



CCSP Deliverable D216
Porvoo, 2013

Janne Andtsjö

Technical report: Comparison of Carbon Capture Methods in Hydrogen Production by Steam Methane Reforming



ccsp

Carbon Capture and Storage Program

CLIC Innovation Oy
ETELÄRANTA 10
P.O. BOX 10
FI-00131 HELSINKI
FINLAND
www.clicinnovation.fi

CLIC Innovation Oy
Carbon Capture and Storage Program (CCSP)
Deliverable D216

Janne Andtsjö

Comparison of Carbon Capture Methods in Hydrogen Production by Steam Methane Reforming



Report Title: Comparison of Carbon Capture Methods in Hydrogen Production by Steam Methane Reforming

Key words: Carbon capture, CCS, SMR hydrogen production, cryogenic separation

Abstract

One possibility to slow down the greenhouse effect is to capture and store CO₂. Gas streams in hydrogen production are an attractive source for CO₂ capture due to high CO₂ concentrations and the low levels of impurities, such as sulphur. The purpose of this report was to compare different CO₂ capture technologies in steam methane reforming (SMR) hydrogen production.

Based on previous research, technology alternatives were screened to find the best suitable options for carbon capture from two steam methane reforming hydrogen plant streams; the off gas from hydrogen purification, and the flue gas from the SMR unit's furnace. After the evaluation, a cryogenic capture process was selected for an engineering analysis. The capture processes consisted of feed compression, CO₂ condensation by expansion and purification by distillation. Technical applicability, investment cost and operating costs were estimated.

The two analysed processes were compared with two other process alternatives described in literature; a process combining cryogenic separation and methanol absorption, capturing CO₂ from the hydrogen purification off gas, and an amine wash process capturing CO₂ from power plant flue gas.

It was concluded, that the most attractive stream in SMR hydrogen production to be used for carbon capture is the off gas from hydrogen purification. Between the two analysed gas flows, the hydrogen purification off gas was economically clearly more competitive than the flue gas. For CO₂ capture from the flue gas, the cryogenic process was found to be less feasible than amine absorption. Regarding the SMR hydrogen purification off gas, the combined cryogenic and methanol absorption process was found to be economically more advantageous compared to the analysed cryogenic process. The estimated production cost for captured CO₂ was in all cases clearly higher than the present emission allowance cost of CO₂.

In conclusion, it can be stated that in order to carbon capture be feasible from the economic point of view, the carbon dioxide emission allowance price has to go up and the overall performance of capture technology must be further developed.



Table of contents

1	Introduction	2
	LITERATURE REVIEW	3
2	Hydrogen applications and production methods.....	3
2.1	Hydrogen applications in fuel production	3
2.2	Hydrogen production methods.....	3
2.3	Description of SMR hydrogen plant	5
3	Basic concepts for carbon capture	7
4	Carbon capture technologies in hydrogen production.....	8
4.1	Absorption	8
4.2	Adsorption	10
4.2.1	Pressure swing adsorption (PSA)	11
4.2.2	Vacuum swing adsorption (VSA).....	14
4.2.3	Temperature swing adsorption (TSA).....	14
4.2.4	Electric-swing adsorption (ESA).....	15
4.3	Cryogenic carbon dioxide capture	16
4.3.1	CO ₂ LDsep	16
4.3.2	FlashCO ₂	18
4.4	Membrane permeation.....	19
4.4.1	Facilitated Transport Membranes.....	24
4.4.2	Hollow Fibre Gas-Liquid Contactors.....	24
4.4.3	Selective Surface Flow membranes.....	25
5	Requirements and methods for transportation and storage of CO₂.....	27
5.1	Transportation, storage and utilization.....	27
5.2	Product purity requirements.....	28
5.3	Economic value of carbon dioxide	28
6	Criteria for selection of CO₂ capture process for SMR	30
	FEASIBILITY STUDY.....	33
7	Auspicious carbon capture processes for steam reformers.....	33
7.1	Selection	33
7.2	Case descriptions.....	33
7.3	Methods.....	38
7.4	Carbon foot print	39
7.5	Operating costs	41
7.6	Equipment selection and sizing	42
7.6.1	Compressor	42
7.6.2	Heat exchangers.....	42
7.6.3	Column	42
7.6.4	Pressure vessels.....	43
7.6.5	Refrigerator.....	43
7.7	Investment cost	43
7.8	Production cost	45



7.9 Sensitivity analyses	46
7.10 Comparison	50
8 Conclusions	53
9 Recommendations	54
10 References	56



1 Introduction

The greenhouse effect is causing the climate to change. One major factor in this process is the increasing amount of carbon dioxide (CO₂) in the atmosphere. In order to slow down the change, methods for decreasing the amount of CO₂ released are studied. In general, these methods are called carbon capture and storage (CCS), sometimes referred to as carbon dioxide capture and storage.

In CCS, carbon (dioxide) is separated from the flue gas or other streams. This is the capture part, which is mainly a process related issue. After the capture part, the carbon dioxide has to be transported and stored, or used as a raw material in order to improve the overall carbon balance. Storing has been found to be the tricky part of CCS, since storing options often face political resistance.

The focus of this report is on the capture of CO₂, not the transport or storage, although these matters are briefly discussed in chapter 5.

In order for the CCS process to be meaningful, the carbon dioxide source has to be somewhat significant. The biggest producers of CO₂ in Finland are power plants, the metal industry, oil refineries and cement factories. (Teir et al., 2010)

The purpose of this study is to screen competitive CO₂ capture methods suitable for hydrogen production, more specifically steam methane reforming (SMR) and to evaluate the feasibility of these methods.

Efficient carbon or carbon dioxide capture from process streams is important. Carbon foot prints describe how much carbon dioxide is produced while doing something. The carbon foot print must be smaller than the amount of captured carbon dioxide, otherwise the whole process is meaningless.

The financial value of CCS forms in emission trading, which determines the price the captured carbon dioxide ton can cost. Carbon dioxide can also be sold to certain industries, such as the food and beverage industry. The market is, however, somewhat limited compared to the amounts of CO₂ produced.



LITERATURE REVIEW

2 Hydrogen applications and production methods

Hydrogen (H₂) is the lightest element in the periodic table. It has relative atomic mass of 1.008 and at standard temperature and pressure it is a colourless, odourless and highly combustible diatomic gas. (Krebs, 2006)

H₂ is the most abundant element in the universe, but on Earth it rarely occurs as elemental hydrogen. Instead, it readily forms covalent compounds with other elements and it is present in water and in most organic compounds. (Krebs, 2006)

2.1 Hydrogen applications in fuel production

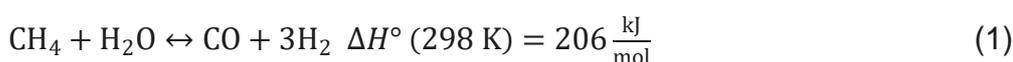
In oil refineries, hydrogen is needed for several processes, such as hydrocracking and hydroprocessing. Hydrocracking is used to produce lighter hydrocarbons and increase their H/C ratio. Hydroprocessing covers the removal of compounds such as sulphur, halides, metals, nitrogen and oxygen. Furthermore, hydrogen is needed for saturation of alkanes and aromatics, isomerization and decyclization or ring-opening. Besides oil refineries, other areas of the process industry use a large amount of hydrogen. (Ramachandran & Menon, 1998)

If other raw materials in the production processes are considered green, it is important to ensure that the green values don't be wasted by the use of fossil-based hydrogen and that the carbon footprint is low.

2.2 Hydrogen production methods

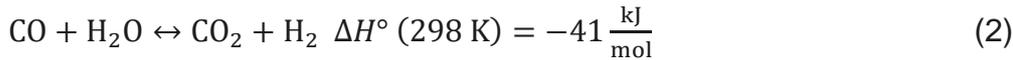
The most common methods for hydrogen production are steam methane reforming, partial oxidation of hydrocarbons, gasfying coal and electrolysis. (U.S. Energy Information Administration, 2008)

The most widely used process for hydrogen production is steam methane reforming (SMR). In SMR, natural gas and steam react in the presence of a catalyst, forming carbon monoxide and hydrogen. The catalyst is often nickel-based and the natural gas usually consists mostly of methane. However, other hydrocarbons can also be used to some extent. (Ramachandran & Menon, 1998)



If the feedstock contains sulphurous components, they have to be removed before the process, since they deactivate nickel-based catalysts. (Dicks, 1996)

Water gas shift (WGS) reactions are used to further convert carbon monoxide and water to hydrogen and carbon dioxide. This is typically done with an iron oxide catalyst.



Combined, the overall process is as follows:



Here we can see that for every mole of methane, 4 moles of hydrogen and one mole of carbon dioxide are formed. Hydrogen can also be produced by other methods, but none are as widely used as SMR. A schematic drawing of the SMR process, in which hydrogen is purified using pressure swing adsorption (PSA), is presented in Figure 1. (Agnew, 2004)

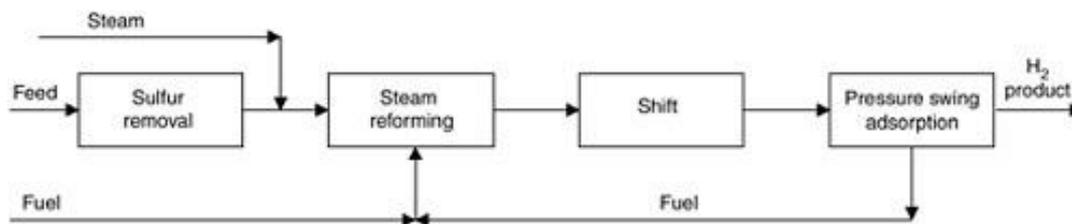


Figure 1 A schematic presentation of the SMR process with hydrogen purification by PSA. (Agnew, 2004)

In the process presented in Figure 1, the hydrogen is separated from the off gas, and the rest is used as fuel gas for the reforming, even though the recycled stream contains CO_2 , which lowers the heat value.

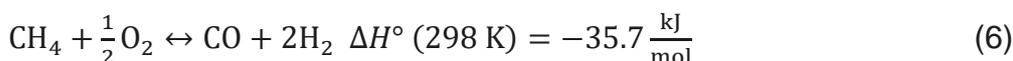
Methanol can also be used as raw material for the reforming: (Cubeiro & Fierro, 1998)



By gasifying coal or coke and making it react with steam, carbon monoxide, hydrogen and some CO_2 as a by-product are formed, as shown below. This method is applicable in areas with rich coal resources and a product demand over $1000 \text{ m}^3/\text{h}$. (Yalian Technology, 2012)



One method is to partially oxidize hydrocarbons, such as methane as shown in equation 6 (Freni et al., 2000) or methanol, as shown in equation 7 (Cubeiro & Fierro, 1998).



Both coal gasification (equation 5) and partial oxidation of methane (equation 6) can, at least in principle, be followed by the same WGS reaction as in SMR in order to yield more hydrogen. By doing so, more carbon dioxide is formed. In addition to



methane, also other hydrocarbons may be used as raw-material as well. By using bio-based C5 hydrocarbons, the end result would be a greener product (Koskinen, 2012).

Even electrolysis of water may be used to produce hydrogen. If an electric current is ran through water, gaseous hydrogen will form at the cathode and gaseous oxygen at the anode:



This is relatively expensive, but the product is pure hydrogen and no separate purifying process is needed.

Some hydrogen is also formed as a side product in processes, such as cracking.

Once the hydrogen is generated, it has to be purified before use. The purity demand varies depending on the application. The two most used purifying methods for hydrogen are pressure swing adsorption (PSA) and membrane permeation.

In PSA, a solid material bed adsorbs impurities at a certain pressure and releases, or desorbs, them at a lower pressure, thus purifying the adsorbent. When multiple vessels are connected in parallel, the process becomes continuous. (Sircar & Golden, 2000)

In membrane permeation, a membrane selectively lets some components of a mixture to permeate through the membrane while the rest stays on the retentate side. (Rousseau, 1987)

In addition to the industrial scale methods mentioned earlier, there are numerous ways of producing hydrogen on a laboratory scale. These are, however, too expensive for industrial purposes due to expensive raw materials or high demand of electricity.

2.3 Description of SMR hydrogen plant

Typical SMR hydrogen plants have four distinctive parts. These include pre-treatment, SMR, WGS and H₂ purification. The block diagram is shown in Figure 1 in paragraph 2.2.

In pre-treatment, the feed gas is compressed and any sulphurous compounds are removed. The feed is typically natural gas or other light alkanes, such as propane. The sulphurous compounds are removed, because they act as catalyst poison in the following stages. There are several sulphur removal technologies available (Kohl & Nielsen, 1997), but these are not covered in this report. The pressure is typically raised to 30-35 bar. The pressure depends on the optimal SMR operating conditions and the desired product pressure. (U.S. Energy Information Administration, 2008)



The SMR process converts the feed gas (in this case, methane) and steam to carbon monoxide and hydrogen according to equation 1. The reaction is endothermic and takes place at high temperatures, typically 700 - 1100 °C in the presence of nickel-based catalysts. The high reaction temperature is achieved by using a furnace. The furnace typically burns natural gas or fuel gases from nearby units.

SMR is followed by WGS, where carbon monoxide and steam are converted to carbon dioxide and more hydrogen, as shown in equation 2. The reaction is slightly exothermic and the equilibrium is highly sensitive to temperature. WGS can be done in two stages, the first one being high-temperature shift (HTS) at 350 °C and the second low-temperature shift (LTS) at 190-210 °C. Catalysts in HTS are primarily iron oxide promoted with chromium oxide and copper on mixed support composed of zinc oxide and aluminium oxide in LTS.

The product stream from WGS contains the hydrogen product along with water, methane, carbon oxides and some nitrogen. The hydrogen is then typically purified via pressure swing adsorption (PSA), where impurities are adsorbed and a pure hydrogen product stream is retrieved. The feed temperature is typically between 30 °C and 50 °C and pressure levels around 20-25 bar. The impurities from the adsorbent beds are desorbed in cycles by changing the pressure levels inside the vessels and retrieved at near ambient pressure. The impurity stream, or PSA off gas, is then either burned in the SMR furnace, or treated in order to capture the carbon dioxide.

Along with providing the necessary temperature for the SMR reaction, furnace heat can also be used to preheat the fuel gas feed, the feed gas itself and to generate extra steam. Additional heat can also be recovered after the SMR, HTS and LTS stages.

In aspects of carbon capture, there are several intermediate streams which contain carbon dioxide. The highest CO₂ concentration is in the PSA off gas, which contains 40-60 mol-% of CO₂ depending on the process. The WGS intermediate product stream contains the same amount of CO₂ than the PSA off gas, but the concentration is lower due to the hydrogen. The flue gas stream also contains CO₂. If no carbon capture takes place, the SMR flue gas has a higher CO₂ level than e.g. power plant flue gases. This is due to the use of PSA off gas as fuel gas. Since the off gas already contains carbon dioxide, the flue gas contains both the carbon dioxide from the off gas and the CO₂ formed in the combustion sequence.



3 Basic concepts for carbon capture

There are basically three different options to decrease the amount of carbon dioxide released to atmosphere; pre- and post-combustion technologies and oxy-fuel combustion. These terms are better suited for combustion processes, but the same terminology may be used in the process industry as well. (Lampinen, 2012)

One way is to remove the carbon from the feed before combustion or processing. This is called pre-combustion carbon capture. In a pre-combustion process, e.g. natural gas is treated with SMR and only the hydrogen is burned. Since there is no carbon in the fuel, the combustion does not produce any carbon dioxide. (Lampinen, 2012)

Another possibility is to use a so called oxy-fuel process. In this process, instead of air, oxygen is used to burn the fuel. This will result in a higher carbon dioxide concentration in the flue gas, making the separation easier or, in some cases, even unnecessary. Compared to air based combustion, temperatures are higher, so retrofitting existing combustion processes may cause problems with design temperatures. (Lampinen, 2012)

A widely used and studied method is the post-combustion method, where carbon dioxide is separated from the flue gas or product stream. There are numerous process alternatives for post-combustion carbon capture, including both chemical and physical separation methods. (Lampinen, 2012)

Even though all of these methods may well be used in power plants, not all options are possible in the process industry. Pre-combustion concepts don't really work and retrofitting old plants to work with oxy-fuel systems is usually not possible. Therefore, only post-combustion technologies are studied further in this report. SMR itself can, however, be considered a pre-combustion process, since carbon is removed from a potential fuel, hydrogen. (Lampinen, 2012)

4 Carbon capture technologies in hydrogen production

As stated earlier, only post-combustion technologies will be studied in this report. Post-combustion technologies with any commercial applications can roughly be divided into the following categories: absorption and adsorption technologies, cryogenic and membrane based separations and microbial or algal systems. Each category can be divided further, as will be explained later. Microbial or algal systems are not discussed in this report. Some common capture methods are shown in Figure 2. (Rao & Rubin, 2002)

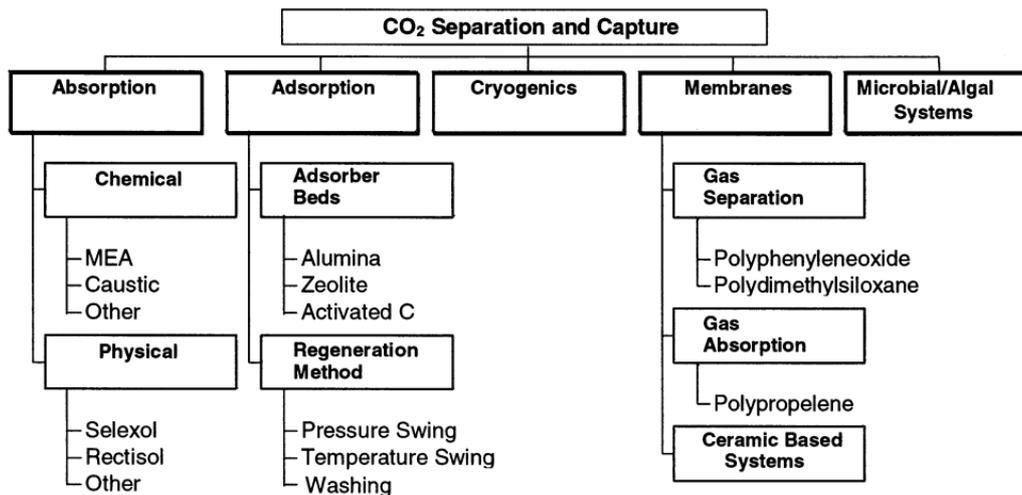


Figure 2 CO₂ capture methods (Rao & Rubin, 2002)

4.1 Absorption

In absorption, a component of a gas mixture is transferred from the gaseous phase into a liquid phase in which the component is soluble. The absorbed component or components are called the absorbate and the liquid, in which the absorbate is transferred to, the absorbent. The reverse process for absorption is stripping. In stripping, a dissolved component from a liquid phase is transferred to a gaseous phase. Absorption is the most important gas purification operation and is widely used. (Kohl & Nielsen, 1997)

Absorption processes can be divided furthermore into three categories based on the interaction mechanism between the absorbate and the absorbent. These are physical absorption, reversible chemical absorption and irreversible chemical absorption.

In physical solution, one component is simply more soluble in the absorbent than the other. No chemical reaction takes place and the equilibrium concentration depends highly on the partial pressure in the gas phase. (Kohl & Nielsen, 1997)

The reversible reaction mechanism involves a chemical reaction between the absorbed component and a component in the absorbent, which together form a loosely bonded reaction product. The new compound can be broken, and the

absorbed component is released. This mechanism is used in CCS, e.g. in the absorption of CO₂ into monoethanolamine (MEA) solution. (Kohl & Nielsen, 1997)

The chemical reaction between a component in the gas mixture and a component in the absorbent can also be (nearly) irreversible. The mechanism is called irreversible reaction. The resulting reaction product is more stable than in the reversible mechanism. (Kohl & Nielsen, 1997)

Absorption processes can be used for streams with both high and low pressures, but a low CO₂ partial pressure, such as flue gases, and they are therefore good for power plant CCS units. However, in the hydrogen production streams, CO₂ has a relatively high partial pressure. (Maroto-Valer, 2010)

The amine wash process (as well as most absorption processes) consists of an amine absorption part and a regeneration stage where the absorbed component is separated from the absorbent. The process is shown in Figure 5.

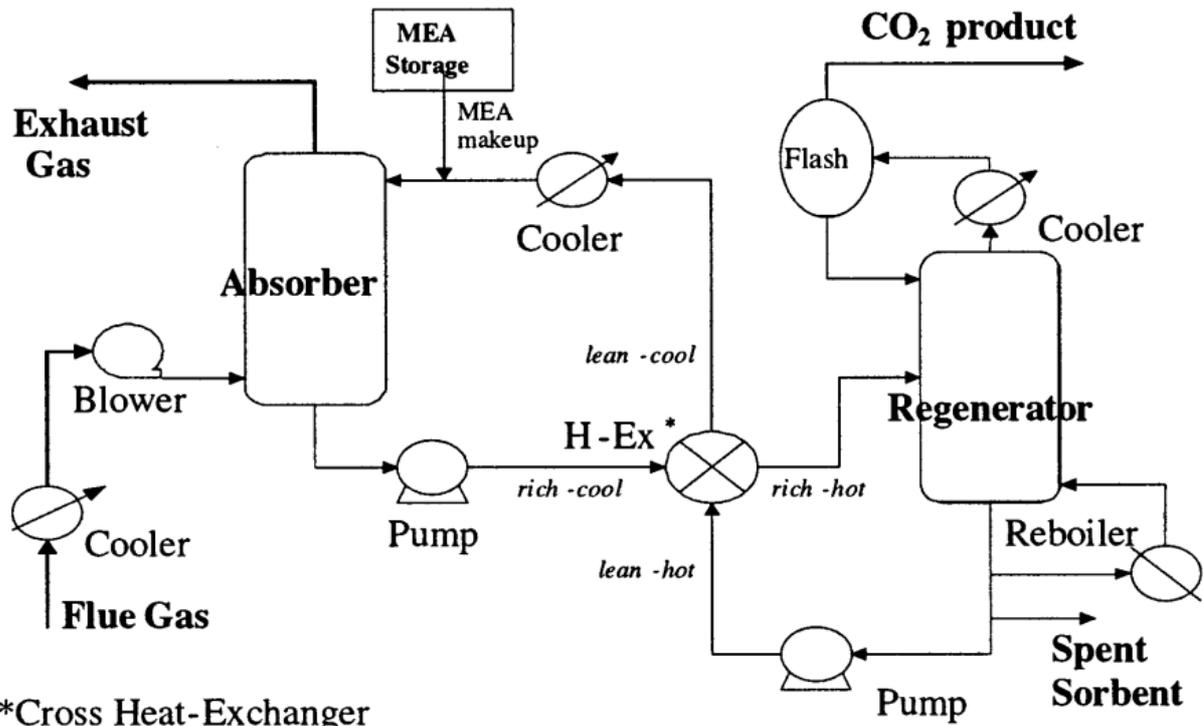


Figure 3 A flow sheet for an amine-based CO₂ capture system (Rao & Rubin, 2002)

Absorption processes are the most used post-combustion CCS technology. This is due to their high efficiency and easy operability. The absorption process provides a large capacity range. (Maroto-Valer, 2010)

Absorption does, however, consume a lot of energy due to the heating needed for regeneration. If a refinery should have lots of waste heat available, it would be beneficial for the energy balance for absorption. Otherwise the carbon foot print due to heating can be significant and cause the overall carbon balance less tempting.



Commercially available absorption processes require 3.2-6.5 GJ/t CO₂ of heating for solvent regeneration. (Merikoski, 2012)

Furthermore, the carbon dioxide product stream has a low pressure and in gaseous phase, and therefore a compressor is required in order for the transportation expenses to be acceptable. The carbon dioxide product stream also contains traces of the absorbent, which could prove problematic in further processing or transportation stages. (Maroto-Valer, 2010)

Amines are the most common absorbents. There are numerous different amine compounds available, such as 2-(butylamino)ethanol (BEA), *N*-methyldiethanolamine (MDEA) and 2-(2-aminoethyl-amino)ethanol (AEEA) (Ma'mun et al., 2007). Other absorbents, such as methanol and ammonia can also be used for CO₂ removal (Pellegrini et al., 2010)

Even though MEA is commonly used for carbon capturing, other amines could prove more efficient for SMR purposes. MEA is often chosen as an absorbent in other processes, because it functions in conditions where oxygen is present, which is not the case in SMR off gases. (Nyman, 2013)

Amine and similar washes will not, however, be discussed in more detail in this report, since the technology has been the subject of many master's thesis and other studies lately. (Merikoski, 2012), (Lampinen, 2012)

4.2 Adsorption

Adsorption is selective concentration of one or multiple components of a gas mixture to the surface of a microporous solid material. The solid material is called the adsorbent and the concentrated component or mixture is called the adsorbate. The forces holding the adsorbate at the surface are not as strong as chemical bonds and therefore the adsorbate can be desorbed (released) from the adsorbent by increasing the temperature or by decreasing the partial pressure of the adsorbed components in the gas phase. (Kohl & Nielsen, 1997)

If an adsorbed component reacts with the adsorbent, it's called chemisorption. Chemisorption is generally not reversible, which means that the adsorbent cannot be regenerated and therefore has to be disposed of and replaced when its adsorption capacity is used. (Kohl & Nielsen, 1997)

Regardless of the type of adsorption, a bed of adsorbent has a limited capacity to adsorb and at some point, the entire bed is exhausted. At this point, the entire stream passes through the bed and no separation takes place. This is presented in Figure 4. The movement of the mass transfer zone can also be seen in Figure 4. (Lenntech, 2012)

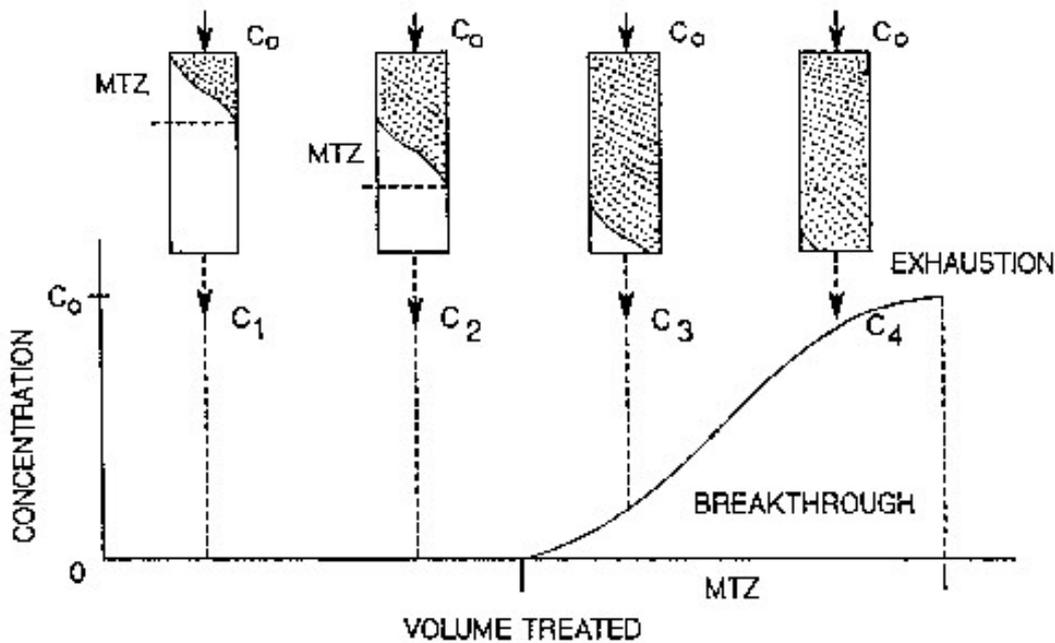


Figure 4 Exhaustion in adsorption beds (Lenntech, 2012)

Different adsorption methods are described below. All these methods are based on an adsorption-desorption cycles.

Separation systems using adsorbent cycles favour large capacities, since the investment cost for large vessels and valves are relatively cheaper than corresponding smaller equipment.

4.2.1 Pressure swing adsorption (PSA)

PSA is the most used adsorption technology in the process industry today. It is used e.g. in the hydrogen production to separate hydrogen from the off-gas. (Sircar & Golden, 2000)

In PSA the gas mixture is fed into a vessel containing adsorbent at a high pressure. One or more components are adsorbed to the surface of the adsorbent, either chemically or physically. When the adsorbent's capacity to adsorb has been used, the feed is diverted into another similar vessel, and the pressure in the first vessel is decreased, thus releasing the captured component or components. If two similar vessels are used, the gas leaving the first vessel can be used to pressurize the second vessel, thus saving costs. A schematic drawing of a PSA process for hydrogen purification is presented in Figure 5. It is to be noted, that PSA systems can be arranged in many different ways. (Sircar & Golden, 2000)

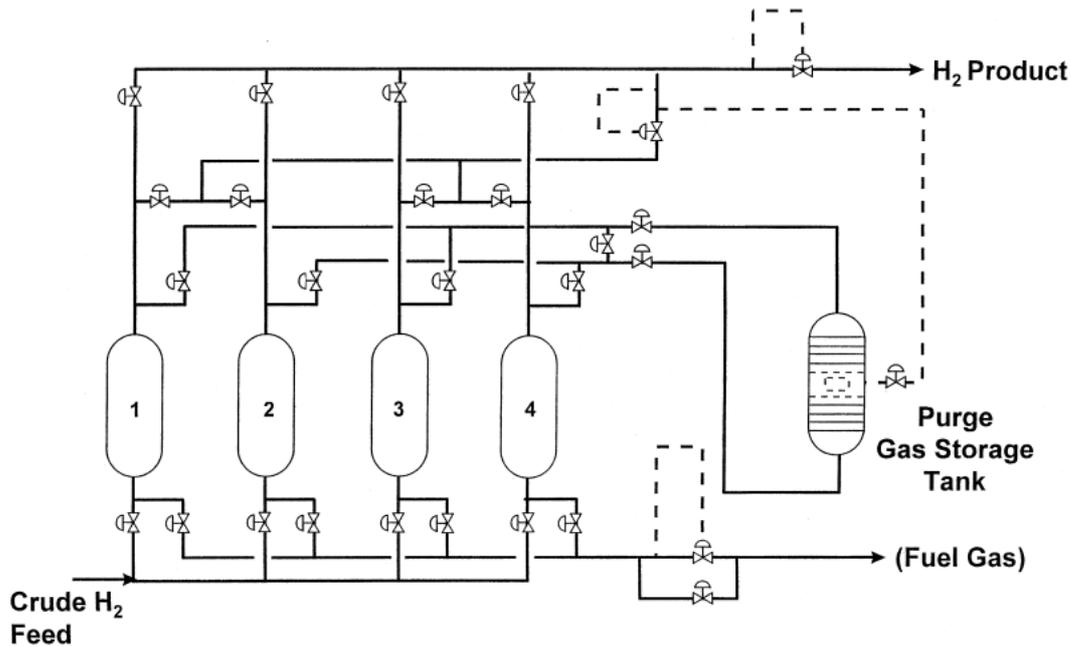


Figure 5 Schematic drawing of a PSA process for hydrogen purification (Sircar & Golden, 2000)

Typical adsorbents for PSA in general are activated carbon, silica gel, alumina and zeolite. Molecular sieves, such as zeolite and some types of activated carbons, utilize their molecular sieve characteristics and exclude some gas molecules based on the size of these molecules. This restricts the adsorption of larger molecules, which can be used to increase selectivity. (Sircar & Golden, 2000)

PSA can nowadays be considered as a common industrial practice. Several different process alternatives have been developed. Some of these, suitable for SMR carbon capture, are described below. (Sircar & Golden, 2000)

4.2.1.1. Gemini®

A specially designed PSA system, Gemini®, can produce two product streams from the steam methane reformer off gas (SMROG), the first being nearly pure hydrogen and the second nearly pure CO₂. The CO₂ stream in this system is in near ambient pressure. (Sircar & Golden, 2000)

The process was patented by Air Products and Chemicals of U.S.A in 1988 (Sircar & Kratz, 1988). The schematic drawing is presented in Figure 6. According to the patent, if the dry feed stream contains 75.4 % H₂, 19.9 % CO₂, 0.96 % CO and 3.73 % CH₄ at a pressure of 18.2 bar and temperature of 21 °C, then the hydrogen product stream purity will be 99.999 %, the hydrogen recovery rate 87.1 % and the pressure the same as feed pressure. The CO₂ stream purity would be 99.4 %, the recovery rate would be 94 % and the pressure would be near ambient pressure. The waste gas contains only 8.1 % CO₂, but a high concentration of hydrogen and methane, and would therefore be a good fuel gas for furnaces. (Sircar & Golden, 2000)

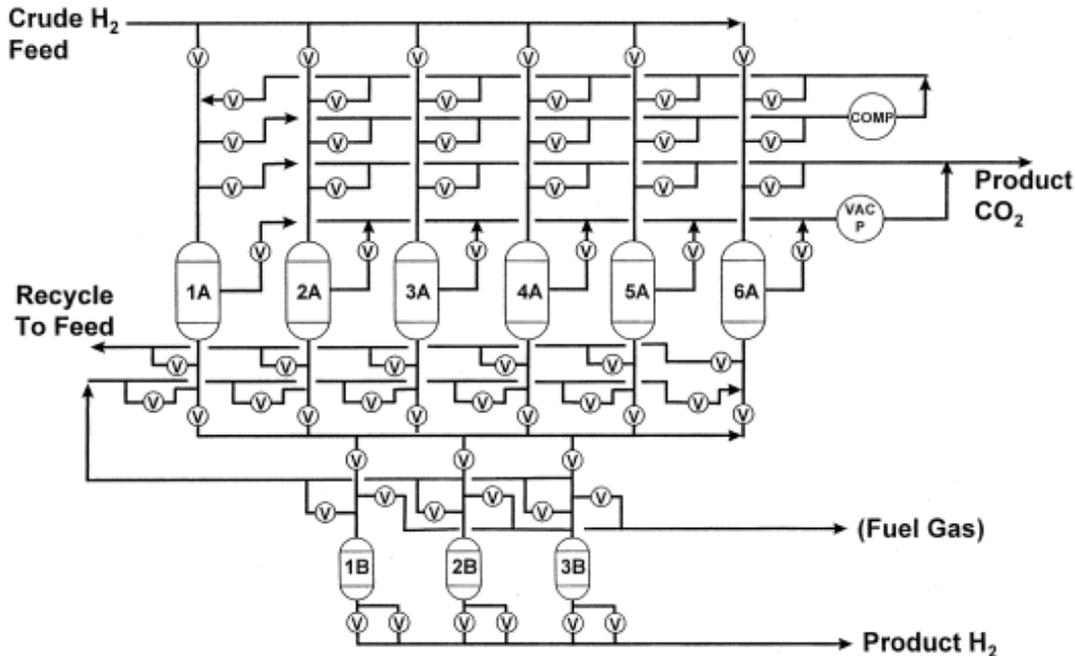


Figure 6 PSA system for simultaneous hydrogen and CO₂ production from SMROG

The system consists of six parallel absorbers (A beds) in series connection with three other parallel absorbers (B beds). The A beds have a six-step cycle and the B beds have a seven-step cycle. (Sircar & Golden, 2000)

The main steps for the A beds are: adsorption, cocurrent CO₂ rinse, countercurrent depressurization, countercurrent evacuation, countercurrent pressurization 1 and countercurrent pressurization 2. For the B beds the cycle contains the following steps: adsorption, countercurrent depressurizations 1, 2 and 3, countercurrent purge, cocurrent pressurization and countercurrent pressurization. (Sircar & Golden, 2000)

The packing in the A beds is activated carbon and it removes CO₂ and water from the SMROG. In B beds the packing is zeolite and it removes the remaining CO₂, CH₄, CO and N₂ from the hydrogen stream. Only a small quantity of CO₂ passes the A beds. (Sircar & Golden, 2000)

4.2.1.2. Duplex PSA

Traditional PSA units based on the Skarstrom cycle, involve four steps, including adsorption, pressurization, blowdown and purge. In the adsorption and purge steps mass transfer zones (MTZ) move from one end of the adsorbent bed to the other, which means that the unit has to be bulky in order to provide sufficient capacity. (Thakur et al., 2011)

In duplex PSA, the MTZ extends over the entire bed, thus making the unit less bulky and saving investment cost. According to Leavitt (U.S. 5,085,674), i.e. air can be fractionated so that both the nitrogen and oxygen products have purities over 99.5

mol-%. Other researches (Thakur et al., 2011) show, however, only purities of 95 mol-% O₂ and 97 mol-% N₂ from a feed containing 20 mol-% O₂ and 80 mol-% N₂.

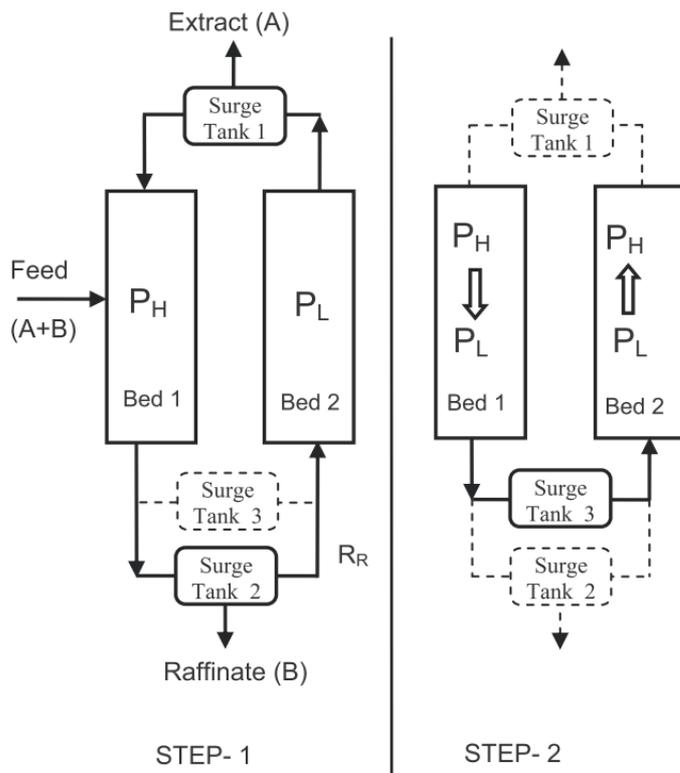


Figure 7 Duplex adsorption (Thakur et al., 2011)

4.2.2 Vacuum swing adsorption (VSA)

Vacuum swing adsorption (VSA) utilizes the same principle as PSA, but uses lower pressures. Where PSA uses high pressure gas for adsorption and above atmospheric pressure for desorption, VSA uses nearly atmospheric feeds for adsorption and even lower pressure for desorption. The desorption pressure is often sub-atmospheric, hence the name. (Kohl & Nielsen, 1997)

4.2.3 Temperature swing adsorption (TSA)

In temperature swing adsorption, the adsorbent is regenerated by increasing the temperature. Even a small increase in temperature can cause a considerable amount of adsorbate to desorb from the adsorbent. Increasing the temperature alone is not, however, used in commercial processes. Instead, a purge gas or steam is passed through the adsorbent bed. This sweeps out the desorbed components. TSA processes are used almost exclusively to treat feeds with low concentrations. (Kohl & Nielsen, 1997)

In order to make a TSA process operate continuously, adsorption beds or vessels can be arranged similarly to PSA, as shown in Figure 8. The process shown in the figure is used to dry natural gas, but the same principle applies to other applications as well. (Netušil & Ditzl, 2012)

4.3 Cryogenic carbon dioxide capture

Cryogenic CO₂ capture can be considered as one application of condensation, just in very low temperatures. In gas purification via condensation, the gas stream is cooled down, causing the component or components with a low vapour pressure to condensate. After this, the condensate can be collected while the rest of the mixture stays in the gaseous phase. In cryogenic carbon dioxide separation, CO₂ is condensed out at low temperature. (Kohl & Nielsen, 1997)

The cold temperatures can be achieved by two methods. One option is to use liquid nitrogen or other cold substances to cool down the stream containing CO₂. The other method, better suitable for industrial scale applications, is to first compress the gaseous stream and then decompress it, causing the temperature to drop. Carbon dioxide does not occur in liquid state at ambient pressure. The phase diagram of CO₂ is presented in Figure 10.

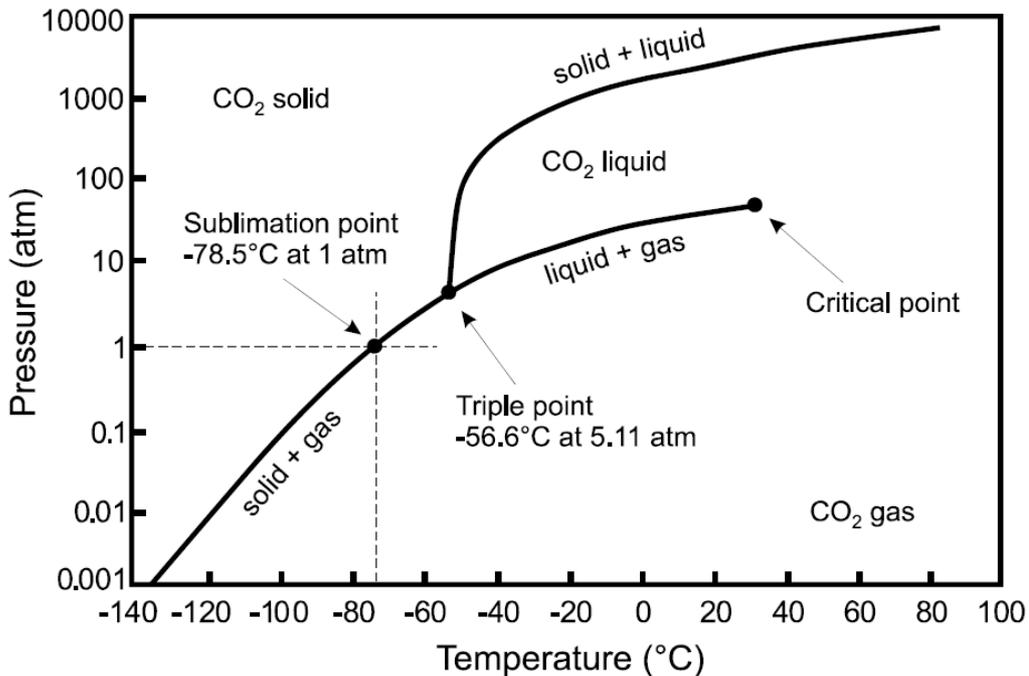


Figure 10 Temperature-pressure phase diagram of carbon dioxide (Shakhashiri, 2008)

Cryogenic CO₂ recovery is typically limited to streams that have a high CO₂ concentration of at least 50 vol-% and preferably over 90 vol-%. It is suitable for a limited amount of processes, one of the viable applications being hydrogen production and especially the PSA off gas stream. (Ebner & Ritter, 2009)

4.3.1 CO₂LDSep

Satish Reddy (Reddy & Vyas, 2009) presents a process called CO₂LDSep for capturing CO₂ from the tail gas (or off gas) of a PSA hydrogen purification unit, as shown in Figure 11. The process is patented by Fluor Enterprises Inc.

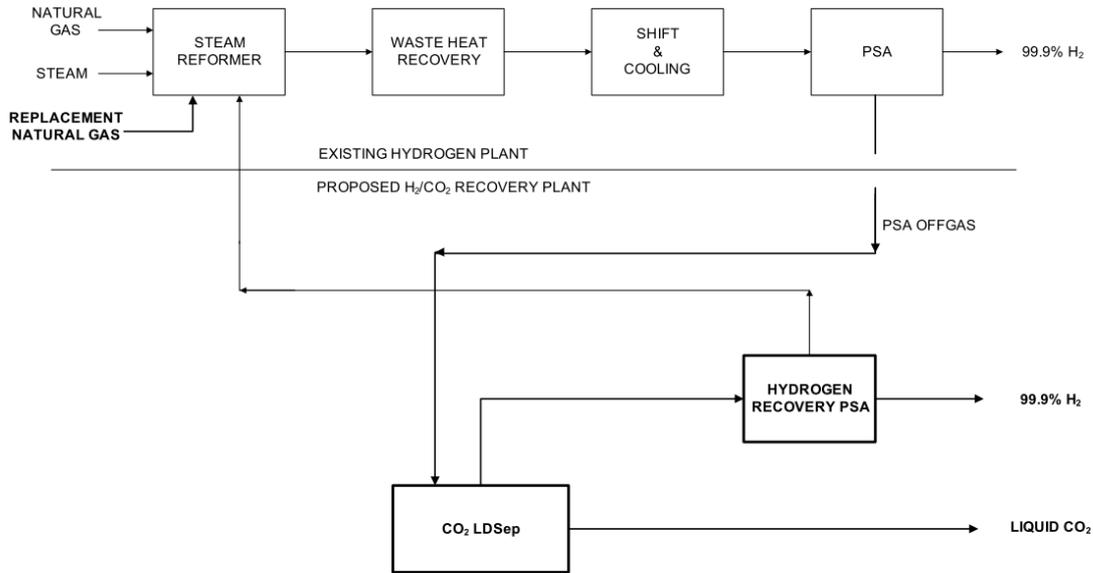


Figure 11 Block diagram of the CO₂LDSep setup (Reddy & Vyas, 2009)

The PSA unit off-gas is compressed, cooled, compressed again, cooled again and then expanded. According to Reddy (Reddy & Vyas, 2009), this can be achieved with one integrally geared compressor package. A part of the CO₂ can be removed through liquefaction due to the auto refrigeration when expanded. If the CO₂ recovery rate needs to be high, supplemental refrigeration may be used. If the purity of CO₂ product has to be food-grade, the liquid CO₂ can be purified in a reboiler stripper (99.99 wt-%). The process is presented in Figure 12.

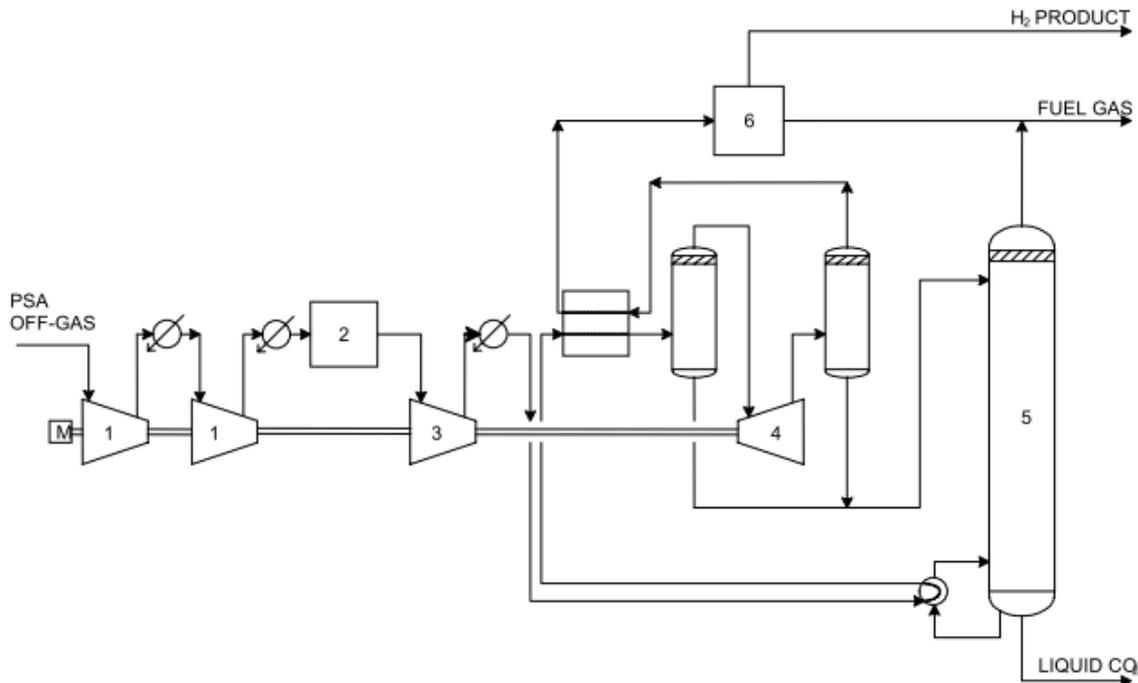


Figure 12 The CO₂LDSep process. The feed is compressed (1), dried, (2) and further compressed (3). The compressed stream is then cooled down with cooling water, in the stripper reboiler and in a cool box. The cool stream is then flashed, and a part of the carbon dioxide condensates. The gas stream is then routed to

an expander (4) where pressure is decreased further down. The expander is geared with the compressor in order to recover energy. The stream from the expander is once again flashed and the liquid product is combined with the previous liquid stream and routed to a stripper (5), where the product carbon dioxide is purified. The gas stream from the last flash is routed to a hydrogen recovery unit (6), where some extra hydrogen can be recovered. The rest of the gas stream and the stripper overhead can be used as fuel gas. (Reddy & Vyas, 2009)

4.3.2 FlashCO₂

The FlashCO₂ (patent pending) process is developed by Union Engineering (Union, 2011) and it utilizes a combination of chilled methanol absorption and liquefaction technology. It captures carbon dioxide from PSA off gas, as shown in Figure 13. The PSA off gas is compressed to approximately 30 bar and the cooled down to -50 °C by flashing the stream, thus condensing a portion of the carbon dioxide. The gas is then routed to a methanol absorption loop. The extracted carbon dioxide is combined with the one recovered via flash, and the product is furthermore purified via means not published. The product stream is food grade liquid carbon dioxide. Hydrogen can be recovered in a similar manner as in the CO₂LDSep process.

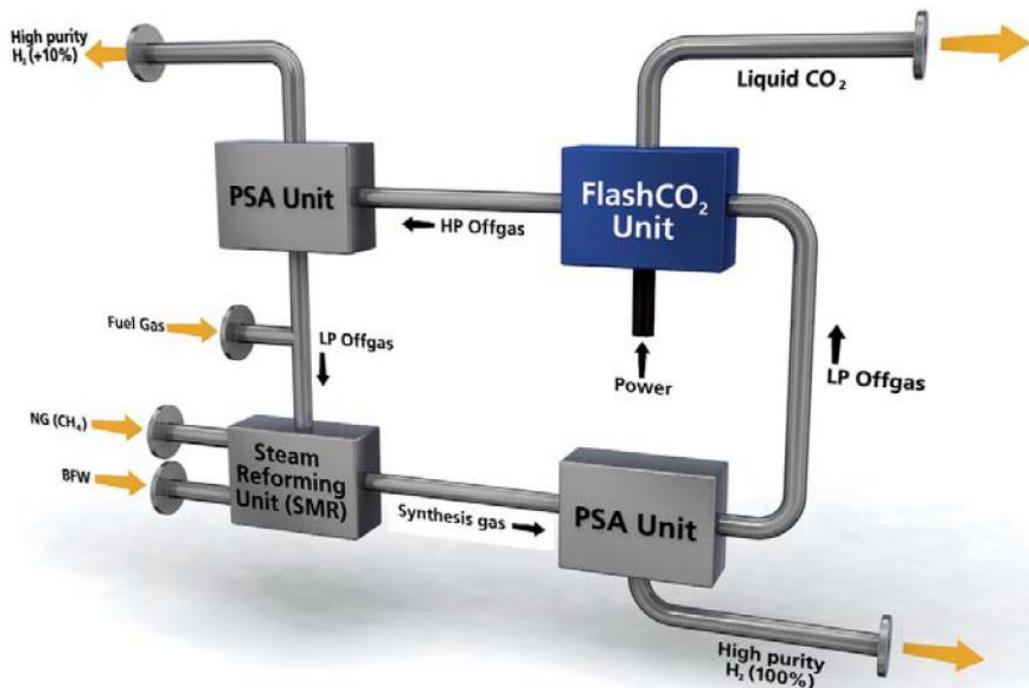


Figure 13 CO₂ capture from H₂ PSA off gas with a FlashCO₂ unit (Union, 2011). BFW stands for boiler feed water.

The FlashCO₂ process was not included in the screening of capture processes, since references to it were found only after the selection process had taken place. It was, however included in the comparison of different processes in chapter 0.

4.4 Membrane permeation

In membrane permeation, polymeric or inorganic membranes separate gases via selective permeation of one or multiple components of a mixture from one side of the membrane to the other. The components dissolve in the membrane surface and are transported through the membrane due to a concentration gradient, which is maintained by a difference in partial pressures of the component on different sides of the membrane. (Kohl & Nielsen, 1997)

The part of the mixture that passes through the membrane is called permeate and the rest is called retentate (Kohl & Nielsen, 1997). A conceptual scheme of a membrane module is shown in Figure 14. Sometimes the components enriched in the permeate stream are called fast components, and components enriched in the retentate side, slow components. (Echt, 2002)

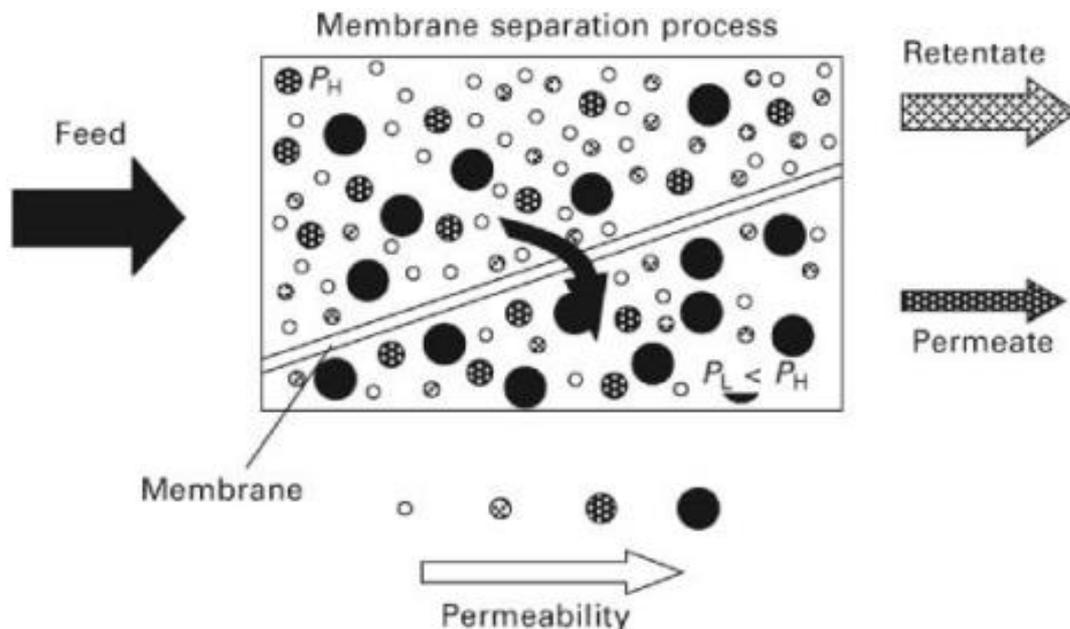


Figure 14 Conceptual scheme of a membrane module (Kohl & Nielsen, 1997)

The main membrane technologies include reverse osmosis and nano, ultra and microfiltration, pervaporation, gas separation, vapour permeation and electro dialysis. Gas separation is used in CO₂ capture. (Maroto-Valer, 2010)

Membranes can also be divided into two main types: porous and non-porous (or dense) membranes. In porous membranes, the separation is based on the molecular sizes of components in a mixture and the gas is separated through small pores in the membrane. Non-porous or asymmetric membranes separate mixtures based on solubility and diffusivity and are more often used in gas separations. (Kohl & Nielsen, 1997)

For both porous and non-porous membranes, there are six significant separation mechanisms: Knudsen diffusion, molecular sieving, surface diffusion, facilitated transport, capillary condensation and solution-diffusion separation. Of these, solution-diffusion occurs in CO₂ separation via polymeric membranes. Solution-diffusion results in a selective gas transport and hence separates the components in a gas mixture. Dense membranes are based on this mechanism. (Kohl & Nielsen, 1997)

Membranes are an attractive and energy efficient way to perform CO₂ capture. Membranes are used in bulk chemistry and the petrochemical industry. Membranes are small, simple to operate and service, compatible, diverse and they don't require any additional chemicals to be used. Membranes are best suited for streams with a high CO₂ content. (Echt, 2002)

Membranes have disadvantages as well. In order for the permeability to increase, the pressure difference over the membrane system has to be increased, which also leads to higher energy consumption. Polymeric membranes require that the feed gas temperature is not more than 100 °C, which usually means that the stream has to be cooled down which furthermore leads to energy loss. In addition, the separation efficiency is not as good as e.g. in absorption. Since the membranes have to withstand the chemical conditions of the process, some otherwise potential membranes cannot be used. (Kohl & Nielsen, 1997)

One problem with membranes is that membranes with a high selectivity have low permeability and vice versa. Besides this, polymeric membrane properties such as their thermal, chemical and plasticization resistances and ageing affects are very important. (Kohl & Nielsen, 1997)

Membranes often require some sort of pre-treatment for their feed. A coalescing filter removes solid particulate matter and liquid traces. A guard bed of activated carbon may be used to remove heavier hydrocarbons, such as lube oil. This bed is usually sacrificial and designed to work for six to twelve months. A particle filter after this bed is used to capture any fine particles or dust from the bed. Finally, a heater may be required to ensure that there is no condensation on the membrane surface. This could take place, because when the CO₂ concentration changes, also the dew point will change. Even though these pre-treatment stages increase the investment and operating costs, they also increase the reliability and element life time of the membranes. A configuration for the pre-treatment is shown in Figure 15. (Echt, 2002)

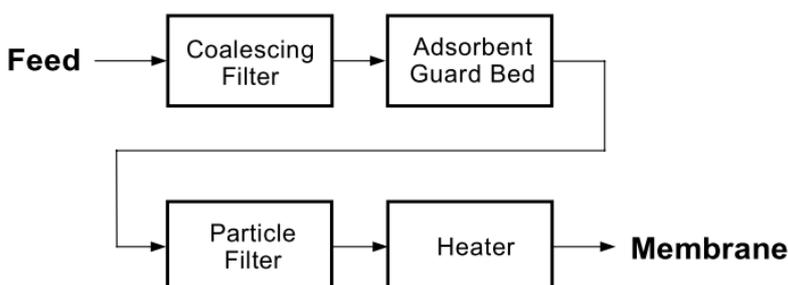


Figure 15 Common pre-treatment steps for the membrane process (Echt, 2002)

Since a part of the slow components end up in the permeate stream, a two-stage system can be used. In this configuration, the permeate stream from the first stage is compressed and fed to the second stage. From the second stage, a purer permeate can be collected, and the retentate is recycled. A flow scheme of the two-stage system is presented below in Figure 16. (Echt, 2002)

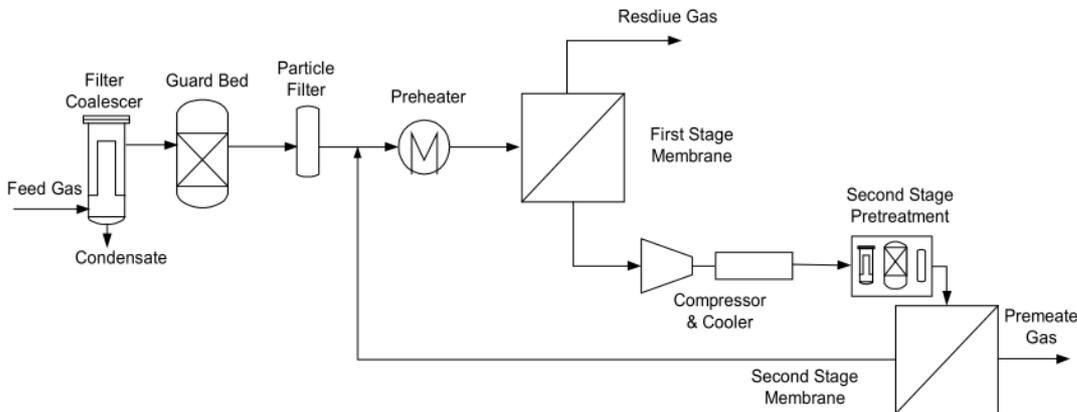


Figure 16 Two-stage membrane system flow scheme (Echt, 2002)

The investment cost of a two-stage system is considerably higher than the cost of a single-stage system, mostly due to the need for a compressor. The benefit comes from a higher recovery rate of slow components. (Echt, 2002)

One idea for making membrane separations a more viable process option is to combine it with some other separation technology, e.g. absorption. This way, the membrane system would be used to separate the bulk quantity and then absorption would be used to polish the remaining gas. This would enable a lower amount of absorbent to be used compared to an absorption system alone. The combined system would, however, mean a more complex separation system and thus make it more expensive and difficult to operate and service. (Echt, 2002)

Hybrid systems that contain a membrane stage and an amine stage are used for separating CO₂ and hydrocarbons (mainly methane) in the U.S. The main objective of these units is, however, to remove CO₂ from the product stream, while the purity of the CO₂ stream is only meaningful via the recovery rate of the product component. According to William Echt these hybrid units prove that membrane technologies can be considered a mature technology. (Echt, 2002)

Some pictures of different membrane types are presented below.

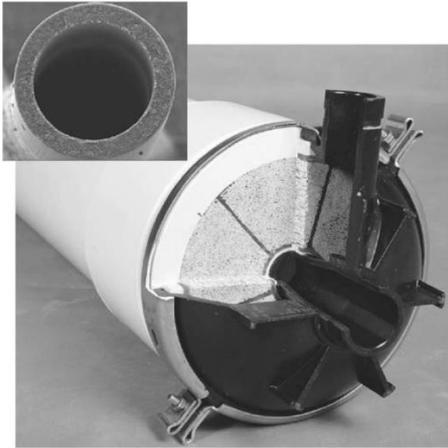


Figure 17 A capillary membrane module. Extruded or spun fibres with membrane on inside circumference (often also on outside). (Kohl & Nielsen, 1997)

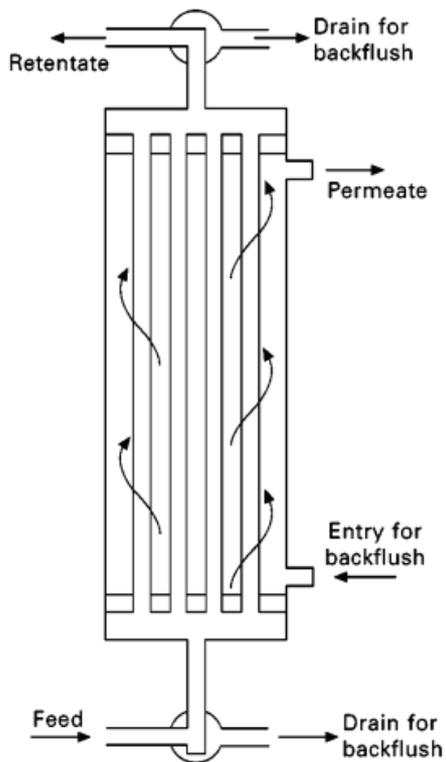


Figure 18 A hollow fibre module. Fine fibres with shell side feed. (Kohl & Nielsen, 1997)

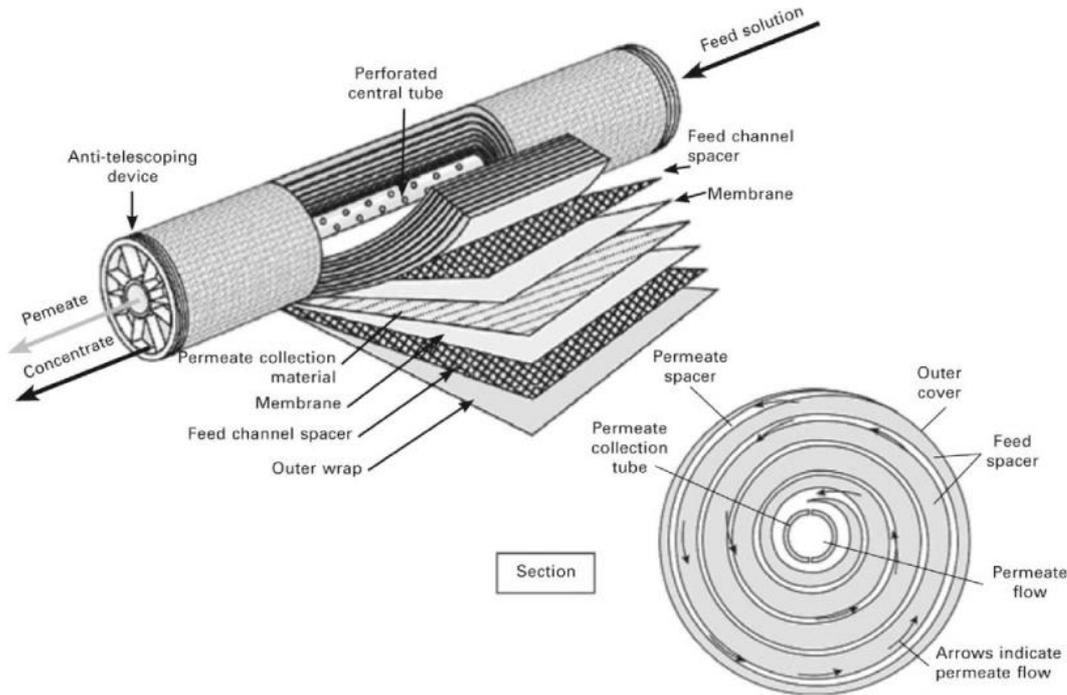


Figure 19 A spiral-wound module. Membrane and permeate channel are wound around a permeate pipe. (Kohl & Nielsen, 1997)

Some key figures concerning membrane economics and performance are shown in Table 1 and Table 2 and some general cost trends in Figure 20.

Table 1 Commercially available CO₂-separation membrane modules, their costs, control of concentration polarization and applications. (Kohl & Nielsen, 1997)

Membrane module	Cost	Characteristics	Packing density [m ² /m ³]	Control of concentration polarisation	Applications
Spiral wound	Low	Flat sheet	700–1000	Good	GS, UF, RO, PV
Capillary	Low	<i>i.d.</i> < 0.5 mm	500–4000	Very good	GS, UF, MF, PV, D, SLM
Hollow fibre	Very low	<i>i.d.</i> < 0.5 mm	4000–30 000	Very poor	GS, RO, PV, D

GS = CO₂ gas separation; MF = microfiltration; UF = ultrafiltration; RO = reverse osmosis; PV = pervaporation; D = dialysis; ED = electrodialysis; SLM = supported liquid membrane.

Table 2 Other parameters for membrane module design (Kohl & Nielsen, 1997)

Parameters	Hollow fine fibres	Capillary fibres	Spiral wound	Plate and frame	Tubular
Manufacturing cost (\$/m ²)	2–10	5–50	5–50	50–200	50–200
Permeate-side pressure drop	High	Moderate	Moderate	Low	Low
Suitability for high-pressure operation	Yes	No	Yes	Marginal	Marginal

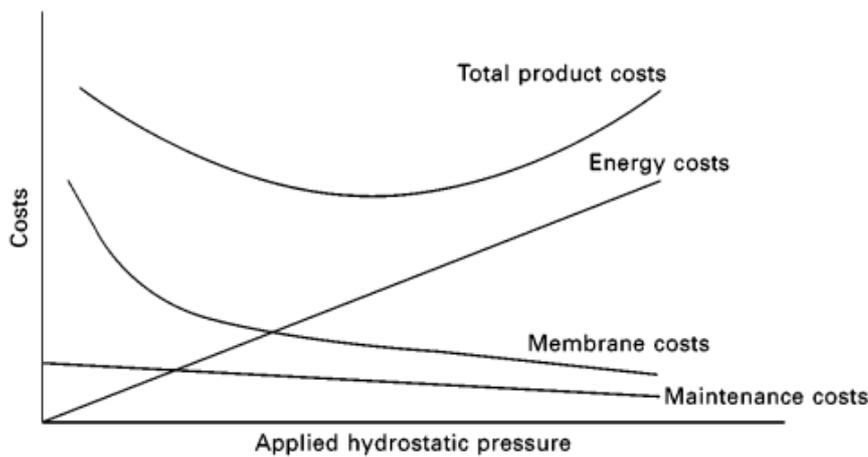


Figure 20 Membrane costs as a function of pressure. (Kohl & Nielsen, 1997)

4.4.1 Facilitated Transport Membranes

Facilitated transport membranes (FTM) have high selectivity and relatively high fluxes. The high selectivity is achieved through the existence of carriers within the membrane. These carriers selectively interact with specific molecules and facilitate their transport through the membrane. FTMs selective towards CO₂ can be used to remove CO₂ from streams with even small CO₂ concentrations. They can, however, be unstable due to the evaporation of the carrier medium (Ebner & Ritter, 2009).

4.4.2 Hollow Fibre Gas-Liquid Contactors

Hollow fibre contactors may be used as an alternative to absorption columns. The concept offers greater contact areas per volume than packed beds in absorption columns. The process has a non-selective membrane, which only acts as a physical barrier between the gas and the liquid phases. The gas stream passes through the membrane and gets in contact with the absorbent. This process offers a larger volumetric mass transfer coefficient compared to packed absorbent beds and a fixed contacting area regardless of altering process conditions, which makes scaling of the process simpler and can also lead to investment and operational cost savings. Unlike

selective membranes, the hollow fibre membrane contactors are not significantly affected by plasticization. (Ebner & Ritter, 2009)

However, if the membranes' pores are wetted or blocked, they lose their efficiency. Absorbents, such as MEA, tend to react with the CO₂ and form precipitates, which cause pore clogging and fouling. (Ebner & Ritter, 2009)

Hollow fibre contactors have high inherent selectivity and relatively large flows and they present a viable option especially for processes such as reforming and gas sweetening. Large scale units have been developed, but the technology has not been commercially successful. (Ebner & Ritter, 2009)

4.4.3 Selective Surface Flow membranes

Selective surface flow (SSF) membranes are nanoporous carbon membranes that separate gas mixtures by a selective adsorption - surface diffusion - desorption mechanism. It permeates the larger and more polar components. The concept is presented in Figure 21. The product stream in this process is usually the retentate-side product, since it can be collected in near feed pressure. In separation of a mixture containing H₂, CO₂ and CH₄, hydrogen is on the retentate side, and therefore SSF can be applied to increase hydrogen recovery rates as hybrid PSA-SSF units, as shown in Figure 22. The use of SSF alongside the PSA may increase the recovery rate of hydrogen to 88.2 % while PSA alone would yield only 75 %. (Sircar et al., 1999)

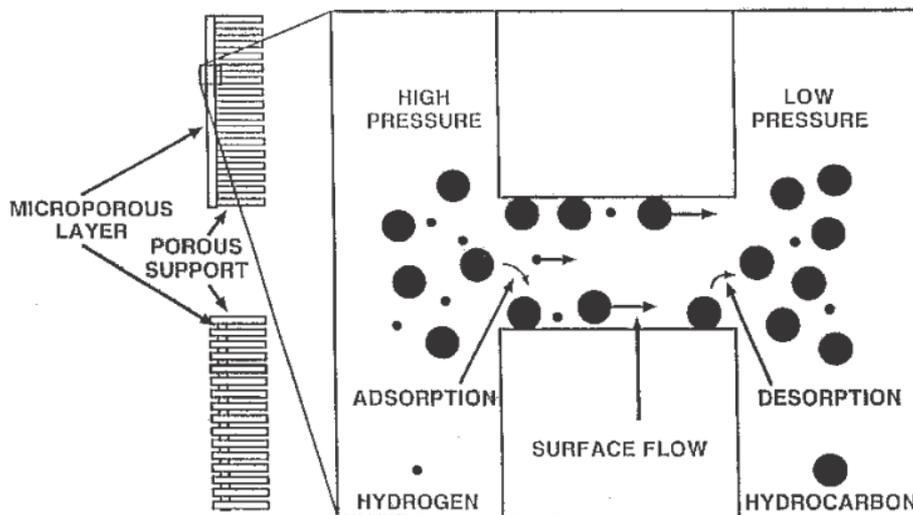


Figure 21 A concept of gas transport mechanism by SSF membrane. The pore size is 0.5-0.7 nm; hydrocarbon diameter is ~0.4-0.5 nm and hydrogen diameter 0.3 nm. (Sircar et al., 1999)

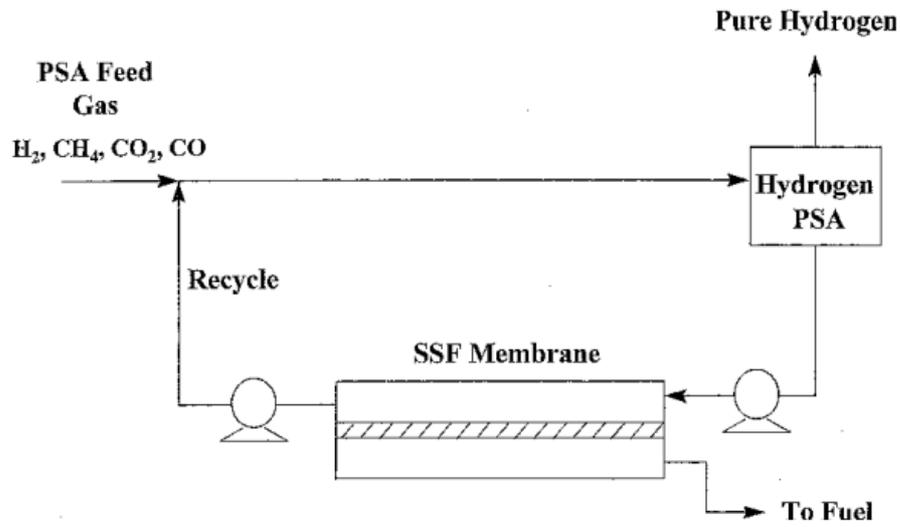


Figure 22 A schematic drawing of a hybrid PSA-SSF process (Sircar et al., 1999)



5 Requirements and methods for transportation and storage of CO₂

As briefly explained earlier, CCS consists of three parts: capture, transportation and storage. In this report, only the capture part is studied. The basics of the other parts are, however, shortly covered here. The financial value of carbon dioxide is also briefly discussed.

5.1 Transportation, storage and utilization

Capacities of feasible carbon capture plants are typically high, which leads to the need for high capacity in transportation as well. Therefore transportation is typically done by pipeline or by ship. The best transportation method depends on the capacity of the CO₂ capture plant, the product phase, purity specifications and distance between the capture plant and the storing or utilization area. Each transportation method requires different product properties, as will be explained in chapter 5.2. (Teir et al., 2010)

For CCS to be meaningful, the carbon dioxide has to be stored or utilized in such a manner, that it won't be released to the atmosphere. CO₂ can be stored in geological formations, in oceans and as mineral carbonates. Storage is typically the trickiest part of CCS in terms of permits and public appearances. (Lampinen, 2012)

Geological storage is the most studied storage method today. Potential formations include deep saline aquifers, depleted oil and gas fields and unexploited deep coal seams. (Allewi et al., 2011)

Enhanced oil (EOR) and gas (EGR) recoveries utilize and store CO₂ at the same time. CO₂ is injected in nearly depleted oil or gas reservoirs to push out the remaining oil or gas, while the majority of the CO₂ will stay in the reservoir. A part of the CO₂ ends up in the gas or oil product. (Rackley, 2010)

CO₂ can react with a variety of minerals, forming mineral carbonates and thus permanently storing the CO₂. The technology for this method is still somewhat experimental. CO₂ can also be stored in oceans via biological, chemical or physical methods. Biological sequestration is basically ocean fertilization, such as algae farming and is commonly considered not suitable for large scale applications. Chemical sequestration in oceans mainly refers to mineral carbonation of oceanic rocks and is also not considered a viable option. Physical sequestration methods include CO₂ dissolution in water and liquid CO₂ isolation. (Rackley, 2010)

Apart from simply storing the captured carbon dioxide, it can also be utilized. In supercritical state, CO₂ can be used as a solvent. Since carbon dioxide is relatively inert, non-toxic and non-volatile, it is an attractive alternative compared with organic solvents. CO₂ is also used in the food industry as a shielding gas and in beverage

industry to acidify drinks. Utilization of CO₂ is discussed in the doctoral dissertation of Turunen. (Turunen, 2011)

5.2 Product purity requirements

EU directive 2009/31/EC (European Parliament and Council 2009) sets some guidelines concerning the transportation and storage of CO₂, but there are no official limits as to purity levels of the captured CO₂ product. Instead, operators have set their own specifications. (Lampinen, 2012)

Isa Lampinen has covered these guidelines and operator specifications in her Master's Thesis (Lampinen, 2012) and the most important figures are presented below, in Table 3.

Table 3 Carbon dioxide purity guidelines for different applications and transport methods.

		Food grade	"Quality guideline"	Pipeline guideline	Ship guideline	Storage	EOR *
Carbon dioxide	CO ₂	>99,9	>95,5-99,5 %	>95,5 %	>99,5 %	>95,5 %	>95,5 %
Water	H ₂ O	40 ppm	< 20-500 ppm	500 ppm	50 ppm	-	< 20 ppm
Non-condensables	N ₂		<300 ppm (EOR) - 4% (all volatiles)	< 4 % (all volatiles)	< 0.2-0.5 % (all volatiles)	< 4 % (all volatiles)	< 300-4800 ppm
	O ₂	100 ppm	< 100 ppm (EOR) - 4 % (all volatiles)				< 100 - 1000 ppm
	Ar		< 0.2-4 % (all volatiles)				-
	H ₂		< 0.2-4 % (all volatiles)				-
	CH ₄		< 0.2-4 % (all volatiles)				< 2 %
Noxious compounds	H ₂ S		< 200 - 9000 ppm	200 ppm	200 ppm	-	< 1500 - 9000 ppm
	CO	10 ppm	< 10 - 2000 ppm	2000 ppm	2000 ppm	-	< 10 - 1000 ppm
Nitrogen and sulphur oxides	NO _x		< 50 - 100 ppm	100 ppm	100 ppm	-	50 ppm
	SO ₂		< 10 - 100 ppm	100 ppm	100 ppm	-	< 10 ppm
	oil	100 mg/m ³					

* EOR = Enhanced oil recovery

In addition to the purity guidelines, other product properties, such as phase, temperature and pressure are important as well. Liquid CO₂ is cheaper to transport than gaseous CO₂, since the density is much higher and since pumping is much cheaper than compressing.

5.3 Economic value of carbon dioxide

The economic value of capture CO₂ arrives from emission allowance trading. In most parts of Europe, including Finland, companies buy allowances from auctions in the European Energy Exchange (EEX) market, located in Leipzig, Germany. At the end of January 2013 allowances were sold at 3.9 €/t CO₂ (Helsingin sanomat, 2013). The development of CO₂ emission allowance cost between 2006 and 2012 is shown in Figure 23. (European Energy Exchange, 2013)

Price



Volume

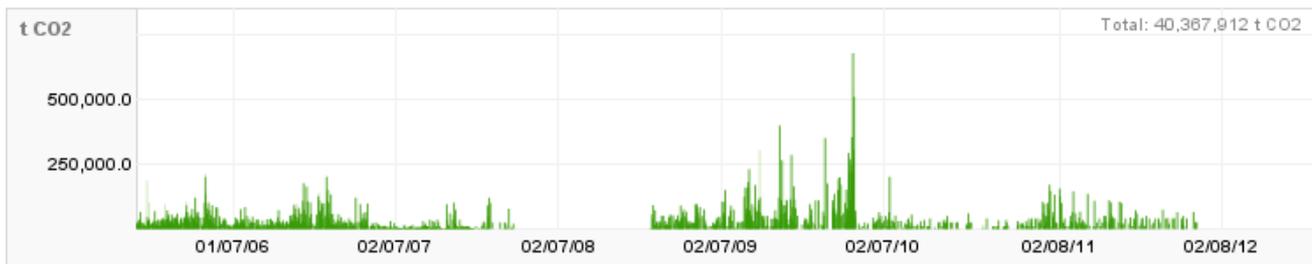


Figure 23 Carbon dioxide emission allowance prices in the EEX market.

The pressure to slow down the greenhouse effect may drive the allowance cost up in the future. Some estimates predict that the cost can be as high as 100 € / tCO₂ in the future. (co2prices.eu)



6 Criteria for selection of CO₂ capture process for SMR

In this report, two carbon capture options for a hydrogen production unit will be studied and their costs will be compared. The selection of these two options will be done by compiling a selection matrix, in which different characters of each technology are presented and compared by both qualitative and quantitative measures.

Several aspects are considered in the selection process. These include the economic aspects, maturity of the technology, capacity and separation efficiency issues and process conditions.

The economy of each process can be assessed by its production costs, which includes the investment and operating costs. These are rated on a high/moderate/low scale.

A technology with higher maturity can be considered as a more secure choice, since previous experience from a full-size unit provides useful information for new cases. Using completely new technology often leads to more start-up problems etc.

Different technologies are suitable for different capacity zones. Technologies that require many types of equipment usually get relatively cheaper at higher capacities since smaller equipment is relatively more expensive than a bigger version. In modular units, where there is lots of equipment in parallel, the price is not as capacity-dependent as in other types of units, since the price of one module does not vary as much. It should also be noted that the capacity can be adjusted more easily in modular units by simply adding more modules, whereas capacity in non-modular units is rather fixed once built. For the selection process, it is important that the technology can achieve a relevant capacity level at a reasonable price.

Challenging process conditions, such as high or very low temperatures or pressures, result in more expensive materials. Also high alkalinity or acidity and many other factors may cause the same result. It should also be noted that if process conditions, especially temperature or pressure, vary a lot between the conditions of upstream and downstream units, it means energy has to be used to achieve the appropriate conditions.

Applicability of some carbon capture technologies to different CO₂ concentrations and desired product purities are shown in Figure 24.

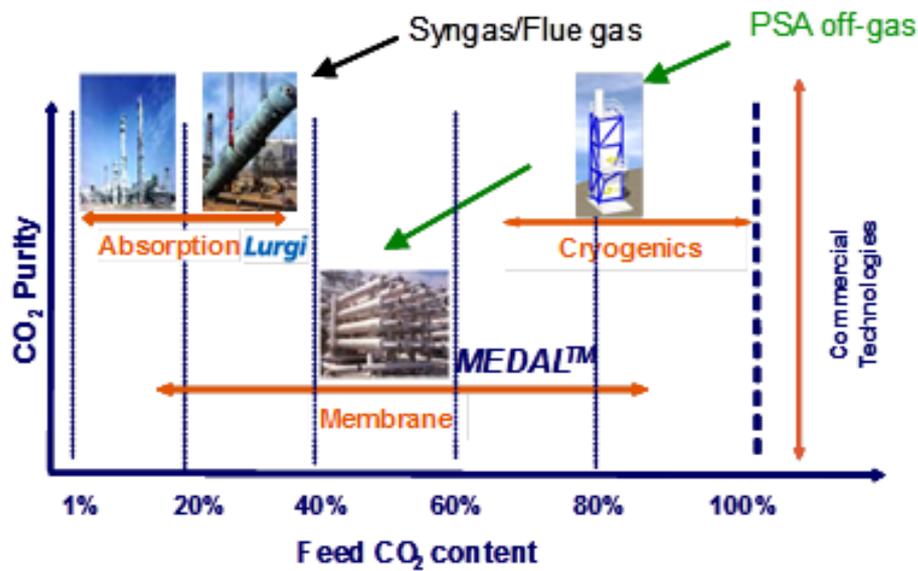


Figure 24 Applicability of membrane, absorption and cryogenic separation methods in different feed and product purities. (Chaubey et al., 2010)

As a result of the screening process in this report, a comparison of currently available process alternatives for carbon dioxide capture was compiled. The comparison is presented in Table 4.

Table 4 Comparison of the main process alternatives for CO₂ capture.

Process	Amine absorption		Gemini®	Duplex PSA	CO ₂ LDSep	FTM		Hollow fiber contactors	
	Based on	Selection criteria				Membrane	Membrane / absorption		
Maturity of Technology	Widely used	Commercially available	Commercially available	Mainly research level	Commercially available	Widely known for stability problems	Large scale units have been developed, but not commercially successful		
Capacity	High	High	High	High	High	Moderate	High		
Preferable CO₂ feed concentration	< 40 vol-%	> 50 vol-%	> 50 vol-%		PSA offgas (>50 %)	low	low		low
Tolerance for feed impurities	Depends on the selected amine	Applicable for PSA off gas stream	Applicable for PSA off gas stream	Moderate	Moderate. Certain compounds may affect the condensation	Low to moderate	Low to moderate		Low to moderate
Preferable feed pressure		PSA off gas pressure	PSA off gas pressure	Higher pressure preferable	Higher pressure preferable	Higher pressure preferable	Higher pressure preferable		Higher pressure preferable
CO₂ product phase and pressure level	Gas, Ambient pressure	Gas, Ambient pressure	Gas, Ambient pressure	Gas, Ambient pressure	Liquid, > 5 bar	Gas, Ambient pressure	Gas, Ambient pressure		Gas, Ambient pressure
CO₂ product purity	High	up to 99.4 %	up to 99.4 %	High	up to 99.99 %	Low	Moderate		Moderate
Process Conditions	Moderate temperatures and pressure levels	Moderate temperatures and pressure levels	Moderate temperatures and pressure levels	Moderate temperatures and pressure levels	Extremely cold temperatures (-100 °C), high pressure levels	Moderate temperatures and pressure levels	Moderate temperatures and pressure levels		Moderate temperatures and pressure levels
Investment Cost	Low to moderate	Moderate to high (rotating equipment, several vessels)	Moderate to high (rotating equipment, several vessels)	Low to moderate (unit size is smaller than traditional PSA)	High	Moderate to high	Moderate		Moderate
Operating cost	High (depends greatly on waste heat availability)	Moderate	Moderate	Moderate	Low to moderate	Low	High (absorbent regeneration needed)		High (absorbent regeneration needed)
Complexity	Low	High	High	Moderate	Low to moderate	Low	Low		Low
Integrability to existing hydrogen plant	Good	Very poor, if hydrogen purification already exists	Very poor, if hydrogen purification already exists	Moderate	Good	Moderate	Moderate		Moderate
Miscellaneous		Is not applicable for retrofitting existing setups.	Is not applicable for retrofitting existing setups.			To avoid stability issues, adding water to the feed may be needed	MEA may react with CO ₂ causing blockages		



FEASIBILITY STUDY

7 Auspicious carbon capture processes for steam reformers

7.1 Selection

In this report the scope was to retrofit an existing hydrogen plant with a carbon capture unit. It is assumed, that the furnace uses air combustion and that oxy-fuel systems cannot be implemented in the retrofitting. It was decided, that two cases would be further studied in this report.

Since the guidelines for shipping carbon dioxide dictates that the CO₂ purity must be over 99.5 vol-%, all membrane based technologies were ruled out. At the moment, single stage membranes can't achieve product purities this high. Furthermore, the main advantage of membrane systems is the low carbon dioxide concentration in the inlet and since especially the PSA off gas stream is rich in CO₂, this advantage is irrelevant.

The Gemini® process is best suited for green field cases. Existing hydrogen plants typically already have a hydrogen purification system, and therefore retrofitting a hydrogen plant with Gemini®, which means that the hydrogen purification system would have to be removed. Furthermore, if any disturbances in the separation occur, the entire hydrogen production is affected. The concept was therefore ruled out for any retrofitting cases. PSA, VSA and TSA systems were deemed to be too vulnerable for failures due to their rather high complexity and number of valves needed. The Duplex technology offers no real advantages over traditional PSA systems except that investment costs are lower than in traditional PSA systems. ESA systems were deemed to be too immature.

The hollow fibre contactor technology offers some advantageous features, but the technology is yet immature. Additionally, the technology is basically an absorption process and the scope of this report was to study technologies apart from absorption.

The CO₂LDSep process along with other cryogenic processes, were deemed to be potentially suitable for hydrogen plant carbon capture, since they are able to produce liquid CO₂ product streams with purities required for CO₂ ship transport. The process is relatively simple and no additive chemicals are needed. Cryogenic processes are best suited for streams with high CO₂ concentration, such as the PSA off gas stream in SMR hydrogen plants. Therefore, a cryogenic process was selected for both cases.

7.2 Case descriptions

For further studies in this report, two cases were studied. In both cases, the capture is based on cryogenic separation, but from different CO₂ sources. The first case uses



the off gas stream from a hydrogen PSA unit. The second case uses the flue gas stream from the SMR furnace.

The feed stream compositions for both cases are based on values from the thesis of Cynthia Tarun (Tarun, 2006). The same stream compositions were used in this report, but mass flow in the PSA off gas case was raised to 95 t / h. The compositions are presented in Table 5.

Table 5 Feed compositions (Tarun, 2006)

Case	PSA off gas		Flue gas	
Mass flow (t / h)	95		147.8	
Temperature (°C)	25		167	
Pressure (bar)	1		1	
Composition	mole fraction	mass fraction	mole fraction	mass fraction
CO ₂	0.51	0.808	0.164	0.248
CO	0.008	0.008	0.001	0.001
CH ₄	0.266	0.153	-	-
H ₂	0.198	0.014	-	-
H ₂ O	0.004	0.003	0.168	0.104
N ₂	0.014	0.014	0.644	0.622
O ₂	-	-	0.022	0.025

It should be noted, that when air combustion furnace processes are used, the flue gas case feed stream should also contain argon, but no argon was present in the studied stream.

The product in both cases is a > 99.5 mol-% liquid CO₂ stream, which can be pumped and transported by ship to the storage site. The two cases differ in some aspects, as will be explained.

A block diagram of case 1 (PSA off gas) is shown in Figure 25.

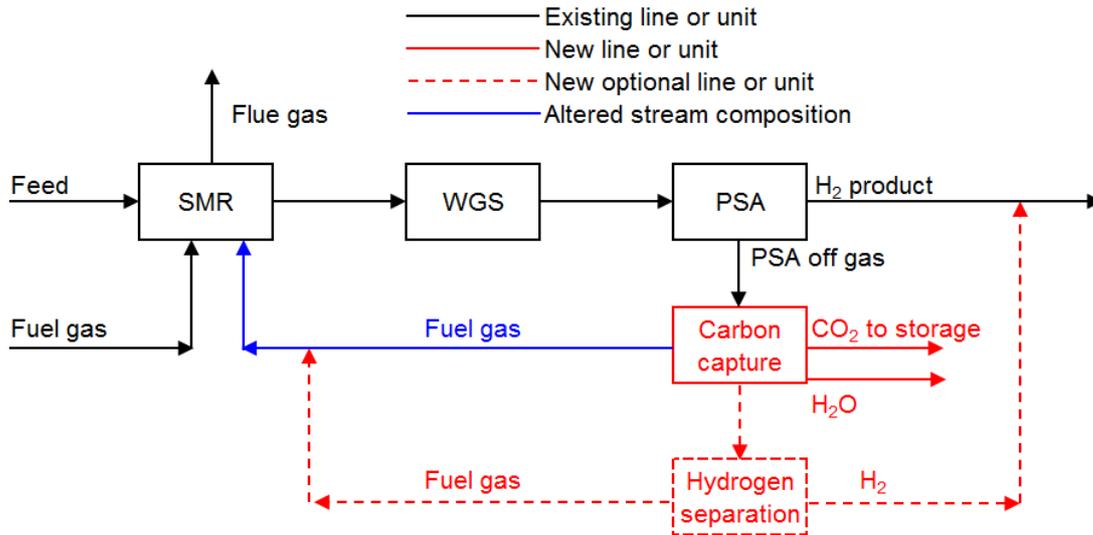


Figure 25 Block diagram of SMR hydrogen plant with carbon capture from PSA off gas stream (case 1).

The feed stream in the PSA off gas case comes from a hydrogen separation PSA unit at ambient pressure and a temperature of 25 °C. The studied stream contains 51 mol-% of CO₂ and the total mass flow is 95 t / h. The feed composition is presented in Table 5 above.

In Figure 25, an optional H₂ separation module is shown with a dotted line. This module could be added to the carbon capture block to enhance the plant's overall hydrogen recovery rate.

A more detailed process diagram of the PSA off gas case is shown in Figure 26. The process in case 1 consists of a four stage compressor, eight heat exchangers, a decompression valve, three flash vessels and a stripper. The overhead from the stripper has to be cooled down to roughly -100 °C for the separation to work properly. This can only be achieved by using a refrigeration unit, which uses a lot of energy. The cold overhead product stream can, however, be used to cool down the expander feed stream.

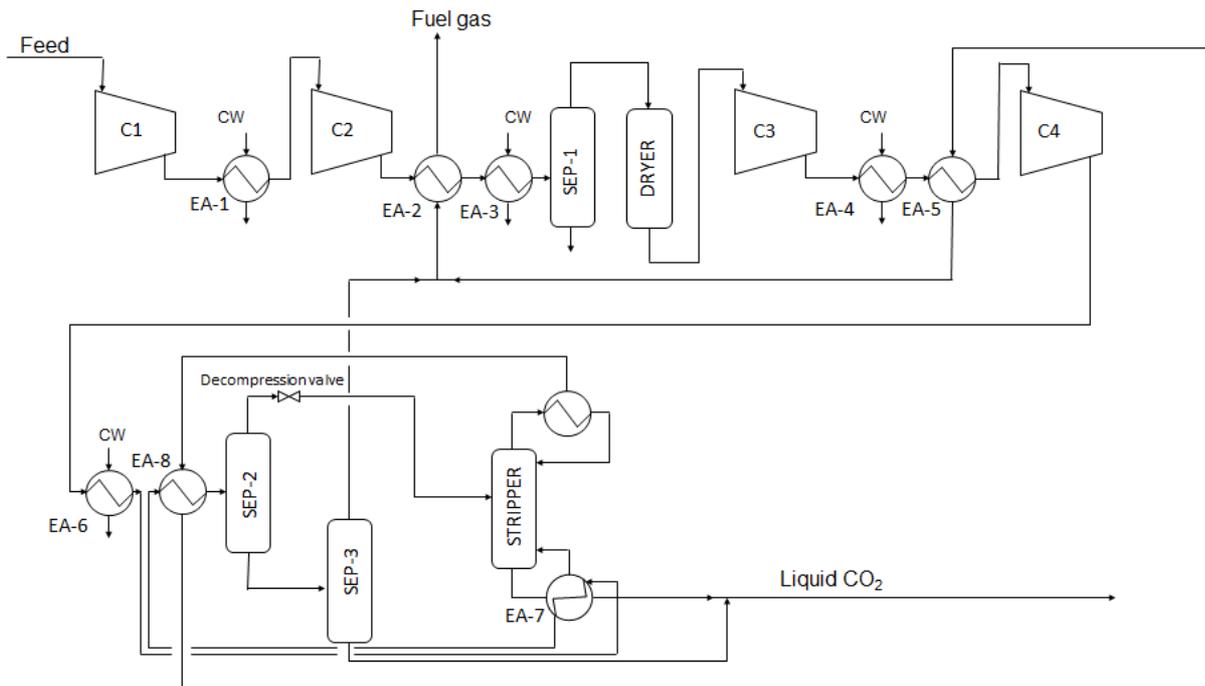


Figure 26 The PSA off gas case. C1, C2, C3 and C4 are different stages of the compressor.

The stripper overhead stream contains hydrogen, which could be separated using a hydrogen separation system, e.g. a PSA unit, and by compressing the product. However, the profitability of the hydrogen separation with current electricity and hydrogen prices is negative and therefore further economical calculations were made without the hydrogen separation. If 75 % of the hydrogen in the stripper overhead stream is recovered, the operating cost for the whole process rises 0.07 €/tCO₂, not taking into account the investment cost.

Typical SMR hydrogen plant furnaces can utilize PSA off gas as fuel gas. If the process in the PSA off gas case malfunctions, the carbon capture process can be bypassed and the off gas can be routed straight to the furnace to be burned, and therefore no redundancy systems are required. The hydrogen production is not allowed to be disturbed by the capture process. However, since the PSA off gas temperature is over 100 °C lower than furnace fuel gas feed temperature, and since CO₂ reduces the average caloric value of the gas; a change in fuel gas feed can cause fluctuations in the SMR temperature. The effect can be reduced by preheating the off gas before feeding it to the furnace.

A block diagram of case 2 (the flue gas case) is shown in Figure 27. The feed stream in the flue gas case comes from the hydrogen plant furnace at ambient pressure and a temperature of 167 °C. The studied stream contains 16.8 mol-% of CO₂ and the total mass flow is 147.8 t / h. The composition is presented in Table 5 above.

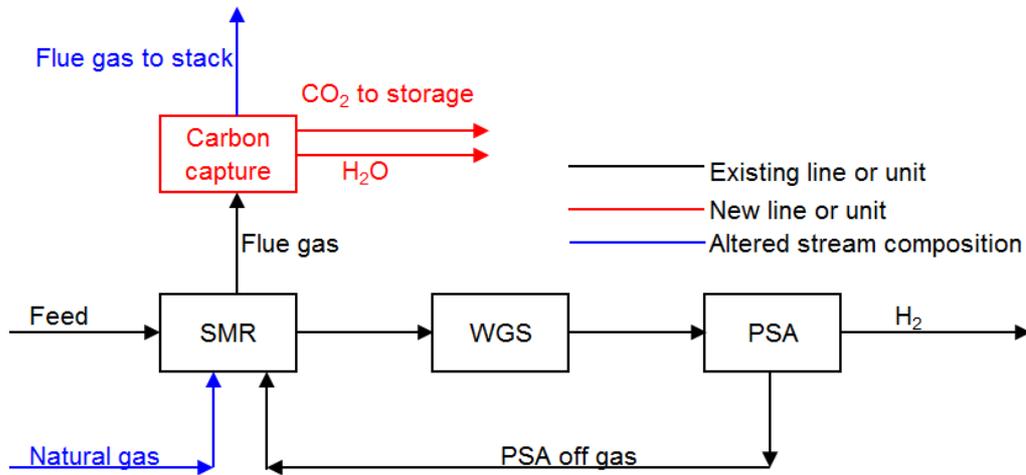


Figure 27 Block diagram of SMR hydrogen plant with carbon capture from flue gas stream. The furnace shall use natural gas as fuel, so that no sulphur removal units are needed.

The process concept in the flue gas case is similar to the PSA off gas case. The main differences are the pre-cooler before the first compressor stage, water condensers between each compressor stage and the lack of flash condenser vessel before the expander. Furthermore, there is no hydrogen in the feed stream, so no hydrogen recovery module is applicable.

Since the flue gas case is an end of pipe solution, it can be bypassed easily by simply routing the entire flue gas stream to the stack. The capture process in case 2 is presented in Figure 28.

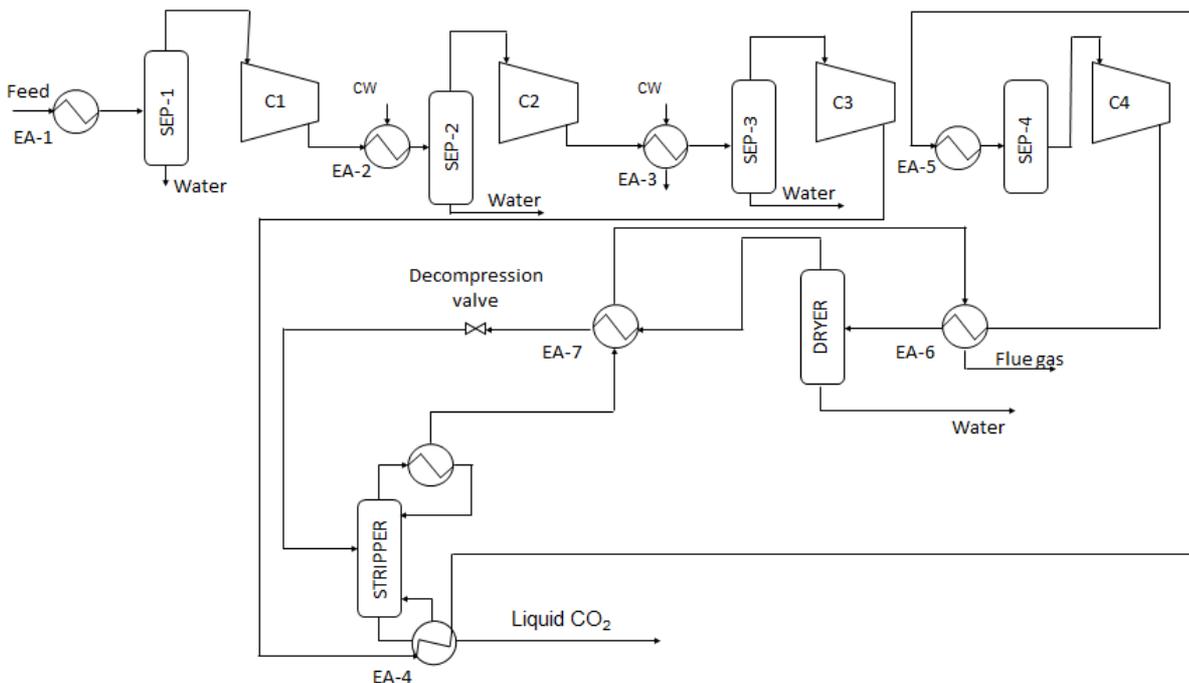


Figure 28 Case 2 (flue gas). Sep-1, Sep-2, Sep-3 and Sep-4 are all for water removal, as well as the dryer.



The economic potential of the flue gas case suffers from the high amount of nitrogen (64.4 mol-%) in the feed caused by the air combustion furnace. Since the entire amount of nitrogen has to be compressed together with the carbon dioxide, the energy consumption per CO₂ product ton rises significantly. The amount of nitrogen could be avoided by using an oxy-fuel process, where pure oxygen is used in the furnace instead of air, which leads to significantly smaller amounts of nitrogen in the flue gas stream. This would make carbon capture more feasible. In this study, however, no oxy-fuel cases were studied. It should also be noted, that the studied stream did not contain any argon, which would be present in a real-life air combustion process. The presence of argon would furthermore worsen the economics of the process, since more stages and condensing power would be required in the stripper for the separation of argon and carbon dioxide to be sufficient enough to meet the specification limit.

The operating cost in the flue gas case was calculated to be 84.6 € / t. See chapter 0 for detailed calculations. Due to high operating costs, the flue gas case was not studied any further. Investment costs were not calculated and no sensitivity analyses were made.

7.3 Methods

Both cases were simulated using Aspen Plus 7.3 software. The Soave modification of Redlich-Kwong equation of state (SRK) with Neste Jacobs Oy in-house binary interaction parameters was used for the process stream as the property method in both cases. For cooling water, normal steam table property methods were used.

Electricity and 30 °C cooling water were assumed to be available. The cooling water was allowed to be heated to 35 °C. No heating media was needed for the process.

For the compressor simulation, an isentropic model with ASME (American Society of Mechanical Engineers) method and an isentropic efficiency of 0.72 were used. Isentropic compression means that the entropy of the compression system is constant. The isentropic efficiency describes the ratio of work input of an ideal isentropic process to the work input of the actual process with same inlet and outlet pressures. ASME covers a large variety of compression related standards common in the industry.

The feed temperature for each stage was cooled down so that outlet temperatures did not exceed 160 °C in the PSA off gas case or 180 °C in the flue gas case. The lower design temperature in the first case was due to hydrogen in the stream. A pressure ratio of three was used for each stage of the compressor in both cases.

The process stream must be dried in order to avoid freezing after the expander. In the flue gas case, there is a significant amount of water in the feed, but majority of it can be separated by using flash condensing vessels between compressor stages. To further remove water from the stream, a dryer is used. The dryer is located before the last compressor stage. The details of the dryer were not calculated in this study, but



a pair of adsorber vessels with silica adsorbent beds should be sufficient. The parallel vessels operate in sequence, where one is adsorbing and the other is desorbing.

According to Pekka Nurmi (Nurmi, 2013), the desorption sequence can be done by counter currently flushing the adsorber with either flue gas from the SMR furnace, or with the process gas itself. If flue gas is used, it can be sent to the stack after the flushing. Assuming that only water is adsorbed in the adsorber, the carbon foot print of the flushing is nearly zero. If process gas is chosen as the flush media, the hot outlet stream from the first compressor stage should be used. The flush gases can be used as fuel gas in the SMR furnace. This means, however, that the carbon dioxide in the flush gas will not be captured, thus decreasing the recovery rate. In further calculations, it was assumed that flue gas is used to flush the adsorbers and no extra operating costs occur.

After simulating the processes with Aspen, carbon footprints were calculated and operating costs for both cases were estimated. Since the operating costs for the flue gas case were deemed to be too high, the flue gas case was disregarded and investment costs and sensitivity analyses were only calculated for the PSA off gas case. Sensitivity analyses were made concerning carbon dioxide emission allowance cost, utility prices, plant lifespan, capacity, interest rate and investment cost. The economics of the PSA off gas case were then compared with other published CCS cases.

7.4 Carbon foot print

All processes require utilities, such as electricity, cooling water or steam. Production of these utilities produces carbon dioxide. The carbon foot print (CFP) describes how much carbon dioxide, or carbon dioxide equivalents, are produced in the process. Carbon dioxide equivalents include other greenhouse gases, such as methane, converted to tons of CO₂ by scaling their greenhouse effects.

When considering carbon capture processes, the CO₂ produced due to the capture process has to be reduced from the product CO₂ in order to get a comparable value.

$$\dot{m}_{\text{CO}_2,\text{avoided}} = \dot{m}_{\text{CO}_2,\text{captured}} - \dot{m}_{\text{CO}_2,\text{produced}} \quad (9)$$

Where

$\dot{m}_{\text{CO}_2,\text{actual}}$ The amount of CO₂ emission avoided due to capture

$\dot{m}_{\text{CO}_2,\text{recovered}}$ The amount of recovered carbon dioxide

$\dot{m}_{\text{CO}_2,\text{produced}}$ The amount of carbon dioxide equivalents produced due to the capture process

Carbon foot prints were estimated for both cases using the average carbon foot print value for electricity in Finland (WWF, 2011). The carbon foot print of cooling water was calculated based on the CFP of electricity using equation 10 and the CFP of

steam was calculated by estimating how much natural gas has to be burned to heat vaporize the water with equation 11.

$$CFP_{CW} = CFP_{\text{electricity}} * W_{\text{pumping}} = CFP_{\text{electricity}} * \frac{\rho gh}{\eta t} \quad (10)$$

Where

CFP_{CW}	Carbon foot print of cooling water $\left[\frac{\text{gCO}_2\text{e}}{\text{t}} \right]$
$CFP_{\text{electricity}}$	Carbon foot print of electricity
W_{pumping}	Electricity required for cooling water pumping
ρ	Density
g	Acceleration of gravity
h	Pump head
η	Pump efficiency
t	Time

$$CFP_{\text{steam}} = Q * \frac{M_{\text{CO}_2}}{\Delta H_{\text{combustion,CH}_4}} \quad (11)$$

Where

CFP_{steam}	Carbon foot print of low pressure steam
Q	Heat required to heat and vaporize water
M_{CO_2}	Molar mass of carbon dioxide
$\Delta H_{\text{combustion,CH}_4}$	Heat produced when burning methane

Using these assumptions and formulas, carbon footprints were calculated for the studied cases. The values are presented in Table 6. It should be noted, that low pressure steam can usually be produced at least partially by using waste heat from other processes, which leads to considerably lower carbon footprints and prices.

Table 6 Carbon foot prints for utilities used in this study

Utility	CFP	Unit of measurement
Electricity	207	gCO ₂ ekv / kWh
Cooling water	47	gCO ₂ ekv / (t CW)
Low pressure steam	147	kgCO ₂ ekv / (t steam)

The carbon footprints of carbon dioxide transport, equipment manufacturing and plant installations were not considered in this study.

7.5 Operating costs

The operating costs were calculated using utility demand figures from Aspen simulations, presented in Table 7, and utility and product prices presented in Table 8. Table 7 also shows the assumed efficiencies for electrical motors and the refrigeration package. The actual electrical usage is calculated by dividing the electrical usage figure from Aspen by the efficiency factor.

Table 7 Utility usage in case 1 (PSA off gas) and case 2 (flue gas)

Case		PSA off gas (case 1)			Flue gas (case 2)		
Feed (t / h)		95			147.8		
		Usage from Aspen (kW)	Efficiency	Actual usage (kW)	Usage from Aspen (kW)	Efficiency	Actual usage (kW)
Electricity	Compression	16 734	0.7	23 906	23 892	0.7	34 131
	Refrigeration	2 167	0.7	3 096	8 175	0.7	11 679
	Electricity total	27 001			45 810		
		Usage (t/h)			Usage (t/h)		
Other	Cooling water	2300			5200		
	Natural gas *	0.04			-		
	Steam	-			-		

* Natural gas, which has to be burned in order to compensate the lost heat value

Table 8 Baseline utility prices and the emission allowance cost of CO₂ used in this study (Tilastokeskus, 2013)

Electricity	0.07	€ / kWh
Cooling water	0.005	€ / (t CW)
LP steam	35	€ / (t steam)
Hydrogen	1100	€ / (t H ₂)
Natural gas	446	€ / (t NG)
CO ₂	10	€ / (t CO ₂)

The operating costs were calculated using equation 12:

$$C_{\text{utility}} = p_{\text{utility}} \frac{\text{utility usage}}{m_{\text{CO}_2, \text{actual}}} \quad (12)$$

Where

C_{utility} Operating cost of a utility $\left[\frac{\text{€}}{\text{tCO}_2} \right]$

p_{utility} Unit price of a utility

Using the values and formulas presented above, the operating costs for both selected cases and amine reference cases were calculated. The operating costs are presented in Table 9 below. Sensitivity analyses of the prices are presented later on.



Table 9 Operating costs for both studied cases.

	Case 1 (PSA off gas)	Case 2 (flue gas)
Electricity (€ / tCO ₂)	28.30	83.69
Cooling water (€ / tCO ₂)	0.17	0.94
Natural gas (€ / tCO ₂)	0.30	-
Operating cost (€ / tCO ₂)	28.77	84.63

As can be seen from Table 9, the operating cost in case 2 is much higher than in case 1. Therefore, case 2 was not studied any further.

7.6 Equipment selection and sizing

The materials for the process equipment were largely dictated by two factors; the presence of hydrogen in the stream or cold temperatures. Therefore all surfaces that become in contact with the process stream have to be made of stainless steel 316. Since the process stream flows on the pipe side in cooling water heat exchangers, the shells can be made of carbon steel, which is cheaper.

7.6.1 Compressor

The most expensive piece of equipment in the process was the compressor. A four stage piston compressor was selected. Four stages were required due to the limited pressure ratio of three per stage and the need to achieve a pressure of 52 bar.

7.6.2 Heat exchangers

Heat exchangers were considered as traditional TEMA type exchangers. TEMA stands for Tubular Exchanger Manufacturers Association, Inc. and is considered as the industry standard. In the selected processes even simpler exchanger types, such as dual pipes, could be used, but for clarity, the investment cost figures were calculated with TEMA types. The heat exchange areas were estimated by using Aspen. A BES type exchanger was selected for the stripper reboiler use and BEU type for all other exchangers. The BEU type is cheap and easy to maintain. The BES type was selected as the reboiler due to vaporization taking place inside the exchanger.

7.6.3 Column

The column has seven valve trays, a condenser and a reboiler. The diameter of the column was estimated to be 1 meter using rating tools in Aspen. The height of the stripper was calculated by assuming 60 cm tray spacing and 1.1 meters of space above the uppermost and 1.5 meters below the lowest tray. According to these assumptions, the column height was calculated to be 6.2 meters.



7.6.4 Pressure vessels

Vertical pressure vessels were selected for the process to be used as flash vessels and gas-liquid separators. The vessels were sized by calculating the terminal velocity in the gas phase and the velocity of the gas exiting the vessel. The minimum diameter could then be calculated and the height could be estimated by using a height to diameter ratio of three.

7.6.5 Refrigerator

In order to achieve the cold temperature in the stripper condenser, a refrigeration package is required. The refrigerator package consists of an ethylene circulation complete with a compressor and heat exchanger. The working principle is similar to the one in a domestic refrigerator. The investment cost of the package was estimated using old in-house cases and the capacity exponent method. The method is described in chapter 7.7.

7.7 Investment cost

Investment costs were calculated using methods described in Process Design Manual by Markku Hurme (Hurme, 2008). Compressor and refrigerator prices were calculated with in-house price estimates for similar, but different sized equipment and by using the capacity exponent method.

With the capacity exponent method, the cost of a new piece of equipment can be estimated, if the capacity and price of another equipment of the same type are known. The price of the new equipment can be estimated using equation 13.

$$C_2 = C_1 \left(\frac{c_2}{c_1} \right)^{\text{capacity exponent}} \quad (13)$$

Where

C_i	Cost of equipment i
c_i	Capacity of equipment i

Hurme has presented some common price estimates for different equipment in the manual. The prices are for equipment made of carbon steel and they apply in year 2006. The equipment purchase price was then calculated by using material correction factors, capacity exponents and installation price estimations for different types of equipment. The used methods are described below.

The methods in the Process Design Manual start from some typical equipment prices in 2006. For example heat exchanger prices are bound to the heat transfer area. These typical prices are for carbon steel equipment, and then equipment specific material correction factors are used to calculate the price of an equally sized heat exchanger made from different material. Equipment installation expenses are



calculated using an installation cost expense table. Finally, the equipment prices are updated to current values by using a plant cost index (Nelson-Farrar).

Based on these methods and the simulated values, the equipment prices were calculated. The prices are presented in Table 10.

Table 10 Equipment prices in the PSA off gas case (case 1)

Equipment type	Price installed (€)
Compressor	33 135 000
Refrigerator	24 997 000
Heat exchangers	466 000
Dryer	207 000
Pressure vessels	94 000
Column	26 000
Total	58 925 000

The entire investment cost consists of equipment prices and piping, instrumentation, structures, insulation, engineering, start-up expenses etc. These expenses were estimated based on Process Design Manual values. However, a larger than normal portion of the total investment costs were assumed to derive from equipment prices. The assumption was made since the studied processes include two very expensive pieces of equipment, and since the studied cases were retrofit cases and therefore don't require as much new infrastructure than green field cases. The used percentages and costs are presented in Table 11. The table also shows the total investment cost of the capture plant based on these calculations.

Table 11 Investment cost in the PSA off gas case (case 1)

	% of total	M€
Purchased equipment (installed)	60	58.9
Piping	6	5.9
Instrumentation & controls	6	5.9
Electrical	5	4.9
Structural steel	1	1.0
Building % HVAC	5	4.9
Insulation & painting	2	2.0
Site preparation	1	1.0
Engineering & supervision	10	9.8
Start-up	4	3.9
Investment cost	100	98.2

It should be noted, that the investment cost calculations only include the capture part of the CCS chain. The entire cost of CCS also includes the transportation and storage expenses. Since comparison between different separation methods can be done by only comparing the capture expenses and since the transportation and storage expenses greatly depend on the plant location in relation to the storage site, it was decided that only the capture expenses would be calculated. Furthermore, if transportation of the product is done by ship, an intermediate storage is required. The

investment cost of a vessel capable of holding the required amount of liquid CO₂ can be somewhat significant.

7.8 Production cost

Production costs were calculated with the equation 14, taking into account the operating cost and annuities of the investment cost. The interest rate was estimated to be 15 % due to the rather unpredictable nature of the economics concerning the process at hand.

$$C_{\text{production}} = C_{\text{operating}} + \text{annuity of the investment cost} \quad (14)$$

Where

$C_{\text{production}}$ Production cost

$C_{\text{operating}}$ Operating cost

The annuity of the investment cost can be calculated using equation 15:

$$\text{annuity of the investment cost} = \frac{IR \frac{(1 + \frac{IR}{100})^{\text{lifespan}}}{(1 + IR)^{\text{lifespan}} - 1} * \text{investment cost}}{\dot{m}_{\text{CO}_2, \text{actual}} * \text{annual operating time}} \quad (15)$$

Where

IR Interest rate

Using equation (14) and the values presented in Table 9 and Table 11, the production cost of the process in the PSA off gas case was calculated. The production cost and product margin in the PSA off gas case are presented in Table 12.

Table 12 Production cost and margin for case 1 (PSA off gas)

Operating costs (€ / tCO ₂)	28.77
Investment cost (M€)	98
Interest rate (%)	7.5
Plant lifespan (a)	30
Annuity of the investment cost (M€ / a)	8.3
Annuity of the investment cost (€ / tCO ₂)	14.75
Manufacturing cost (€ / tCO ₂)	43.52
Product value (€ / tCO ₂)	10.00
Margin (€ / tCO ₂)	-33.52

Since the margin is negative, no payback time was calculated.

7.9 Sensitivity analyses

Sensitivity analyses were conducted for variations in CO₂ emission allowance cost, utility and hydrogen prices, plant capacity, plant lifespan and interest rate of the investment.

Sensitivity analysis for the emission allowance cost of carbon dioxide was calculated using the value range presented in Table 13. The low end of the CO₂ emission allowance cost is the cost at which allowances were sold at the end of January 2013. The high end was chosen based on estimates on future prices, which are greatly affected by decisions in climate policy. The analysis is visualized in Figure 29.

Table 13 CO₂ emission allowance cost variations

CO₂ emission allowance cost	Emission allowance cost (€ / tCO ₂)	% of normal	Margin (€ / tCO ₂)
Lowest cost	20	40 %	-23.52
	50	100 %	6.48
Highest cost	100	200 %	56.48

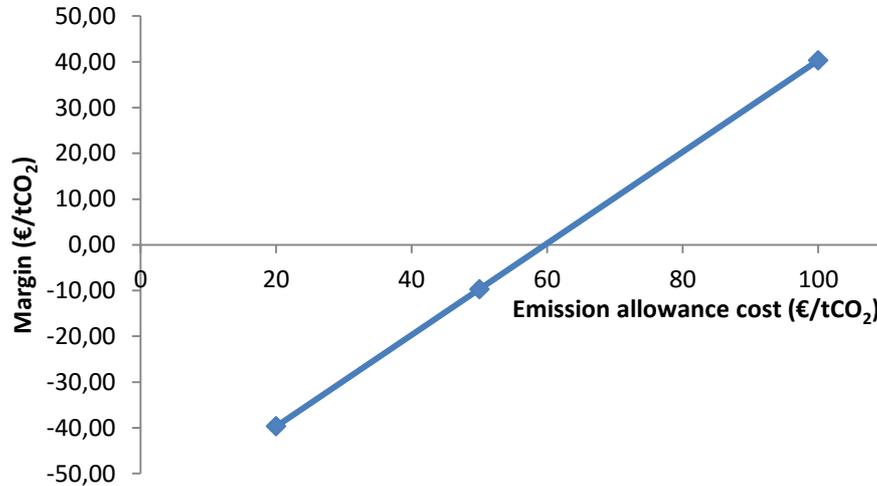


Figure 29 Sensitivity analysis of carbon dioxide emission allowance cost variations

Variation ranges for utility prices are shown in Table 14 and the sensitivity analyses are presented in Figure 30.

Table 14 Utility price variations

Utility prices	Electricity		Cooling water		Natural gas		LP steam	
	€/ kWh	Margin (€/ tCO ₂)	€/ t CW	Margin (€/ tCO ₂)	€/ t NG	Margin (€/ tCO ₂)	€/ t steam	Margin (€/ tCO ₂)
Lowest price	0.035	-19.37	0.0025	-33.43	300	-33.42	17.5	-33.52
Normal	0.07	-33.52	0.005	-33.52	446	-33.52	35	-33.52
Highest price	0.14	-61.82	0.01	-33.69	600	-33.62	70	-33.52

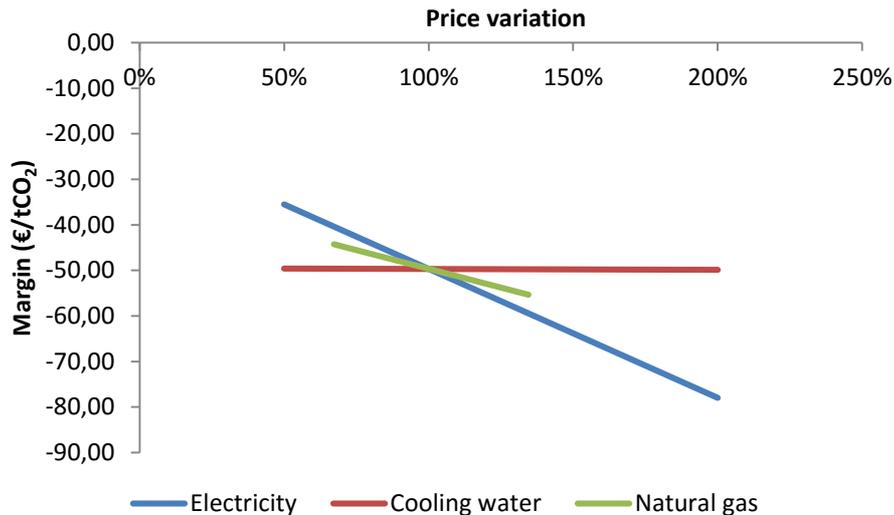


Figure 30 Sensitivity analyses of utility price variations.

Sensitivity analyses were also conducted for plant capacity, estimated life span, interest rate and investment cost. The effect of plant capacity was calculated using the capacity exponent with a capacity exponent of 0.7. The effects of these variations are presented in Table 15 and Figure 31.

Table 15 Life span, interest rate and plant capacity variations.

	Life span		Interest rate		Plant capacity		Investment cost	
	years	Margin (€/ tCO ₂)	%	Margin (€/ tCO ₂)	Feed (t/h)	Margin (€/ tCO ₂)	M€	Margin (€/ tCO ₂)
Lowest	20.0	-35.86	5.0	-30.10	30	-39.61	70	-29.28
	22.5	-35.03	5.6	-30.92	46	-37.07	77	-30.34
	25.0	-34.40	6.3	-31.76	63	-35.49	84	-31.40
	27.5	-33.90	6.9	-32.63	79	-34.37	91	-32.46
Normal	30.0	-33.52	7.5	-33.52	95	-33.52	98	-33.52
	32.5	-33.21	9.4	-36.29	109	-32.93	111	-35.46
	35.0	-32.96	11.3	-39.20	123	-32.44	124	-37.41
	37.5	-32.76	13.1	-42.21	136	-32.01	137	-39.35
Highest	40.0	-32.60	15.0	-45.30	150	-31.63	150	-41.30

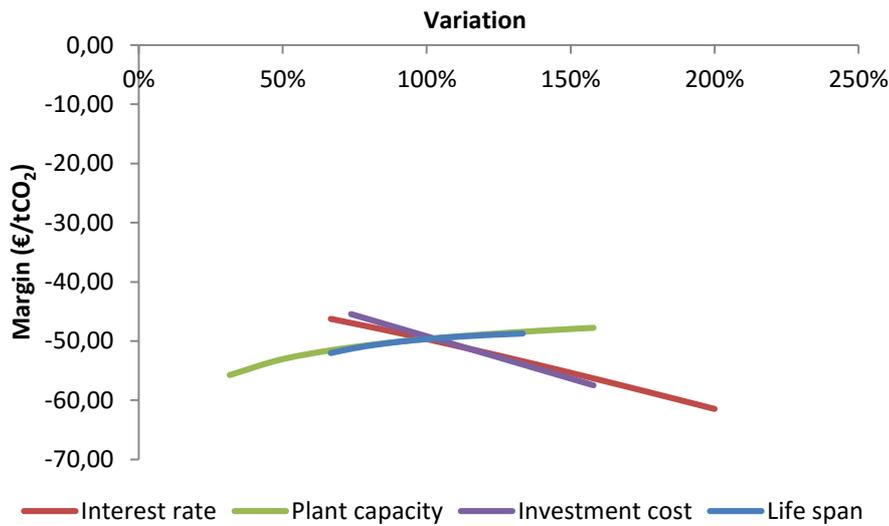


Figure 31 Sensitivity analysis of plant lifespan, capacity, interest rate and investment cost variations.

It was previously calculated, that with current hydrogen, electricity and fuel gas prices, the recovery of hydrogen from the off gas would be unprofitable. A sensitivity analysis of these prices was also conducted. The results are presented in Table 16 and Figure 32.

Table 16 Variations of hydrogen, fuel gas and electricity prices and their impact on the profitability of the extra hydrogen recovery.

H ₂	Hydrogen price		Natural gas price		Electricity price	
	€/ t H ₂	Impact on margin (€/ t H ₂)	€/ t NG	Impact on margin (€/ t H ₂)	€/ kWh	Impact on margin (€/ t H ₂)
lowest	500	-751	200	451	0.035	-116
	800	-451	323	150	0.053	-134
normal	1100	-151	446	-151	0.070	-151
	1300	49	523	-340	0.085	-166
highest	1500	249	600	-528	0.100	-181

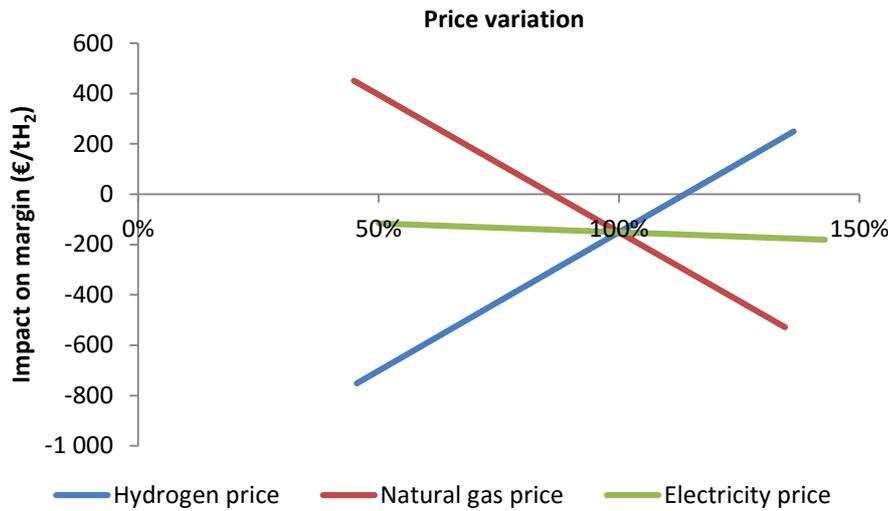


Figure 32 Sensitivity analysis of the profitability of hydrogen recovery after the carbon capture.

Based on these analyses, it can be concluded, that the most important factor concerning the margin of the PSA off gas case is the emission allowance price of carbon dioxide. Since a lot of electricity is needed for the process, the price of electricity also plays a vital role concerning the profitability. It should also be noted, that if the emission allowance price goes up, the price of electricity also goes up. Prices of cooling water and natural gas are nearly irrelevant, if no hydrogen is recovered. If, however, hydrogen is recovered, it has to be replaced by natural gas containing an equal amount of energy than the recovered hydrogen. At this point, the natural gas price becomes significantly more important.

The typical feed for SMR processes is natural gas. This leads to a price link between hydrogen and natural gas. Due to this link, it is unlikely that the price of hydrogen goes up while the natural gas price goes down. This should be taken into consideration when analysing the hydrogen production profitability. It should also be noted, that if more hydrogen production capacity is needed, and the recovery of hydrogen from the fuel gas stream would fulfil the extra capacity requirement, then the profitability of the recovery should be compared to the profitability of building an entirely new hydrogen plant.

Since the investment cost is high, the interest rate has a huge impact on the profitability. Further raising the capacity doesn't significantly increase the economic potential, but smaller capacities become increasingly more unsustainable. It should also be noted, that if capacity is raised beyond the point where one compressor is sufficient, the investment cost is considerably higher. The figure shows, that increasing the lifespan beyond 30 years slightly increases the profitability, but one should remember that increasing the life span also increases service expenses, which are not included in this sensitivity analysis.



7.10 Comparison

The set-up and results of studied cases were compared to literature information available for other processes. Information concerning the economics of carbon capture processes, especially from the PSA off gas stream, is scarce and incomplete. Two reference points were used; FlashCO₂ for the PSA off gas stream, and KS-1 for furnace flue gases.

The FlashCO₂ process is described earlier in chapter 4.3.2. As can be seen from Figure 13, the process is identical to the cryogenic separation process on a block diagram level, only the separation method differs from case 1. According to Union Engineering, the operating cost of the process is 20-30 €/tCO₂. (Union 2011)

The operating cost seems to be somewhat in line with operating costs with the cryogenic process studied in this report. In both processes, the entire PSA off gas stream must be compressed to higher pressure. Union does, however claim (Union 2011), that a pressure of 30 bar is sufficient, whereas the process simulated in this study, requires roughly 50 bar for the flash tank to operate decently and therefore the compression cost of the FlashCO₂ is lower. The cryogenic process studied in this report needs a large refrigerator to condense the overhead in the final column, but since the FlashCO₂ process utilizes methanol absorption, it needs no external refrigeration. Furthermore, regenerating methanol does not necessarily require steam, but instead the compressor intercoolers heat can be used for regeneration. Therefore, no extra operating costs occur and the comparable overall operating cost is lower. If the process simulated in this study would only use 30 bar compression as well, and if no external refrigeration was used, the operating cost would be the same as in FlashCO₂. The investment cost of FlashCO₂ would be lower than in the simulated case, due to the same components of the process. The main process equipment in both processes is similar, except for the smaller compressor, missing refrigeration package and the extra absorber and regenerator in the FlashCO₂ process.

For further calculations concerning the cost of FlashCO₂, more accurate process details are needed, but they are not publicly available. Methanol absorption is, however, studied in the Master's Thesis by Kalliola. (Kalliola, 2007)

Riku Merikoski covers a variety of amine based CO₂ capture processes in his Master's Thesis. For the comparison, the Mitsubishi KS-1 process was selected since it presents the lowest utility usage figures. An overview of the process is presented in Figure 33. It is rather typical absorption process with an absorber, regenerator, heat exchangers, pumps and some auxiliary equipment.

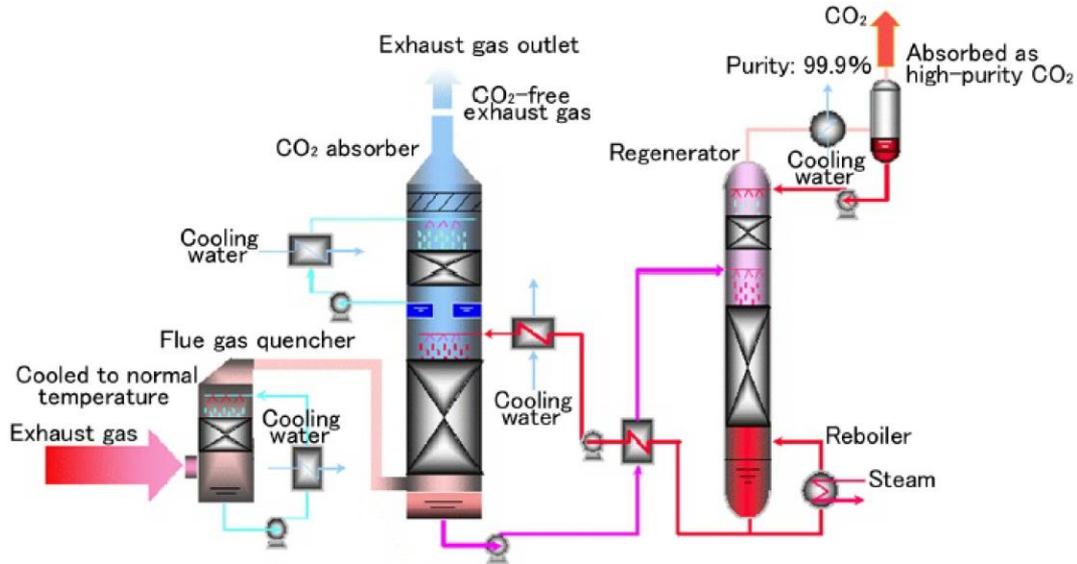


Figure 33 The KS-1 process

Operating costs of the process were calculated based on heat, electricity, cooling water and solvent consumptions reported in the master's thesis by Merikoski (Merikoski, 2012). Since the product is gaseous by default, it should be liquefied by compressing and condensing the carbon dioxide. An estimate for the operating cost of liquefaction was done. The operating cost is presented in Table 17.

Table 17 Operating cost of the KS-1 process

Electricity (€ / tCO ₂)	0.77
Cooling water (€ / tCO ₂)	0.75
LP Steam (€ / tCO ₂)	40.76
Amine makeup (€ / tCO ₂)	0.04
Liquefaction (€ / tCO ₂)*	18.0
Operating cost (€ / tCO ₂)	60.31

* Liquefaction cost estimated

Investment costs were also roughly estimated. The investment cost is presented in Table 18. It should be noted, that cost figures should be calculated with more accurate values in order to get more reliable results.

Table 18 Investment cost estimation for the KS-1 process with 15 t/h CO₂ product capacity

Absorber & Regenerator (k€)	330
Heat exchangers (k€)	240
Quencher (k€)	50
Pumps (k€)	1 000
Liquefaction (k€)	17 030
Equipment total (M€)	18.65
Total investment cost (M€)	37.3

The operating costs for the two simulated cases, along with the operating costs for two reference point processes are compiled into Table 19. Calculated investment costs for the studied PSA off gas case and estimated investment costs the two reference processes are also shown.

Table 19 Operating parameters and costs of the two studied cases and two reference cases.

Case	case 1 (PSA off gas)	case 2 (flue gas)	KS-1	FlashCO2
Feed (t/h)	95	147.8	10 000 t/d and above	First commercial: 5t/h
CO ₂ captured (t/h)	72.85	34.827	n/a	n/a
CO ₂ recovery rate (%)	95.0	95.0	n/a	n/a
CO ₂ product phase	liquid	liquid	liquified	liquid
CO ₂ product pressure (bar)	13.0	7.8	> 5	n/a
CO ₂ product temperature (°C)	-33.4	-46.4	n/a	n/a
CO ₂ purity (%)	99.9	99.5	EOR *	>99,9
CO ₂ avoided (t/h)	67.12	27.72	n/a	n/a
Electricity (kWh / t CO ₂)	404	1196	11	n/a
Cooling water (t CW/ t CO ₂)	34.8	188.1	149.3	n/a
LP Steam (t LPS / t CO ₂)	0	0	1.2	n/a
Solvent consumption (kg / t CO ₂)	0	0	0.35	n/a
Natural gas (kg NG / t CO ₂)	0.7	0	0	n/a
Operating costs (€ / t CO ₂)	28.8	84.6	42.31 **	20-30 **
Investment cost (M€)	98	n/a	37	lower than case 1

* EOR specification for purity is 95.5 vol-%

** KS-1 and FlashCO2 costs were estimated based on literature

A few aspects should be noted when comparing the figures presented in Table 19. First of all, the Mitsubishi KS-1 process captures CO₂ from a flue gas stream, which has a considerably lower CO₂ concentration than the PSA off gas stream. Since amine absorption processes require great amounts of heat, the price is highly dependent on the availability of waste heat streams in the surrounding processes, or if no waste heat is available, the price of low pressure steam. Also, the uncertainty of the operating cost accuracy in the FlashCO₂ case is very high due the limited knowledge concerning the process.



8 Conclusions

According to the operating cost estimation studies, it became obvious that carbon capture is more feasible from a PSA off gas stream than from a flue gas stream. The PSA off gas stream doesn't have to be cooled down before the capture process as the flue gas must.

Furthermore, the CO₂ concentration in the PSA off gas is higher than in the flue gas. The PSA off gas doesn't contain any nitrogen, whereas the flue gas does, which means that a smaller amount of feed has to be treated in order to capture the same amount of CO₂.

Even though the selected process, especially in the PSA off gas case, was somewhat competitive compared with other available carbon capture technologies, the operating margin at current CO₂ allowance price was still negative. The same applies to the FlashCO₂ process, which had the lowest production cost. Basically this means, that unless CO₂ allowance prices go up, investing in carbon capture is economically unsustainable.

The recovery of hydrogen is not profitable with current hydrogen, natural gas and electricity prices. If, however, hydrogen prices go up and natural gas prices go down, the recovery could be profitable. Also, if investing in an entirely new hydrogen plant can be avoided by recovering the hydrogen from the fuel gas produced in the cryogenic process, the savings could be significant.

The PSA off gas from the SMR hydrogen production process was found to be an attractive source for carbon capture due to its high CO₂ concentration and lack of nitrogen and impurities, such as sulphurous compounds. Compared to flue gases from the SMR process, the water concentration in the PSA off gas is also low and the temperature is lower, thus making any precooling unnecessary.

In the analysed cases, the most important factor regarding the profitability of carbon capture was the emission allowance price of carbon dioxide, followed by the price of electricity. The price of cooling water seemed to have nearly no effect at all. If hydrogen were to be recovered from the fuel gas leaving the capture process, the price of hydrogen and natural gas would also be important in terms of feasibility. The capacity of the capture process is also important, since bigger equipment is relatively cheaper than smaller equipment.



9 Recommendations

Both studied cases along with both reference cases were deemed to be unprofitable with current prices. If the emission allowance cost of carbon dioxide goes up in the future, the processes could become economically profitable.

The operating cost for the flue gas case was deemed to be too high for any further studies. This was, however, greatly due to the high nitrogen content in the stream, which could be avoided by using oxy-fuel furnaces. It is, however usually difficult or impossible to retrofit existing furnaces to function with oxy-fuel systems. However, when building new hydrogen plants, oxy-fuel furnaces could be considered, which would lead to lower nitrogen contents and thus a higher relative carbon dioxide concentration. Furthermore, this would lead to a less expensive carbon capture process. Since there is no nitrogen present in the combustion, no NO_x emissions occur, which is a significant improvement. Therefore, a study of an oxy-fuelled furnace with cryogenic carbon capture process from the flue gases is recommended.

Also, since the PSA case feed stream contains considerable amounts of hydrogen, a more efficient hydrogen separation system alongside the carbon capture process could lead to better profits. In this study, it was deemed, that with current hydrogen and utility prices the additional hydrogen recovery unit actually makes the operating profit worse due to its electricity consumption and the need to replace the hydrogen with natural gas in the furnace. If, however the value of hydrogen goes up compared to electricity and fuel gas prices, the recovery module becomes more profitable.

Current compressor types don't allow the outlet temperature of the process stream to exceed 160 or 180 °C. If compressor with higher outlet temperature limits come commercially available, it would be possible to utilize these higher temperatures via steam production, which could have a considerable impact on the economic sustainability of the process alternatives.

Current single stage membrane systems can only produce product streams with below specified purities. Cryogenic processes, among others, favour higher CO₂ concentrations in their feeds. Then again, especially the flue gas has a low CO₂ content. Therefore combining these technologies could prove viable. A single stage membrane system could be used to raise the CO₂ concentration to above 50 vol-%, followed by a cryogenic separation step. Other combinations should be studied as well.

If a process for the PSA off gas stream is chosen, a detailed study of the effects on the SMR furnace should be made. The fluctuations caused by fuel gas feed changes should be studied to insure that no unwanted effects occur.

Even if the capture process would become feasible at future CO₂ allowance costs, the overall production cost should be calculated thoroughly. Even though separation



costs are typically the biggest expense in the chain, intermediate storage facilities, transportation and storage expenses should be calculated as well.



10 References

Agnew, William G. 2004. *The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs*. ISBN: 0-309-09163-2. 256 p. Available online: http://www.nap.edu/openbook.php?record_id=10922&page=199

Allevi, C., Blew, W., Claus, G., Chevallier, F., Dinka, P., Gardzinski, W., Lichtscheidl, J., Lyde, C., Maas, W., Mahoney, L., Mendes, A., Parks, G., Riesco Garcia, J.M., Rucker, S., Sinnen, H., Sopramzetti, A., Zaninbelli, L., Reid, A., Bauld, J., Larivé, J. 2011. *The potential for application of CO₂ capture and storage in EU oil refineries*. Report 7/11, CONCAWE, Brussels.

Chaubey, T., Terrien, P., Valentin, S., Vauk, D., Tranier, J-P., Shanbhag, U. 2010. *Clean Hydrogen Production from SMR*. Air Liquide, Newark, DE, USA. CO₂ Summit: Technology and Opportunity, Eds, ECI Symposium Services, Volume P12 (2010). Available: http://dc.engconfintl.org/co2_summit/40

co2prices.eu. *Analysis of the EU CO₂ Market*. Website, accessed 17.2.2013
Available: <http://www.co2prices.eu/>

Cubeiro, M.L. & Fierro, J.L.G., 1998. *Selective Production of Hydrogen by Partial Oxidation of Methanol over ZnO-Supported Palladium Catalysts*. Journal of catalysis, 179:1. 150-162. [Cited 31.10.2013]. Available:doi:10.1006/jcat.1998.2184

Dicks, Andrew L., 1996. *Hydrogen generation from natural gas for the fuel cell systems of tomorrow*. Journal of Power Sources, 61:1. 113-124. [cited 15.11.2012]. Available:doi:10.1016/S0378-7753(96)02347-6.

Ebner, Armin D. & Ritter, James A. 2009. *State-of-the-art Adsorption and Membrane Separation Processes for Carbon Dioxide Production from Carbon Dioxide Emitting Industries*. Separation Science and Technology, 44:6, 1273-1421. [Cited 6.11.2012]. Available: doi:10.1080/01496390902733314.

Echt, William. 2002. *Hybrid Systems: Combining Technologies Leads to More Efficient Gas Conditioning*. Laurance Reid Gas Conditioning Conference.

European commission, 2012. *NER300 - Moving towards a low carbon economy and boosting innovation, growth and employment across the EU*. Commission staff working document. 19 p. [Cited 17.2.2013]. Available: http://ec.europa.eu/clima/news/docs/2012071201_swd_ner300.pdf

European Energy Exchange. 2013. *EU Emission Allowances – Prices and Trading Volumes, 2012/01/02*. Website. [Cited 26.2.2013]. Available: <http://www.eex.com/en/Market%20Data/Trading%20Data/Emission%20Rights/>

European Parliament and Council. 2009. *Directive 2009/31/EC on the geological storage of carbon dioxide*, Directive, Strasbourg, EU. Available: <http://eur->



lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0114:0135:EN:PDF

Freni, S., Calogero, G & Cavallaro, S., 2000. *Hydrogen production from methane through catalytic partial oxidation reactions*. Journal of Power Sources, 87:1-2. 28-38. [Cited: 31.10.2012]. Available:doi:10.1016/S0378-7753(99)00357-2

Arola, Heikki. 2013. *Valtio saa laihat tulot päästökaupasta*. Helsingin sanomat, 30.1.2013. [Cited 17.2.2013]. Available:
<http://www.hs.fi/talous/Valtio+saa+laihat+tulot+p%C3%A4st%C3%A4st%C3%B6kaupasta/a1359436903543>

Hurme, Markku. 2008. *Process Design Manual*. 1st edition. Otaniemi, Espoo.

Kalliola, Lotta. 2007. *Biomassan kaasutuksessa muodostuvan synteetisikaasun puhdistaminen fysikaalisella absorptiolla*. Master's thesis. Helsinki University of Technology, Department of Chemical Technology. Espoo. 127 p.

Kohl, Arthur L & Nielsen, Richard B. 1997. *Gas Purification (5th Edition)*, 1439 p. ISBN 978-0-88415-220-0.

Koskinen, Jukka. 2012. Professor at Aalto University. Espoo, Finland. Personal communication 8.11.2012.

Krebs, Robert E. 2006. *The history and use of our earth's chemical element: A reference guide*. Greenwood Publishing Group. ISBN: 978-0313334382.

Lampinen, Isa. 2012. *Carbon Capture from Oil Refineries - a Concept Study*. Master's thesis. Aalto University, School of Chemical Technology. Espoo. 37 p.

U.S. 5,085,674. 1992. *Duplex Adsorption Process*. Union Carbide Industrial Gases Technology Corporation, Danbury, Connecticut, US. (Leavitt, Frederick W.) 603,479, 25.10.1990. Publ. 4.2.1992. 14p.

Lenntech 2012. Website. Accessed: 17.2.2013. Available:
<http://www.lenntech.com/library/adsorption/adsorption.htm>

Ma'mun, Sholeh; Svendsen, Hallvard F., Hoff, Karl A. & Juliussen, Olav. 2007. *Selection of new absorbents for carbon dioxide capture*. Energy Conversion and Management, 48. 251-258. [Cited 31.10.2012]. Available:doi:10.1016/j.enconman.2006.04.007.

Maroto-Valer, M. Mercedes (editor). 2010. *Developments and Innovation in Carbon Dioxide (CO₂) Capture and Storage Technology, Volume 1 - Carbon Dioxide (CO₂) Capture, Transport and Industrial Applications*. Woodhead Publishing. 574 p. ISBN: 978-1-84569-533-0.



Merikoski, Riku. 2012. *Flue Gas Processing in Amine-Based Carbon Capture Systems*. Master's thesis. Tampere University of Technology, Programme in Environmental and Energy Technology. Tampere. 102 p.

Moon, Seung-Hyun & Shim, Jae-Woon. 2006. *A novel process for CO₂/CH₄ gas separation on activated carbon fibers - electric swing adsorption*. Journal of Colloid and Interface Science, 298. 523-528. [Cited 2.11.2012]. Available:doi:10.1016/j.cis.2005.12.052.

Netušil, Michal & Ditzl, Pavel. 2012. *Natural Gas Dehydration, Natural Gas - Extraction to End Use*, Dr. Sreenath Gupta (Ed.), ISBN: 978-953-51-0820-7, InTech, Available:doi:10.5772/45802.

Nurmi, Pekka. 2013. Consultant at Neste Jacobs Oy, Porvoo, Finland. Personal communication 1.2.2013.

Nyman, Timo. 2013. Associate at Neste Jacobs Oy, Porvoo, Finland. Personal communication 4.1.2013.

Pellegrini, G., Strube R., Manfreda, G. 2010. *Comparative study of chemical absorbents in postcombustion CO₂ capture*. Energy, 35:2. 851-857. [Cited 17.2.2013]. Available:doi:10.1016/j.energy.2009.08.011

Rackley, S.A. 2010. *Carbon capture and storage*, Butterworth-Heinemann, Burlington MA. ISBN: 978-1-85617-636-1.

Ramachandran, Ram & Menon, Raghu K. 1998. *An Overview of industrial uses of hydrogen*. International Journal of Hydrogen Energy, 23:7. 593-598. [Cited: 23.10.2012]. Available:doi:10-1016/S0360-3199(97)00112-2.

Rao, Anand B. & Rubin, Edward S. 2002. *A Technical, Economic, and Environmental Assessment of Amine-based CO₂ Capture Technology for Power Plant Greenhouse Gas Control*. Environmental Science & Technology, 36:20. 4467-4475. [Cited 31.10.2012]. Available:doi:10.2021/es0158861.

Reddy, Satish & Vyas, Sunil. 2009. *Recovery of Carbon Dioxide and Hydrogen from PSA Tail Gas*. Energy Procedia, 1:1. 149-154. [Cited 7.11.2012]. Available:doi:10.1016/j.egypro.2009.01.022.

Rousseau, Ronald W (editor). 1987. *Handbook of Separation Process Technology*. John Wiley & Sons. 1048 p. ISBN: 978-0-471-89558-9.

Shakhashiri. 2008. *Chemical of the week – Carbon Dioxide, CO₂*. Web article. Available: <http://scifun.chem.wisc.edu/chemweek/pdf/carbondioxide.pdf>

Sircar, S. & Kratz, W.C. 1988. *Simultaneous Production of Hydrogen and Carbon Dioxide from Steam Reformer Off-gas by Pressure Swing Adsorption*. Separation Science and Technology. 23:14-15. 2397-2415. [Cited 31.10.2012]. Available:doi:10.1080/01496398808058461.



Sircar S., Rao, M.B. & Tharon M.A. 1999. *Selective Surface Flow Membrane for Gas Separation*. Separation Science and Technology, 34:10. 2081-2093. [Cited 6.11.2012]. Available:doi:10.1081/SS-100100757.

Sircar, S. & Golden, T.C. 2000. *Purification of Hydrogen by Pressure Swing Adsorption*. Separation Science and Technology, 35:5. 667-687. [Cited 5.11.2012]. Available:doi:10.1081/SS-100100183.

Tarun, Cynthia B. 2006. *Techno-Economic Study of CO₂ Capture from Natural Gas Based Hydrogen Plants*. Thesis for the degree of Master of Applied Science in Chemical Engineering. University of Waterloo. Ontario, Canada. 100 p.

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, Finland: VTT Technical Research Centre of Finland. 188 p. ISBN: 978-951-38-7661-6 (printed). ISBN: 978-951-38-7662-3 (Electric).

Thakur, R.S., Kaistha, Nitin & Rao, D.P. 2011. *Process intensification in duplex pressure swing adsorption*. Computers & Chemical Engineering, 35:5. 973-983. [Cited 6.11.2012]. Available:doi:10.1016/j.compchemeng.2011.01.024.

Tilastokeskus. 2013. *Energy prices*. [e-publication]. Helsinki: Statistics Finland. [Cited 26.2.2013]. Available: <http://tilastokeskus.fi/til/ehi/2012/03/>

Turunen, Helka. 2011. *CO₂-balance in the atmosphere and CO₂-utilisation. An engineering approach*. University of Oulu, Faculty of Technology, Department of Process and Environmental Engineering, Mass and Heat Transfer Process Laboratory

Union, 2011. *CO₂ Capture from Fossil Fuel-Based Hydrogen Production. A Special Applications Report from Union Engineering*. Cryogas International, May 2011.

U.S. Energy Information Administration, 2008. *The Impact of Increased Use of Hydrogen on Petroleum Consumption and Carbon Dioxide Emissions, Appendix C. Existing Hydrogen Production Capacity*. Released: 08/2008 Available: <http://www.eia.gov/oiaf/servicerpt/hydro/appendixc.html>

WWF. 2011. *Ilmastolaskurissa käytetyt oletuskertoimet ja -arvot*. [Cited 26.2.2013]. Available <http://ilmastolaskuri.fi/web/storage/files/>

Yalian Technology, 2012. Website. Accessed 30.8.2012. Available: http://www.yalian.cn/en/gas_03.shtml