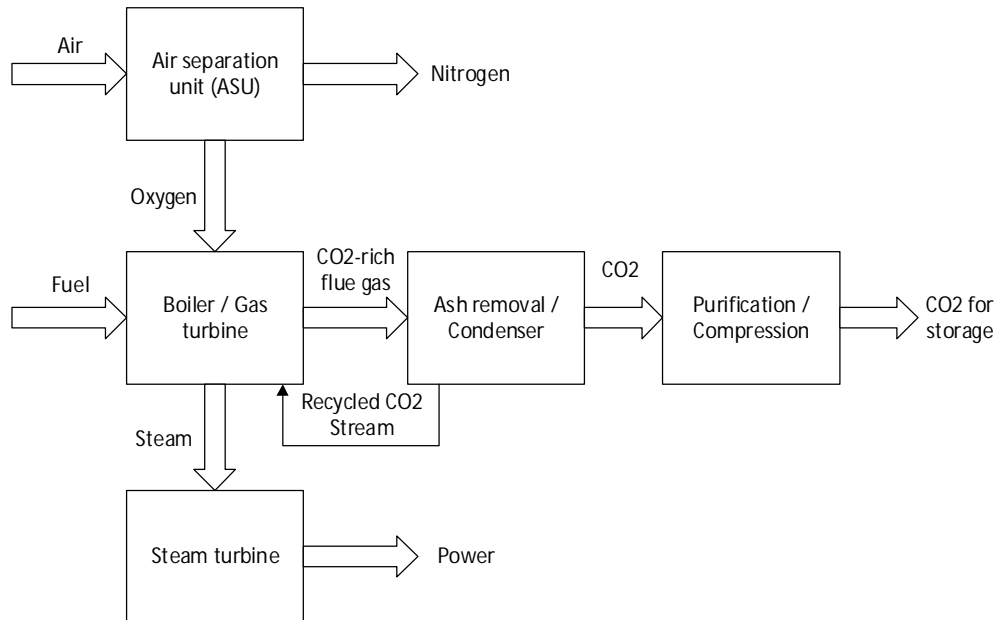


Figure 10. Basic oxyfuel-process. (Wall et al. 2009)

The product flue gas, after condensing all the water vapor, typically contains roughly 80-95 % (dry basis) CO₂. This number is affected by the fuel type, excess oxygen, air-in leakage and the type of flue gas processing chosen. Various industrial scale pilot plants operated between 1980 and 2000 have been able to reach concentrations of 90-95% CO₂. This high concentration of CO₂ in the flue gas eliminates the need for energy intensive CO₂ separation units that are employed in post-combustion capture. After the harmful corrosive agents are removed from the flue gas, it can be compressed and transported for storage. (IEAGHG, 2010.)

The main differences in oxy-combustion when compared to normal air combustion are a result of the properties of CO₂ and N₂ which are the main diluting gases in the combustion process. CO₂, which is the main dilute for Oxyfuel, has higher density, heat capacity and emissivity when compared to N₂. These fundamental differences in the properties of the gas must be taken into account when designing and operating Oxyfuel process. The main differences will be listed below.

- Reaching the same adiabatic flame temperature in Oxyfuel requires higher concentration of oxygen (30%) than in similar air fired process (21%).

- The high concentrations of CO₂ and H₂O in the flue gas will result in higher gas emissivity, thus increasing radiative heat transfer.
- The volume of flue gases flowing through the furnace is reduced and the power plant produces roughly 80% less flue gases.
- Excess air ratio decreases from 20% (for coal) in air fired boiler to about 3-5% for Oxyfuel boiler.
- Due to the high recycle ratio of the flue gases (roughly 60%), the concentration of some undesirable components (SO_x, NO_x) may increase unless the flue gases are processed before recycling.
- Oxyfuel is typically less efficient per unit of energy produced than equivalent air-fired process due to the auxiliary power consumption of the ASU and flue gas compression. (Wall et al. 2009) With the existing technologies oxygen production via cryogenic ASU and compression of CO₂ impose a net efficiency penalty of 8-12 % points to electricity production. (Scheffknecht et al. 2011)

3.1.2.1 Chemical looping combustion

Chemical looping combustion (CLC) is a special case of oxygen combustion. In CLC the oxidation and reduction reactions are separated into two reactors. The process is made possible by looping a metal oxide which acts as an oxygen carrier between the two reactors. Metal oxidation occurs in the air reactor where the oxygen carrier reacts with ambient air and forms metal oxide. The metal oxide is then fed into fuel reactor where it is reduced by the combustion with the fuel. The reduced oxygen carrier is then returned back to air reactor. The flue gases from fuel reactor consist of CO₂ and water and with the chemical looping the use of energy intensive air separation units is avoided, thus decreasing the energy penalty of CCS operation. (Metz et al. 2005).

Circulating fluidized beds are preferred choice for reactors as it makes possible to move solids between reactors and ensures sufficient heat and mass transfer between the solids and the fluid. The fluidized bed places the oxygen carrier under considerable stress and one of the issues of this technology is ensuring sufficient mechanical and chemical stability of the oxygen carrier. (Metz et al. 2005). The research on CLC has focused on gaseous fuels but in recent studies the focus has shifted on adapting the process for solid fuels. Smaller CLC pilot plant studies have been realized with solid fuels. (Lyngfelt et al. 2013). The technology utilizing gaseous fuels has been successfully demonstrated in a

number of small scale pilot studies and is ready to be scaled up to 1-10 MW scale. Plants operating with gaseous fuels have shown excellent performance with 100% CO₂ capture and fuel conversion. For solid fuel reactors the incomplete conversion of fuel reactor gas is a problem and can only be attained with very expensive oxygen carriers. Char leakage to the air reactor and with the fuel reactor flue gases has also been reported. Although further development is required, the CLC technology has considerable promise in reducing the large costs and energy penalties involved in CO₂ capture. (Abanades et al 2015).

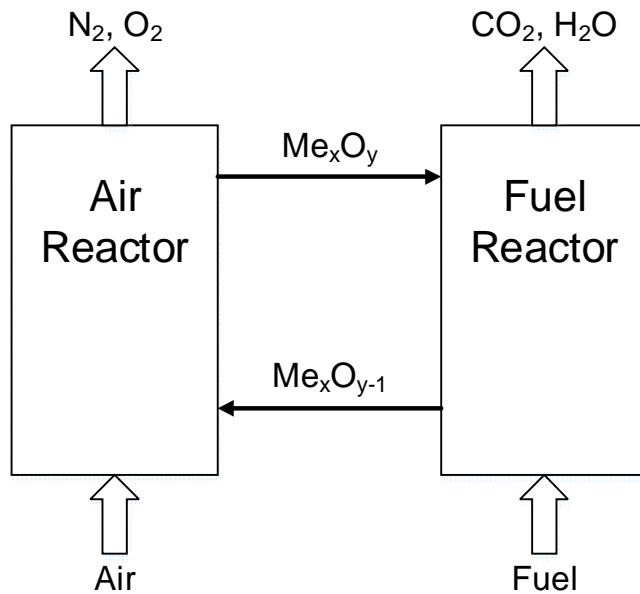


Figure 11. Basic CLC process. (Lyngfelt et al. 2013).

3.1.3 Pre-combustion technologies

In pre-combustion technologies the fuel must first be processed to a form where the carbon separation is possible. Practically this means production of synthesis gas from primary fuel either by addition of steam (steam reforming) or oxygen to the process. If the fuel is a fluid then the oxygen addition is called “partial oxidation” and if the fuel is a solid it is called “gasification”. (Metz et al. 2005).

One application of pre-combustion technology used for energy production is the integrated gasification combined cycle (IGCC) which resembles natural gas combined cycle (NGCC). The main difference is that instead of using natural gas as a fuel the facility employs solid coal which is gasified to produce a flue gas with high concentration of CO₂ and H₂. The high operating pressure in combination to high partial pressure for CO₂ makes

it possible to utilize solvents based on physical absorption. Physical solvents are characterized by weaker binding forces than amine based chemical solvents which enables their regeneration by using pressure swing method. Physical solvents release the captured CO_2 when the operating pressure is dropped, thus decreasing the energy demand for solvent regeneration when compared to chemical solvents. However the gasification and water gas shift reactors among other components still cause substantial energy penalty. (Rubin et al. 2012).

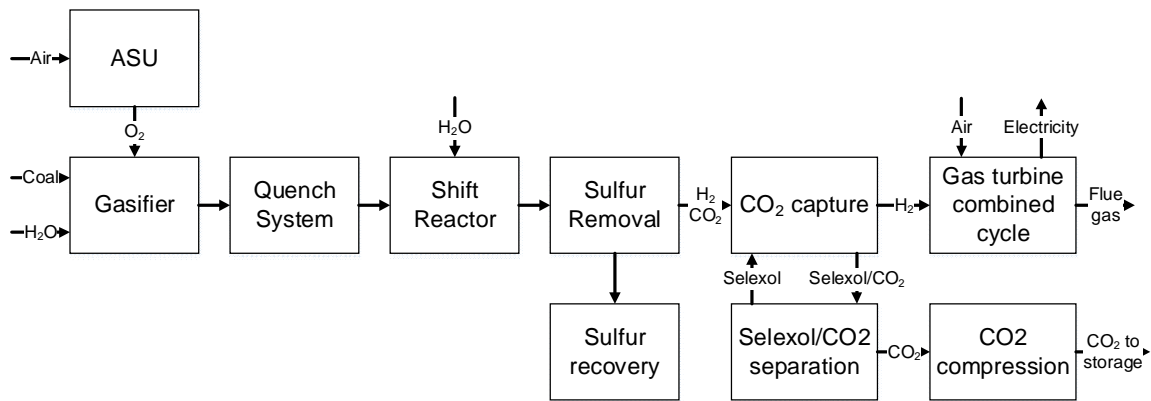


Figure 12. Basic Pre-combustion process. (Rubin et al. 2012).

Pre-combustion method is utilized in commercial processes for syngas purification as well as in other industrial applications to remove impurities such as sulphur, nitrogen and CO_2 . As of yet the technology has not been utilized at electric power plants. (Rubin et al. 2012).

3.2 Potential CO_2 sources

Potential CO_2 sources include CO_2 from combustion processes and CO_2 from by-product streams of industrial processes. CO_2 capture directly from the atmosphere is also technically feasible. Different CO_2 sources are listed in Figure 13 with their respective CO_2 concentrations in the flue gas or by-product gas. (Reiter, Lindorfer 2015). The partial pressure of CO_2 is one of the most important aspects when considering the available CO_2 separation technologies for the process. When the partial pressure of flue gas CO_2 decreases it also narrows down the available separation technologies considerably. Generally lower partial pressures require more energy intensive separation methods. The flue gas CO_2 content of a combustion process varies depending on the fuel and excess air ratio used, however the combustion processes are characterized by low CO_2 concentrations. Some industrial

processes produce almost pure streams of CO₂ as a result of the process. One such example is the fermentation of sugars to produce alcohol. (Metz et al. 2005).

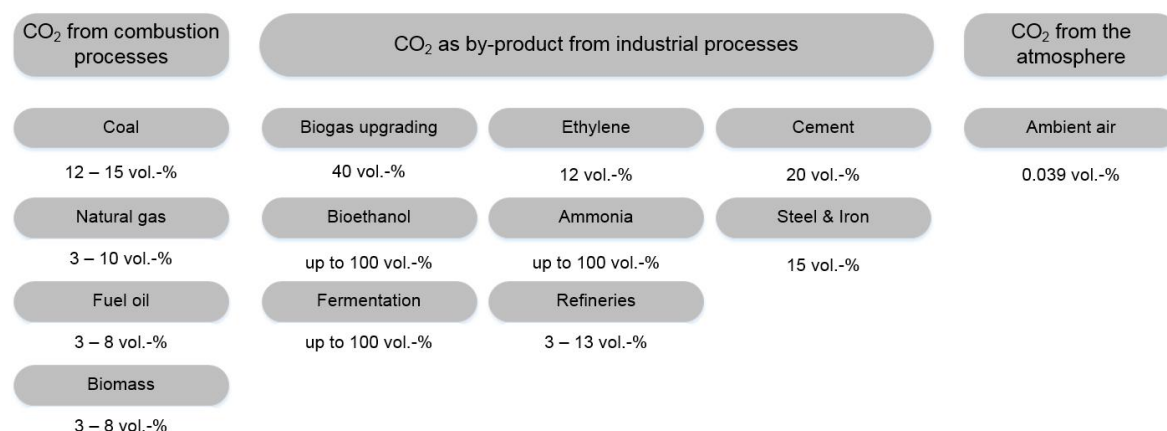


Figure 13. Potential CO₂ sources and their respective CO₂ concentrations.

Some industrial processes require that undesired components, such as CO₂, are removed from the product gas. This type of product gas cleaning is utilized by petrochemical industry in various processes such as ammonia production and natural gas sweetening. As a result, the gas cleaning process produces concentrated stream of CO₂. (Metz et al. 2005). The potential CO₂ sources will be explored in the following subchapters.

3.2.1 Power plants

Energy production by combustion of fuels is significant producer of CO₂ and as such could provide considerable amount of CO₂ for methanation (Reiter, Lindorfer 2015). Traditional combustion processes and fuels produce relatively low-concentration CO₂ streams which make amine-based solvents most suitable for carbon separation. Implementation of CCS will have considerable effect on plant efficiency and it will increase the required energy input per produced power output. (Rubin et al. 2012). Reiter and Lindorfer (2015) studied the effect of different CCS technologies on the efficiency of several power plant setups. Their results are presented in the table 3. It can be concluded that CCS will typically decrease plant efficiency by 7-13 %-points. The increase in required energy input varies between 16.3 % and 29 % for plants operating with fossil fuels. The high energy cost is associated with the high regeneration heat of chemical solvents required for flue gases with low CO₂ partial pressure, or with the ASU operational costs for plants utilizing oxyfuel technology. (Reiter, Lindorfer 2015).

The exceptional data of calcium looping system in table 3 is not directly comparable to other values. Although the additional energy input of the process is very high, effectively doubling the fuel consumption of the plant, the resulting heat from the carbon capture process is of high quality and can be utilized to produce steam, thus increasing the overall energy production and leading to relatively good efficiency. Therefore the additional primary energy requirement for calcium looping is not directly comparable with other presented values. (Mantripragada, Rubin 2014).

Table 3. Effect of CCS on new power plants. (Reiter, Lindorfer 2015). *(Mantripragada, Rubin 2014). ** (Kvamsdal et al. 2007)

Fuel and capture technology	Net efficiency		Energy penalty		
	No carbon capture	With carbon capture	Efficiency reduction in %-points	Additional energy input	Additional primary energy in MJ/kgCO ₂ captured
Pulverized coal power plant					
Post-combustion (chemical absorption)	40.0 %	31.0 %	9.0 %	29.0 %	2.7
Pre-combustion (IGCC, physical absorption)	40.0 %	33.0 %	7.0 %	21.2 %	1.9
Oxyfuel (with ASU)	40.0 %	32.0 %	8.0 %	25.0 %	2.3
Calcium looping*	39.0 %	36.0 %	3.0 %	88.5 %	4.8*
Natural gas (NGCC) power plant					
Post-combustion (chemical absorption)	50.0 %	43.0 %	7.0 %	16.3 %	2.9
Pre-combustion (IGCC, physical absorption)	50.0 %	42.0 %	8.0 %	19.0 %	3.0
Oxyfuel (with ASU)	50.0 %	41.0 %	9.0 %	22.0 %	3.6
Chemical looping**	56.7 %	51.3 %	5.4 %	-	-
Biomass power plant					
Post-combustion (chemical absorption)	47.0 %	44.0 %	3.0 %	6.8 %	1.3
Pre-combustion (IGCC)	47.0 %	34.0 %	13.0 %	38.2 %	5.5

The captured CO₂ gas quality varies considerably depending on the fuel, combustion technology and carbon separation technology used (Reiter, Lindorfer 2015). For example various coals and heavy fuel oils contain high amounts of sulphur and heavy metals. The likely impurities, which result from capturing CO₂ from such sources, include SO₂ for conventional steam plants and H₂S for IGCC pre-combustion capture. (IEA 2004).

In the table 4 the effect of different separation technologies on the captured CO₂ quality are listed for coal and NG fired power plants. It should be noted that SO₂ concentration for oxyfuel and the H₂S concentration for pre-combustion capture are for cases where impurities are left on purpose in the CO₂- stream to decrease capture costs. (Metz et

al. 2005). From the table it can be observed that when utilizing post-combustion technologies the trace amounts of harmful substances are limited. From this point of view the methanation process favours post-combustion separation technologies.

Table 4. Trace components in dried CO₂ stream after capture, % by volume. (Metz et al, 2005).

Coal fired plants	SO ₂	NO	H ₂ S	H ₂	CO	CH ₄	N ₂ /Ar/O ₂	Total
Post-combustion capture (MEA)	<0.01	<0.01	0	0	0	0	0.01	0.01
Pre-combustion capture (IGCC)	0	0	0.01-0.6	0.8 - 2.0	0.03 - 0.4	0.01	0.03 - 0.06	2.1 - 2.7
Oxyfuel	0.5	0.01	0	0	0	0	3.7	4.2
Gas fired plants	SO ₂	NO	H ₂ S	H ₂	CO	CH ₄	N ₂ /Ar/O ₂	Total
Post-combustion capture (MEA)	<0.01	<0.01	0	0	0	0	0.01	0.01
Pre-combustion capture (IGCC)	0	0	<0.01	1	0.04	2	1.3	4.4
Oxyfuel	<0.01	<0.01	0	0	0	0	4.1	4.1

For PtG applications the utilization of CO₂ from power plants can be challenging. During times of excess renewable production the CO₂ producing power plants decrease their production to accommodate for the excess supply. This leads to sharp decrease in CO₂ emissions which may affect the availability of CO₂ for methanation. Some form of temporary CO₂ storage may be required to ensure sufficient CO₂ availability if power plants are utilized as a source.

3.2.2 Byproduct CO₂

Several different industrial processes produce CO₂ either as a byproduct of the chemical process or as a result of intensive energy consumption required in the production. These CO₂ producing processes include steel and cement industry, ethylene, ethylene oxide, ammonia, bioethanol and biogas production. (Metz et al. 2005). On Finnish scale the pulp and paper industry is another substantial CO₂ producer.

The characteristics of different industrial sectors are now examined with respect to carbon capture.

3.2.2.1 Iron and Steel industry

Iron and steel sector emitted worldwide 2.3 Gt of CO₂ in the year 2007, which equals to 10% of total CO₂ emissions and 30% of the direct CO₂ produced by industry (Kuramochi et al. 2012). Integrated steel mills account for over 80% of CO₂ emissions in steel production (Metz et al. 2005). In typical integrated steel mill the major CO₂ sources are the coke oven

gas which is caused by coke production from coal, ore preparation where iron ore is sintered before it is fed to blast furnace (BF), lime kiln where limestone is calcined to produce quicklime, blast furnace where iron ore is reduced to pig iron and basic oxygen steelmaking process where the carbon content of pig iron is reduced by injection of oxygen to produce steel. (Wiley et al. 2011). The oxygen consumption is roughly 53 m³ per ton of pig iron (Great Soviet Encyclopedia 1979). Roughly 70% of the carbon supplied to a steel mill is present in the blast furnace gas which is used as a fuel for energy generation within the steel mill. The CO₂ can be captured either before or after combustion. The CO₂ concentration of the gas is 20% before and 27% after the combustion with air. These values are higher than typical CO₂ concentrations of power plants thus making CO₂ capture easier. The other point sources within steel mills could also provide large amounts of CO₂, such as oxygen-steel furnace which produces flue gas with 16% of CO₂ and 70% of CO. (Metz et al. 2005).

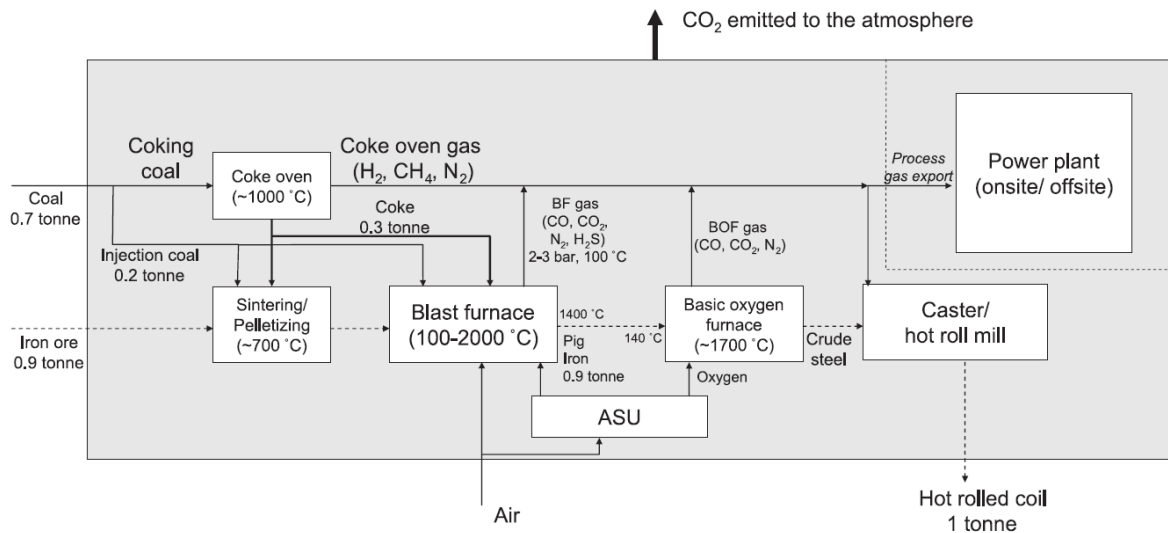


Figure 14. Typical blast furnace – basic oxygen furnace -based steel mill.

Sulphur (SO_x, H₂S) is typically removed from the blast furnace gas before combustion in hot stoves and power plant, thus resulting in very low concentrations of Sulphur in the flue gas ready for capture (Arasto et al. 2013). Typical flue gas characteristics for various steel mill point sources are shown in the table 5 (Romano et al. 2013).

The specific energy consumption and specific cost for different carbon separation methods when applied to steel mills are presented in table 6. The capture methods are separated into three main categories: post combustion capture in air-blown BF, which means retrofitting existing BF with carbon capture without modifications to the BF itself.

Table 5. Flue gas characteristics for steel mill CO₂-point sources. (Romano et al. 2013)

CO ₂ -sources	concentration of carbon species, % by vol.	Other components and impurities	% of total emissions
Power plant flue gas	Boiler: 15 - 25 Combustion turbine 7-12	O ₂ , N ₂ , Sox 10-30ppm, NO _x 30-60ppm	40 - 70
Hot stoves flue gas	CO ₂ : 15 - 25	O ₂ , N ₂ , Sox 10-30ppm, NO _x 30-60ppm	15 - 30
Lime kiln	CO ₂ : 20 - 30	O ₂ , N ₂ , low NO _x , low SO _x	
Coke plant flue gas	CO ₂ : 15 - 25	O ₂ , N ₂ , high Nox	15 - 20
Sinter plant	CO ₂ : 5 - 10	O ₂ , N ₂ , Dust, SO ₂ , Dioxins, Heavy metals, Nox	
Blast furnace gas	CO ₂ : 20 - 25 CO: 20 - 25 CnHm: <1	H ₂ , N ₂ , dust	-
Coke oven gas	CO ₂ : 2 - 5 CO: 4 - 7 CnHm: 20 - 50	H ₂ , N ₂	-
Basic oxygen furnace gas	CO ₂ : 10 - 18 CO: 55 - 80	H ₂ , N ₂ , dust	-

Second is the top gas recycling BF (TGRBF), where the BF is modified to enable oxy-combustion which results in high concentration of CO₂ and CO in the BF top gas. The CO₂ is then removed and CO is recycled as a reducing agent back to the BF.

Table 6. Specific capital costs and energy consumption for iron mills with CCS.

CO2 capture technique	Specific energy consumption [GJ/(t CO2 captured)]		Specific capital cost [€/ (t CO2 captured/a)]
	Steam	Electricity	
Air-blown BF			
Chemical absorption (MEA)	3.2 - 4.4	0.51 - 0.55	70 - 90
Chemical absorption (adv.solvents)	2.2 - 2.5	0.5	70
Physical absorption (Selexol)	-	0.77	180
Selective carbon membrane	-	0.69 - 0.89	80
Top gas recycling BF			
Chemical absorption (MEA)	3.3	0.62	60
Vacuum pressure swing adsorption	-	0.94	50
Physical absorption (Selexol)	0.21	0.93	60
selective carbon membrane	-	0.79 - 0.88	60 - 90
COREX			
Chemical absorption (MEA)	4.4	0.45	40
Physical absorption (Selexol)	-	0.97	40

And lastly the COREX process, which is based on smelting reduction that replaces conventional BF by combining the coal gasification and melt reduction of iron ore into single

unit. When the coke preparation is not needed the energy consumption of entire process is diminished and the COREX process produces flue gases with high content of CO₂ for easier capture. (Kuramochi et al. 2012).

The post combustion capture technologies for air-blown BF share the same technological maturity as in other fields of industry. The TGRBF and COREX have been studied extensively to reduce energy consumption in the steel mills and the TGRBF can be commercialized in the short- to mid-term. The COREX process is commercially available and operating in at least one location in South Africa. (Kuramochi et al. 2012).

3.2.2.2 Cement industry

Cement industry produced 2 Gt of CO₂ worldwide in the year 2007. This makes it the second most CO₂ intensive industry. The high CO₂ emissions are caused in combination with the high energy requirement of the process and due to the emissions from raw materials. (Kuramochi et al. 2012). Basic cement production process consists of raw material preparation, clinker production and clinker grinding and cement production. 50% of the CO₂ emissions are a result from the calcination of limestone in the clinker production phase while 40% of the CO₂ is from combustion of fuels needed to provide energy for calcination. In calcination limestone (CaCO₃) is heated up to 900°C where it reacts according to following equation:



The limestone reacts with heat to produce CO₂ and calcium oxide which is further converted to clinker. (Bosoaga et al. 2009). The flue gas CO₂ concentration of cement kilns depends on the production process and the type of cement produced. Typically the concentrations are higher than in power generation processes. (Metz et al. 2005). Some SO₂ and NO_x is present at the flue gases from cement kilns. An evaluation on German cement kilns shows that NO_x concentration is on average at around 410 ppm/m³, while SO₂ concentration is considerably lower with 50% of plants emitting less than 100mg/m³. SO₂ concentration is highly dependent on the limestone quality and is quarry specific. This should be considered when appropriate CO₂ separation technique is chosen. (IEAGHG 2013b).

For carbon capture in cement plants three main options are presented here: Post-combustion capture, oxy-combustion modification of the kiln and calcium looping process for the pre-calciner. Post combustion capture is considered more challenging for cement plants when compared to power plants due to the lack of low-grade heat available for solvent regeneration. Thus the regeneration heat must be produced at the plant or imported from nearby source. If the regeneration heat is produced onsite, the choice of fuel will have considerable effect on the performance of the plant. Some of the required regeneration heat can be obtained from waste heat sources onsite. It is estimated that between 13% and 50% of the regeneration heat could be obtained from clinker flue gas and clinker cooling. The capture will in any case increase the energy demand of the cement production. (Kuramochi et al 2012).

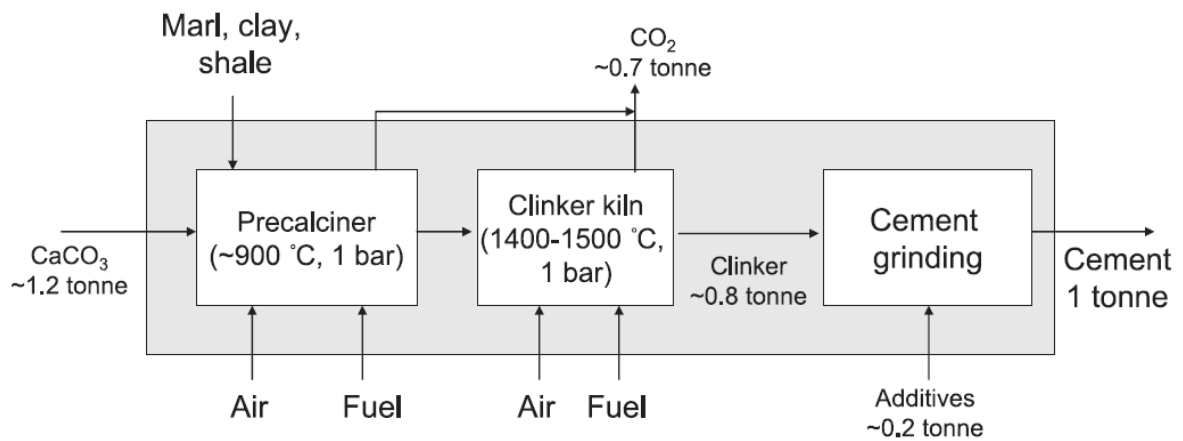


Figure 15. Basic cement plant. (Kuramochi et al. 2012).

The oxy-combustion option would require reconstruction of large central components of the plant. Modification of just the pre-calciner is considered technologically the safest option, however the technology is currently in the modeling and laboratory phase and the oxy-combustion of pre-calciner has not been proven. (Kuramochi et al 2012).

In the calcium looping cycle it is assumed that there is power plant or equivalent CO₂ source where CO₂ is being captured by the calcium looping cycle. The spent sorbent CaO from the carbon capture is then utilized for cement production, thus indirectly reducing the CO₂ emissions of the cement production. (Kuramochi et al 2012).

In the table 7 are presented the estimated cost and energy demands for different carbon capture methods with different stages of process integration. Advanced solvents with

the steam import or calcium looping cycle provide the most cost-effective alternatives. (Kuramochi et al 2012).

Table 7. Specific energy consumption and capital cost of CO₂ capture at cement plants.

CO ₂ capture technique	System details	Retrofit possible?	Specific energy consumption [GJ/(t CO ₂ capture)]			Incremental capital cost [€/ (t CO ₂ captured/a)]
			Primary energy	Steam	Electricity	
Post-combustion capture (MEA)	Steam import	Yes	-	3.7 - 4.4	0.37 - 0.73	60 - 160
Post-combustion capture (MEA)	Onsite NG-CHP	Yes	3.6	-	0.13	160
Post-combustion capture (MEA)	Onsite coal CHP	Yes	5.5	-	-0.35	310
Post-comb. capt. (adv.solvents)	Steam import	Yes	-	2.7	0.54	80
Oxyfuel kiln	Pre-calciner only	Yes (major modification of pre-calciner)	0.06 (coal)	-	0.73	150
	Entire kiln	New plants	0.86 (coal)	-	0.99	110
Calcium looping	Pre-calciner only	Yes (major modification of pre-calciner)	1.6 (coal)	-	0.54	50

3.2.2.3 Petroleum refineries

Petroleum refineries account for close to a 1 Gt/a of CO₂ emissions worldwide. The CO₂ emitted at refineries are produced from multiple sources which are typically scattered around wide areas. Onsite heat and electricity generation is responsible for bulk of the CO₂ emissions while the regeneration of fluid catalytic crackers is the second most important source. (Kuramochi et al. 2012). The hydrogen production facility is another substantial source of CO₂.

In the figure 16 is presented the distribution of CO₂ emissions by the source. Majority of the CO₂ is produced by sources which emit low concentrations of CO₂. The flue gas CO₂ concentration is known to range from 3% to 12%. Therefore amine based solvents are the preferred method for carbon capture. (Kuramochi et al. 2012).

Typical values for flue gas characteristics of the different point sources present at the refineries are shown in the table 8. When we take into account all the different processes utilized and consider all the available configurations, we can say that the compositions of flue gases and its contaminants are unique to each refinery. (Romano et al. 2013).

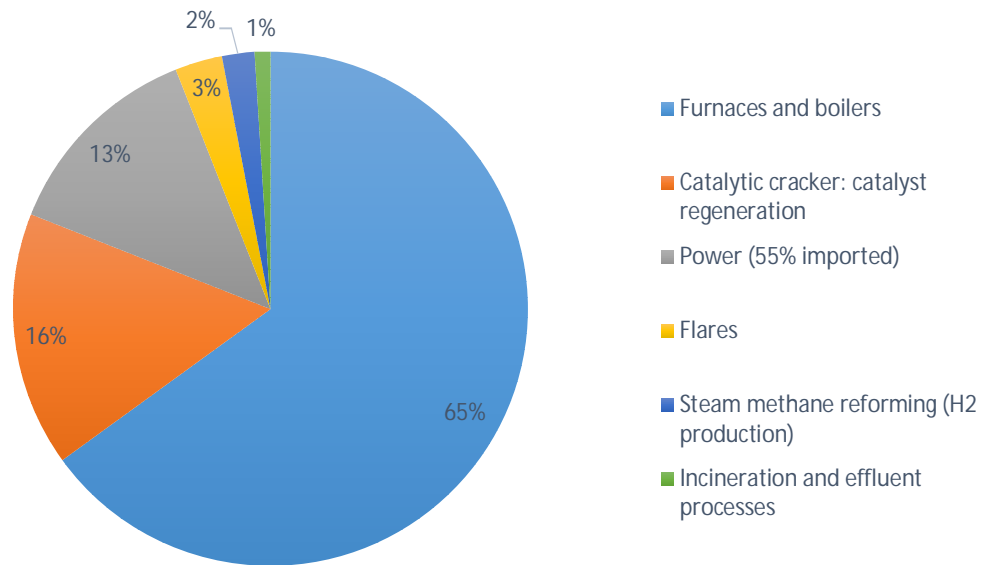


Figure 16. Typical breakdown of CO₂ emissions from petroleum refineries. (Kuramochi et al. 2012).

Table 8. Typical CO₂ point sources and flue gas characteristics at refineries. (Romano et al. 2013)

CO ₂ sources	CO ₂ concentration, % by vol	Other components and impurities	% of total emissions
Process heaters and utilities flue gas	Gas-fired: 3 - 6	O ₂ (2-6 %-vol), SO ₂ (gas fired: 10-20ppm, oil fired: 50-600 ppm), SO ₃ , NO _x	Process heaters: 30 - 60
	Oil-fired: 7 - 12		Utilities: 20 - 50
Fluid catalytic cracker flue gas	8 - 12	O ₂ (1-2 %-vol), SO ₂ (1000-15000ppm), catalyst dust, CO, SO ₃ , NO _x	20 - 35
H₂ production plants			
Syngas	15 - 35	H ₂ , CO, CH ₄ , N ₂	-
PSA off-gas	40 - 50	H ₂ , CO, CH ₄ , N ₂	-
Regenerator off-gas	95 - 99	Traces	-
FTR furnace flue gas	5 - 20	O ₂ (2-6 %-vol), NO _x	5 - 20

Specific energy consumption and capital costs are listed in the table 9 for different emission sources and capture technologies. The considered technologies are post combustion capture with MEA, oxy-combustion with oxygen produced either by cryogenic or more advanced oxygen conducting membrane (OCM) method and pre-combustion capture with water-gas shift membrane reactor (WGSMR). OCM method operates at high temperatures (800-900 °C) and produces high-quality oxygen with 35-68% lower specific energy consumption when compared to conventional ASU. In the WGSMR process the water gas shift reaction and H₂ separation occur simultaneously. The post-combustion

capture with MEA can be utilized in the short term (<10 years) while OCM and WGSMR are considered available in the long term (>20 years).

Since power plants and processes at refineries are typically run with high annual operational hours, they can be considered more reliable source for CO₂ when compared to power plants operated for the grid. However for refineries which consume hydrogen it would be more effective to utilize the hydrogen produced by electrolysis directly for the processes instead of methanation. This therefore reduces the suitability of refineries as a CO₂ source for PtG operation.

Table 9. Specific cost and energy consumption of different carbon separation methods for petrochemical industry. (Kuramochi et al. 2012)

Emission source	CO ₂ capture technique		Specific energy consumption [GJ/tCO ₂ captured]			Incremental capital cost [€/tCO ₂ captured/a]
			Primary energy (NG)	Steam	Power	
Combined stack	Post-combustion (MEA)	Onsite NG-CHP	5.7	-	-0.65	250
		Steam import	-	3.3 - 4.4	0.48 - 0.62	100 - 210
	Oxyfuel (cryogenic)	Onsite power	1.9 - 2.5	-	-0.24 to -0.06	200 - 240
		Steam import	-	-	2	150
	Oxyfuel (OCM)	Onsite power	5.3 - 16.4	-	-8.5 to -1.5	170 - 390
Catalytic cracker	Oxyfuel	Pre-combustion WGSMR	4.8	-	-0.1	150
		Steam import	-	4.6	0.6	150
		Cryogenic	-	-3.1 to -3.3	2.4 - 2.5	190 - 200

3.2.2.4 Chemical and petrochemical industry

Petrochemical industry was responsible for 1.3 Gt of CO₂ in the year 2007. Main sources of CO₂ are the steam boilers and CHP plants (Kuramochi et al. 2012). Other considerable point sources include ethylene production and ammonia production with CO₂ emissions of 258 and 113 Mt respectively (Metz et al. 2005). Ethylene is produced via steam cracking of light hydrocarbons, which is the most CO₂ intensive process in the chemical and petrochemical industry. Steam cracking produces 180 Mt of CO₂ annually and most of it is caused by combustion of fuels to provide heat for the cracking process. The CO₂ concentration of the ethylene furnace flue gas is comparable to that of the other combustion processes at about 12 vol-%. (Kuramochi et al. 2012).

Ammonia production is another considerable industrial process which produces CO₂ byproduct streams. Ammonia production requires hydrogen and the current hydrogen production methods include cracking of natural gas or liquefied petroleum gas. Ammonia production based on natural gas consumes 45% of the natural gas in the form of fuel for cracking and 55% as a raw material for hydrogen. The excess carbon is typically removed via absorption by amine solutions or pressure swing adsorption. (Onarheim et al. 2015). The separated CO₂ stream is practically pure and the CO₂ from the combustion process depends on the fuel used, but is typically around 8 vol-%. (Metz et al. 2005). However it is not practical to use hydrogen for methanation when the CO₂ available is generated from hydrogen production. It would be more efficient to directly replace the fossil fuel-based hydrogen with renewably produced hydrogen in the ammonia production, thus decreasing the overall fossil fuel consumption.

3.2.2.5 Pulp and paper industry

The biogenic CO₂ emissions of pulp and paper industry in the Nordic countries exceed 41 Mt of CO₂ (Teir et al 2010). In Nordic pulp and paper industry the kraft process is the most prominent pulp producing process. Kraft process emits roughly three times the CO₂ of a mechanical pulp process. In kraft process the wood chips are dissolved in high alkali, temperature and pressure environment, the resulting pulp is extracted and the water content of leftover liquid is reduced through evaporation to produce black liquor. The black liquor is then combusted to produce heat and to recover the inorganic materials such as sodium sulphide (Na₂S) and sodium carbonate (Na₂CO₃). Calcium oxide (CaO) is fed into the process to regenerate sodium carbonate into sodium hydroxide NaOH. The byproduct of this causticising process is calcium carbonate (CaCO₃) which is regenerated in a separate lime kiln to produce CaO and CO₂. Due to wood being the main raw material and fuel in the kraft mills up to 90-100% of the CO₂ emissions are biogenic. The main CO₂ producer is the recovery boiler. (Onarheim et al. 2015). Smaller point sources include bark boiler and lime kiln (Mesfun, Toffolo 2013).

CCS in pulp and paper industry has not been studied extensively, mainly due to the biogenic nature of CO₂ involved. Capture of biogenic CO₂ would result in negative emissions, i.e. removing CO₂ from atmosphere. However the current policies do not recognize negative emissions and therefore no fiscal incentive exists for CO₂ capture from biogenic sources. (Teir et al. 2010).

CCS from pulp and paper is however believed to be more complex than in traditional power plants due to strong chemicals used and thus flue gases including more pollutants (Teir et al. 2011). Trace emissions include H_2S , SO_2 , NO_x , HCl , NH_3 , CO , methanol and other organic compounds. Then again, most pulp and paper mills have extensive flue gas cleaning facilities as a result of strict environmental regulations, thus reducing the emissions. (Tran, Vakkilainen 2007).

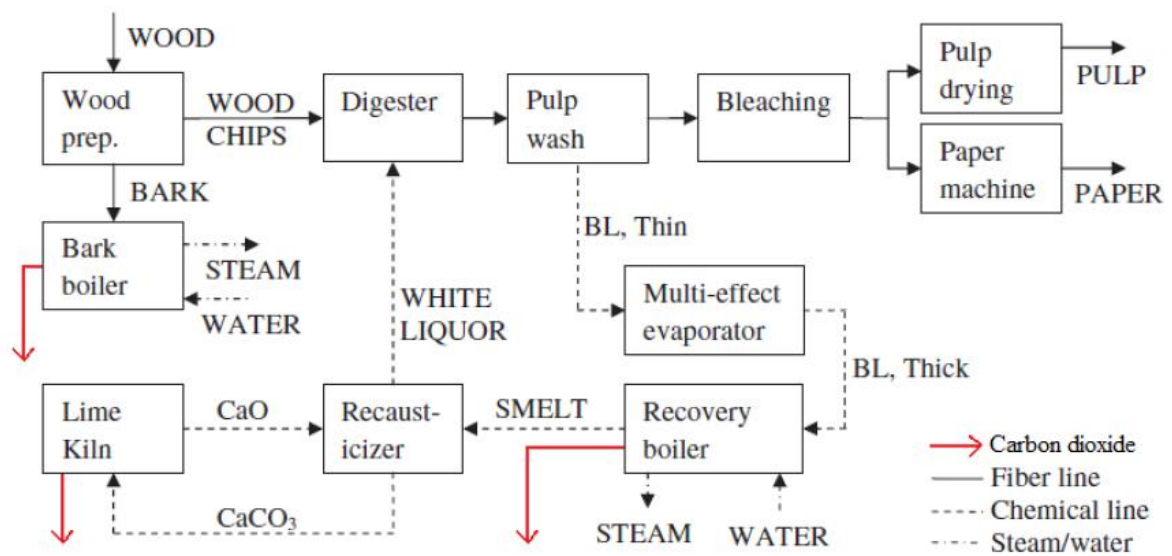


Figure 17. Kraft mill process. (Leeson et al. 2014).

There are two processes in kraft process which utilize oxygen or hydrogen: Oxygen delignification and bleaching. In delignification oxygen is fed into the pulp with steam to remove excess lignin from the pulp, thus decreasing chemical consumption in the bleaching stage of the pulp production. Bleaching utilizes hydrogen peroxide, which is either produced on-site or imported. (Vakkilainen, Kivistö 2014). Production of hydrogen peroxide requires both hydrogen and oxygen. The oxygen is typically obtained from ambient air while hydrogen has to be produced by other means. (Chen 2006). In this sense the pulp mill could profit from electrolysis directly as a source of raw materials if the price of electricity is sufficiently low.

3.2.2.6 Bioethanol production

Much like ethanol produced for alcohol based beverages the bioethanol is produced by fermentation of six-carbon sugars by yeast. The chemical reaction follows the reaction equation below:



Fermentation of sugars to ethanol produces by-product stream of almost pure CO₂ at atmospheric pressure. The few impurities contained in the gas are organic substances such as ethanol, methanol, H₂S, water and dimethyl sulphide. Since no CO₂ separation is needed the cost of CO₂ capture is relatively low. (Xu et al. 2010). However the existence of H₂S can cause issues with chemical methanation and additional purification may be required, thus increasing capture costs.

The worldwide fuel ethanol production in the year 2013 was 87.2 billion liters (Gupta, Verma 2015). Using the reaction equation presented above, we can calculate that the CO₂ generated in the ethanol production equals to 65.7 Mt of CO₂. There is considerable untapped potential in the use of biomass for bioethanol potential, as studied by Gupta, Verma 2015. By utilizing lignocellulosic biomass the ethanol production could be increased by 440 billion liters worldwide. Utilizing different agricultural wastes could provide additional 440 billion liters of bioethanol. The production of 880 billion liters of bioethanol would generate up to 660 Mt of biogenic CO₂ annually. (Gupta, Verma 2015).

3.2.2.7 Biogas

Biogas refers to gas produced through anaerobic digestion from biogenic carbon sources such as animal manure, slurries and digestible organic waste. The two main components of biogas are methane and CO₂ with typical concentrations around 50-75% for methane and 25-45% for CO₂. (Seadi et al 2008). Trace components include water vapor, hydrogen sulphide, siloxanes, hydrocarbons, ammonia, oxygen, carbon monoxide and nitrogen (Ryckebosch et al. 2011). Anaerobic digestion is widely applied to treat waste materials from different sources and to produce biogas. Biogas is produced at municipal waste water and solid waste treatment plants, agricultural biogas plants, landfill gas recovery plants and industrial biogas plants. (Seadi et al 2008). In European Union, the primary energy production from biogas was 13.4 Mtoe in the year 2013 (EurObserv'ER 2014). If average CO₂ content of biogas is assumed to be 35%, the amount of CO₂ generated in biogas production equals 18.2 Mt.

3.2.3 Atmospheric CO₂

Technology exists for atmospheric CO₂ extraction. However, due to the fact that CO₂ concentration in the atmosphere is 370 ppm the energy cost for the required separation process is roughly 3.4 times the energy cost of a point source with 10 vol.-% CO₂ concentration. With chemical absorption the process energy requirement would be in the range of 5.4-9.0 MJ/kg_{CO2} which results in specific costs of 150-320 €/kg_{CO2}. (Reiter, Lindorfer 2015). It can be argued that as long as there are higher concentration point sources it will be more effective to capture CO₂ from the source instead of the atmosphere.

3.3 Energy penalty and capture cost of CCS

The energy penalty of different carbon capture technologies and industrial setups can be seen on table 10. Values are as represented by Reiter, Lindorfer 2015. The CO₂ capture at the refinery includes capture from steam cracking, fuel combustion, hydrogen and ethylene production with either chemical absorption or oxyfuel process. The steelmaking processes are based on CO₂ capture by chemical absorption. Likewise the cement production assumes post-combustion capture by chemical absorption.

Table 10. Energy penalties for different industries with variable carbon capture options. (Reiter, Lindorfer 2015). *(Gardarsdottir et al. 2014)

CO2 source and capture technology	Additional energy in MJ per kg CO2 captured
Refinery (Combined stacks, catalytic cracker)	
Post-combustion (MEA)	2.07
Oxyfuel	3.88
Steel & Iron production	
Blast furnace - post combustion (MEA)	3.76
Top gas recycling	4.91
COREX	3.87
Cement production	
Post-combustion (MEA)	5.06
Pulp and paper (reboiler flue gases)*	
Post-combustion (MEA)	3.76
Post-combustion (Ammonia)	2.80
Atmosphere	5.4 - 9.0
Power plant	
Pulverized coal post-combustion (MEA)	2.7
Natural gas post-combustion (MEA)	2.9

Pulp and paper mill values are based on the capture from reboiler flue gases with chemical absorption. Capture from atmosphere and power plants likewise assume chemical absorption.

The chemical absorption based post-combustion capture is chosen due to the technology's relative maturity for implementation in the short term. In the long term the situation is likely to change as more energy-efficient methods for carbon capture in various industries are developed.

The cost of CO₂ capture from different sources is shown in figure 18. The sources are ranked from cheapest to the most expensive. Biogas and bioethanol provide by far the most economical sources for CO₂. However if the CO₂ is separated from the biogas, the costs increase considerably. This magnitude of biogas cleaning costs are typically associated with biogas upgrade before injection into the natural gas pipelines. Even in such case the CO₂ can be regarded as a waste product that would have to be separated anyway and therefore it can be treated as “free”. (Reiter, Lindorfer 2015). When the large scale industrial sources are considered, pulp and paper mill capture costs are lowest, followed by steel mills, ammonia production, refineries and cement production. Post combustion capture for pulverized coal power plants costs roughly twice the amount of pulp and paper mill CO₂ capture, while for natural gas plants it would be three to four times as expensive.

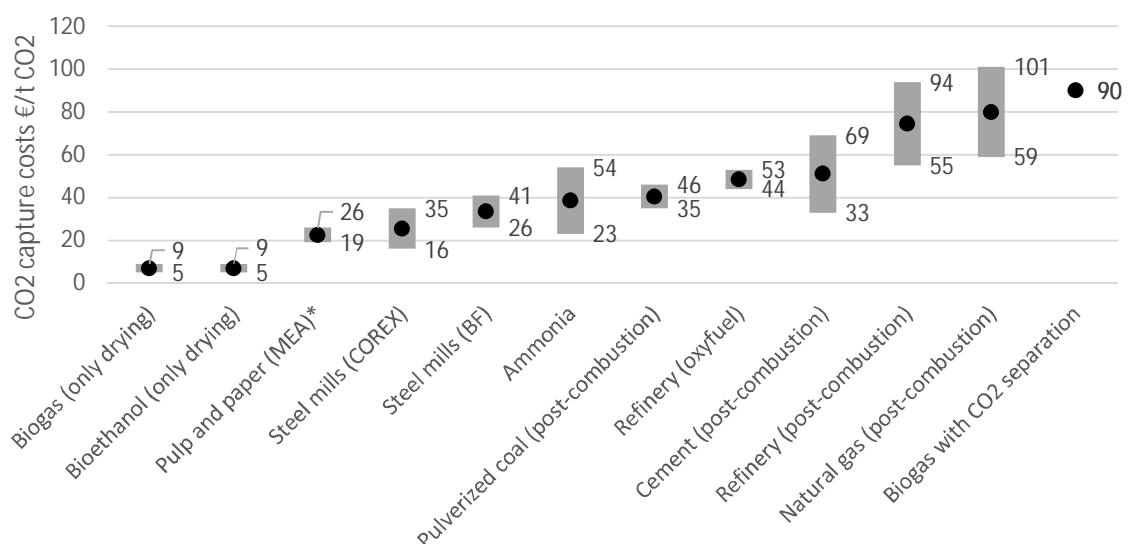


Figure 18. CO₂ capture costs for different sources with different separation techniques. (Reiter, Lindorfer 2015). *(Onarheim et al. 2015)

3.4 Effect of CCS on PtG efficiency

Power-to-Gas chain can be seen as a process containing three crucial components: the electrolysis, methanation and carbon separation. However most literature sources include only electrolysis and methanation when calculating the PtG process chain efficiency. The carbon is in most cases assumed to be “free”. However capturing carbon takes considerable effort and causes large energy penalty. If we consider the PtG process chain with electrolysis and methanation efficiencies of 80% each, the total PtG efficiency is 64 %. When the energy demand from carbon separation process, such as amine scrubbing with MEA which consumes roughly 4.0 GJ/tCO₂, is included the PtG process efficiency drops to 56 %. Efficiency is calculated by equation 14.

$$\eta_{PtG} = \frac{LHV_{CH_4}}{e_{CCS} + e_{EL}} \quad (14)$$

Where

η_{PtG}	is the PtG efficiency
LHV_{CH_4}	is the lower heating value of the produced SNG
e_{CCS}	is the specific energy consumed by the carbon capture process
e_{EL}	is the specific energy consumed by the electrolyzer

In Figure 19 the PtG process efficiency is graphed as a function of the carbon separation energy penalty. In the figure we may also see various carbon sources plotted on the graph. The carbon capture energy penalty data is from table 10 and post combustion capture is assumed for all cases. It can be seen that refineries and pulverized coal plants offer best PtG efficiency. Steel mills with blast furnace and pulp and paper mills are the next most effective, having equal capture penalties. Capture from cement production and from atmosphere have the largest efficiency decrease. It should be noted that as the technology chosen for this comparison is the MEA based amine scrubbing, the carbon capture penalty is relatively high. As more advanced technologies for CCS become available for steel and cement industry the associated energy penalty is likely to drop significantly. For example cement plant using CaL-based CCS can has energy penalty of only 1.6 GJ/tCO₂ in primary energy and 0.54 GJ/tCO₂ in electrical energy, which would bring the associated PtG efficiency on par with the presented refinery and pulverized coal CCS.

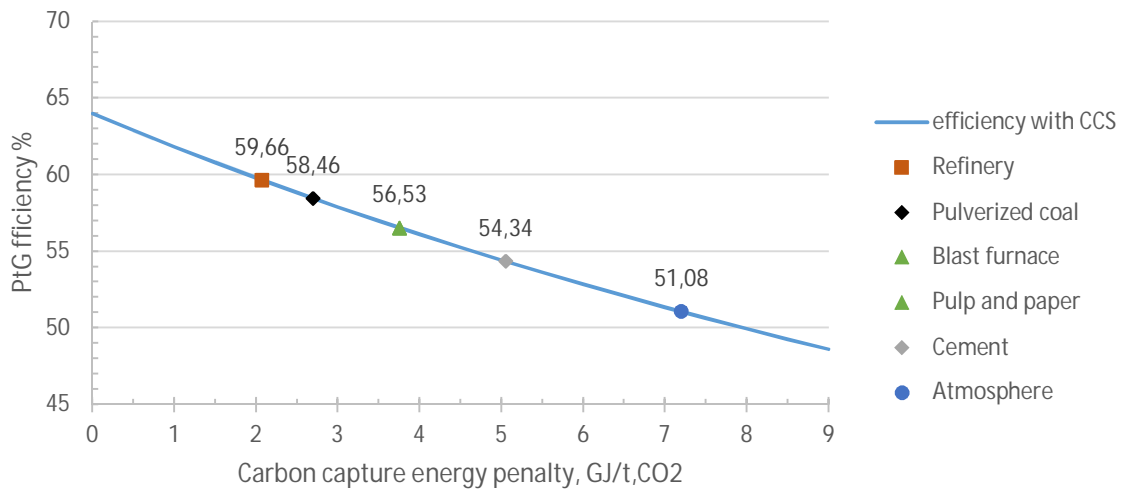


Figure 19. PtG Process efficiency as a function of CCS energy penalty. Efficiencies for MEA based amine-scrubbing.

3.5 100% Renewable Finland 2050

For the purposes of this thesis it is beneficial to estimate the amount of CO₂ required for national PtG system. The estimate is based on 100% renewable Finland 2050 scenario by Michael Child and Christian Breyer (2015). Their study is built upon EnergyPLAN tool developed 1999 at Aalborg University in Denmark. It allows for energy systems analysis on an hourly resolution for a period of one year. The model includes analysis of electricity, heating and transport sectors and uses historical data for a calendar year. The scenario is based on 100% renewable energy production by wind, solar, hydro and biomass. The installed capacity for onshore wind is 30 GWe and for offshore wind 5 GWe. Installed solar capacity is 30 GWe, hydro 3.5 GWe and biomass CHP 9 GWe. The installed PtG capacity is 23.5 GWe with full load hours of 2583h, which produces 31 TWh of SNG. It should be noted that the scenario takes into account the energy consumption of industrial-, transportation- and heating sectors, which means that the purpose of PtG system in the scenario is not only to store the excess energy produced by the renewables, but also to produce the fuels consumed by industry, transportation and heating. (Child, Breyer 2015). In the figure 20 is presented the hourly PtG production in megawatts on hourly resolution. It can be seen that majority of the PtG production is distributed from January to mid-May (hours 1 to 2600) and from late August to mid-November (hours 5600 to 7700). The PtG production is linked to the onshore wind production. Although solar power does contribute

large amounts of power when it is available, on a yearly basis the wind power generation contributes most to the PtG operation. (Child 2015). The maximum production capacity of the PtG system is 12 GW of methane, which equals to peak consumption of 2400 tons of CO₂ per hour.

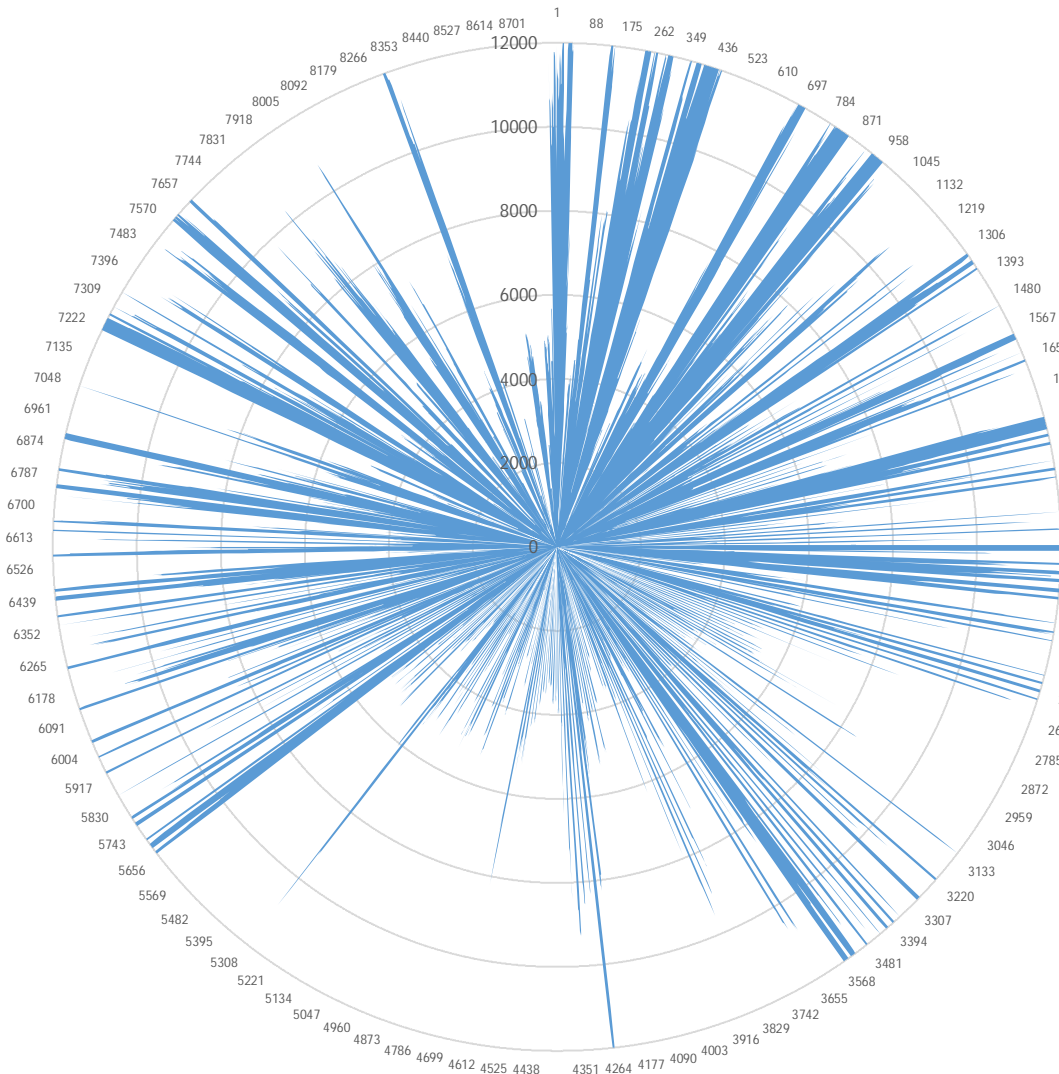


Figure 20. Hourly data of PtG production from 100% renewable Finland 2050 case. Production in MW of gas (CH₄) produced. 730 hours equals roughly a one month. (Child 2015).

In the figure 21 the typical energy production and consumption is presented for one summer week of the case study. The production is dominated by the high spikes of solar production, with the wind power generation picking up after three days. On the electricity demand, or consumption, figure we can see how the electricity which is not consumed is used to charge batteries on electric vehicles (BEV) and stationary installations as well as to run PtG to

provide fuel for industry, heating and traffic. It can be observed that the longest uninterrupted period of PtG production corresponds with the period of increased wind power generation. Figure 22 represents the same data for one week during the winter at the time of highest electricity consumption. As it happens, this period of time coincides with a time of high winds, resulting in large PtG production and even some electricity production losses due to full use of battery and PtG capacities. (Child 2015).

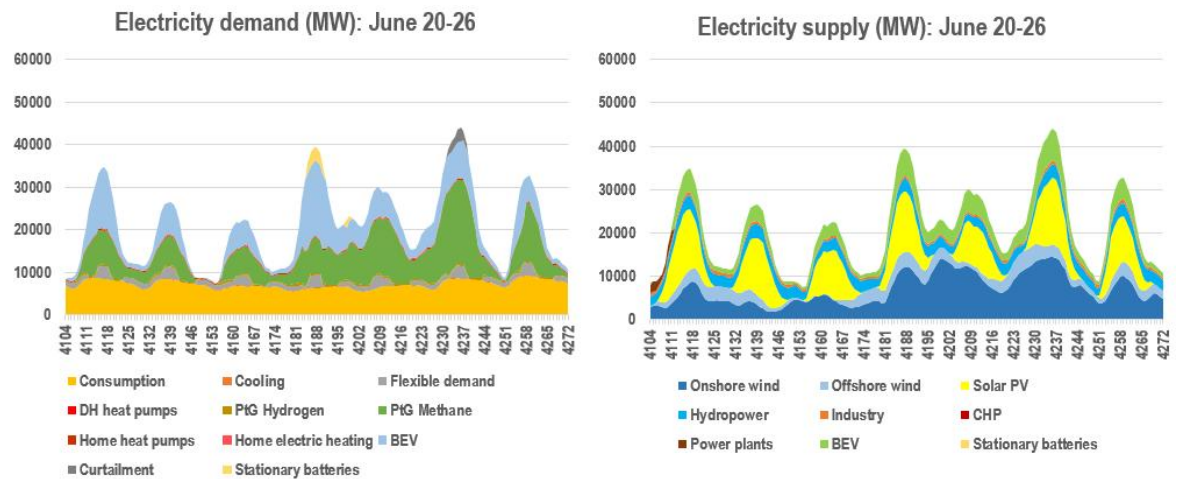


Figure 21. Electricity production and consumption for one summer week from the renewable Finland case study. (Child 2015).

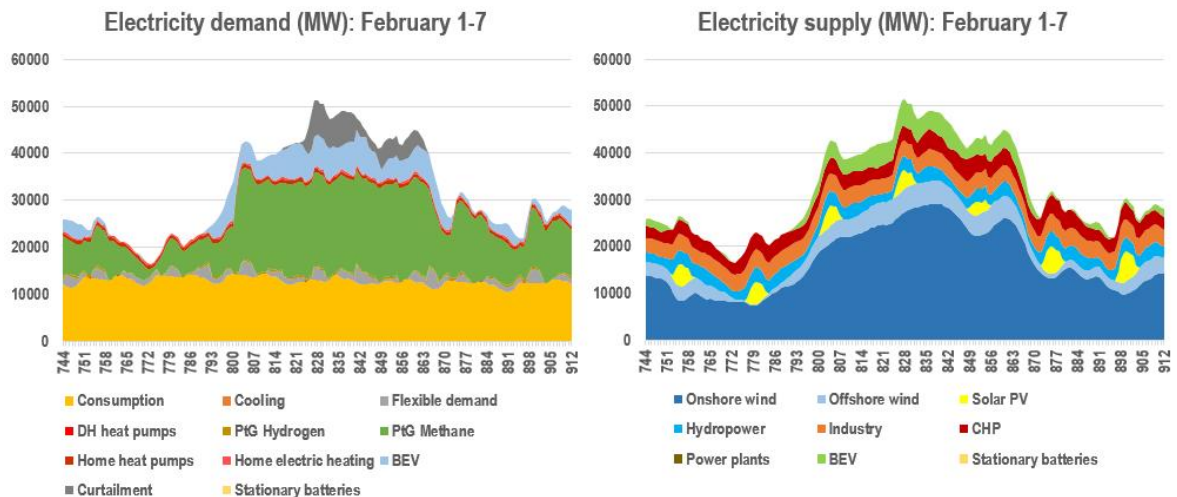


Figure 22. Electricity production and consumption for one winter week from the renewable Finland case study. (Child 2015).

To operate the PtG system at the level proposed by the 100% renewable Finland 2050 scenario, up to 6.1 Mt of CO₂ is required annually for the PtG system. This estimate of 6.1 Mt of CO₂ will be the target when estimating the CO₂ resources in Finland.

4 CO₂ AVAILABILITY IN FINLAND

From PtG point of view it has some relevance whether the CO₂ was captured from fossil or biogenic sources. Utilizing biogenic CO₂ would effectively render the methane produced by PtG process a renewable fuel. On the other hand, utilizing fossil fuels would not prevent the CO₂ emissions from the fossil source, rather just store it in the chemical energy carrier for the period of the storage before it is released in the air upon consumption. If we are to achieve fully renewable energy sector, the carbon circulation in the atmosphere must be closed.

The Finnish industry and energy production sector produces annually 59.6 million tons of CO₂ (2012 level). This number includes fossil and biogenic CO₂. Forest, chemical and metal industries together with energy production sector account for 96% of these emissions. The share of each sector is represented in Figure 23. (Tilastokeskus, 2012)

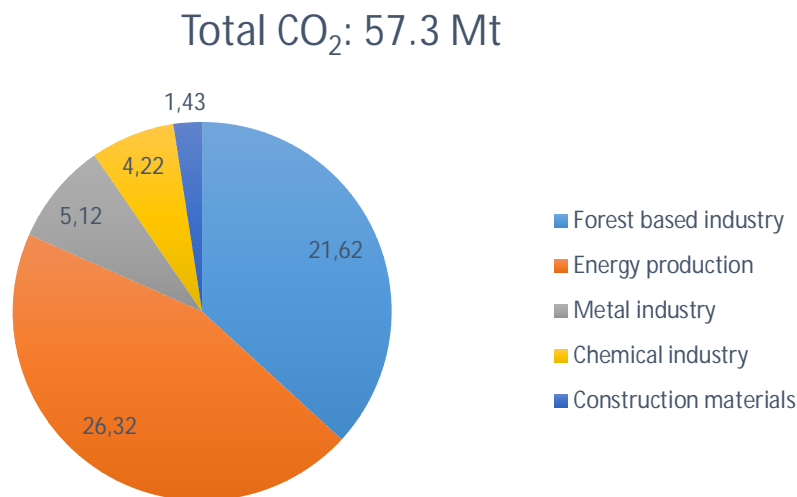


Figure 23. CO₂ production by sector. Construction materials include cement, lime and plaster production.

The share of biogenic CO₂ is 27.3 million tons of CO₂. As can be seen from figure 24, pulp and paper industry together with energy sector are the largest producers of biogenic CO₂ with combined share of 97% of all industrial biogenic emissions. (Ilmanpäästöt toimialoittain, 2012). It should be noted that although pulp and paper industry together with energy sector produce considerable amounts of biogenic CO₂, the CO₂ has to be captured from combustion flue gases with low partial pressure which require the use of energy intensive carbon separation methods. For this reason carbon sources that either produce

concentrated stream of CO₂ or in other ways avoid the CO₂ separation process, such as biogas, should also be considered for the PtG process.

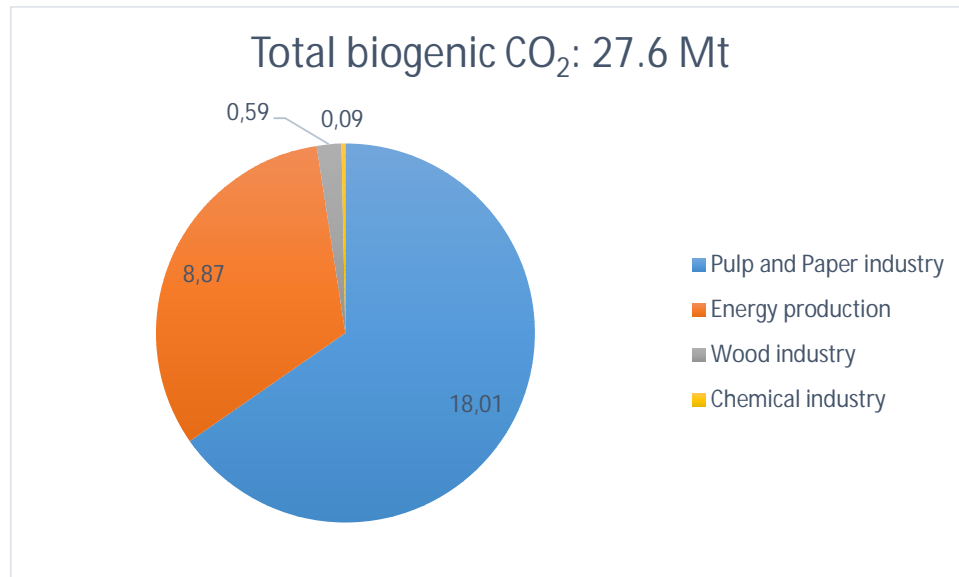


Figure 24. Biogenic CO₂ production by sector.

In addition to biogenic CO₂ produced in the industry and energy sector, there exists 42 biogas plants in Finland with a combined biogas production of 59.1 million cubic meters. The biogas produced is composed mainly of methane and CO₂. Assuming average concentration of CO₂ to be 40%, this would result in 43 thousand tons of biogenic CO₂ available for methanation. (Huttunen, Kuittinen, 2014). In recent W-fuel project the biogas potential of southern Finland (Turku, Salo, Helsinki, Kymenlaakso) was estimated to be around 2.2 TWh produced from 50 new biogas plants (Rasi et al. 2012). This is equivalent to 254 thousand tons of biogenic CO₂ annually. Total theoretical biogas potential for Finland is estimated to be 23.2 TWh with the share of technically and economically utilizable biogas being 9.2 TWh. (Tähti, Rintala 2010). The amount of technically utilizable biogas is equivalent to one million tons of biogenic CO₂ per year. Although in the terms of quantity the biogas production does not compete with industrial sources for CO₂, there are other benefits for biogas use such as the ability to use in-situ biomethanation and the potential integration with CHP production units to provide power.

The different CO₂ sources will be evaluated in the following chapters. Subchapter 4.1 includes biogas based carbon sources while subchapter 4.2 will focus on CO₂ streams available from industrial applications. Industrial sources which produce less than 100,000

tons of CO₂ and require carbon separation methods for capture are not included in this study. However industries which emit pure CO₂ streams will be evaluated even if the produced amount of CO₂ is below 100,000 tons due to the ease of CO₂ capture.

4.1 Biogas

Largest biogas plant utilizing anaerobic digestion (AD) reactor in Finland is the one located in Viikinmäki, Helsinki. The plant produces roughly 8.7 tons of CO₂ annually which would translate to CO₂ mass flow of 1 kg/h. (Huttunen, Kuittinen, 2014). For such a small units the biomethanation has numerous advantages over chemical methanation, such as simplicity due to the operation in low temperatures and at atmospheric pressure. To utilize biogas the chemical methanation would require extensive flue gas cleaning to remove impurities such as hydrogen sulphide from biogas. Also the load management is not considered an issue for biomethanation. For these reasons the biomethanation is the preferred option for biogas utilization in PtG.

Two different ways to utilize biological methanation in biogas methanation have been proposed. The in-situ methanation (figure 25) in the biogas digester and methanation in a separate reactor (figure 26). (Götz et al. 2014).

The in-situ biological methanation refers to the use of the digesters of biogas plants as a methanation reactor by directly injecting hydrogen into the digester. The excess CO₂ and hydrogen will be converted into methane by the methanogenic bacteria present in the reactor. (Bensmann et al. 2014). This results in a biogas with higher methane- and energy content. The methane production is limited by the low Methane Formation Rate (MFR, $q_{v,CH_4,out}/V_{reactor}$) of biogas plants. Typical MFR values for biogas digesters are $< 0.1 \text{ h}^{-1}$. The low MFR is however compensated by the low investment cost since no external reactor is required. The achievable increase in methane content varies depending on the biomass used in the digester. For energy crops the potential methane content increase is from 52% to 75%, whereas plants utilizing different waste materials and residues can achieve 97% methane content. Current research efforts aim to validate the compatibility of biogas digesters with hydrogen injection. (Götz et al. 2014).

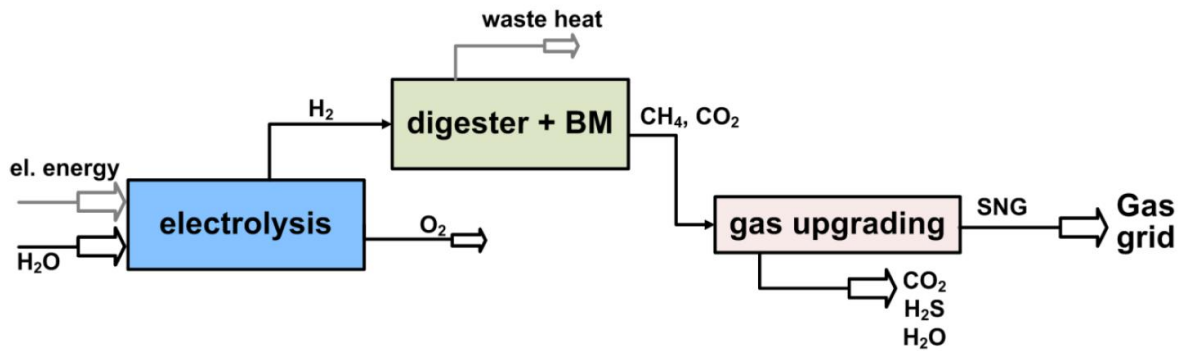


Figure 25. Process flow diagram of in-situ biological methanation. (Götz et al. 2014).

External reactors are able to utilize pure cultures of methanogenic bacteria to gain considerable increase in MFR. Götz et al 2014 cites study results by MicrobEnergy GmbH and Krajete GmbH which have shown wide range of MFR's for external reactors, from 2.5 to 22.4 h⁻¹. Another advantage is that external bioreactors can utilize other CO₂ sources besides biogas. However, due to the poor solubility of hydrogen to liquid, the methanation rate is limited by the rate of hydrogen supply to the bacteria. (Götz et al. 2014).

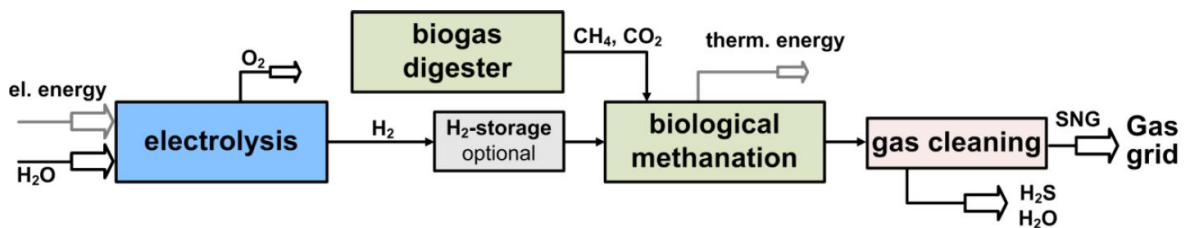


Figure 26. Process flow diagram for external reactor. (Götz et al. 2014).

For the purposes of this thesis it is assumed that the in-situ methanation in the digester is feasible, and due to the simplicity of the configuration it is the preferred option for biomethanation. The cases presented in this thesis are based on biogas production in continuously stirred-tank reactors (CSTR) which are then coupled with hydrogen injection.

For in-situ methanation in digester, the H₂ injection flowrate is limited in stationary operation by the CO₂ output flowrate due to reaction stoichiometry. This limitation is named the biological limit. However, the biological limit can be exceeded for short periods of time provided that the total amount of inorganic carbon contained in the digester is not exceeded. This type of digester overloading increases the partial pressure of hydrogen in the output gas composition until the injected hydrogen has reacted with CO₂. Requirements on the output biogas quality may have further limitations on the amount of injectable hydrogen in this type

of overloading scenarios. Despite these operational limitations, bio-methanation unit based on anaerobic digester has considerable dynamical flexibility with respect to the H_2 injection rate. This type of flexibility is especially beneficial when considering the fluctuating nature of renewable power sources. (Bensmann et al. 2014).

Typically the biogas generated through anaerobic digestion is either upgraded to produce fuel-grade biogas for traffic use or utilized on site to produce heat and electricity in a CHP plant. The most widely used biogas upgrade methods are based on CO_2 removal from the biogas stream. Commonly applied CO_2 separation methods are absorption (amine scrubbing), adsorption (pressure swing adsorption) or membrane separation. (Jürgensen et al. 2014).

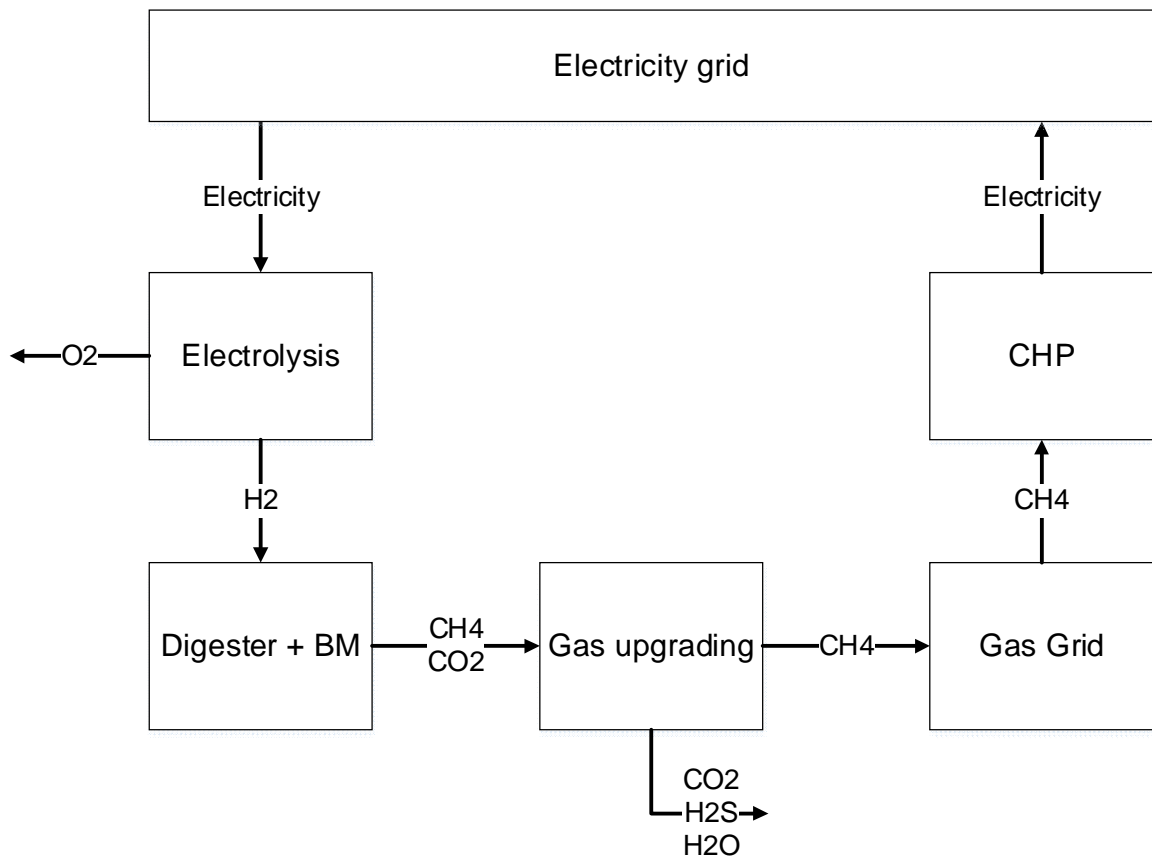


Figure 27. Biogas plant combined with hydrogen injection and CHP.

From PtG point of view the CHP power generation could provide valuable balancing power to even out the fluctuations in the renewable power generation. Hahn et al. studied the potential of biogas-fueled CHP units to produce secondary (activated 5-15 min. after system imbalance) and tertiary (activated 15 min. after system imbalance and lasts for 4

hours) balancing power. In Germany there exists 7300 biogas plants with installed electrical capacity of 3 GW. The annual operational hours are estimated to be around 7000 hours. By decreasing annual operational hours to 2000-4000 hours the installed capacity could be increased to 6-12 GW thus increasing the balancing power available. Dynamical operation of CHP plants would require more flexible supply system for biogas. Expanded biogas storage, dynamic biogas production and upgrade to biomethane are proposed as control methods for biogas supply. (Hahn et al. 2014). If we consider the biogas plant as a unit which includes not only the digester and CHP unit, but also the electrolyzer for hydrogen production, the balancing capacity of the entire unit is increased beyond that of plain CHP plant. Figure 27 proposes one potential way to integrate biogas plants into PtG operation. During times of excess power generation the electrolyzer is utilized to upgrade biogas and during times of power deficit the biogas is used to fuel CHP plant and to provide balancing power. (Jürgensen et al. 2014).

In the biogas-cases studied in this thesis the potential electrolyzer capacity is designed to provide sufficient hydrogen to reach the biological limit of the digester. Or in other words, to match the CO₂ production rate so that all produced CO₂ is converted into methane which would (in stationary operation) result in biogas methane content of 95%. This means that the possibility of overloading discussed in above chapter is not taken into account. This is to simplify the estimates on electrolyzer capacity potential. The electrolyzer capacity required to exceed biological limit to achieve beneficial hydrogen overloading scenarios is optimization problem which requires economic considerations. Such optimization is not within the scope of this work and sufficient information about the potential electrolyzer capacity can be obtained from the simpler estimates made in this thesis. In the next subchapters the biogas PtG potential is evaluated in three different scenarios: The current existing infrastructure, the potential biogas infrastructure in southern Finland proposed by W-fuel report and the maximum utilization of all available biomass. Each case estimates the capacity which can be installed to biogas plants without exceeding the biological limit. To estimate the amount of methane produced by hydrogen injection it is assumed that the electrolyzers are operated 2583 hours per year, which is the PtG full load hours for 100% renewable Finland 2050 scenario. To estimate the amount of CHP balancing capacity it is assumed that all produced biogas can be stored and utilized by the CHP plant. The CHP is assumed to have identical full load hours to the CHP in 100% renewable 2050 scenario, which is 1641 h/a. In this thesis the electrical efficiency of combustion engine is

assumed to be 35 %. The total balancing capacity provided by the biogas plant will therefore be the sum of electrolyzer and CHP capacity.

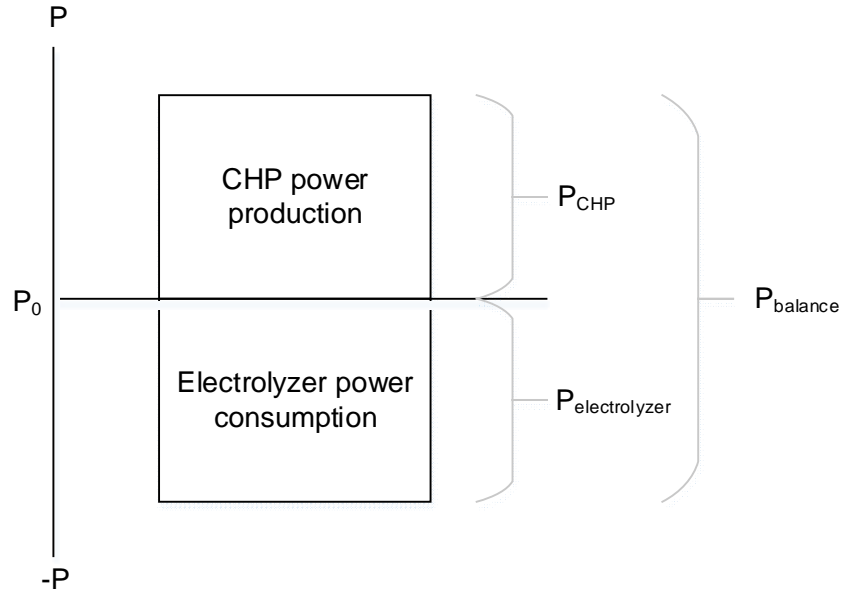


Figure 28. Energy consumption & production in combined CHP and biogas plant coupled with hydrogen injection.

4.1.1 Low utilization case: Existing biogas plants

This case evaluates the PtG potential of existing biogas infrastructure in Finland. In the year 2013 there were 16 operational biogas reactor plants at municipal wastewater treatment sites, 3 operational industrial wastewater treatment plants, 12 farm-scale biogas plants and 11 plants treating solid municipal waste. The combined biogas production of reactor installations was 59.1 million m³. On top of this 40 landfill gas recovery plants produced 94.8 million m³ of biogas. However, since the landfill gas recovery units operate in a different way compared to the anaerobic digesters, the in situ- hydrogen injection is not feasible for landfill gas. For this reason only the biogas production from the reactor plants is accounted for. (Huttunen, Kuittinen, 2014).

Industrial wastewaters are treated anaerobically in three locations. These locations employ different anaerobic reactors, like the type of UASB- through-flow reactors (upflow anaerobic sludge bed). Suitability of this kind of reactors for hydrogen injection is unknown, thus these reactors are not accounted for in this study. The farm scale digesters are operated in 12 locations. The biogas production volumes on farm scale are comparatively low when

compared to municipal waste treatment plants, thus the total effect of these plants is considered negligible and are not accounted for in this thesis.

Table 11. Biogas production at municipal water treatment units in Finland.

Wastewater treatment plant	Prod. biogas 1000 m ³	CH ₄ %	Prod. CH ₄ 1000 m ³	Additional CH ₄ potential 1000 m ³	P _{electrolyzer} MW _e
Espoo, Suomenoja	3926	63	2473	1256	2.53
Forssa	569	70	398	142	0.29
Helsinki, Viikinmäki	13322	62	8260	4396	8.85
Hämeenlinna, Paroinen	643	62	399	212	0.43
Joensuu, Kuhasalo	923	65	600	277	0.56
Jyväskylä, Nenäinniemi	2107	63	1327	674	1.36
Kuopio, Lehtoniemi	1166	68	793	315	0.63
Lahti, Kariniemi, Ali-Juhakkala	1925	60	1155	674	1.36
Maarianhamina, Lotsbroverket	413	40	165	227	0.46
Mikkeli, Kenkäveronniemi	418	67	280	117	0.24
Nurmijärvi, Klaukkala	61	70	43	15	0.03
Riihimäki	650	65	423	195	0.39
Salo	465	62	288	153	0.31
Tampere, Rahola	652	65	424	196	0.39
Tampere, Viikinlahti	2551	65	1658	765	1.54
Total	29791	-	18686	9616	19.36

The 16 municipal wastewater treatment plants produced total 29.790 million m³ of biogas with methane content between 40-70 %. The plants are listed in the table 11 with their respective biogas production, CH₄ content in biogas, total amount of CH₄ produced and the potential for additional CH₄ production with hydrogen injection.

Although Götz et al. mentioned that the maximum methane content of biogas upgraded through hydrogen injection varies between 75-97 %, it is, for the sake of simplicity, assumed here that the biogas will be upgraded up to 95% methane content. $P_{electrolyzer}$ is the electrolyzer power needed to produce enough hydrogen to reach the biological limit of the bioreactor. The resulting sum of installed electrolyzer capacity is 19.4 MW. Assuming that the electrolyzer operational hours are the 2583h, the hydrogen injection would result in additional 2.8 million m³ of methane. This equals to 28 GWh in energy content.

Tähti and Rintala note in their study that 60% of the sludges available for wastewater treatment facilities are not utilized in biogas production. Utilization of this sludge could effectively double the current biogas potential and electrolyzer capacity.

Production of the hydrogen for biomethanation also produces considerable amounts of oxygen as a side product. The 19.36 MW installed capacity of electrolyzers would produce annually 27,500 tons of oxygen. One potential end-use for the oxygen is within the wastewater treatment facilities which use aeration to treat the wastewater. Aeration is the process step where atmospheric oxygen (air) is fed via compressors into the sludge to oxidize organic material (van Haandel, van der Lubbe 2012). Replacing the air with pure oxygen could potentially decrease the required compressor work through decreased volumetric flow and increase the efficiency of aeration. More research on the subject is required before any conclusions about the benefits of pure oxygen aeration can be made.

The 11 biogas plants treating municipal solid wastes produced 27.058 million m³ of biogas with methane content of 60-70 %. The plants are listed in Table 12.

Table 12. Biogas production in municipal solid waste treatment units in Finland.

Municipal waste treatment	Prod. biogas 1000 m ³	CH ₄ %	Prod. CH ₄ 1000 m ³	Additional CH ₄ potential 1000 m ³	P _{electrolyzer} MW _e
Biokymppi oy, kitee	1824	60	1094	638	1.29
Biovakka suomi oy, turku	4600	67	3082	1288	2.59
Biovakka suomi oy, vehmaa	4682	66	3090	1358	2.73
Envor Biotech Oy, Forssa	5240	65	3406	1572	3.16
Kymen Bioenergia oy, Kouvola	1886	66	1245	547	1.1
Laihian kunta	144	60	86	50	0.1
Lakeuden Etappi, Ilmajoki	2619	65	1702	786	1.58
Oy Pohjanmaan biokaasu, Kokkola	360	61	220	122	0.25
Satakierto Oy, säkylä	270	63	170	86	0.17
Stormossen, Koivulahti	1738	61	1060	591	1.19
VamBio oy, Vampula	3694	70	2586	924	1.86
Total	27057	-	17741	7962	16.02

The potential for installed electrolyzer capacity totals 16 MW. With electrolyzer yearly operating hours of 2583, the total amount of methane produced as a result of hydrogen injection would result in additional 2.3 million m³. This equals to 23 GWh in energy content. The combined amount of CO₂ from municipal waste and wastewater treatment equals to 14,700 tons of CO₂.

The total electrolyzer capacity which can be installed on existing biogas infrastructure is 35 MW. The total amount of produced biogas amounts to 411 GWh, out of which 51 GWh is due to hydrogen injection. The hydrogen injection therefore results in

~14% production increase. When all of the produced biogas is used to fuel CHP plants operating at 1641 full load hours, the CHP electricity production capacity can reach ~88 MW. The total balancing capacity for biogas plants will be $P_{balance} = P_{electrolyzer} + P_{CHP} = 35 + 88 = 123$ MW.

4.1.2 Medium utilization case: W-fuel report biogas plants

This case estimates PtG potential if biogas production would follow the estimate of “From Waste to Traffic Fuel” –project’s final report. The report estimates available biomass in southern Finland, namely in Turku, Salo, Kymenlaakso and Helsinki regions. The theoretical estimate for biomass based energy potential is 3 TWh. The report uses geographical information system to identify potential biogas plant locations and finds that 50 plants with production capacity between 2.1 to 14.5 MW could be installed in the study region. Their combined biogas production corresponds to 2.2 TWh of energy. (Rasi et al. 2012).

Table 13. Biogas production by region in W-fuel report.

Biogas plants W-Fuel scenario	Biogas prod. capacity MW	Annual biogas production MWh	CH ₄ %	CH ₄ potential 1000 m3	P _{electrolyzer} MWe
Turku	97.7	787300	60	46442	93.48
Salu	74.6	598440	60	35301	71.06
Kymenlaakso	69.2	553770	60	32666	65.75
Helsinki	38.9	312137	60	18413	37.06

The calculated potential $P_{electrolyzer}$ power is shown in table 13. The total potential for installed electrolyzer capacity is ~270 MWe, which will increase the methane production by 387 GWh when electrolyzer operational hours are assumed to be 2583 h. This equals to 39 million m³ of methane. The size of individual electrolyzer units varies depending on the size of biogas production facility and ranges from 3.7 MWe to 25.9 MWe.

The total biogas production will be 2.25 TWh with additional 0.39 TWh increase due to hydrogen injection, totaling 2.64 TWh. Or in the terms of carbon, 260,000 tons of CO₂. When all of the produced biogas is utilized in CHP production with the full load hours of 1641 h/a, the electricity production capacity of CHP plants will reach ~560 MW. The total balancing capacity will be $P_{balance} = P_{electrolyzer} + P_{CHP} = 270 + 560 = 830$ MW.

4.1.3 High utilization case: Theoretical maximum

This case estimates the PtG potential in Finland in the case of maximum biomass utilization for biological methanation in digesters and coupled with hydrogen injection. The estimate of available biomass is based on a study by Tähti and Rintala (2010) which estimates biomethane and –hydrogen production potential in Finland. The study estimates the entire theoretical potential for biomethane production to be 23.2 TWh. When technical and economic considerations are taken into account the share of utilizable biomethane decreases to 9.2 TWh. After the share of landfill gas is excluded from this number, the biogas potential of biomass utilizable in digesters is 8.7 TWh. It should be noted that the estimates on theoretical biomass available differ greatly from study to study. The estimates vary between 14 and 95 TWh. (Tähti, Rintala 2010).

When the methane content of biogas is assumed to be 60%, the amount of CO₂ produced amounts to 1.7 Mt. The electrolyzer power required to produce sufficiently hydrogen for the methanation of this entire biogas pool is 1030 MW. With annual electrolyzer operating hours of 2583h, the hydrogen injection will result in additional 1.5 TWh of methane. If all the produced biogas is used to fuel CHP plants, with CHP full load hours of 1641 h/a, the CHP units' total electricity production capacity will reach 2180 MW. The total balancing capacity will be $P_{\text{balance}} = P_{\text{electrolyzer}} + P_{\text{CHP}} = 1030 + 2180 = 3210 \text{ MW}$.

As the renewable Finland 2050 scenario assumes the biomass CHP power to be 9 GWe, the biogas plants with CHP could provide roughly 24 % of the required CHP power capacity. The PtG capacity (in the form of electrolyzer power) is only 4 % out of the 23.5 GWe required. Additional sources of carbon for PtG operation are therefore required. The biogas production can however provide considerable amount of PtG capacity together with substantial amount of the required CHP, making it desirable unit for PtG and GtP operations.

4.2 Large scale point sources

Compared to the biogas-based CO₂ the magnitude of CO₂ available from industrial sources is considerably higher. The biogenic CO₂ alone provides 27.6 Mt of CO₂ annually, compared to high-utilization scenario of biogas which could provide 1.7 Mt of CO₂.

There are 18 industrial plants in Finland which produce annually over one million tons of CO₂ when both biogenic and fossil CO₂ are included. (Teir et al. 2011), (Energiavirasto 2015). The industries emitting more than 1 Mt of CO₂ can be seen in figure 29 with their respective CO₂ emissions.

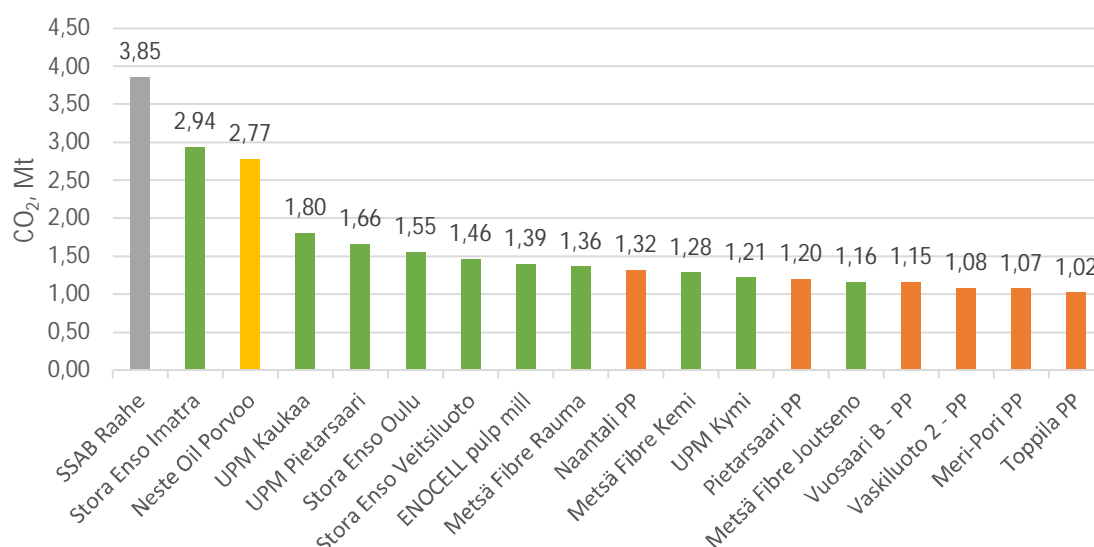


Figure 29. Over 1 Mt of CO₂ emitting point sources in Finland.

SSAB Raahe steel mill and Neste Oil Porvoo refinery represent 23% of the emissions from large point sources (>1 Mt). Rest of the large point sources are either pulp and paper mills (10 plants) or power plants (6 plants). When medium sized point sources (100,000 – 1,000,000 tons of CO₂) are included the number of point sources is increased to 68 plants. The medium point sources include 12 pulp and paper mills, 29 power plants, a steel mill, an oil refinery, two chemical production plants, two cement plants and three lime production facilities. In total the medium and large point sources account for 49 Mt of CO₂. In the Figure 30 the CO₂ emissions of each branch of industry is represented.

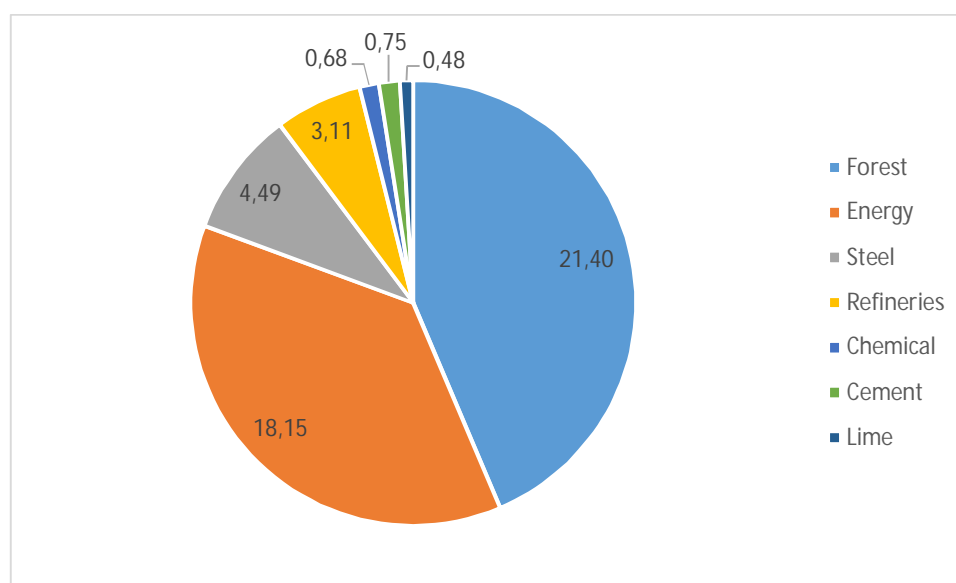


Figure 30. Total CO₂ emissions (Mt) of major industrial sectors for point sources >0.1 Mt.

If only biogenic CO₂ is considered then there are 10 plants producing over 1 Mt of CO₂ and 24 producing over 100,000 tons of CO₂. (Teir et al. 2011). The 10 plants producing over one million tons of biogenic CO₂ are all part of the pulp and paper industry. In the range of 100,000 – 1 Mt of biogenic CO₂ there are eight pulp and paper mills and five power plants. It should be noted that the table by Teir et al which is the source for biogenic CO₂ emissions is for the year 2008. The table included various plants which have since been shut down and had to be removed from the list. There are also numerous plants which have since been taken into operation and can be found Energy authority's list of CO₂ producing facilities, yet have no information on the amount of biogenic CO₂ produced. Particularly the biogenic emissions of power plants can change in short period of time just by switching from fossil fuels to wood based fuels. However for the purposes of this thesis the information is sufficient (the mapping of different CO₂ sources and their scale) but for more in-depth studies the quantities of biogenic CO₂ should be rechecked.

4.2.1 Power plants

Today power plants in Finland are major contributor to the national CO₂ emissions with 26.3 Mt of CO₂ produced annually and considerable share of this is from biogenic fuels (8.9 Mt). The energy system of 100% renewable Finland 2050 assumes that in high biomass scenario the total energy available from combustible biomass is 89 TWh_{th}. (Child, Breyer 2015). When the biomass is assumed to have LHV of 19 MJ/kg and carbon content of 48% from the dry mass, it can be calculated that this 89 TWh_{th} of biomass produces 15.3 Mt of CO₂ annually. This could easily provide the 6.1 Mt of CO₂ required by the national PtG system. Before the 100% renewable scenario is reached there will be transition phase where the share of biomass as a fuel increases while fossil fuel consumption decreases. At the same time, the scenario assumes that the CHP power full load hours decrease from 4106h to 1641h while the capacity increases from 3490 MWe to 9000 MWe. (Child, Breyer 2015). If CO₂ capture from power plants for PtG is to be utilized, then the chosen power plants should be limited to CHP units as purely condensing units are likely to be shut down in the near future. One must also consider the changing role of CHP units as the transition progresses towards 100% renewable 2050 scenario. While CHP units operate at medium (~4000h) full load hours today, in the future their role is to balance the fluctuations of wind and solar production, leading to the lower operational hours (~1600h). This causes problems in the sense of CO₂ availability, as majority of the CO₂ is produced within relatively short period of time. When

the solar and wind production is high, other power plants have to adjust by lowering their production, thus decreasing CO₂ available for PtG operation. Therefore some form of seasonal CO₂ storage is needed if CO₂ from biomass-fired CHP units is to be utilized. However investments to large storage facilities while more reliable CO₂ sources are available seems unreasonable. It should be considered that decrease in full load hours also translates into increased capital costs in relation to operating costs, thus low full load hours make investments in carbon separation facilities economically unprofitable.

In conclusion it could be argued that while more reliable (high full load hours) carbon sources with higher CO₂ partial pressure are available, those sources should be utilized first.

4.2.2 Steel industry

There exists two steel mills in Finland which produce over 100,000 tons of CO₂ annually, the SSAB Raahe mill and Outokumpu Tornio steel mill. The plants produce 3.85 Mt and 0.64 Mt of CO₂ respectively. (Energiavirasto 2015). The steel mills typically operate at high capacity factors (91 - 97%), thus CO₂ is available throughout the year. (Kuramochi et al. 2012). However the CO₂ is produced from fossil sources and although the CO₂ concentration is higher than in combustion processes on average, the capture still requires energy intensive separation methods. If fossil fuels were replaced by renewable alternatives, such as biogenic SNG, the share of biogenic CO₂ in the flue gases would likewise increase, but considering the immense energy consumption in steelmaking processes it would be very difficult to produce entirely biogenic SNG. From the economic point of view the CO₂ capture from steel mills is relatively low cost, being close to the price of CCS from pulp and paper mills. The pulp mills however have the advantage of biogenic CO₂. Therefore it can be concluded that while CO₂ is available from pulp and paper mills these sources should be utilized first.

4.2.3 Cement and lime production

In Finland there are two cement plants and three lime production plants. The individual CO₂ emissions are shown in the table 14. When summed up the combined emissions equal 1.2 Mt of CO₂. From the perspective of scale the Finnish cement industry could provide substantial amount of CO₂ for the national PtG system. 90 % of the CO₂ emissions in the cement production are caused in the calcination process, i.e. in the production of lime. 50%-points is attributed to the CO₂ released from the limestone while 40%-points is from the combustion of fuels to produce heat for the process. Limestone is the key ingredient of

cement and as such difficult to replace, however the fuel used for heat production can be replaced with renewable fuels, like SNG from PtG process. PtG could therefore offer potential route in decarbonizing the cement production by capturing some of the unavoidable CO₂ emissions.

Table 14. Finnish cement and lime production plants

	t _{CO2}
Finnsementti Parainen	497 465
Finnsementti Lappeenranta	250 369
Nordkalk Tytyri	162 942
Nordkalk Raahe	161 231
SMA Mineral Röyttä	150 880

The high energy penalty (5.06 MJ/kg_{CO2}) and specific costs (33 – 69 €/t_{CO2}) of MEA-based post-combustion capture at cement plants make cement industry less attractive option for carbon capture in the short term. However the new technologies, such as calcium looping and oxyfuel, can offer considerable decrease in the energy requirement of carbon separation in the long term. According to Kuramochi et al. 2012, the energy penalty of cement CCS with pre-calciner modified to operate as oxyfuel kiln can be as low as 0.06 MJ/kg_{CO2} primary energy and 0.73 MJ/kg_{CO2} electricity. However the technical immaturity and relative difficulty of retrofitting existing plants with entirely new kiln make utilization of oxyfuel or CaL technologies implausible in the short term.

4.2.4 Pulp and Paper industry

The pulp and paper industry is single largest producer of CO₂ in Finland. Majority of this CO₂ is biogenic as a result of the wood based raw materials employed by the industry. Finnish pulp and paper mills which have annual CO₂ emissions over 100,000 tons are listed in the Table 15 (2008 values). The total CO₂ emitted amounts to 22.2 Mt, out of which 18.5 Mt is of biogenic origin. (Teir et al. 2011).

The three largest pulp and paper mills could easily provide the CO₂ required for PtG system. However, as the biogenic carbon is released from combustion processes its concentration is low and thus the CO₂ separation process will require considerable amounts of energy.

Table 15. Pulp and paper based CO₂ emissions. *unknown value.

	total[t _{CO2}]	fossil[t _{CO2}]	bio[t _{CO2}]
Stora Enso Imatra	2 938 217	165 259	2 772 958
UPM Kaukaa	1 798 537	134 021	1 664 516
UPM Pietarsaari	1 655 034	30 638	1 624 396
Stora Enso Oulu	1 547 873	375 369	1 172 504
Stora Enso Veitsiluoto	1 464 560	357 049	1 107 511
ENOCELL pulp mill	1 391 413	40 435	1 350 978
Metsä Fibre Rauma	1 358 530	36 530	1 322 000
Metsä Fibre Kemi	1 282 597	64 597	1 218 000
UPM Kymi	1 213 381	58 411	1 154 970
Metsä Fibre Joutseno	1 159 597	71 597	1 088 000
Metsä Fibre Äänekoski	820 164	18 164	802 000
Stora Enso Varkaus	816 874	117 016	699 858
Rauhalahti PP	739 215	454 415	284 000
UPM Tervasaari	685 385	244 253	441 000
UPM Jämsänkoski	615 633	135 787	479 846
Kotkamills Kotka	517 362	261 627	255 735
Stora Enso Anjalankoski	474 239	400 463	73 776
UPM Kaipola	463 543	94 539	369 004
Stora Enso Sunila	359 579	39 579	320 000
Stora Enso Heinola Fluting	346 792	163 716	183 076
Sappi Finland Kirkniemi	265 800	159 500	106 300
Powerflute Savo pulp	121 484	121 484	*
Metsä Board Simpele	104 814	104 814	*

Since the pulp mills produce large amounts of CO₂ it might not be sensible to capture it all for PtG process as this would require considerable buildup of electrolyzer and methanation capacity in the vicinity of the mill. In this sense the scattered point sources of the mills are an advantage: by tapping to the smaller point sources, such as lime kiln or bark boiler instead of recovery boiler it is possible to utilize only a fraction of the CO₂ produced. The costs of pulp and paper CO₂ capture are lowest of the industrial point sources and the CO₂ is biogenic, thus making it ideal for PtG utilization.

4.2.5 Refineries

There are two large refineries in Finland, the Neste Oil Porvoo and Naantali refineries. Porvoo refinery produces 2.8 Mt of CO₂ annually which makes it one of the largest CO₂ emission sources in Finland. Refinery in Naantali is relatively small with emissions of 340,000 tons of CO₂. (Energiavirasto 2015). The CO₂ produced is low concentration gas and in the case of fluid catalyst cracking it may contain considerable amounts of problematic

impurities. Typically the fuels and raw materials used are from fossil sources, thus reducing the attractiveness of carbon capture from refineries. As can be seen in chapter 3.3, the cost of carbon capture at refineries is typically at the higher end of the spectrum.

Another point to consider is the hydrogen consumption: the Neste Oil Porvoo refinery alone consumes 14 t/h of hydrogen which is produced by steam reforming of natural gas and butane. (Länsi-Suomen ympäristölupavirasto 2006). From the point of view of efficiency it is more effective to utilize the hydrogen for the processes in the refinery instead of methanation, as a share of the energy is lost in the conversion process to methane.

4.2.6 Petrochemical industry

Borealis Polymers Ltd plant at Kilpilahti produces 537,000 tons of CO₂ annually. (Energiavirasto 2015). The CO₂ is produced by cracking and regeneration units, process heaters and flares. The raw materials include oil-derived hydrocarbons from the Neste Oil Porvoo refinery and fuels used are either combustible process gases or natural gas. The carbon capture technologies are same as the ones used at refineries, with same energy penalties and capture costs. (Uudenmaan ympäristökeskus 2006).

Yara Suomi Ltd plant at Uusikaupunki produces annually 149,000 tons of CO₂. (Energiavirasto 2015). The main products of the plant are Nitric acid, nitrates and fertilizers. 15,200 tons of the CO₂ is associated to the oil-fired process heaters. However, no other CO₂ emitting sources are mentioned by the environmental license, leaving the source for rest of the CO₂ unknown. (Länsi-suomen ympäristölupavirasto 2008).

4.2.7 Bioethanol production

Bioethanol is produced on five locations in Finland by St1. The plants at Lahti, Vantaa, Hamina and Hämeenlinna produce 1 Ml/a per plant while the plant in Jokioinen produces 7 Ml/a, bringing the combined bioethanol production is 11 million liters of bioethanol. (St1 2015). From reaction stoichiometry it can be seen that production of one mole of ethanol produces one mole of CO₂. Thus from this production data it is possible to indirectly calculate the CO₂ emissions from the fermentation process: 8300 tons of CO₂. In addition to this there is the Altia ethanol plant at Koskenkorva, producing 23,800 tons of ethanol annually. The plant produces excess 20,000 tons of CO₂ which is currently sold to AGA-company. (Altia 2014).

Suomen Bioetanoli Oy (SBE) is planning to start a bioethanol plant at Myllykoski, Kouvola in the premises of decommissioned paper mill. The plant is designed to produce 72,000 tons of bioethanol annually. (SBE 2015). Such quantity would produce roughly 69,000 tons of CO₂ as a side product. Although the CO₂ available from ethanol production is limited, the pure stream of biogenic CO₂ produced as a byproduct is very attractive for PtG carbon source.

5 RESULTS AND DISCUSSION

From the data collected and assumptions made it can be concluded that there exists sufficient CO₂ sources in Finland to supply PtG operated energy storage system. Therefore the determining factor in choosing the CO₂ source should be its renewability, availability and ease of capture. From this point of view the bioethanol and biogas production would stand out as the most favorable sources due to the high partial pressure of CO₂ and biogenic origin. Biogas and bioethanol is followed by the pulp and paper industry due to the biogenic origin, relatively low capture costs and steady supply of CO₂. Power plants can also contribute considerable amounts of biogenic CO₂ if solely biogenic fuels are used and the carbon production and consumption can be balanced. It could also be argued that different carbon sources are suitable for different storage scales. For example biogas digesters can very flexibly accommodate small and fast fluctuations in the power grid and provide power back to the grid via CHP unit. This makes biogas units attractive for grid balancing operations. Large scale point sources could be more suited for long term energy storage. Large scale chemical methanation would be used when there are large amounts of predictable renewable power available, such as photovoltaic production during summer, to produce large amounts of SNG for long term energy storage or for traffic fuel consumption.

Table 16. Potential CO₂ sources in Finland.

*(Reiter, Lindorfer 2015) **Only includes the emissions from recovery boiler. (Gardarsdottir et al. 2014)

CO ₂ source	Fossil CO ₂ [Mt]	Biogenic CO ₂ [Mt]	Number of plants	Carbon capture energy penalty [MJ/kgCO ₂]	Specific capture costs [€/tCO ₂]	Capture efficiency [%]*
Power plants	17.50	8.90	35	2.7 - 2.9	35 - 46 (coal) 59 - 101 (NG)	90
Steel plants	4.49	-	2	3.76 - 4.91	16 - 35 (COREX) 26 - 41 (BF)	75
Cement & lime plants	1.22	-	5	5.06	33 - 69	85
Pulp & paper plants	3.60	18.50	23	2.80 - 3.76	19 - 26	60**
Refineries & petrochemical	3.79	-	2	2.07 - 3.88	44 - 53 (oxyfuel) 55 - 94 (post-combustion)	75
Bioethanol	-	0.03	5	-	5 - 9	100
Biogas, existing AD	-	0.02	26	-	5 - 9	100
Future potential						
Biogas, max. utilization	-	1.00	-	-	5 - 9	
Biomass CHP (2050 scenario)	-	15.30	-	1.3 - 5.5	-	

As 100% carbon neutral energy system cannot be achieved without including traffic fuels, it is likely that large scale methanation is needed to produce sufficient amounts of traffic fuels from biogenic CO₂ and renewable energy.

The most prominent advantages and disadvantages of different carbon sources can be seen in table 17. The bioethanol and biogas can be seen as the most promising carbon sources for PtG due to high concentration and biogenic origin of the CO₂. These sources are however very limited today and even with maximum utilization of biomass cannot provide all of the CO₂ required by the 100% renewable 2050 scenario. The pulp and paper industry could provide all the biogenic carbon required. Up to date, the carbon capture at pulp and paper mills has not been studied extensively and there is some uncertainty regarding the cost and energy penalty associated with the capture.

Table 17. Advantages and disadvantages of various different carbon sources.

	Advantages	Disadvantages
Power plants	-CCS has been studied extensively -Large amounts of CO ₂ available	-CO ₂ production does not correspond with PtG production
Steel plants	-Large amounts of CO ₂ available	-Fossil origin -Energy intensive
Cement & lime plants	-Large amounts of CO ₂ available	-Fossil origin -Energy intensive without waste heat integration -High capture costs
Pulp & paper plants	-Large amounts of biogenic CO ₂ available	-Very few studies of CCS in pulp&paper industry - Uncertainty of costs and energy penalty
Refineries & Petrochemical	-Large amounts of CO ₂ available -Heat integration offers relatively low energy penalty	-Fossil CO ₂ -Plants likely to consume produced hydrogen
Bioethanol	-Biogenic -Pure CO ₂ stream	- Limited quantities available
Biogas	-Biogenic -Very high CO ₂ concentration -Potential for large amounts of CO ₂	-Limited quantities available

The last of the biogenic CO₂ sources considered here are power plants utilizing biomass. Carbon capture at power plants has been studied the most and the technology is relatively mature for implementation. The main problem lies within the disparity in carbon capture from the power plant and consumption at the PtG facility. Some form of CO₂ storage is ultimately required to balance the supply and demand of carbon, thus increasing the overall

costs for this carbon source. Then again, even a fraction of the CO₂ emissions of a large power plant is sufficient for large quantities of SNG. For example capturing only 20% of the carbon from a power plant emitting 500,000 tons annually would be enough for 14,200 MWh of SNG. Or in terms of electricity production the CO₂ would be enough for the conversion of the annual production of 470 MW of wind power to SNG.

The steel, cement and petrochemical industry are problematic due to the fossil origin of the carbon involved. Steel production could in theory be decarbonized by utilization of renewable SNG, but due to the large energy consumption it is very difficult to supply sufficient quantities of fuel. Utilization of renewable SNG in cement industry could decrease the fossil CO₂ emissions by half, but there is still the unavoidable fossil carbon of limestone involved which is released in the calciner. Refineries and petrochemical industry consume very high amounts of hydrogen, therefore these industries are likely to use the produced hydrogen without further conversion into SNG by methanation. Although in this sense petrochemical industry can greatly benefit from PtG, it is not suitable for SNG production.

One could also argue that during the transition phase the fossil carbon sources can be utilized as it makes no practical difference where the carbon is captured if the net atmospheric carbon balance is increasing. The fossil carbon sources produce concentrated stream of carbon which is relatively easy to capture. However if the 2050 scenario of 100% renewable Finland is to be realized, the fossil emission sources must be hitherto replaced with biogenic sources.

The estimates for carbon capture costs presented in this thesis are from several different sources. This may result in a bias towards some carbon sources such as the pulp and paper industry, where the data was gathered from two separate studies. Then again, most carbon capture studies assume that the aim of carbon capture is to remove all of the produced CO₂ emissions, which leads to high full load hours for the installed capacity. The PtG operation is based on the assumption that CO₂ is captured only for the methanation process. This leads to considerably lower full load hours when compared to traditional carbon capture and therefore affects the economics of CO₂ capture. Additionally, most carbon separation technologies are not designed for part load operation with swift load changes which is the requirement if the carbon capture is to be run in parallel with the methanation process. Some form of intermediate CO₂ storage is likely required to act as a buffer between CO₂ production and consumption. In any case, more in-depth study of carbon capture operation at partial loads or at low full load hours is necessary for more accurate cost calculations.

It should be noted that this thesis focused on the specific PtG application of converting renewable energy to methane for the purpose of energy storage. The thesis does not consider other similar energy conversion processes, such as Power-to-Hydrogen or Power-to-Liquids. It is very much possible that these other applications may have better technical and economical prerequisites for operation.

6 CONCLUSIONS

Methanation, as a part of PtG process, turns CO₂ from waste product into an asset and a valuable resource. However to supply fully renewable energy system the CO₂ itself must be renewable, which greatly limits potential CO₂ sources. Biogas plants provide biogenic CO₂ which can be utilized via in-situ biological methanation without additional carbon separation methods. Coupling biogas plant with a CHP unit turns the plant into electricity storage and discharge unit, capable of balancing the electricity grid. This makes biogas plant ideal source for carbon in a PtG system. Pulp and paper industry is the single largest producer of biogenic CO₂, followed by the energy sector. Refineries, steel mills and cement plants produce high quantities of CO₂ but suffer from the fossil origin of the CO₂. Carbon capture from these plants is typically more expensive when compared to pulp and paper mills, thus there is no incentive to capture CO₂ from these plants while biogenic option from pulp mills exists. Power plants could provide large amounts of biogenic CO₂ but they have to adjust their energy production to accommodate for renewable power generation. This results in decreased CO₂ supply during times of highest PtG usage. This problem could be circumvented with intermediate CO₂ storage, at the price of increase in capital and operational costs.

LÄHTEET

Abanades, J.C., Arias, B., Lyngfelt, A., Mattisson, T., Wiley, D.E., Li, H., Ho, M.T., Mangano, E., Brandani, S. 2015. Emerging CO₂ capture systems. *International Journal of Greenhouse Gas Control*. doi:10.1016/j.ijggc.2015.04.018

Akinyele, D.O., Rayudu, R.K. 2014. Review of energy storage technologies for sustainable power networks. *Sustainable Energy Technologies and Assessments*, vol. 8, pp. 74-91.

Altia 2015. Altia Financial statements 2014. Available from: <http://www.altiacorporation.com/eng/Company/Publications/>. Cited 4.6.2015.

Arasto, A., Tsupari, E., Kärki, J., Pisilä, E., Sorsamäki, L. 2013. *International Journal of Greenhouse Gas Control*, vol. 16, pp. 271-277.

Bartholomew C.H. 2001. Mechanisms of catalyst deactivation. *Applied Catalysis A: General*, vol. 212, pp. 17–60

Benjaminsson G., Benjaminsson, J., Rudberg, R.B. 2013. Power-to-Gas – A technical review. SGC Report 2013:284. Svenskt Gastekniskt Center.

Bensmann, A., Hanke-Rauschenbach, R., Heyer, R., Kohrs, F., Benndorf, D., Reichl, U., Sundmacher, K. 2014. Biological methanation of hydrogen within biogas plants: A model-based feasibility study. *Applied Energy*, vol. 134, pp. 413-425.

Bosoaga, A., Masek, O., Oakey, J.E. 2009. CO₂ Capture Technologies for Cement Industry. *Energy Procedia*, vol. 1, pp. 133-140.

Burkhardt, M., Busch, G. 2013. Methanation of hydrogen and carbon dioxide. *Applied Energy*, vol. 111, (2013) pp. 74-79.

Carmo, M., Fritz, D.L., Mergel, J., Stolten, D. 2013. A comprehensive review on PEM water electrolysis. *International journal of hydrogen energy*, vol. 38, pp. 4901-4934.

Chen, Q. 2006. Development of an anthraquinone process for the production of hydrogen peroxide in a trickle bed reactor—from bench scale to industrial scale. *Chemical Engineering and Processing: Process Intensification*, vol. 47, pp. 787-792.

Child, M. 2015. Personal communication. 29.7.2015. Junior researcher, Lappeenranta University of Technology.

Child, M., Breyer, C. 2015. Visions and initial feasibility analysis of a recarbonised Finnish energy system. Internet source, available: <http://www.lut.fi/documents/10633/70751/LUT-Vision-and-initial-feasibility-of-a-recarbonised-Finnish-energy-system-for-2050.pdf>. Cited 18.6.2015.

Dean, C.C., Blamey, J., Florin, N.H., M.J. Al-Jeboori, Fennell, P.S. 2011. The calcium looping cycle for CO₂ capture from power generation, cement manufacture and hydrogen production. *Chemical Engineering Research and Design*, vol. 89. pp. 836-855.

Energiavirasto 2015. Laitoskohtaiset todennetut päästöt vuosilta 2008-2014. Available: <http://www.energiavirasto.fi/paastotiedot>. Accessed: 26.5.2015.

EurObserv'ER, 2014. BiogasBarometer 2014. Available from: <http://www.eurobserv-er.org/biogas-barometer-2014/>. Accessed 25.5.2015

EU, 2011. A Roadmap for moving to a competitive low carbon economy in 2050. EU commission. Online source, available: http://eurlex.europa.eu/resource.html?uri=cellar:5db26ecc-ba4e-4de2-ae08-dba649109d18.0002.03/DOC_1&format=PDF. Cited: 8.6.2015.

Gandía, L.M., Arzamendi, G., Diéguez, P.M. 2013. *Renewable Hydrogen Technologies: Production, Purification, Storage, Applications and Safety*. Amsterdam: Elsevier.

Gardarsdottir, S.O., Normann, F., Andersson, K., Johnson, F. 2014. Process evaluation of CO₂ capture in three industrial case studies. *Energy Procedia*, vol. 63, pp. 6565 – 6575.

The Great Soviet Encyclopedia, 3rd Edition, 1970-1979. "Basic Oxygen Process." The Gale Group, Inc.

Gupta, A., Verma, J.P. 2015. Sustainable bio-ethanol production from agro-residues: A review. *Renewable and Sustainable Energy Reviews*, vol. 41, pp. 550-567.

Götz, M., Koch, A.M., Graf F. 2014. State of the Art and Perspectives of CO₂ Methanation Process Concepts for Power-to-Gas Applications. International Gas Union Research Conference, September 17-19, Copenhagen, Denmark.

Haandel, A.C., Lubbe, J.G.M. 2012. *Handbook of Biological Wastewater Treatment, Design and Optimisation of Activated Sludge System*. London: IWA Publishing.

Hahn, H., Krautkremer, B., Hartmann, K., Wachendorf, M. 2014. Review of concepts for a demand-driven biogas supply for flexible power generation. *Renewable and Sustainable Energy Reviews*, vol. 29, pp. 383-393.

Harrison, K., Levene, J.I. 2008. Solar Hydrogen Generation – Toward a Renewable Energy Future. pp. 42-63. New York: Springer.

Hoekman, S.K., Broch, A., Robbins, C., Purcell R. 2010. CO₂ recycling by reaction with renewably-generated hydrogen. *International Journal of Greenhouse Gas Control*, vol. 4, pp. 44–50.

Huttunen, M.J., Kuittinen, V. 2014. Suomen biokaasulaitosrekisteri n:o 17. Reports and Studies in Forestry and Natural Sciences, No 19. Joensuu: University of Eastern Finland.

IEA 2004. Impact of Impurities on CO₂ Capture, Transport and Storage. IEA: London.

IEAGHG, 2010. Oxyfuel Combustion of Pulverised Coal. Report 2010/07, August 2010.

IEAGHG, 2013. Iron and Steel CCS Study (Techno-Economics Integrated Steel Mill), 2013/04, July, 2013. Cheltenham: IEAGHG.

IEAGHG, 2013b. Deployment of CCS in the Cement Industry. Report: 2013/19, December 2013. Cheltenham: IEAGHG.

Tilastokeskus 2012. Ilmanpäästöt toimialoittain. Online source, available: http://www.stat.fi/til/tilma/2012/tilma_2012_2014-09-25_tie_001_fi.html ISSN=2323-7589. Helsinki: Tilastokeskus [Cited: 11.5.2015].

Klaus, T., Vollmer, C., Werner, K., Lehmann, H., Müschen, K. 2010. Energy target 2050: 100% renewable electricity supply. German Federal Environment Agency: Dessau-Roßlau.

Kvamsdal, H.M., Jordal, K., Bolland, O. 2007. A quantitative comparison of gas turbine cycles with CO₂ capture. Energy, vol. 32, pp. 10 – 24.

Kopyscinski, J., Schildhauer, T. J., Biollaz, S. M. A. 2010. Production of synthetic natural gas (SNG) from coal and dry biomass – A technology review from 1950 to 2009. Fuel, vol. 89, pp. 1763-1783.

Kuramochi, T., Ramírez, A., Turkenburg, W., Faaij, A. 2012. Comparative assessment of CO₂ capture technologies for carbon-intensive industrial processes. Progress in Energy and Combustion Science, vol. 38, pp. 87-112.

Leeson, D., Fairclough, J., Petit, C., Fennell, P. 2014. A Systematic Review of Current Technology and Cost for Industrial Carbon Capture. Imperial College London, Grantham institute, Report GR7.

Lehner, M., Tichler, R., Steinmüller, H., Koppe, M. 2014. Power-to-Gas: Technology and Business Models. Springer.

Länsi-suomen ympäristölupavirasto 2008. Lupapäätös, Nro 85/2008/2, Dnro LSY-2004-Y-398 and Nro 86/2008/2, Dnro LSY-2007-Y-398.

Länsi-Suomen ympäristölupavirasto 2006. Ympäristölupapäätös Nro 29/2006/2. Dnro LSY2004Y120. Länsi-Suomen ympäristölupavirasto 31.10.2006.

Mantripragada, H.C., Rubin, E.S. 2014. Calcium looping cycle for CO₂ capture: Performance, cost and feasibility analysis. Energy Procedia, vol. 63, pp. 2199 – 2206.

Mao, C., Feng, Y., Wang, X., Ren, G. 2015. Review on research achievements of biogas from anaerobic digestion. Renewable and Sustainable Energy Reviews, vol. 45, pp. 540–555.

Mello, L.F., Pimenta, R.D.M., Moure, G.T., Pravia, O.R.C., Gearhart, L., Milios, P.B., Melien, T. 2009. A technical and economical evaluation of CO₂ capture from FCC units. *Energy Procedia*, vol. 1, pp. 117-124.

Mesfun, S., Toffolo, A. 2013. Optimization of process integration in a Kraft pulp and paper mill – Evaporation train and CHP system. *Applied energy*, vol. 107, pp. 98-110.

Metz, B., Davidson, O., Coninck, H., Loos, M., Meyer, L. 2005. *IPCC Special Report on Carbon Dioxide Capture and Storage*. New York: Cambridge University Press.

Onarheim, K., Mathisen, A., Arasto, A. 2015. Barriers and opportunities for application of CCS in Nordic industry – A sectorial approach. *International Journal of Greenhouse Gas Control*, vol. 36, pp. 93-105.

Rasi, S., Lehtonen, E., Aro-Heinilä, E., Höhn, J., Ojanen, H., Havukainen, J., Uusitalo, V., Manninen, K., Heino, E., Teerioja, N., Anderson, R., Pyykkönen, V., Ahonen, S., Marttinen, S., Pitkänen, S., Hellstedt, M., Rintala, J. 2012. *From Waste to Traffic Fuel – projects Final report*. Jokioinen: MTT Agrifood Research Finland.

Reiter G., Lindorfer J. 2015. Evaluating CO₂ sources for power-to-gas applications – A case study for Austria. *Journal of CO₂ Utilization*, vol. 10, pp. 40-49.

Romano, M.C., Anantharman, R., Arasto, A., Ozcan, D.C., Ahn, H., Dijkstra, J.W., Carbo, M., Boavida, D. 2013. Application of advanced technologies for CO₂ capture from industrial sources. *Energy Procedia*, vol. 37, pp. 7176-7185.

Rubin, E.S., Mantripragada, H., Marks, A., Versteeg, P., Kitchin, J. 2012. The outlook for improved carbon capture technology. *Progress in Energy and Combustion Science*, vol. 38, pp. 630-671.

Ryckebosch, E., Drouillon, M., Vervaeren, H. 2011. Techniques for transformation of biogas to biomethane. *Biomass and Bioenergy*, vol. 35, 1633-1645.

SBE 2015. Internet source. Available: <http://www.sbe.fi/SBE.html>. Cited: 18.6.2015.

Scheffknecht, G., Al-Makhadmeh¹, L., Schnell, U., Maier, J. 2011. Oxy-fuel coal combustion—A review of the current state-of-the-art. *International Journal of Greenhouse Gas Control*, vol. 5, pp. 16-35.

Seadi, T.A., Rutz, D., Prassl, H., Köttner, M., Finsterwalder, T., Volk, S., Janssen, R. 2008. *Biogas handbook*. Esbjerg, Denmark: University of Southern Denmark.

St1 2015. Internet source. Available: <http://www.st1biofuels.com/solutions>. Cited: 18.6.2015.

Teir, S., Arasto, A., Tsupari, E., Koljonen, T., Kärki, J., Kujanpää, L., Lehtilä, A., Nieminen, M., Aatos, S. 2011. Hiilidioksidin talteenoton ja varastoinnin (CCS:n) soveltaminen Suomen

olosuhteissa. VTT tiedotteita – Research notes 2576. Kuopio: VTT Technical Research Centre of Finland.

Teir, S., Hetland, J., Lindeberg, E., Torvanger, A., Buhr, K., Koljonen, T., Gode, J., Onarheim, K., Tjernshaugen, A., Arasto, A., Liljeberg, M., Lehtilä, A., Kujanpää, L., Nieminen, M. 2010. Potential for carbon capture and storage (CCS) in the Nordic region. Espoo 2010. VTT Tiedotteita – Research Notes 2556.

Tran, H., Vakkilainen, E. 2007. Advances in the kraft chemical recovery process. 3rd ICEP international colloquium on eucalyptus pulp, Belo Horizonte, Brazil.

Tähti, H., Rintala, J. 2010. Biometaanin ja – vedyn tuotantopotentiaali Suomessa. Jyväskylän yliopiston bio- ja ympäristötieteiden laitoksen tiedonantoja 90. University of Jyväskylä.

Uudenmaan ympäristökeskus 2006. Ympäristölupapäätös, Dnro UUS-2004-Y-287-111.

Vakkilainen, E., Kivistö, A. 2014. Forest industry energy consumption – trends and effect of modern mills. Lappeenranta: Lappeenranta university of Technology.

Varone, A., Ferrari, M., 2015. Power to liquid and power to gas: An option for the German Energiewende. Renewable and Sustainable Energy Reviews, vol.45, pp. 207–218.

Wall, T., Liu, Y., Spero, C., Elliot, L., Khare, S., Rathnam, R., Zeenathal, F., Moghtaderi, B., Buhre, B., Sheng, C., Gupta, R., Yamada, T., Makino, K., Yu, J. 2009. An overview on oxyfuel coal combustion—State of the art research and technology development. Chemical engineering research and design, vol. 87, pp. 1003-1016.

Wiley, D.E., Ho, M.T., Bustamante, A. 2011. Assessment of Opportunities for CO₂ Capture at Iron and Steel Mills: An Australian Perspective. Energy procedia, vol. 4. pp. 2654-2661.

Xu, Y., Isom, L., Milford H.A. 2010. Adding value to carbon dioxide from ethanol fermentations. Bioresource Technology, vol. 101, pp. 3311–3319.