LAPPEENRANTA–LAHTI UNIVERSITY OF TECHNOLOGY LUT
School of Energy Systems
Department of Environmental Technology
Sustainability Science and Solutions
Master's thesis 2019

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Sustainable carbon capture in oil refineries

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TIIVISTELMÄ

Lappeenrannan–Lahden teknillinen yliopisto LUT
School of Energy Systems
Ympäristötekniikan koulutusohjelma
Sustainability Science and Solutions

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Kestävä hiilidioksidin talteenotto öljynjalostamoilla

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Hakusanat: Hiilidioksidi, CO_2, hiilen talteenotto, CCS, absorptio, adsorptio, amiini, elinkaariarviointi, öljynjalostamo, jalostamo, GHG, päästö, vety, vedyntuotanto, FCC, prosessiuuni, PSA

Hiilen talteenotto on radikaali tapa vähentää kasvihuonekaasupäästöjä maailmanlaajuisesti ja hillitä ilmastonmuutosta, kun talteenotettu CO_2 varastoidaan pysyvästi tai hyötykäytetään kestävästi. Modernit öljynjalostamot ovat suuria päästölähteitä, mitkä ovat vastuussa huomattavasta osasta raskaan teollisuuden kasvihuonekaasupäästöistä.

Tämän diplomityön tarkoitus on päivittää tietoa hiilen talteenotosta, perehtyä erilaisiin CO_2 lähteisiin öljynjalostamoilla ja niiden potentiaalisiin talteenottotekniikoihin sekä niiden kestävyyarviointiin. Elinkaariarvioinnin tarkoitus on määrittää valittujen tekniikoiden hiilijalanjäljet ja päästöprofiilit sekä vertailla niiden tehokkuutta talteenottaa CO_2 niiden omien ympäristövaikutusten perusteella. Empiirisessä osassa tehdään elinkaariarviointi vedyntuotannossa syntyvän hiilidioksidin talteenotolle. Vertailu talteenottotekniikaksi valittiin yleisesti käytössä oleva amiini absorptio, vertailtaviksi talteenottotekniikoiksi fysikaalinen absorptio ja kiintopeti adsorptio, jotka kaikki sijaitsevat vedyn erotuksen jälkeisessä virrassa. Elinkaariarvioinnin tulokset osoittavat että vertailtavien tekniikoiden hiilijalanjäljet ovat pienemmät kuin amiini tekniikalla.

CO_2 talteenottoa voitaisiin hyödyntää jalostamoiden konsentroituneisiin CO_2 virtoihin ja siitä voi tulla pakollista lähitulevaisuudessa. Kannustimia, lainsäädännöllistä ja poliittista kehystä kuitenkin tarvitaan laaja-alaiseen käyttöönottoon.

ABSTRACT

Lappeenranta–Lahti University of Technology LUT
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Sustainable carbon capture in oil refineries

Master’s thesis
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141 pages, 37 figures, 18 tables and 8 appendices

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Keywords: Carbon dioxide, CO_2, carbon capture, CCS, absorption, adsorption, amine, life cycle assessment, oil refinery, refinery, GHG, emission, hydrogen, hydrogen production, FCC, process furnace, PSA

Carbon capture is a radical way to reduce greenhouse gas emissions globally to mitigate the effects of climate change when CO_2 is stored permanently or utilized sustainably. Modern oil refineries are large stationary emitters, that are accountable of notable share of heavy industry greenhouse gas emissions.

Objectives for this master's thesis are to update information regarding the carbon capture, study CO_2 sources at oil refineries, introduce potential capture technologies and their sustainability assessments. The goal of the life cycle assessment is to determine the carbon footprint and emission profile of selected technologies and compare their effectiveness to capture CO_2 based on their own environmental impacts. In the empirical part, a life cycle assessment is conducted for CO_2 capture from the hydrogen production. Amine absorption was selected as a base technology and physical absorption and fixed bed adsorption as comparable technologies, that are applied to stream after hydrogen production. Life cycle assessment results show that carbon footprints of the compared technologies are smaller than amine absorption.

CO_2 capture could be applied to CO_2 concentrated refinery streams and it may become a necessity in the near future. However, incentives, regulatory and political framework are needed for wide scale adoption.

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After two years in LUT, it's exciting to be finishing my studies as well as my master's thesis. It is now time to start my career and a new chapter in life. As my educational journey is about to end, I would like to thank LUT for providing quality education and lifelong tools that come in handy. After my bachelor studies in HAMK University of Applied Sciences, I am happy for choosing the path that led me to master studies, during which I learned even more than I anticipated. I gained a lot of knowledge and experience during my time at LUT and would recommend it to others.

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In Porvoo 28th of October 2019

Jussi Sippola

TABLE OF CONTENTS

APPENDICES

Appendix 1. Capture costs

Appendix 2. CO_2 quality requirements for range of applications

Appendix 3. Low- and high temperature sorbents for CO_2 adsorption

Appendix 4. Physical absorption advantages and disadvantages

Appendix 5. Chemical absorption advantages and disadvantages

Appendix 6. Amine treatment LCA model

Appendix 7. Selexol capture LCA model

Appendix 8. Selective PSA capture LCA model

Abbreviations

ASU	Air separation unit
CCC	Cryogenic carbon capture
CCS	Carbon capture & storage
CCU	Carbon capture & utilization
CFP	Carbon footprint
DEA	Diethanolamine
ETS	Emission trading scheme
GHG	Greenhouse gas
IGCC	Integrated gasification combined cycle
LCA	Life cycle assessment
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MER	Membrane enhanced reaction
MGA	Membrane gas separation
NG	Natural gas
PSA	Pressure swing adsorption
SER	Sorption enhanced reaction
SEWGS	Sorption enhanced water-gas shift
SMR	Steam methane reformation
TSA	Temperature swing adsorption
WGS	Water-gas shift

1. Introduction

Climate change is the major challenge of the modern society and the anthropogenic emissions are increasing due to growing population, continuous consumption and increased need for energy. Human activities have had a large impact on climate and growth of CO_2 emissions since the industrial revolution. Currently the atmospheric CO_2 concentration is 412 ppm (CO2.earth) and it has increased steadily over the last two decades at the speed of 2 ppm per year.

Oil refineries are accountable for a large share of heavy industry CO_2 emissions and many refining processes are energy intensive. Carbon capture is used to separate CO_2 from flue gas or other gas streams away from the more desired and valuable refinery streams. New more effective and less energy intensive capture technologies are needed for emission reduction and for more efficient capture of CO_2. Amine scrubbing is a common sour gas treatment in refineries, that utilizes chemical solvent absorption to capture acid gases. Capture agents require regeneration that reverses the separation and causes parasitic load for energy generation and decreases the viability of capture. This thesis is motivated by the need to find suitable technologies and improve CO_2 capture by studying its sustainability.

Objectives for this thesis are to get familiar with different sources of CO_2 emissions in modern oil refineries and focusing on finding and introducing potential capture technologies for these sources. This thesis focuses specifically on oil refinery surroundings and capture part only. Many of the new capture technologies are in R&D stage and their development is driven by emission reduction targets by the EU and the EU's strategy to become carbon neutral economy by 2050 (EU 2018). Many new innovative solvents and solid adsorbents are under development and research have been also done for effecting traditional capture processes. Post-combustion technologies are considered to be most promising for stationary sources and new applications are under development (Wang et al.

2017). Technical focus is on evaluating potential capture technologies and their sustainability. LCA methodology will be applied for potential technologies.

Sustainability is the key driver for this thesis, and it is an important aspect for oil refineries as well as corporate responsibility for stakeholders and mitigation of climate change. Some large oil companies are offsetting their emissions abroad and buying allowances, though real emission reduction is needed, not just compensation. ETS is one of the key drivers for emission reduction in refineries along with maintaining competitiveness in global markets and being ahead of the curve. ETS price for CO_2 has been low and it's been more viable to release CO_2 into the atmosphere by using allowances than capture it. Carbon capture could become more popular as the ETS price increases and approaches capture price of CO_2. Climate change has been acknowledged to be great challenge of our generation and sustainable innovations to reduce emissions are needed.

1.1 Objectives and scope

Objective for this thesis is to present suitable and sustainable development- and commercial stage capture technologies for the refinery sources. Theoretical sections objective is to present a typical CO2 oil refinery emission sources, identify emission characteristics and present and compare suitable capture technologies. Theory section gets familiar with various capture technologies and gives a comprehensive technical overview during the search for potential refinery capture technology. Economic data is presented if found and determined to be reliable. Amine treatment is used as a comparison technology. Couple of technologies are chosen for the empirical LCA and carbon footprint quantification, which is conducted specifically for the capture part, because only it would be applied in refinery plot.

Many of the novel capture technologies are in development- or test stage so it is difficult to give a comprehensive conclusion about their potential. However, with technological comparison, available data and LCA, potential technologies can be drafted, and evaluated.

One goal for this thesis is to update information regarding the carbon capture and new innovative technologies that are under development or approaching commercial status. Some potential technical solutions could gain commercial status in a few years, so immediate actions might not be the best way to proceed.

The goal of this thesis is defined by research questions that also set the parameters. This study should provide answers for at least the following questions:

- What kind of potential capture technologies are there?
- What are the main refinery CO_2 emission sources and their characteristics?
- What capture technologies could be suitable for these refinery emission sources?
- What are the most energy efficient and effective capture technologies compared to traditional amine treatment?
- When could carbon capture become competitive against ETS price variations?

1.2 Structure and parameters

This master's thesis is divided into two theory chapters and empirical chapter that consists the LCA of chosen technologies. These chapters are designed and structured so that logical and systematic approach can be made for tackling the research problem. All the chapters should provide qualitative knowledge form large variety of sources such as textbooks, research papers and scientific journals. The main parameters for this thesis are identifying potential refinery CO_2 emission sources for CO_2 capture, introduction of the capture technologies that are suitable for oil refineries and the LCA for most potential capture technologies. Literature view of refinery emissions and carbon capture are the first two main chapters of the thesis, which tackle the given topic by providing theoretical background. The following first chapter presents the typical modern refinery CO_2 sources.

2. Refinery emission flows & characteristics

During the first chapter, the main singular CO_2 emission sources are identified and characterized. Modern refineries produce various emissions and following sources are chosen for potential CO_2 capture due to their volumes, CO_2 concentration and role in refinery total emissions. Suitable capture technologies are selected and evaluated by studying emission composition and volumes.

2.1 Typical refinery CO_2 emission sources

Modern refineries are complicated facilities and have a number of processes in operation simultaneously. Refineries can differ from each other by size, age, crude oil quality and complexity. Crude can be refined to different kinds of products depending on the complexity of refinery. Production efficiency is important and some components from crude are utilized as an energy or further refined into specialized products for the markets. In the process of refining, CO_2 is emitted by fuel combustion or by chemical conversion. Refinery sector is accountable for 6 % of industrial CO_2 emissions, which is 3 - 4 % of total anthropogenic emissions in EU area (CONCAWE 2011) and 4 % globally which accounts over billion tons of CO_2 annually (van Straelen et al. 2009).

Although, modern refineries are complex, they have similar unit processes for intermediate product refining. These few processes presented in table 1.1 can be found almost every refinery and have not changed much in decades. Steam methane reforming (SMR) and fluid catalytic cracking (FCC) are processes that can be found from most modern refineries. There are also process furnaces that are used in everyday operations to heat hydrocarbon streams. During next sub-chapters, these processes are presented and their emission shares and characteristics can be found in figure 1.1 & table 1.2.

Table 1.1 Typical refinery emission sources and brief description (van Straelen et al. 2009)

CO_2 emitter	Description
Furnaces and boilers.	Heat required for the separation of liquid feed and to provide heat of reaction to refinery processes such as reforming and cracking
Utilities	CO_2 from the production of electricity and steam at a refinery.
Fluid catalytic cracker	Process used to upgrade a low hydrogen feed to more valuable products
Hydrogen manufacturing	For numerous processes, refineries require hydrogen. Most refineries produce this hydrogen on site.

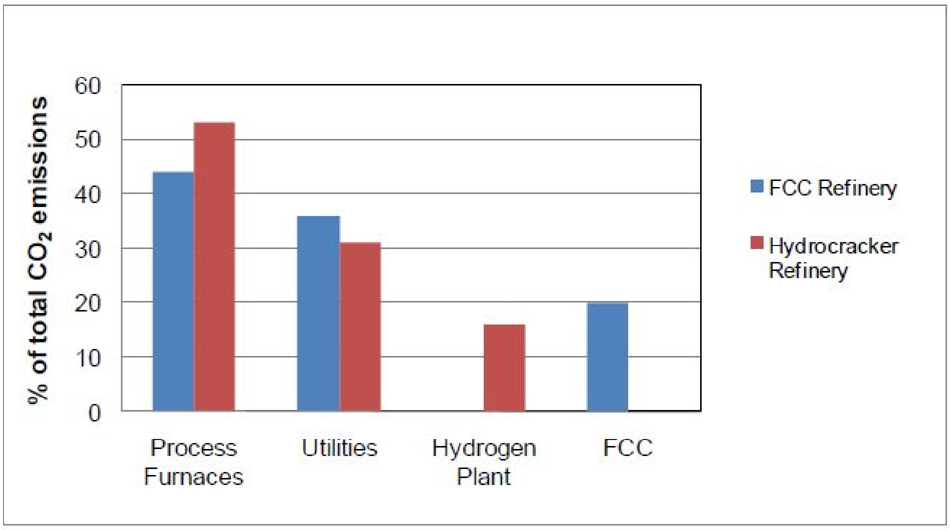


Figure 1.1 Distribution of CO_2 emissions between main sources (CONCAWE 2011)

Table 1.2 Refinery emission source properties (CONCAWE 2011)

Emission sources	CO_2 % v/v	Oxygen % v/v	SO_2 ppmv	Other contaminants
Gas Fired Process/Utility Furnaces [1]	3-6	2-6	10-20	SO_3
Oil Fired Process/Utility Furnaces [2]	7-12	2-6	50-600	SO_3
FCC Regenerator Stack	8-12	1-2	1000-15,000	Catalyst Dust, CO, SO_3
Hydrogen via steam reforming:				
Solvent absorption	95-99 [3]	0	0	Clean
PSA	40-50	0	0	CO, H_2
Hydrogen via residue gasification (POX)	95-99 [3]	ppm levels	ppm levels	H_2S, COS
SRU Incinerator	2-7	1-8	200-6000 [4]	COS, CS_2, Sulphur, SO_3

Notes

(1) Assuming refinery gas at < 200 ppmv H_2S

(2) Assuming heavy fuel oil at up to 1% m/m sulphur

(3) From solvent regenerator

(4) High variation depending on type of tail gas unit

2.1.1 Steam methane reformer

Steam methane reforming is by far, most utilized technology for H_2 production in refineries and is globally accountable for over 50 % of produced H_2 (Cherbanski & Molga 2018). H_2 is utilized in cracking processes and its production is essential for refineries as well as being self-contained with H_2 to ensure production stability. SMR unit is accountable for ⅕ of total refinery CO_2 emissions. (CONCAWE 2011) SMR CO_2 emissions from total emissions is usually between 10 - 50 % depending on refining scheme and refinery complexity, due to need of H_2 in lighter hydrocarbon cracking (Digne et al. 2014). Total emissions vary depending on the fuel used, though light NG is used (CSFL 2018).

In SMR process, catalyzed conversion process is done for lighter hydrocarbon feedstock and it is the most economical technology to produce high purity H_2 (Marsh 2016). NG is the main fuel for SMR but also other heavier (C2+) hydrocarbons can be used, though impurities such as sulfur S and chlorine Cl must be removed prior. Impurities can poison the pressure swing adsorption (PSA) adsorbent, affect H_2 purity and reduce the yield of H_2 (Oliveira 2009). Demand for H_2 is growing in refineries due to stringent requirements for light transportation fuel specifications (Colloidi & Wheeler n.d.). Steam reforming is well established technology and achieves cost of 1,5 $/kg$H_2$ (in 2012 NG values). H_2 production is costly and energy intensive. According to CSFL (2018), H_2 price is affected by SMR unit lifetime, cost of NG & feedstocks, location and industrial applications. NG price is the key factor for profitability, because NG prices can vary by location and season (CSFL 2018).

Current SMR process faces several challenges and high reaction thermodynamics require high exit temperature for high degree CH_4 conversion during reforming. SMR H_2 production results H_2, CO_2, vapor and small amounts of CO and CH_4 (Equations 1 & 2). SMR unit is integrated with PSA unit, that is used for H_2 purification. PSA also produces a CO_2 rich side stream that is called tail gas, which is the leftover from raw syngas H_2 separation. (CONCAWE 2011) Tail gas could be beneficial stream for CO_2 capture and doesn't contain much nitrogen, whereas the reformer flue gas does and has a higher CO_2 concentration compared to reformer flue gas (Reddy & Vyas 2009). SMR unit CO_2 emissions are an important consideration when designing new units due to their effect on refinery CO_2 emission balance (Shahani & Kandziora 2014).

$$CH4 + H2O \text{—>} CO + 3H2 \qquad (1)$$

$$CO + H2O \text{—>} CO2 + H2 \qquad (2)$$

Producing ton of H_2 emits on average 10 tons of CO_2 depending on the feedstock. Usually lighter CH_4 or propane is used as a feed. NG is mainly CH_4 if impurities are not considered and its refining potential is low, which makes it an excellent feed. CH_4 has also an H_2 mass content of 25 %, whereas propane C_3H_8 has H_2 mass content of 18 %. (CONCAWE 2011) According to Zhang et al. (2014): "About 95% of hydrogen produced today comes from carbonaceous raw materials, primarily fossil in origin". H_2 is produced from hydrocarbons by breaking the bond between C and H (C-H). This bond is strong and requires a notable amount of energy to be broken. Steam or high temperature heat is used to break C-H bond with catalyst. (Zhang et al. 2014)

Before feeding NG and recycled raw H_2 to reformer (Figure 1.2), the feed mixture is desulphurized in first reactor section (Figure 1.3, page 17). Reformer catalytic fixed bed reactors usually contain zinc oxide ZnO as adsorbent and some sort of catalyst, thats main goal is to maximize H_2 production and conversion. Reactor produces hydrochloric acid HCl and hydrogen sulfide H_2S from organic sulfur that are later scrubbed via chemisorption. Important variables for reforming are gas exiting temperature, steam/carbon ratio, typically 3:1 and pressure. (Marsh 2016)

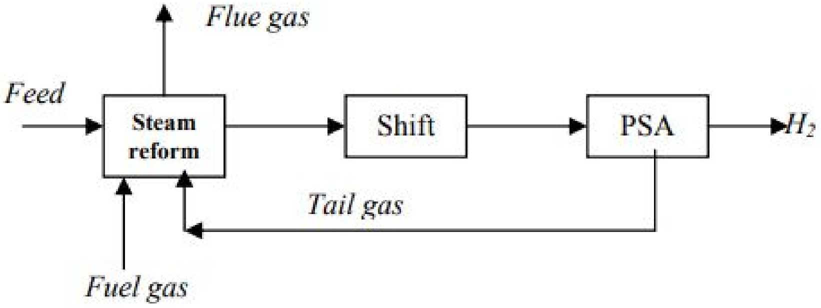


Figure 1.2 Simplified SMR block flow diagram (Colloidi & Wheeler)

Two reactions in SMR are reforming and water-gas shift (WGS) (Equations 1 & 2). Reforming is highly endothermic and requires outside energy to happen, whereas the WGS is slightly exothermic which makes overall reaction very endothermic. NG reacts with vapor in temperature of 700 - 1100 °C and H_2 and CO are formed. Reforming reaction is usually carried out above 750 °C and at the 14 - 20 bar pressure due to reaction reversibility. (Cherbanski & Molga 2018) SMR usually have two WGS reactors, low- and high temperature reactors where CO is converted to H_2 (Equation 2). They are used as secondary reformer for adjusting the H_2/CO ratio. (Speight 2016) Higher temperature WGS reactor operates between 250 - 475 °C where most of the conversion is done. Low temperature WGS reactor operates between 200 - 250 °C, that converts the rest of the CO via steam to CO_2 & H_2 and leaves CO concentration less than a few percentage (Figure 1.4, page 18). Low temperature WGS requires generally more catalyst to happen. CO conversion is done for maximizing H_2 production and for air pollution control perspective due to oxidation of CO to CO_2 when released into the atmosphere. (Zhang et al. 2014)

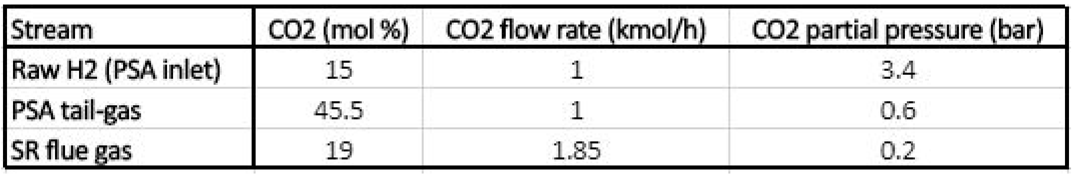
Heat energy for NG and vapor reaction is provided by reformation furnace by combusting low value refinery gases and PSA tail gas. Reaction between CH_4 and H_2O is done in reformer tubes filled with nickel catalyst and NG is fed 3 times more than H_2O to reduce risk of carbon coking in tubes. Typical catalysts for process are Ni, Ru, Rh, Pd, Ir or Pt. CO is later converted in WGS reactor to H_2 & CO_2 by steam. (Zhang et al. 2014) Complete conversion for CH_4 is never possible (Cherbanski & Molga 2018). This reaction is done at high pressure, since pressurized H_2 is desired product and PSA purification and conversion reaction favors high pressure feed, so it doesn't have to be pressurized. (Zhang et al. 2014) Reformers high temperature is due for available selection of catalysts, which show activity just under 400 °C. Catalysts require higher temperature to catalyze the conversion and this causes high energy demand for endothermic conversion. (Rostrup-Nielsen & Rostrup-Nielsen n.d.)

Most SMR units have PSA unit for H_2 product purification and recovery. Stream from SMR unit is divided into syngas and tail gas. Syngas is the shifted gas from reformer and tail gas is from PSA unit where product H_2 is separated. PSA can recover 75 - 90+ % of converted H_2. H_2 concentration and pressure in PSA feed gas can affect product H_2 recovery rate. PSA can achieve high H_2 purity rate of 99.99 % and it is an ideal technology for specifically H_2 separation. (Reddy & Vyas 2009) Hydrocracking experts according to Lindsay et al. (2009) indicate that H_2 purity of ≥ 95 % is acceptable for cracking operations. There is however unrecovered H_2 in PSA tail gas and if it could be recovered at low cost, it could benefit refinery profitability. (Reddy & Vyas 2009)

In earlier SMR unit designs, H_2 purification was done via amine scrubbing and regeneration cycle. Scrubbing of reformer product stream was energy- and capital intensive and resulted a product stream of 95 - 97 % purity H_2 and around 99 % pure CO_2. During the 1980s, PSA started to replace scrubbing for two main reasons, 1) PSA achieves 99.9 % purity for H_2 2) overall energy efficiency of SMR unit was increased by introducing PSA. Due to these reasons, PSA is been favored design for H_2 purification ever since for refineries. Transition towards PSA purification caused the stream purity reduction and near-sequestration quality CO_2 was traded to purer H_2. (Lindsay et al. 2009) CO_2 has different concentration and partial pressure in all the three sources in SMR unit (Table 1.3) (Colloidi & Wheeler n.d.).

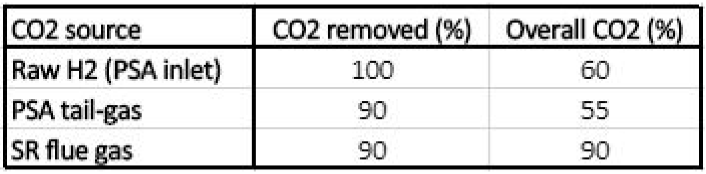
CO_2 capture can be done from three different places; reformer flue gas, syngas or PSA tail gas, which are presented later. It is possible to combine flue gas capture with syngas/tail gas capture to achieve over 90 % capture rate as two-point capture (Table 1.4), but it is not economically feasible. (Colloidi & Wheeler n.d.). Modern SMR unit emits 60 % of CO_2 by chemical conversion from NG to H_2 and 40 % in combustion via reformer (Figure 1.2), which means that a smaller amount of feed would be treated for larger amount of CO_2 if captured from tail gas instead of flue gas. (Colloidi & Wheeler n.d.). SMR unit is potential place for CO_2 capture due to its high pressure and concentration.

Table 1.3 SMR CO_2 streams (Colloidi & Wheeler n.d.)



Stream	CO2 (mol %)	CO2 flow rate (kmol/h)	CO2 partial pressure (bar)
Raw H2 (PSA inlet)	15	1	3.4
PSA tail-gas	45.5	1	0.6
SR flue gas	19	1.85	0.2

Table 1.4 SMR achievable CO_2 capture for different streams (Colloidi & Wheeler n.d.)



CO2 source	CO2 removed (%)	Overall CO2 (%)
Raw H2 (PSA inlet)	100	60
PSA tail-gas	90	55
SR flue gas	90	90

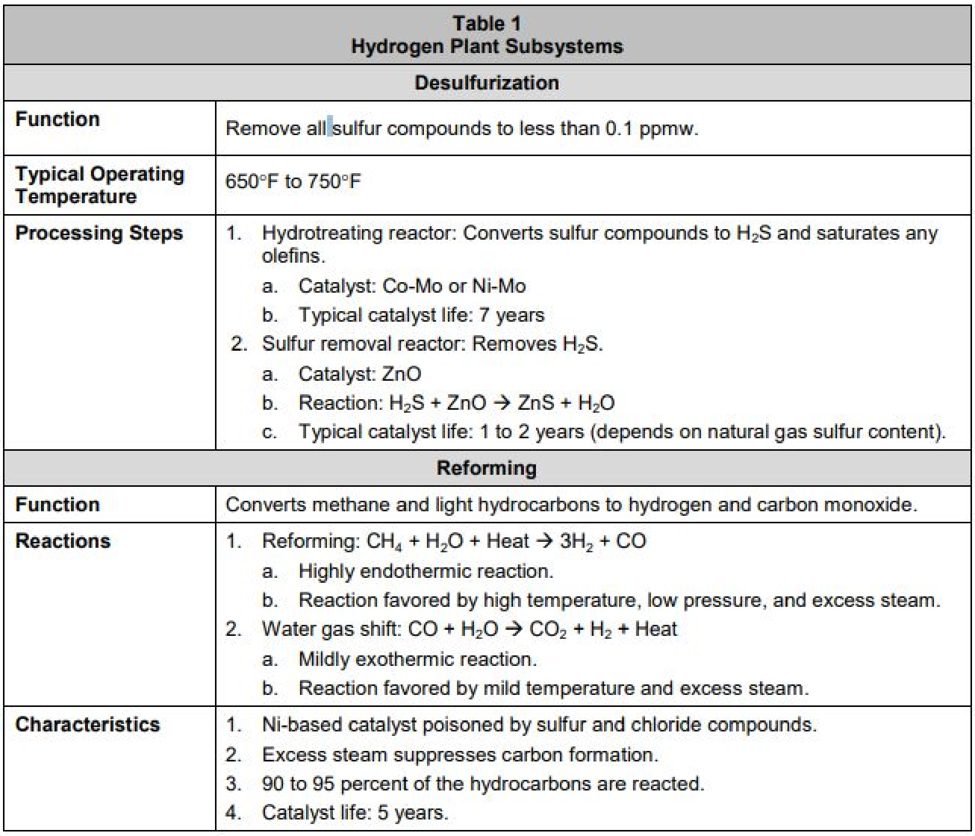


Table 1 **Hydrogen Plant Subsystems**	
Desulfurization	
Function	Remove all sulfur compounds to less than 0.1 ppmw.
Typical Operating Temperature	650°F to 750°F
Processing Steps	1. Hydrotreating reactor: Converts sulfur compounds to H_2S and saturates any olefins. a. Catalyst: Co-Mo or Ni-Mo b. Typical catalyst life: 7 years 2. Sulfur removal reactor: Removes H_2S. a. Catalyst: ZnO b. Reaction: $H_2S + ZnO \rightarrow ZnS + H_2O$ c. Typical catalyst life: 1 to 2 years (depends on natural gas sulfur content).
Reforming	
Function	Converts methane and light hydrocarbons to hydrogen and carbon monoxide.
Reactions	1. Reforming: $CH_4 + H_2O + \text{Heat} \rightarrow 3H_2 + CO$ a. Highly endothermic reaction. b. Reaction favored by high temperature, low pressure, and excess steam. 2. Water gas shift: $CO + H_2O \rightarrow CO_2 + H_2 + \text{Heat}$ a. Mildly exothermic reaction. b. Reaction favored by mild temperature and excess steam.
Characteristics	1. Ni-based catalyst poisoned by sulfur and chloride compounds. 2. Excess steam suppresses carbon formation. 3. 90 to 95 percent of the hydrocarbons are reacted. 4. Catalyst life: 5 years.

Figure 1.3. SMR unit process description (Bonaquist 2010)

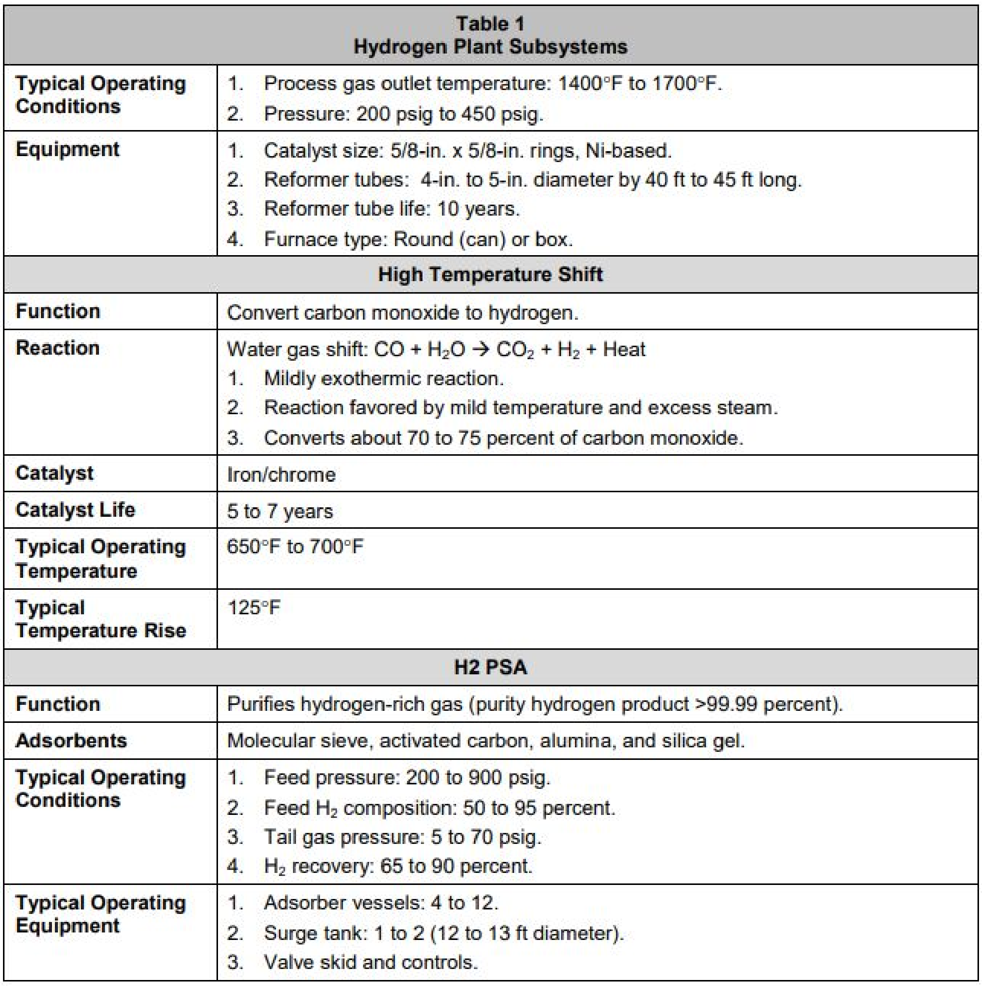


Table 1 **Hydrogen Plant Subsystems**	
Typical Operating Conditions	1. Process gas outlet temperature: 1400°F to 1700°F. 2. Pressure: 200 psig to 450 psig.
Equipment	1. Catalyst size: 5/8-in. x 5/8-in. rings, Ni-based. 2. Reformer tubes: 4-in. to 5-in. diameter by 40 ft to 45 ft long. 3. Reformer tube life: 10 years. 4. Furnace type: Round (can) or box.
High Temperature Shift	
Function	Convert carbon monoxide to hydrogen.
Reaction	Water gas shift: $CO + H_2O \rightarrow CO_2 + H_2$ + Heat 1. Mildly exothermic reaction. 2. Reaction favored by mild temperature and excess steam. 3. Converts about 70 to 75 percent of carbon monoxide.
Catalyst	Iron/chrome
Catalyst Life	5 to 7 years
Typical Operating Temperature	650°F to 700°F
Typical Temperature Rise	125°F
H2 PSA	
Function	Purifies hydrogen-rich gas (purity hydrogen product >99.99 percent).
Adsorbents	Molecular sieve, activated carbon, alumina, and silica gel.
Typical Operating Conditions	1. Feed pressure: 200 to 900 psig. 2. Feed H_2 composition: 50 to 95 percent. 3. Tail gas pressure: 5 to 70 psig. 4. H_2 recovery: 65 to 90 percent.
Typical Operating Equipment	1. Adsorber vessels: 4 to 12. 2. Surge tank: 1 to 2 (12 to 13 ft diameter). 3. Valve skid and controls.

Figure 1.4. SMR unit process description 2. (Bonaquist 2010)

Blue hydrogen

Due to high energy intensity of H_2 production, blue hydrogen is seen as the potential path for the future. Blue hydrogen is H_2 produced with CCS, where zero carbon emissions are emitted. It's been noted that international interest towards clean hydrogen is growing and clean H_2 has an important part in global energy transition towards a more sustainable production. H_2 is versatile fuel and energy carrier that can be produced from a variety of fuels and utilized by the energy sector. H_2 origin is important, when producing clean H_2 and now it's been converted from NG, which is accountable for significant CO_2 emissions in refineries that utilize SMR technology. (van Hulst 2019) H_2 produced from NG without CCS is called grey hydrogen and H_2 produced via electrolysis, from biogas or through gasification with CCS is called green hydrogen (NIB 2016) (van Hulst 2019). Currently, the grey hydrogen is cheaper than the two previous, with the price of 1,50 $/kg, though the price can vary due to NG price variations in the global markets. (van Hulst 2019) According to NAVIGANT (2019) technological potential for blue H_2 based on CCS or CCU in EU area is small, although CCS applications for blue H_2 production could be scaled to large quantities in short timeframe. Challenge with scale-up is political acceptance and electrolysis development is linked to growing wind or solar power generation. Early scale-up could accelerate fuel decarbonization in EU area and meet 2050 targets to become a carbon neutral economy. (NAVIGANT 2019)

It was found that clean H_2 is still too expensive for wide adoption and in some estimates, prices may not decrease until 2030. Uncertainty always surrounds energy sector and transition is always slow, but there were some signs that clean H_2 could become more affordable before 2030. Number of EU countries want to establish a base CO_2 price, that would gradually increase during the next 10 years to 30 - 40 €/tCO_2. It would mean that CO_2 emission costs would add almost 0,50 € per kg/H_2 in EU area. Latest estimates about applying CCS to H_2 production vary from 50 - 70 €/tCO_2 captured. This puts the price of blue H_2 above grey H_2, but the gap is expected to narrow down due to CO_2 emission price increase in the coming years. Price of green H_2 is estimated to be between 3,50 and 5 €/kg currently. (van Hulst 2019) These factors make the CO_2 capture from H_2 production more interesting for further research.

2.1.2 Fluid catalytic cracker

Fluid catalytic cracking is critical process in refineries and its main function is to convert crude oil and heavy fractions to lighter products and high-boiling petroleum fractions to higher value fuels. FCC is accountable for about 10 - 20 % of refinery total emissions (Figure 1.1, page 12) (CONCAWE 201) (Digne et al. 2014). NPTEL (n.d.) states that FCC unit produces about 50 % of transportation fuels alone and approximately 35 % of gasoline pool. FCC is key process for modern refineries and its operation determine mainly if the refinery can be competitive in the markets. Purpose for FCC technology utilization is to increase profitability of refinery. Crude oil always contains heavy components, but markets for these products have gone cold. Catalytic cracking provides conversion capacity to decrease production of these not desired components and refines them to more valuable form. Modern FCC has an excellent ability to crack heavier fractions with catalysts. Feeds for FCC are from crude unit where atmospheric distillation into intermediate products like naphtha, kerosene, diesel and gas oil is done. Gas oil from atmospheric column, vacuum column and delayed coker are the feeds for FCC unit. FCC feeds are fractions from crude oil that boil between 330 - 550 °C. (Sadeghbeigi 2012)

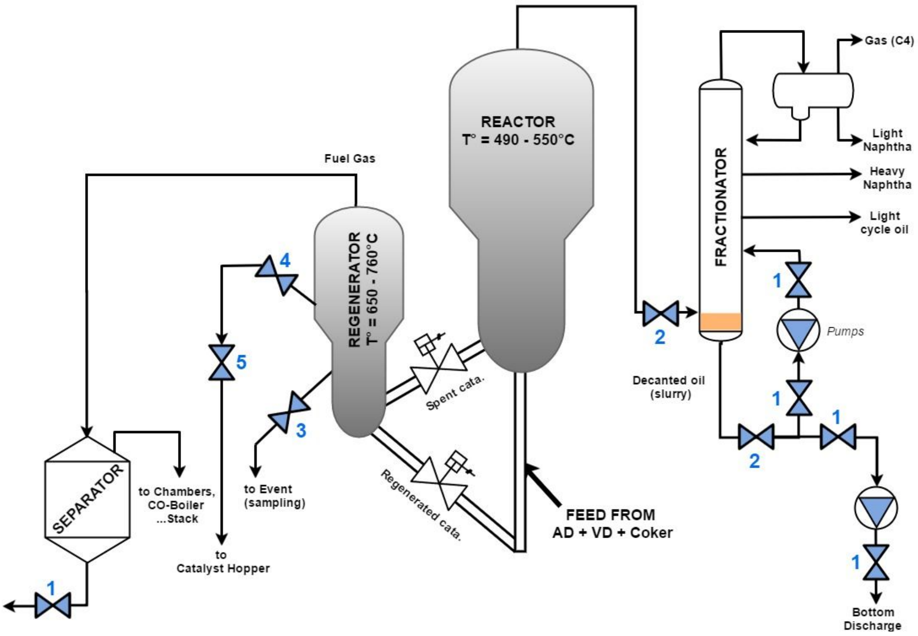
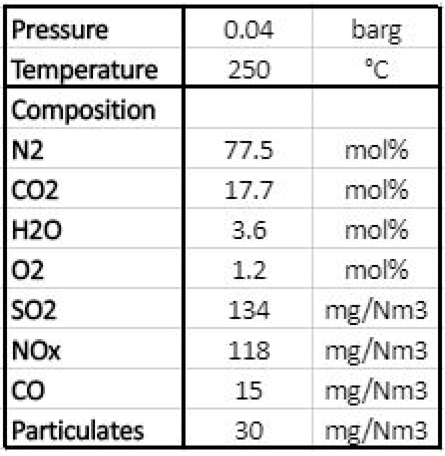


Figure 1.5 Typical FCC process (Guichon valves n.d.)

Modern FCC is a complex process but has three basic functions, reaction, regeneration and fractionation (Figure 1.5). Catalytic reaction occurs in reactor feed channel where feed and catalyst contact and mix. Catalytic reaction between feed and catalyst results lighter hydrocarbons that are directed to fractionator. Catalyst is then regenerated by combusting coke that is attached to the catalyst particles during the process. (Sadeghbeigi 2012) Catalyst coke combustion is the source of FCC CO_2 emissions. Combusted coke is mainly high purity carbon that produces CO_2 rich flue gas that can be up to 20 % CO_2 (Table 1.5). (CONCAWE 2011) Catalyst regeneration process is exothermic, and after regeneration, catalyst is cycled back to the reactor (Sadeghbeigi 2012). Recovering the catalyst activity via combustion of coke is also used for vaporizing the hydrocarbon feedstocks and to reach desired outlet temperature for process streams. Energy balance between regeneration and reactions sections in key factors of FCC. (Digne et al. 2014) Catalysts are solid materials that are fluidized by steam and hot process liquids in feed channel. Fresh catalyst must be added to process to replace worn-out catalyst and to balance cracking process. In fractionation, product hydrocarbons are distilled into products such as liquid petroleum gas and gasoline. (Sadeghbeigi 2012)

Table 1.5 Typical FCC outlet gas composition (Digne et al. 2014)



Pressure	0.04	barg
Temperature	250	°C
Composition		
N2	77.5	mol%
CO2	17.7	mol%
H2O	3.6	mol%
O2	1.2	mol%
SO2	134	mg/Nm3
NOx	118	mg/Nm3
CO	15	mg/Nm3
Particulates	30	mg/Nm3

2.1.3 Process furnaces

Furnaces are utilized throughout the process industry to produce heat by combusting various fuels. Process furnaces in refineries are used as a heat source or reactor that provides favorable conditions for desired reactions. Process/utility furnaces transfer heat via combustion of light refinery fuels and are accountable for 17 % of total refinery CO_2 emissions or according to Digne et al. (2014) or around 40 - 55 % according to CONCAWE (2011). Process furnace heat up fluids by transferring heat via radiation 60 to 70 % and convection (preheats the feed) furnace section to tubes that carry the process fluid. There are many types of furnace designs that can vary based on their function and during the past decade, new complex furnaces are designed for better efficiency and reduced fuel consumption. There are some similarities in furnaces such as burner operation. Burners are provided with fuel and combustion air which results oxidation of fuel and heat. Furnace can have several burners and their arrangement can differ, depending on furnace heat profile. (NPTEL)

Refineries utilize process furnaces in everyday operations for fossil feedstock heating, fractionation, thermal cracking or high temperature processing. Furnaces use fossil sources of energy due to low-grade fractions that can be combusted rather than refined. Process furnaces have been designed so that they provide a specific amount of heat energy that is needed with suitable residence time in heat section. When using and designing a process furnace, idea is that right amount of heat energy is absorbed to process fluid by adjusting firing rate and fluid flow. Outlet temperature in the furnace is a challenge and can lead to product degeneration and feedstock damage if not operated properly. Also, flue gas temperature must not let drop under dew point, when acids and other corrosive compounds are formed (Furu 2016). Good balance in process can be achieved by disposition of tubes in furnace like in boiler operation, adjusting the firing rate of fuel and fluid flow in furnace. In furnace design stage, fuel consumption, furnace wall thickness, tubes and maximal operating conditions are determined. Process furnaces are typically vertical cylinder shaped equipment. that are used when large heat output is not required. (NPTEL n.d.) Cylinder-shaped furnace maximal output is around 30 MW whereas box shaped furnaces can deliver up to 60 MW power. Both designs use vertical tube construction mainly. (Furu 2016) Typical process furnace can have heat transfer rate of 50 kW/m^2 and power between 3 - 60 MW. (NPTEL n.d.)

3. Carbon capture

In this second chapter, theoretical background for carbon capture is introduced with capture concepts and technologies. Technologies are presented by getting familiar with technical properties as well as their principles of function. First subchapter gets familiar with background of CO_2 capture. Also, in later subchapter, development of capture technologies are introduced and new innovative technologies are pointed out.

3.1 Theoretical background

Industries like oil refining are guided by incentives, legislation and political decision making. Fuel consumption has increased, and lighter fuels are refined more than ever. Fossil fuel dependency should be eliminated and replaced by renewable energy sources. Currently, there are no solutions that could replace the share of fossil fuels, so the crude oil refining must be improved. CO_2 is produced as a by-product and there are recovery processes where it can be separated (Alexandre et al. n.d.). For CO_2 capture, it would be beneficial that there would be a mechanism in place that provides incentives for capture technology implementers so that industrial sector could benefit from practical experience and reduce the cost of future capture projects. (CONCAWE 2011)

Carbon capture and sequestration (CCS) was a trend back in early 2010s, but political situation, legislation, technical maturity and price per ton of CO_2,were barriers for its large-scale adoption. Also, there were no sufficient economic drivers and incentives for CCS market lock-in (Berger & Bhown 2013). Capturing CO_2 from flue gas has received attention in past years (Mirzaei et al. 2015). Now, CCS sector capacity is size of 30 Mt/CO_2 annually, that is from the steel industry, electricity generation and SMR (Kreijkes et al. 2018). Only geological storage is seen effective due to ocean injection opposition, limited capacity and impermanence of land storage (Stephens & Van Der Zwaan 2005). Usually CO_2 separation term is used when CO_2 is removed from other fractions. It doesn't mean that every time the CO_2 is separated, it is stored or utilized. Typically, it is released into the atmosphere, because it is cheaper to do so, due to emission trading scheme (ETS) price. On the other hand, refining margins have been low in Europe after 2013 and financial constraints related to CO_2 emissions will impact negatively to refineries. This scenario implies that there could be need for capture technologies in order to reduce CO_2 emissions in European refineries for better revenues. (Digne et al. 2014)

CO_2 capture is designed for large volume stationary sources like power plants, oil refineries and steel production. There are countless sources for CO_2 emissions that are produced in various stages during oil refining. Naturally, CO_2 is found from NG as a component, from which it is separated during purifying process. CO_2 emissions in refineries are not generally captured but most concentrated streams could be potential places for economical and high efficiency capture. Higher the capture efficiency, the higher the cost (Rubin et al. 2010).

Selecting the suitable capture technology for refinery benefits sustainability, energy consumption and process operation. CO_2 separation from high value refinery streams is important when refining gasoline or other high-quality oil products. Capture is performed mainly for CO_2 removal from the more valuable refinery streams. CO_2 separation from NG and crude oil mixtures is important so that volumes can be decreased, and heating value and energy content can be increased so that concentrations of valuable fractions is high, and the amount of impurities low. (CONCAWE 2011)

Flue gas capture is technically and economically challenging and differs from capturing high concentration CO_2 stream due to low concentration (3 - 15 %) of CO_2 (Teir et al. 2009). Flue gas composition could be improved by introducing fuel mixes that produce higher concentration of CO_2 when combusted. For example, replacing coal with NG, which produces CO_2 and H_2O when combusted, if impurities are excluded (IEA Greenhouse gas R&D Programme). Most of the fuels used in refineries are low-grade light hydrocarbons, that have no refining value except energy generation. Self-generated energy is way to reduce energy costs and the amount of imported fuels. (CONCAWE 2011)

CO_2 and H_2S are acid gases and can be found from liquid hydrocarbons such as propane and butane. Propane and butane are also known as liquid petroleum gas (LPG). (Berger & Bhown 2013) Acid gases are compounds that require separate removal processes for environmental- and further utilization reasons. There is a so called "clean air legislation" that requires most industrial countries to remove acid gases from emissions to very low concentrations before release to atmosphere. (David & Jones 2008) From the two acid gases, H_2S is the one with more negative effects and higher selectivity and is usually primarily removed. (Teir et al. 2009) When H_2S is released into the atmosphere, it reacts with O_2 forming dilute sulfuric acid H_2SO_4 and CO_2 forms carbonic acid H_2CO_3. Both acids are a risk for human health and cause corrosion to metallic objects. Difference between these two acid gases is that H_2S is found from refinery gases as an impurity whereas CO_2 is produced in combustion, conversion or gasification (David & Jones 2008) CO_2 is not the most desired compound to be primarily separated, such as in the case of H_2S that have actual limits that must be met. CO2 is an inert gas, so it doesn't react to temperature or pressure easily and gives it more ways to be captured.

There is a process called enhanced oil recovery (EOR) that is 1st generation CCS technology, where produced CO_2 in oil drilling operations is injected into depleted oil well, where CO_2 mainly stays in gaseous form and some carbonation occurs during period of time. CO_2 injection enhances the recovery rate of NG and crude oil. This method is driven by increased oil production and not environmental reasons. (Teir et al. 2009) According to IEA (2016) 73 % of all global capture projects are related to EOR and contributing to increased crude oil production. Most of the crude oil related emissions are from fuel combustion and not production, so the enhanced oil recovery CO_2 sequestration will not outweigh the emission of increased crude production. So, it can be generally determined that so far, CCS sector has been a contributor to climate change rather than mitigating it. (IEA 2016) Captured CO_2 can be also utilized instead of storage or release. There are multiple solutions for utilization for example using it as an inert gas, protective gas in food packages, purifying it to high grade CO_2 and pH stabilizer in industrial solutions. Although, there are many utilization applications, it doesn't change the fact that every utilization method will eventually release the CO_2 into the atmosphere in some way. (Teir et al. 2009)

Challenge of the capture process is its energy consumption during regeneration of capture agent that creates a parasitic load for energy generation. Every capture technology uses some form of energy and this consumption plays an important role when choosing the suitable technology. Overall operating costs are tried to reduce, and technological innovations are searched (Rubin et al. 2010). Post-combustion technologies are dominant and believed to remain that way due to easier retrofitting to already existing power plants and potential to utilize available low-grade thermal energy in facility, which could be provided by flue gas system for example. (I&EC research 2016)

3.2 Motivation for effective CO_2 capture

Mitigation and actions against climate change are driven by EU climate- and energy package. It is targeting to reduce GHG emissions rapidly and set strict targets and plans for future emissions while keeping competitiveness in the markets. EU has been interested in low emission technologies as in figure 2.1 and that's why CCS has surfaced again. Paris climate agreement was ratified 2016, and all the agreement parties had together 55 % share of global GHG emissions. The main goal of the agreement is to reduce total GHG emissions and keep global warming under 1,5 °C. First overall review of Paris agreement intermediate results will be in 2023 and new measures to reduce impacts of global warming will be discussed (UNFCCC). Pressure towards high emitting industries such oil refining has been reinforced by two stages of current ETS system. Third stage (2013 - 2020) has a target that 21 % reduction of CO_2 is achieved compared to 2005 values. (Digne et al. 2014)

Current refinery processing implies that even with the high energy efficiency, modern refineries continue to consume high amounts of energy and CO_2 emissions are not decreasing although, efforts are being made. Solution for rapid decrease of CO_2 emissions could be through CCS.

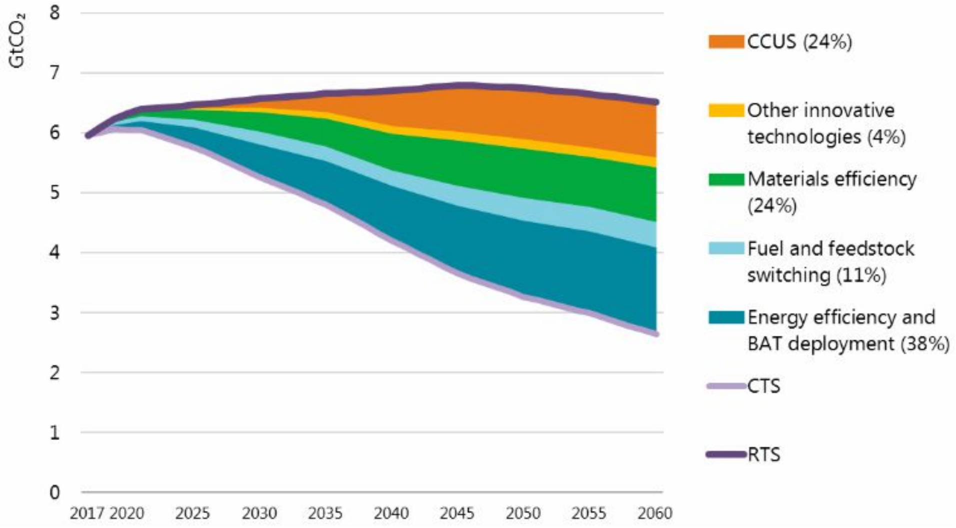


Figure 2.1 Global CO_2 reduction scenario for various technologies, RTS = Industry direct CO_2 emissions & CTS = Total direct CO_2 emissions (IEA 2019)

Fossil sources of energy are still dominant and crude oil, NG and coal extraction results annually almost 400 Mt of CO_2 globally and their refining to higher grade fuels produces approximately 700 Mt of CO_2 annually due to bad quality crude oil, these emissions are expected to increase. (Teir et al. 2009) (IEA 2008) EU refineries are accountable for 140 - 150 Mt/a of CO_2 annually. CONCAWE (2011) states that modern EU refineries have an average calorific consumption of 6,5 to 7 % of the incoming crude, although there can be variation between complexity of refineries. (CONCAWE 2011) van Straelen et al. (2009) estimated the calorific consumption to be between 1.5 - 8 % for different type of refineries depending the complexity. These values mean that over 200 kg CO_2 is produced when ton of crude oil is refined. There are obviously differences between refineries and CO_2 value per ton of crude oil is used as a generic indicator to present intensity of refining. 98 EU area refineries total CO_2 emissions can be seen in figure 2.2. EU area refineries collective emissions have been increasing over the years due to product quality requirements and demand for “middle distillates” (diesel, gas oil and jet fuel) has rapidly grown. Demand for

H_2 has also increased because fuel products are required to become gradually lighter so that more refining is required. (CONCAWE 2011) Also, crude oil is getting heavier and sourer globally (Shahani & Kandziora 2014).

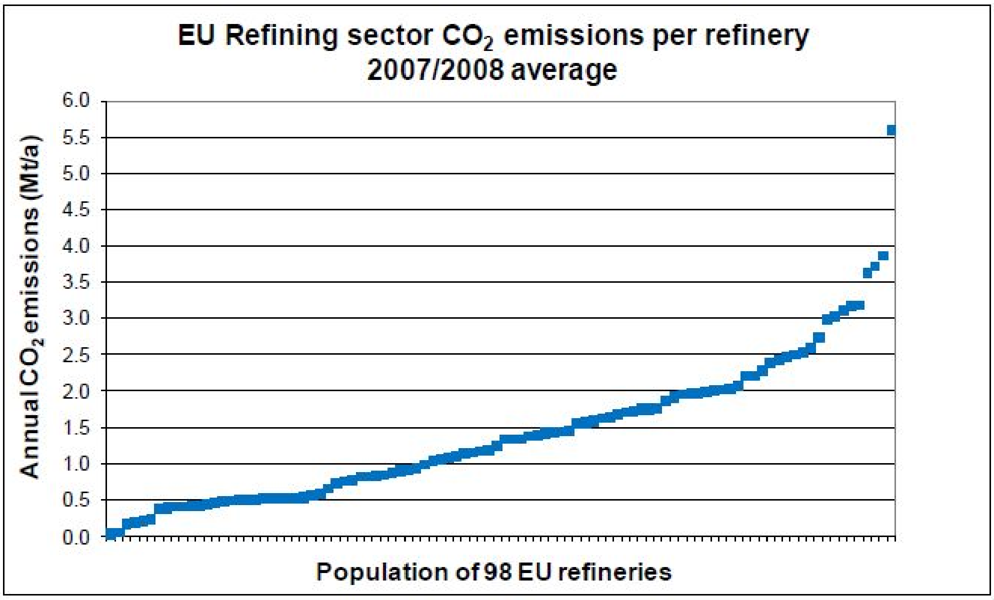


Figure 2.2 CO_2 emissions of 98 EU area refineries (CONCAWE 2011)

On January 2005, the oil refineries were included in ETS, which increased the cost of emitted CO_2. During the same time, the directive 2003/17/EC on the quality of petrol and diesel fuels required further refining for oil products. Refining will demand measures for energy saving and potential technical solutions are implemented at the refineries constantly. After ETS implementation, fuels that produce high CO_2 emissions cause additional cost for users. (Holmgren & Sternhufvud 2008) (EU)

3.3 Carbon capture in general

There are two ways to capture CO_2. Capturing it from process gas stream and leave process unchanged or changing the process to directly produce rich CO_2 stream. (CONCAWE 2011) CO_2 can be captured power plant flue gas, industrial streams or even directly from air. When captured CO_2 is compressed and stored, process can become a carbon sink for the atmospheric CO_2 if biomass is used (Guo et al. 2012). Capture is more effective for larger source than multiple smaller ones. Major disadvantage for refineries is that they are not one-point emitters but have scattered CO_2 sources around the plot. Effective capture in modern refineries requires focusing on most concentrated and large volume emission sources. (Kreijkes et al. 2018) Suitable and effective capture technology can depend on several factors such as emission flow, CO_2 content, composition, volume, temperature and pressure (Keskitalo 2013). Potential and least costly CO_2 sources for capture are ones with the high pressure and CO_2 concentration, which allows the CO_2 separation facility to be smaller and compression of feed gas is not needed (Carbon Management 2001). These kinds of sources can be found from H_2 unit and will approximately count for 5 - 20 % of the refinery's emissions. Capture cost can increase over 25 % when CO_2 content drops from 12 to 4 %. Also, lack of scaling drives capture cost up if potential source emits less than 500 kt annually. Due to refinery plot size and space utilization, combined emission routing for one capture unit is not attractive solution due the routing costs and modifications to pipe network. (van Straelen et al. 2009) According to van Straelen et al. (2009):” The costs of capture from such sources based on available amine technology will be about 3-4 times higher than the current carbon trading values.”

3.3.1 Capture concepts

Carbon capture concepts are characterized broadly by the stage of CO_2 capture. CO_2 can be separated from fuel as “pre-combustion” or from flue gas as “post-combustion”. (Teir et al. 2010) There are also an oxy-fuel combustion that utilizes stoichiometric O_2 injection to produce rich CO_2 flue gas stream with low amount of NOx or nitrogen gas and chemical looping combustion where metal oxygen carriers provide O_2 for combustion by oxidation and reduction reactions.

Pre-combustion capture is done prior to combustion, where fuel is converted to syngas which consists of H_2, CO and CO_2. Separation of CO_2 or so called decarbonization of fuel is done via gasification, where CO_2 is captured from raw syngas. Usually pre-combustion technology is used for converting coal, NG or liquid fuels to syngas due to low emissions and easier fuel handling. (Teir 2009) Advantage for pre-combustion capture is easier separation of H_2 and CO_2 rather than separation from N_2 rich flue gases due to large difference between molar masses after combustion with post-combustion technologies. (Rackley 2010) Pre-combustion technology is commercialized technology with high capital, operating, fuel handling- and maintenance costs. Pre-combustion technology is utilized in integrated gasification combined cycle (IGCC) plants. IGCC technology enables the usage of low-quality fuels and poorly combustible materials. IGCC utilizes gas turbine to produce power and exhaust gas that is used to produce steam that is directed to steam turbine and there to condenser for district heating for example. (Teir et al. 2009)

Post-combustion capture technologies refer to a capture process that is done after combustion or conversion. Capture of CO_2 can be done with absorption or adsorption for example. (Teir et al. 2010) Variety of membranes can be also utilized to intensify CO_2 capture as well (Keskitalo 2013). Post-combustion technologies can achieve over 90 % capture rate by utilizing chemical solvents (Teir et al. 2010). Aqueous solvents are mostly utilized in post-combustion capture and this method is used and adopted by many industrial sectors (Berger & Bhown 2013). Chemical absorption is usually applied when the concentration of CO_2 is low and physical adsorption when concentration of CO_2 is high (Teir et al. 2010). Post-combustion is most researched method compared to others.

3.4 Capture technologies

Capture process is based on physical and chemical properties of the CO_2. In chemical absorption, CO_2 will dissolve in desired conditions and reacts with absorbent and is regenerated by stripping. (Teir et al. 2010) Technologies are dependent on the emission source and some compounds must be separated prior. Capture technologies don't separate 100 % of CO_2 and high capture rate for low concentration CO_2 streams is expensive. Capture installations depend on site specific properties such as size, efficiency, retrofitting potential and opportunity to utilize available low-grade heat, which can lead to cost reduction (IEAGHG 2010). Energy consumption of carbon capture system is referred to as a parasitic load, which affects the total amount of power generated in power plant due to capture system power demand. When choosing a suitable capture technology, there are some factors to consider (IEAGHG 2010) (Keskitalo 2013):

- Techno-economic benchmarking, user experience & technical evaluation
- Process risk assessment, scale-up challenges & future strategy
- Retrofit or design for new facility or process
- Finance and long-term commitment
- Global CO_2 capture R&D and commercial technologies
- Technical study assessing new technologies, development and innovations
- CO_2 capture potential and capacity
- Feed gas mixture properties
- Energy requirement
- Involvement with EU and CCS programs
- Environmental effects

Capture technologies in figure 2.3 like any other technical applications are divided into categories depending on the physical or chemical phenomenon that they are based on. There are commercial technologies and many novel technologies in development status, meaning either laboratory stage of small-scale piloting. (Rubin et al. 2010) These types of capture technologies are presented during next subchapters.

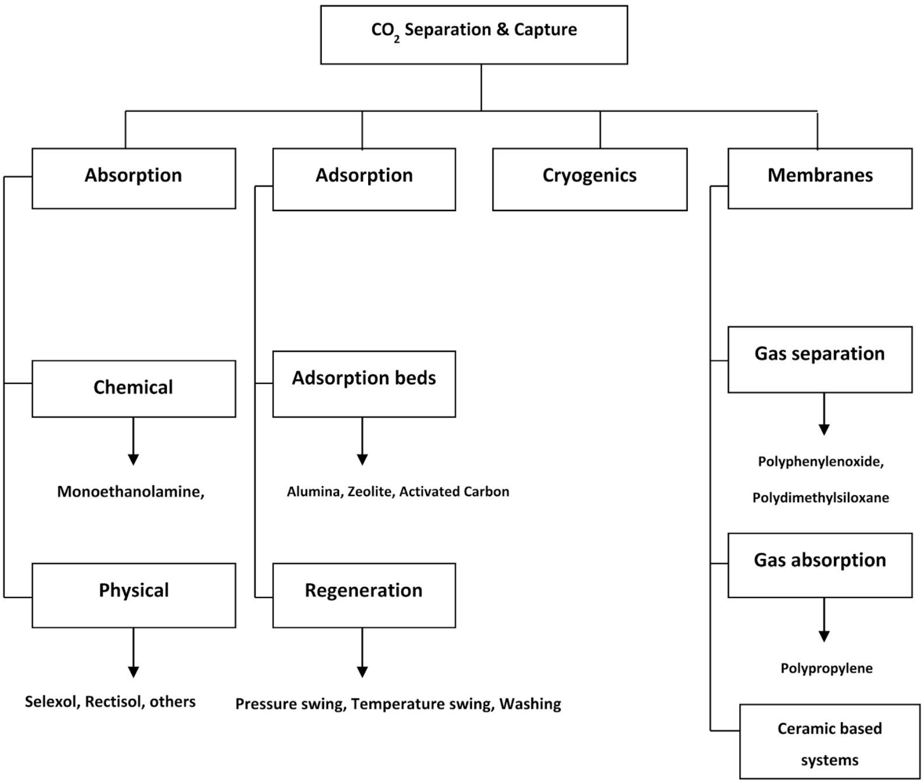


Figure 2.3. CO_2 capture technologies (Yoro & Sekoai 2016)

3.4.1 Absorption

According to Warren et al. (1986): "In gas absorption, a soluble vapor is absorbed by means of a liquid in which the solute gas is more or less soluble, from its mixture with an inert gas." Absorption is a physicochemical reaction, where substance is soluble and its atoms, molecules or ions enter to another substance, absorbent. The counter process for absorption is stripping where solvent is thermally regenerated. Stripping in chemistry means separation of component or components from liquid to gas by applying steam. (Kohl & Nielsen 1997) Absorption is mainly applied for purifying gaseous mixtures and for gas separation in chemical processes for components like H_2S, NOx and CO_2 (Mirzaei et al. 2015). Absorption based capture provides highly selective method for CO_2 capture (IPCC 2015). In general, low pressure absorption capture technologies that are most effective are also the ones with the largest regeneration energy input (CONCAWE 2011).

Post- or pre-combustion capture facility captures 85 - 90 % of the CO_2, though the values are not in technical limits or in optimal economic point (IEA 2007).

Absorption medium is called absorbent and the reaction is generally carried out in vertical absorber column in which the solvent is fed in countercurrent from the top of the column where direct contact with gaseous CO_2 and liquid solvent occurs (Ruthven 1997) (Mirzaei et al. 2015). Columns come in large variety and packed columns with regular geometric structures are typical design among others due to excellent performance with effective mass transfer and minimize pressure drop (Mirzaei et al. 2015) (Ruthven 1997). Packed columns are simple and provide cheap solution if diameter is reasonable. Packed columns are used mainly for corrosive gases, due to ceramic or plastic packing materials. The fundamental principles of gas absorption are solubility of gas known as capacity and the rate of mass transfer. (Ruthven 1997) Also, selected solvent musty have selectivity over N_2 when applied in post-combustion (Mirzaei et al. 2015). Driving force and mass transfer are important factors when sizing absorption equipment to determine absorption of a given amount of solvent per unit time. Mass transfer is "the rate at which the solute is transferred from the gas to the liquid phase". (Ruthven 1997)

Absorption can be used for high and low concentration streams and flue gas and NG are typical subjects for applications (Kothandaraman et al. 2009). Post-combustion solvent absorption can have capture rate around 90 % (Teir et al. 2010). With physical solvents, CO_2 dissolves into solvents surface in high pressure and is released when pressure decreases. Physical absorption has weaker bonds between CO_2 molecules and solvent molecules compared to chemical absorption (Teir et al. 2009) (Rubin et al. 2010). Heat or pressure is needed when bonds or forces between CO_2 and solvent are broken (IPCC 2005). As can be seen in figure 2.4, most of the capture technologies for refineries are limited to chemical solvent absorption due to low CO_2 concentrations in gas streams, except H_2 production. Alkaline solvents are effective due to CO_2 concentrations and low pressure. Variations between CO_2 partial pressures in gas streams affect the effectiveness of capture and cause variable recovery. Flue gases in refineries are at atmospheric pressure, and cause disadvantage for processes that require higher operating pressures. It mainly limits the utilization of physical solvents, which require high CO_2 concentration and partial pressure. (CONCAWE 2011)

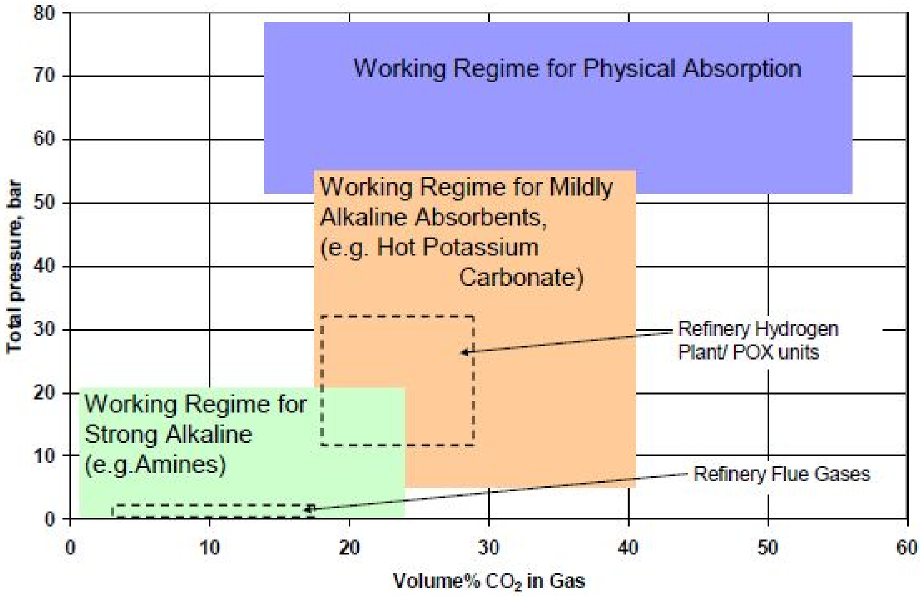


Figure 2.4 Capture technology selection for absorption (CONCAWE 2011)

Kohl & Nielsen (1997) divided absorption into three categories based on mechanism between substances in absorption; 1) separation based on physical solution, 2) separation based on reversible chemical reaction, and 3) separation based on irreversible chemical reaction. Physical absorption is dependent on CO_2 partial pressure (Figure 2.5), temperature and pressure whereas chemical absorption for CO_2 is based on acid-based neutralization reaction (Mirzaei et al. 2015).

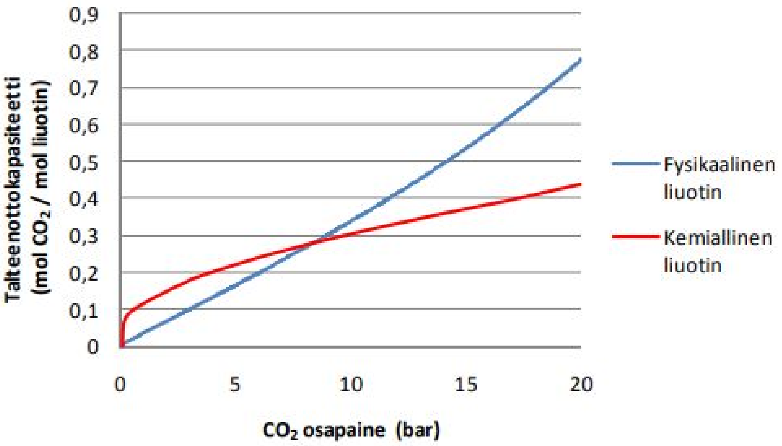


Figure 2.5 Solvent CO_2 capacity dependency on CO_2 partial pressure (red represents chemical solvents & blue represents physical solvents) (Teir et al. 2011b)

When utilizing absorption-based capture technology for CO_2, there are technical and economic factors to be considered according to IPCC (2005):

- Flue gas & solvent flow for absorber sizing
- Flue gas composition, CO_2 partial pressure, SO2, NOx, O2 and particles
- Capture rate, CO_2 solubility and capacity and their effects to capture cost
- Total energy consumption is determined by adding regeneration energy to equipment power consumption
- Environmental cost and toxicity (Mirzaei et al. 2015)

Chemical solvent treatment

Chemical solvents are based on reversible chemical reactions between solvent and CO_2 when its captured (Wang & Stiegel 2017). Thermally regenerable aqueous alkanolamine solvents are dominant technology for acidic CO_2, H_2S and S based compounds removal from industrial sour gases as those found from oil refineries (Weiland et al. 2004) (Kohl & Nielsen 1997). There are primary, secondary and tertiary amines and their structural characteristics play an important role in reaction chemistry between solvent and acidic compound causing different removal capabilities for different solvents. Alkanolamines react with sour gases when contacted and amine solvent acid and amine bases form a complex, a salt when reacting with acid gas. Chemical carbamate formation (salt), only occurs with primary and secondary amines because CO_2 reacts with amine molecules and firstly produce carbamate intermediate and secondary reacts with another amine group to form the amine salt. Due to previous reaction, primary and secondary amines can essentially achieve almost complete removal of acidic H_2S and CO_2. (Sheilan et al. 2015) Carbamate formed by primary and secondly amines is stable water-soluble compound and requires more energy to be reversed compared to tertiary amines (Keskitalo 2013) (Knuutila et al. 2019). Whereas, reaction rates and temperatures with primary and secondary amines are high, tertiary amines, absorption temperature is low, and the reaction rate is slow. (Knuutila et al. 2019) Lindsay et al. (2009) determine that amine absorption product CO_2 stream is ideal for sequestration for example and just requires dehydration and compression.

Absorption solvents behavior depends on its amino nitrogen group to react with acidic component and limiting factor for the reaction is its equilibrium (David & Jones 2008) (Keskitalo 2013). Each of the amine solvents have hydroxyl group that reduces solvent vapor pressure and at least one amino group that accounts for alkalinity. (Kohl & Nielsen 1997) (David & Jones 2008) Alkanolamines have three basic functional groups, an alcohol (hydroxyl), alkane (hydrocarbon) and an amino nitrogen (Figure 2.6) (Sheilan et al. 2015). Ethanol amines such as MEA and DEA are produced by the reaction between ammonia and ethylene oxide (Luis 2016).

It is critical to maintain the quality/activity of solvent, which is maintained by regeneration, temperature and with regenerative heat exchanges (IPCC 2005). Amine solvents have lower thermal stability compared to physical solvents and cannot be reused effectively due to thermal or oxidative degradation, which makes stripping more challenging (Mirzaei et al. 2015). It is important to minimize the solvent degradation and intermediate products such as nitrosamines and nitramines which are potentially harmful for humans and for the environment (IPCC 2005) (Leung et al. 2014) (Eide-Haugmo et al. 2009). Also, ammonia and aldehydes could be a concern (Voice & Rochelle n.d.). Environmental effects only occur when amine solvents evaporate from absorber column unintentionally (Luis 2016). Amines also tend to break down because the influence of SO_2, NO_2 and O_2 in the flue gas. Additive chemicals are needed for those compounds and for pH optimizing and corrosion reduction. (Linnanen 2018) Corrosion by amines is the limiting factor for amine concentration in capture solvents and creates additional cost due to more dilute aqueous solutions (Mirzaei et al. 2015). More chemical absorption properties can be seen in appendix 5.

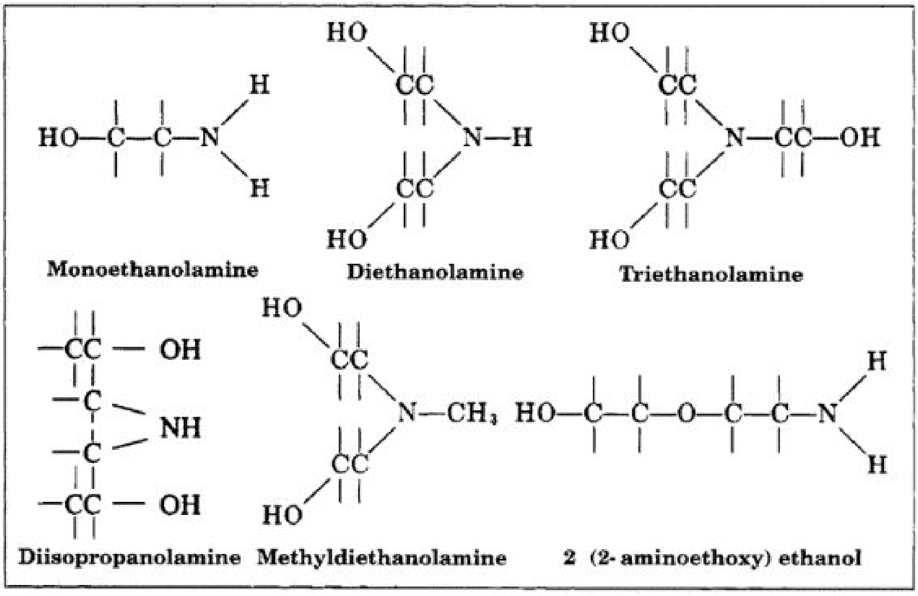


Figure 2.6 Alkanolamines structural formulas (Kohl & Nielsen 1997)

Additives can also be used to improve CO_2 absorption. Dang & Rochelle (2003) in their study stated that MEA and MDEA solvents can be modified by adding piperazine as a promoter. Piperazine addition to aqueous MEA as 0,6 - 1,2 M, resulted in 1,5 to 2,5-time better absorption rate compared to traditional aqueous MEA. (Dang & Rochelle 2003) PZ should increase the absorption rate of CO_2 and the capacity of absorbed CO_2. PZ is less sensitive to thermal degradation and decreases thermal and oxidative degradation of MEA. Piperazine has potential to reduce operating costs. (Fisher et al. 2007)

Aqueous amine solvents can form heat stable salts, which are thermally unregenerable compounds that are formed during scrubbing process. These salts are reaction products between alkaline amines and organic/inorganic acids, which can influence significantly to scrubbing process even in low concentrations. (Weiland et al. 2004) Heat stable salts are formed when other acidic components than H_2S or CO_2 react with amine. The salts formed by H_2S or CO_2 during gas sweetening operation are weak intermediate products that can be reversed by applying heat in regeneration stage at stripper column. Other salts have more tightly bonds and are called heat stable salts due to undesirable quality. These salts cause the corrosion and erosion of metal components in process equipment (Figure 2.7). (Sheilan et al. 2015)

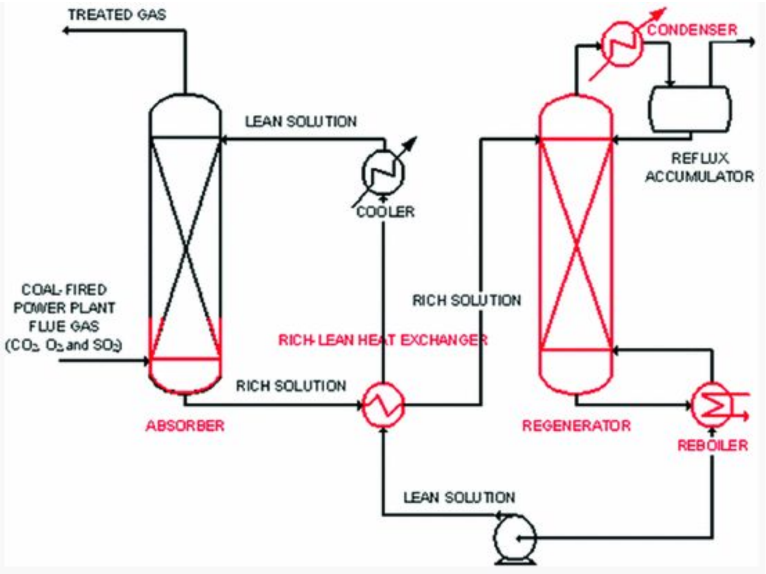
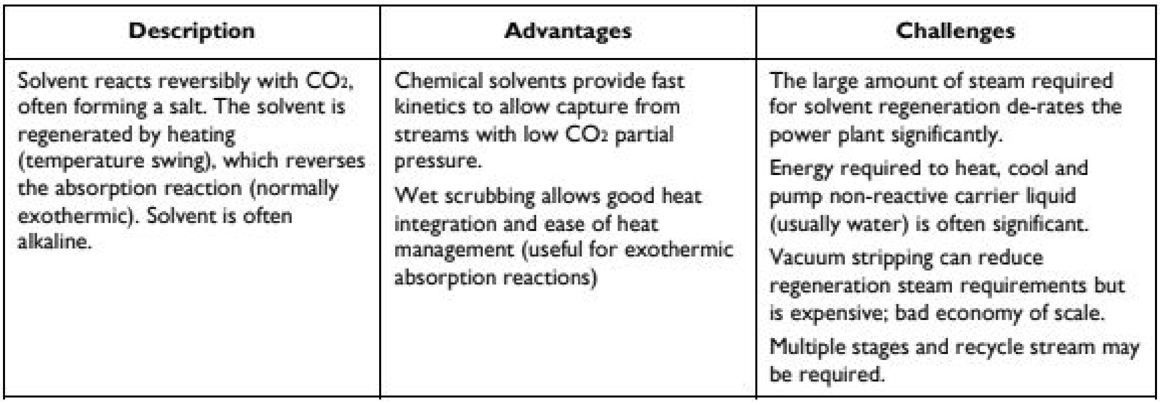


Figure 2.7. Potential heat stable salt corrosion and accumulation positions (Liu et al. 2018)

Table 2.1 Chemical solvent absorption advantages and challenges (Rubin et al. 2010)



Description	Advantages	Challenges
Solvent reacts reversibly with CO_2, often forming a salt. The solvent is regenerated by heating (temperature swing), which reverses the absorption reaction (normally exothermic). Solvent is often alkaline.	Chemical solvents provide fast kinetics to allow capture from streams with low CO_2 partial pressure. Wet scrubbing allows good heat integration and ease of heat management (useful for exothermic absorption reactions)	The large amount of steam required for solvent regeneration de-rates the power plant significantly. Energy required to heat, cool and pump non-reactive carrier liquid (usually water) is often significant. Vacuum stripping can reduce regeneration steam requirements but is expensive; bad economy of scale. Multiple stages and recycle stream may be required.

Chemical solvents are generally less expensive than physical solvents and can achieve a more complete removal of CO_2. Amines can achieve 98.5 % purity when operating at 0.5 - 1.5 bar (Colloidi & Wheeler) They are also more utilized due to their ability to capture CO_2 with low partial pressure at higher capacity. Chemical solvents have higher CO_2 absorption rate and their thermal and chemical stability are also suitable for low concentration CO_2 capture. Most of the developed absorption applications are chemical based and are done with aqueous amines, ammonia and carbonates for example. (Keskitalo 2013) More information can be seen in table 2.1. Requirements for chemical CO_2 absorption solvent selection set by Keskitalo (2013):

- High reactivity & fast reaction kinetics with CO_2
- Low regeneration energy & high absorption capacity
- High thermodynamic stability & low solvent degradation
- Low environmental impacts and harmfulness (health and corrosivity for equipment)
- Solvent price, availability and easy to recover

There are various solvents available for CO_2 separation, and the most common is the monoethanolamine MEA (Teir et al. 2009). Diethanolamine DEA is also widely used and there is a mixture of MEA and DEA called MDEA. Research about MEA is currently focussing on minimizing the regeneration energy. (Luis 2016) One top of the line, solvent research facility is Technology Center Mongstad in Norway. They do research and test various solvents for CO_2 absorption and can develop modified custom solvents to meet client's needs. They also provide testing site for companies to study novel solvents in practice. IEAGHG (2010) requirements for solvent based capture process:

- Can be retrofitted to existing facility
- Is proven technology
- Large research base and continuous R&D
- Energy penalty
- Capital cost and commitment
- Experience and data from other facilities
- Capture solvent degradation, evaporation and corrosiveness challenges
- Environmental impacts

Typical aqueous MEA solution contains 20 - 30 % MEA by weight in water and additives for preventing foaming and equipment corrosion. (Teir et al. 2009) It can also be mixed with some other non-reactive solution. Additives can also cause foaming and evaporation of the solvent (Rochelle & Jassim 2006). MEA oxidizes when air is present, so the storage must be air sealed and inert gas can be used to protect solvent and avoid premature oxidation. (David & Jones 2008)

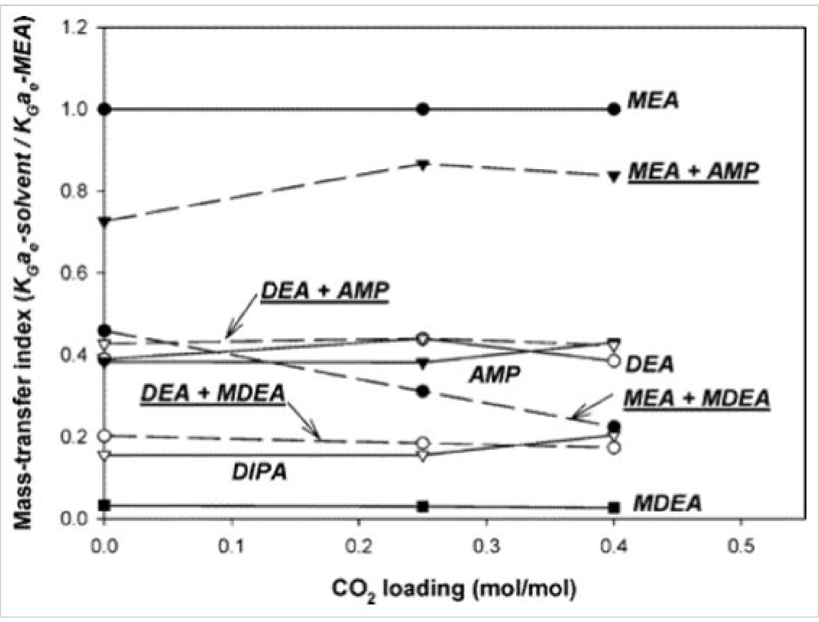


Figure 2.8 Amine solvent mass transfer coefficients. (Aroonwilas & Veawab 2004)

Amine treatment is mostly utilized for H_2S removal due to its harmfulness, but in the case of CO_2, solvent should be selective over H_2S (Kohl & Nielsen 1997). MEA solvent is non-selective when absorbing acid gases and H_2S absorbs faster than CO_2 and the difference between compounds isn't that large that separation could be available. There is a small difference in molar masses between the two compounds and MEA absorbs them by mole-to-mole basis, see figure 2.8. Absorption capacity refers to a solvents ability to bind CO_2,which is also referred to as solvent loading. MEA has the lowest molecular weight between all available amine solvents which means its capture capacity for acid gases occurs by unit weight or volume basis. (David & Jones 2008) Huertas & Garzon (2015) stated that nominal absorption capacity of MEA is 720 gCO_2/kg MEA. To achieve nominal capacity, very high pressure is required. (Huertas & Garzon 2015)

CONCAWE (2011) divided CO_2 capture via amine scrubbing into five steps:

- Flue gas cooling, ash removal, SOx removal and water content reduction
- Compression of flue gas with fan to overcome pressure drop

- MEA injection in absorber for CO_2 absorption
- Flue gas release into the atmosphere after MEA capture
- Rich solvent routing to Stripper for regeneration and lean solvent back to absorber

CO_2 scrubbing is done at 40 - 65 °C, but operating temperatures can be as moderate as 15 - 35 °C while pressure can go up to 70 bar. (Teir et al. 2010) (Knuutila et al. 2019) MEA and amines generally have few disadvantages when applied to flue gas capture, thermal degradation, chemical degradation and corrosivity (Fisher et al. 2007). also, amines degrade after 125 °C and destruct around 150 °C (Rochelle & Jassim 2006). According to (van der Giesen et al. 2017) amines are consumed during operations and typical consumption of MEA that has to be supplemented is around 0,5 - 3 kg/tCO_2 captured in power plant operations. Due to low temperature resistance, amine regeneration cannot utilize superheated steam as an energy source in power plants. There are water scrubber applications that are applied to amine scrubbers by fitting the water unit to the top of the amine scrubber for preventing evaporated solvent to escape by cooling and condensing (Pfaff 2010).

Thermal degradation is an operating feature that can be managed via cooling, but chemical degradation means that flue gas treatment must be done prior to capture (IPCC 2005). Voice & Rochelle (n.d.) estimated that absorption solvent degradation can be responsible for 10 % of the total CO_2 capture costs due to decreased capture system performance, solvent compensation costs and reduced equipment lifetime. When MEA is degraded, ammonia is formed and emitted into the atmosphere. Ammonia emissions are estimated to be around 0.136 kg NH_3/tCO_2 captured, though lower values have been reported. Also, MEA by itself is emitted and normally evaporation is around 0.014 - 0.063 kg MEA/tCO_2 captured. (van der Giesen et al. 2017) Minimizing the solvent oxidation is important and solvent make up will reduce system performance and can add capture costs by 1 - 2 \$/tCO_2 captured. (Voice & Rochelle)

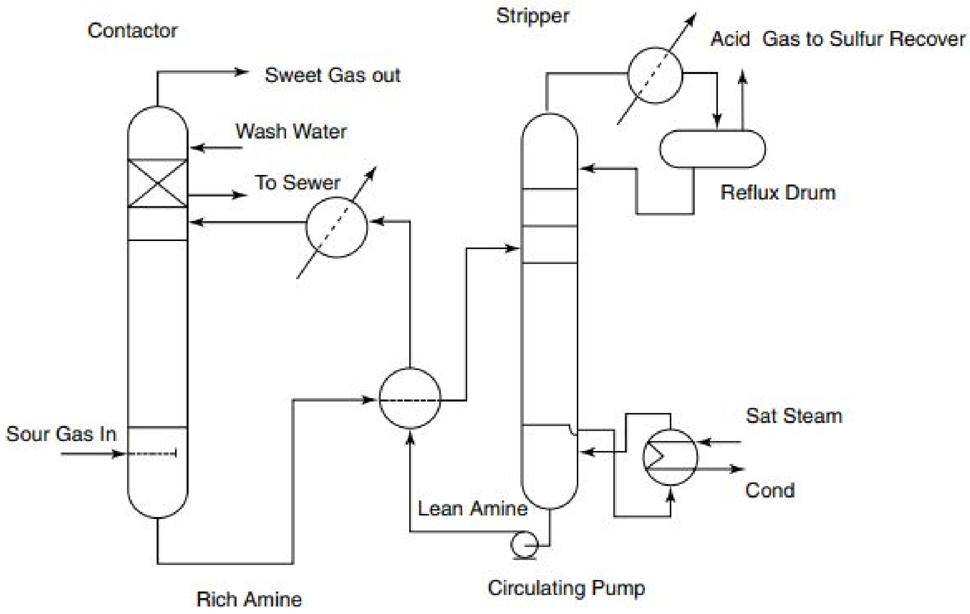


Figure 2.9 Post-combustion amine scrubbing process (David & Jones 2008)

Absorber is the largest and the most expensive part of amine treatment equipment and its sizing is done based on CO_2 concentration and feed gas flow (Figure 2.10). Absorbers metallic packing structure ensures evenly flow of gases and liquids. Packed column structure provides the contact area for absorption and there are specially designed liquid distributors for amine solvent. As the flue gas mixture flows upwards in absorber, counter current sprayed solvent captures CO_2 and rest other gases head to water wash. Concentration of CO_2 in flue gas stream decreases steadily during flow upwards in absorber and at the same time CO_2 content in amine solvent increases steadily. Water wash in absorber is the secondary action to treat hot gases and recover amine solvent so that loss of solvent is reduced and to protect the environment from harmful amines. After water wash, “sweet gas” or “decarbonized gas” without CO_2 is released into the atmosphere and the CO_2 rich solvent is routed to stripper where the addition of steam will reverse the absorption and the solvent is regenerated as in figure 2.9. (Technology Center Mongstad 2010) Higher degree of purification can be achieved by vacuum, inert gas stripping or applying heat to solvent (Tande et al. 2013).

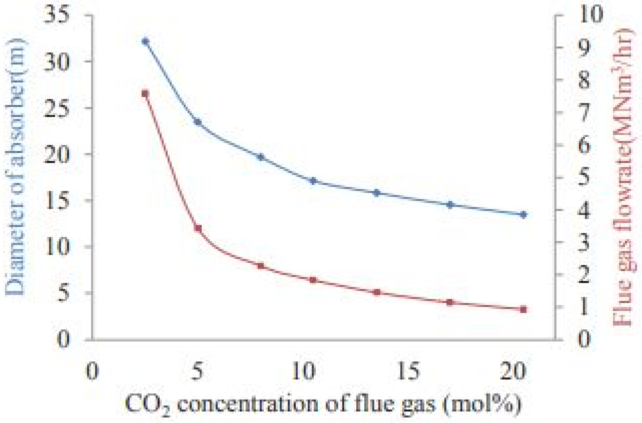


Figure 2.10 Illustration of CO_2 concentration effect on absorber sizing and flow rate with Aspen Plus simulation (Husebye et al. 2012)

Desorber is also a column with structured packing and much smaller than absorber due to lower gas volume and less need for contact area because reverse reaction is done via heat (Technology Center Mongstad 2010). Reactions between CO_2 & H_2S and solvent are reversed via steam approximately at 118 °C and 69 kPa (Stewart & Ken 2011). In stripper, CO_2 rich amine solvent is fed into column from the top and steam is fed to the bottom of the column where it rises to get contact with amine solvent. (Technology Center Mongstad 2010) Due to contact with the heat, preheated solvents bonds break between acidic component and amine (Stewart & Ken 2011). The amine solvent that has gone through absorber pre-heated in crossflow heat exchanger where energy is collected, and too early release of CO_2 is prevented. Solvent then heated up to 120 °C in reboiler where the CO_2 is stripped off. (Teir et al. 2010) Reboiler is utilized to transfer heat from steam to solvent indirectly and is accountable for most of the energy consumed in regeneration. Regeneration energy is referred sometimes as “reboiler duty”. (Jung et al. 2013) When aqueous solvent is heated in the bottom of desorber, steam is produced by vaporizing solvent and it provides the heat reverses the absorption and strips the CO_2 (Technology Center Mongstad 2010).

Stripper column has a reflux system that supplies water for CO_2 wash before leaving the stripping section. Washed vapors are condensed with cooled condenser and the residual steam is separated from CO_2 stream and can be utilized in reflux system. (Technology Center Mongstad 2010) Absorber operation pressure is around or slightly over 1.0 bar whereas stripper can have higher pressure than absorber but nowadays, vacuum strippers are used to boil solvent with low-pressure steam that reduces energy consumption (Liu et al. 2018). Temperatures in the absorber and stripper are generally in the range of 40–60°C and 120–140°C respectively (Technology Center Mongstad 2010). Stripper column can be divided into several sections where different operation pressures done by compressors can effectively release the CO_2 from the solvent. (Liu et al. 2018)

Amine process have adopted the reclaimer system that takes the side stream of amine solvent, around 3 %, that is pumped through charcoal filter that clean the impurities from the solvent during operation. Reclaimer in MEA operation is located at the bottom of the stripper where solvent is heated to boil the water while some heat stable salts are retained. reclaimer is used periodically and collected impurities are discharged from the system with low amounts of solvent. (Stewart & Ken 2011)

Reaction enthalpy in CO_2 absorption process with MEA is exothermic and reverse reaction is endothermic, which means that heat must be applied for regeneration (Technology Center Mongstad 2010). Liu et al (2018) estimated that regeneration energy demand accounts for approximately 80 % of the total solvent capture systems energy consumption. Chemical solvents used for CO_2 absorption, require 2.7 to 3.3 GJ/tCO_2 captured depending on the process (IPCC 2005). Hamborg et al. (2014) performed numerous MEA CO_2 capture simulations with Aspen Plus software for typical flue gas and thermal energy demand varied between 4,06 to 4,16 GJ/tCO_2 and recovery rate varied between 91,3 % and 95,5 %. Recovery rate was defined as "Ratio of the sum of the CO_2 flow in depleted flue gas and the product CO_2 flow divided by the CO_2 flow in the flue gas supply". (Hamborg et al. 2014) Luis (2016) reported 3,2 - 5,5 GJ/tCO_2 range for 30 %wt MEA solvent regeneration and 2,9 GJ/tCO_2 in more recent study with 35 % MEA and advanced stripper configurations. Merikoski (2012) estimates that commercial amine-based technologies energy demand could be as high as 5 - 6,5 GJ/tCO_2. Generally, CO_2 concentration in the feed gas has a direct effect to reboiler duty and power consumption as seen in figure 2.11.

According to Yu et al (2012): “the theoretical minimum energy required for recovery of CO_2 from a flue gas and compression of CO_2 to 150 bars is 0,396 GJ/ton CO_2.” Many solvents are aqueous mixtures of water and some absorption agent. These solvents are in straight contact with flue gas or other feed gas that contain CO_2. (Yu et al. 2012) Regeneration energy is accountable for 1⁄4 to 1⁄3 of steam consumption in coal fired power plant (Hongqun et al. 2008). When steam is utilized for regeneration instead of power generation, total efficiency of power plant can decrease 20 - 35 % (Nummelin et al. 2015) or according to Teir et al. (2010) 9 - 15 percentage points. That kind of efficiency reduction is notable. (Nummelin et al. 2015)

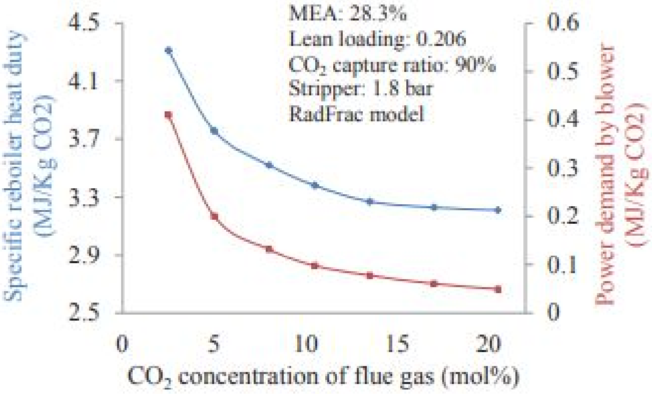


Figure 2.11 Illustration of MEA regeneration energy demand in Aspen Plus simulation (Husebye et al. 2012)

In addition, regeneration process requires electrical energy for pumps, fans and compressors, so the average electricity consumption per captured ton of CO_2 is between 0,06 - 0,11 GJ/t CO_2 (IPCC 2005). Rochelle & Jassim (2006) simulated and tested the MEA solvent energy consumption for CO_2 absorption to be 0,878 MWh per t/CO_2. This energy consumption has been reduced by adding MDEA solvent to MEA resulting 3,33 MWh reduction to energy consumption per t/CO_2 captured (Rochelle & Jassim 2006). Rochelle (2009) states that for a practical operation, an energy consumption of 0,72 GJ/t of

CO_2 is hopefully achieved. Since the absorption-based capture is usually applied to low concentration CO_2 streams, it causes elevated energy penalty due the need to reach 95,5 % CO_2 purity for further applications and their purity requirements (Appendix 2). US national energy technology laboratory estimated post-combustion capture to increase electricity production cost by 70 % (Leung et al. 2014). Furthermore, current novel amine-based solvents offer around a 25 % cost reduction compared to traditional MEA and even then, the capture costs are still about 3 - 4 times the current ETS trading value (van Straelen et al. 2009). Generally, investment cost reduction, new absorption solvents and reduced regeneration energy are required for this technology to be attractive.

There is an industrial case study by Digne et al. (2014) about technical and economical evaluation of FCC capture, where absorption via 40 wt-% MEA was employed. Capture was done by evaluating HiCapt+™ pilot technology that is modified amine absorption process with pre-treatment of wet- and dry-scrubbing of flue gas. Used MEA solvent is added with high performance oxidative inhibitors that reduce solvent oxidation and solvent has higher amine concentration. It was found that FCC flue gas requires prior treatment before capture and flue gas had to be cooled down to 50 °C before entering the absorber. Wet-scrubbing and dry-scrubbing for flue gas were applied for flue gas to reduce temperature, SO_2 and particulate matter. Also, electrostatic precipitator was needed to meet particle emission levels. It was concluded that HiCapt+™ requires between 3,1 - 3,3 GJ/tCO_2 for solvent regeneration and reached 74 % capture of FCC CO_2 emissions which accounts for more than 14 % of study size refinery total CO_2 emissions. Price of capture CO_2 ton was determined to be 75€. This cost can be reduced by better compressors, applying low-pressure steam in back pressure turbine and recovering excess heat from process and flue gas cooling. (Digne et al. 2014) All in all, challenges remain yet to be solved with FCC capture and large volumes can cause scaling problems. When applying capture for such a large source, transport, compression and storage of CO_2 should be solved beforehand.

Physical solvent treatment

In physical absorption, some components of the feed mixture are more soluble for selective absorbent and interact with absorbent. When physical solvent is applied to capture, no chemical reaction takes place between feed gas and the absorbent. (Mirzaei et al. 2015) Generally, physical solvent absorption process is more complex compared to amines but can be economically more attractive (Sheilan et al. 2015). Physical solvents rely mass transfer of gas molecules and capacity which are greatly dependent on Henry's law, feed gas temperature and the partial pressure of CO_2 (Maroto-Valer 2010) (Svensson et al. 2013). Desired operating temperature is lower, and pressure is higher than with chemical solvents. Physical solvents are most effective in low temperatures and cooling of feed gas is essential for effective absorption. (Mirzaei et al. 2015) Also, physical absorption is utilized when the concentration and partial pressure of CO_2 are high, which means physical absorption is not applicable for flue gas capture due to low partial pressure, high temperature and flue gas pressurization (Mirzaei et al. 2015) (Teir et al. 2009). Typically, CO_2 should have concentration > 30 % and partial pressure of 0,7 MPa. (CONCAWE 2011)

Many of the used physical solvents are organic and used for acidic components (Mirzaei et al. 2015). Typical currently available solvents are for example selexol (dimethyl ethers of polyethylene glycol), rectisol (methanol), purisol (N-methyl-2-pyrrolidone), fluor solvent (propylene carbonate) and ammonia (Alexandre et al. n.d.). Rectisol is well known process and employed methanol capture is operated at - 30 to 60 °C, which means refrigeration duty is required via refrigerant and electricity is consumed to maintain operating conditions. CO_2 partial pressure should be > MPa and usually, capture rate is between 60 - 75 % though rectisol can be used to capture multiple components. Disadvantages for rectisol are complex process, high refrigeration duty, high operating costs and high solvent evaporation. (Miller 2015)

Physical solvents are used for acid gas removal from NG and syngas streams. Hydrocarbons are also soluble to physical solvents and as the weight of hydrocarbon increases, its solubility increases. Hydrocarbon solubility is the main reason that physical solvents are mostly applied to gasification syngas than steam reforming syngas due to hydrocarbons in the feed gas. Solvents selectivity can be increased by using multiple solvents simultaneously. (Tande et al. 2013) Unlike in chemical absorption, physical solvents are nonreactive to feed gas and avoid the formation of heat stable salts (Rackley 2010). Physical solvents favor low temperatures that increase the acidic compounds solubility, although the temperature isn't as major factor than pressure. Some physical solvents require stripping in addition to pressure swing but reboiler duty requirements are much lower. Physical solvents work for bulk removal also. (Stewart & Ken 2011)

Advantage for physical solvents is their lower heat demand for regeneration, although it also necessitates lower operating temperatures at the absorption stage to achieve high solvent loading without early release. More Solvent loading capacity is directly proportional to the CO_2 partial pressure and physical absorption favors high pressure conditions. (Rackley 2010) According to Tande et al. (2013): “The regeneration step for selexol can be carried out by either thermally, or flashing, or stripping gas depending on the process design, treated gas required specifications and acid-gas composition.” In flashing, rich solvent from the bottom of absorber is regenerated in stages via pressure swing. Pressure swing causes acidic components partial pressure decrease and the acid component evolve to the vapor phase and is separated. (Stewart & Ken 2011) Physical solvents typically have lower overall regeneration energy demand when compared to chemical solvents but the main disadvantage is the solvent acid components loading, which is determined entirely by the components partial pressure in this case CO_2 (Svensson et al. 2013). Physical absorption also provides opportunity for partial regeneration by reducing pressure which decreases regeneration energy consumption (Tande et al. 2013). Some physical solvents must be regenerated via stripping, or it can be used for effecting the regeneration and improve solvent loading by more complete removal of CO_2 from the solvent (Stewart 2014). More physical absorption properties can be found in appendix 4.

Key parameters for effective physical absorption are feed gas flow and the solvent circulation rate that affects absorber sizing and every other equipment. Most critical factor is the feed gas and solvent contact temperature, which in lower temperatures improves solvent capacity and reduces the solvent amount. Low temperature also benefits acid gas solubility to solvent and it minimizes the hydrocarbon loss in syngas. Need for higher partial pressure of CO_2 and pressure is a challenge and feed gas pressure must be increased to the level that physical absorption would be more effective than chemical. Syngas presents one potential target for high pressure and partial pressure source of CO_2. (Tande et al. 2013)

There is no stoichiometric limit for physical absorption as in chemical one, which means that physical solvents could have potential to capture more CO_2 in favorable operating conditions (Mirzaei et al. 2015). Most of the traditional flue gases are N_2 rich which means that energy is wasted by compressing large amount of feed gas for capturing small amount of CO_2. This is the main reason with low CO_2 concentration why chemical absorption is used for flue gas. Physical absorption is not economical or applicable capturing CO_2 from flue gas. (Rackley 2010) (Mirzaei et al. 2015) Physical solvents need to have low vapor pressure in ambient temperature to prevent solvent loss, low viscosity and be non-corrosive and non-reactive. (Tande et al. 2013)

However, there are some challenges such as pressure loss of feed gas and CO_2 during separation due to flash drums which operates in atmospheric pressure. Also, low temperatures present an economic challenge because solvent refrigerating isn't cheap and feed gas must be effectively cooled also. If syngas or raw H_2 product is used as a feed, they must be preheated again before further processing. Also, H_2 can be lost with CO_2 during process though this isn't a problem with PSA tail gas. These challenges cause energy penalty and require additional equipment. (Tande et al. 2013)

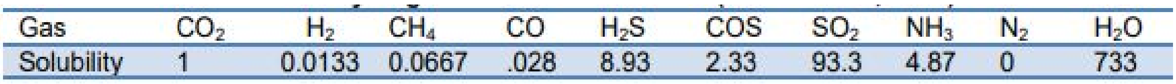
Selexol

Dimethyl ethers of polyethylene glycol (formulation of $CH_3(CH_2CH_2O)nCH_3$, where n is between 3 and 9) is a physical solvent that has a trade name Selexol (Tande et al. 2013) (Maroto-Valer 2010). It is used in physical absorption of acid gases from NG and syngas mostly and was commercialized in the 1970s. Selexol process is very similar to earlier presented amine treatment but with cooled feed gas stream (0 - 20 °C) and flash drums that separate the liquid components. Feed gas for selexol process should have 5 - 60 % of acid gas by volume at feed pressure of 2 - 16 MPa and CO_2 partial pressure of 0,7 - 3 MPa. (Rackley 2010) Mokhatab et al. (2014) suggest that acid gas components should have at least 50 psi (3,45 bar) partial pressure, whereas Alexandre et al. state that physical absorption can be utilized when CO_2 gas concentration is between 15 % to 40% in the feed gas and has high partial pressure so that physical solvents could be applied advantageously.

Selexol can achieve approximately 85 % CO_2 removal and is economical when acidic components have high partial pressure and heavy end hydrocarbons are absent from feed gas. Process normally don't meet the pipeline requirements due to feed gas and many impurities are co-absorbed as well. Diisopropylamine (DIPA) can be added to selexol solvent to meet the pipeline requirements, though it increases the stripper heat duty when regenerated by stripping. (Stewart & Ken 2011) Depending on purpose, selexol can be optimized for either trace- or bulk removal of acidic components. Operating temperature must be kept low to ensure high CO_2 loading to solvent and also maintain partial pressure of H_2O low due to its over 730 times greater solubility to selexol compared to CO_2 as in table 2.2 (Thande et al. 2013). Due to high H_2O and hydrocarbon solubility to selexol, it can be used as a dew point control method (Svensson et al. 2013). Presence of heavy hydrocarbons and aromatics should be evaluated case by case for selexol functionality (Stewart & Ken 2011). Every physical absorption process has advantages relative to the others in certain applications and according to Stewart & Ken (2011) at least the following facts should be considered when planning to apply physical solvent:

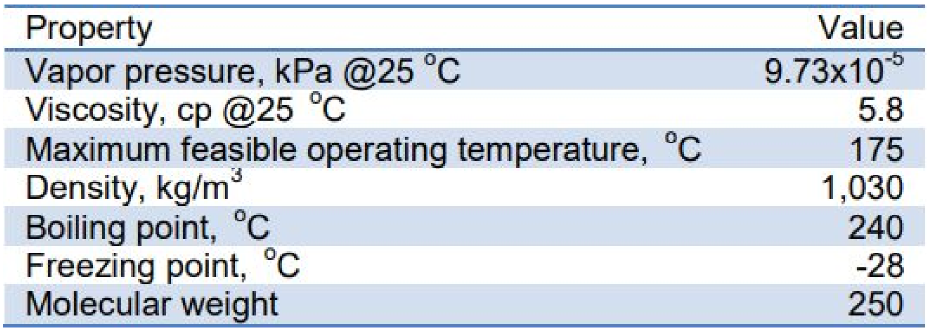
- Acidic components present in the feed gas
- Concentration of each contaminant and degree of removal desired
- Volume to be treated along with temperature and pressure
- Selectivity or feasibility of recovering desired component or co-absorption

Table 2.2 Different components relative solubility to Selexol solvent (Tande et al. 2013)



Gas	CO_2	H_2	CH_4	CO	H_2S	COS	SO_2	NH_3	N_2	H_2O
Solubility	1	0.0133	0.0667	.028	8.93	2.33	93.3	4.87	0	733

Table 2.3 Selexol solvent basic properties (Tande et al. 2013)



Property	Value
Vapor pressure, kPa @25 °C	9.73x10^{-5}
Viscosity, cp @25 °C	5.8
Maximum feasible operating temperature, °C	175
Density, kg/m^3	1,030
Boiling point, °C	240
Freezing point, °C	-28
Molecular weight	250

Selexol is typically operated between 5 - 40 °C. Compared to other physical solvents, selexols has the ability to operate in those temperatures which reduces costs by reducing the refrigeration duty (Table 2.3). (Maroto-Valer 2010) Size of selexol molecule ensure the desired vapor pressure and good viscosity to prevent solvent losses via evaporation and lower pumping costs respectively. Selexol process is offered for license for example by Universal Oil Products UOP, which is part of Honeywell that also produces selexol solvent. (Tande et al. 2013)

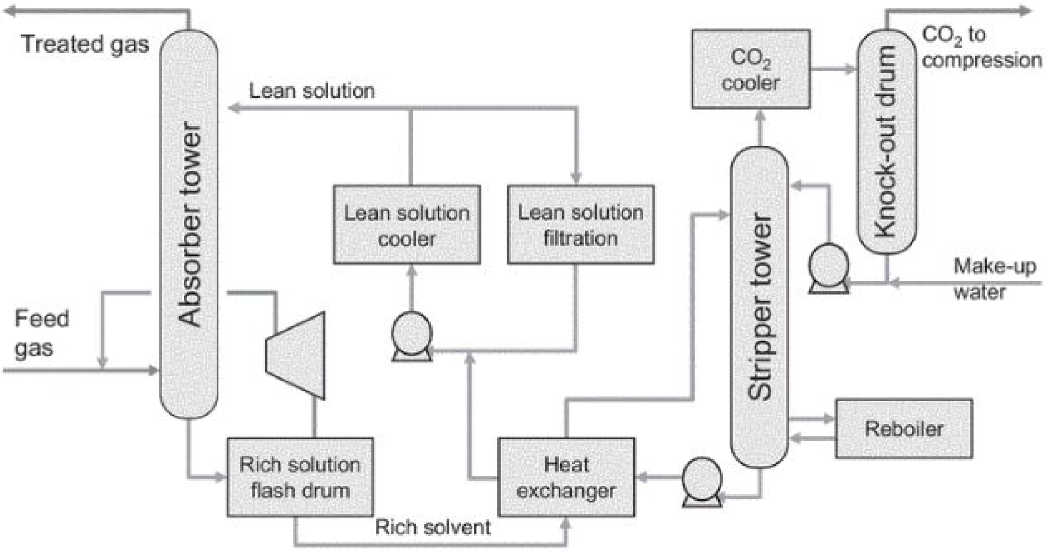


Figure 2.12 Schematic selexol process (Rackley 2010)

Selexol has low vapor pressure compared to amines and other physical solvents and has high capacity for CO_2 absorption in favorable conditions due to oligomer end group methyl ether. Oxygen in the methyl ether group increases CO_2 solubility to solvent by Lewis base interaction with CO_2 molecule. It also has wide operating temperatures and good selectivity when removing acidic components. (Tande et al 2013) Selexol process flow chart in figure 2.12 exhibits typical physical absorption system where the stripper pressure/temperature swing or intermediate flash drums allow recovery of co-absorbed syngas components such product H_2 and CO to be recovered (Miller 2017). Selexol advantages according to Tande et al. (2013) are:

- High capacity for acid gases
- Very low vapor pressure that limits its losses to the treated gas
- Low viscosity to avoid large pressure drop
- High chemical and thermal stability
- Nontoxic, non-corrosive and inherently non-foaming
- Compatibility with gasifier feed gas contaminants
- High solubility for HCN and NH_3
- Low heat requirements for regeneration
- High flash point ensures ease and safety in handling

- Requires no mixing, formulating, diluting or activating agents
- A fairly wide range of operating temperature (-18 to 175 °C)
- High loadings at high CO_2 partial pressure- reduces recirculation rate
- High affinity for water so it simultaneously dehydrates the gas stream

Lemonidou (2017) states that latest selexol process, modeled by Spallina et al. (2014) has a reboiler duty of 189 kJ/kgCO_2 and power consumption of 303 kJ/kgCO_2 at 200 °C conditions for reboiler. Energy for compression was reported to be 252 kJ/kgCO_2. At the same operating conditions, MDEA solvent was compared to selexol and its reported regeneration energy and electricity demand were 887 kJ/kgCO_2 and 84 kJ/kgCO_2. (Lemonidou 2017)

Guo et al. (2012) studied physical absorption power requirement and separation efficiency for simplified selexol process by utilizing Aspen Plus simulation software. Selexol was used to separate CO_2 from crude synthetic NG (SNG) and upgrade its heating value and reduce its volume. Selexol process is an alternative for other available technologies such as absorption via alkaline solvents, membrane permeation and adsorption. When selecting suitable technology for CO_2 removal from crude SNG, partial pressure of CO_2, temperature, pressure and facility size should be considered. Guo et al (2012) state that CO_2 capture via selexol absorption achieves reasonable energy demand separation For CO_2 capture from CHP plant, PSA was reported to have energy demand of 459 kJ/kgCO_2, while MEA and DEA solvents have energy demand around 275 kJ/kgCO_2. When considering crude SNG composition, selexol, PSA and membranes are reported technologies to be suitable for CO_2 separation. Guo et al. (2012) reported that another research group had studied different designs of membrane systems for SNG CO_2 removal and determined the optimal power consumption for the system to be about 620 kJ/kgCO_2 due to pressurization. (Guo et al. 2012)

Guo et al. (2012) determined physical absorption via selexol to be the most attractive solution and in the case of raw SNG containing over 10 % CO_2. Physical absorption achieves to keep the energy demand on reasonable level with high potential for large industrial scale applications. Generally, physical solvents have no stoichiometric limit for CO_2 loading and solubility of solvent is dependent either high partial pressure or low temperature. Either one of the factors can lead to higher solubility and solvents performance can be estimated by its solubility at the given conditions. (Guo et al 2012)

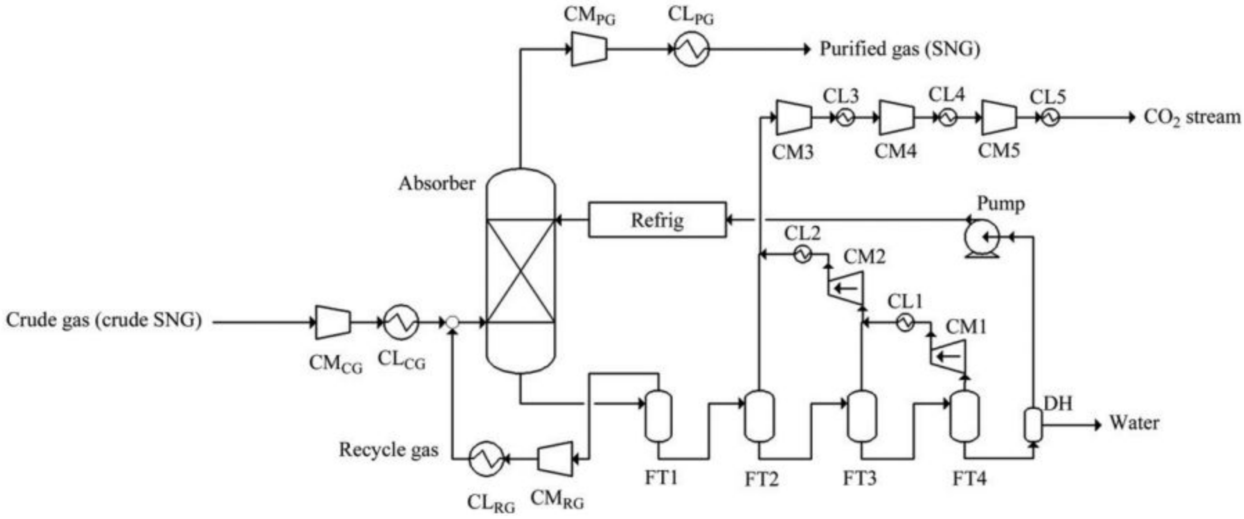


Figure 2.13 Flow sheet of selexol process for CO_2 separation (Guo et al. 2012)

Figure 2.13 presents the general flow sheet by Guo et al. (2012) for selexol capture, where raw SNG is compressed prior to capture. Before feed gas is fed to absorber, feed SNG is mixed with recycle gas from the first flash tank FT1 what separates the liquid and gaseous substances. Mixed raw SNG is fed to the absorber and selexol is sprayed counter current. Flash tanks are used for multistage separation of CO_2 and as in figure 2.12 & 2.13, CO_2 is separated at every flash tank during stripping and selexol is simultaneously regenerated. FT1 is operated at 6 bar and FT2 - 4 at 4.2, 2.3, 1 bar respectively. CO_2 released from secondary or further flash tank can be considered as a waste. After FT4, selexol is dehydrated, its pressure is increased via circulation pump and it flows through refrigeration unit before entering absorber. There is no reboiler duty due to the nature of selexol process and only electricity consumption should be considered. Heat can be used for regeneration, but pressure swing is more economical and simpler to arrange. (Guo et al. 2012)

Flow rate of solvent is first variable to be solved when designing selexol process and secondly removal performances of flash tanks should be determined, which has straight effect on compressing the separated CO_2 and recycle gas in the first flash tank. It must be noted that solvents temperature increase will influence the selexol flow rate. According to Guo et al. (2012), there are typically two main reasons for solvent temperature increase; 1) heat transfer between feed gas and selexol, and 2) the absorption heat of removed gases. Due to the possibility of solvent temperature increase, cooling every stream that enters to absorber is advised. There should not be any heat transfer between feed gas and the solvent. Guo et al. (2012) designed their absorber to operate in 25 °C and the solubility of selexol was predicted at 25 °C. Operating pressure for absorber and syngas was set at 15 - 30 bar. Error in solvent mass flow modeling could influence systems power demand. In addition, selexols temperature increases about 2 °C due to compression in flash tanks and it creates a temperature difference between refrigeration unit inlet and outlet flow. (Guo et al. 2012)

Figure 2.14 shows that specific power consumption (SPC) of selexol process which varies from 566 - 1020 kJ/kgCO_2. In figure 2.15, Specific power consumption excluding raw SNG & SNG compressions (SPCE) varies slightly at given pressures with different removal efficiencies. At any given removal efficiency, SPC increases with the increase of absorber pressure (PA). Guo et al (2012) case study results indicate that energy efficiency of CO_2 removal favors less difference between feed gas pressure and absorber pressure. When feed gas pressure and absorber pressure are both at 20 bar, SPC reaches its minimum value of 566 kJ/kgCO_2. Also, SNG volume was reduced and its heating value was increased due to capture from 17,5 to 33,2 MJ/Nm^3. The SPC of simulated selexol process is slightly lower than earlier reported membrane systems 620 kJ/kgCO_2. Sensitivity analysis indicated that CO_2 separation efficiency influences greatly on total power consumption when CO_2 compression was considered. Removal efficiency didn't have such high influence on the specific power consumption than total power consumption. It was reported that SPC would be about 281 kJ/kgCO_2 higher when compression is added. CO_2

removal efficiency should be determined prior to process with technical limits with respect to CO_2 content in the feed gas. (Guo et al. 2012)

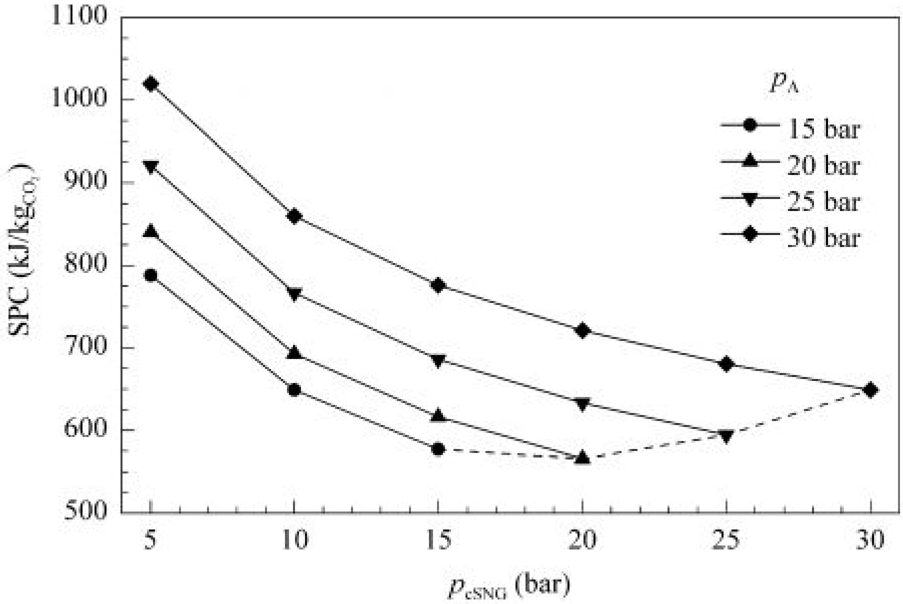


Figure 2.14 SPC of CO_2 removal with selexol and 95 % capture rate at various SNG pressures (*P*SNG) and absorber pressures (*P*A) (Guo et al. 2012)

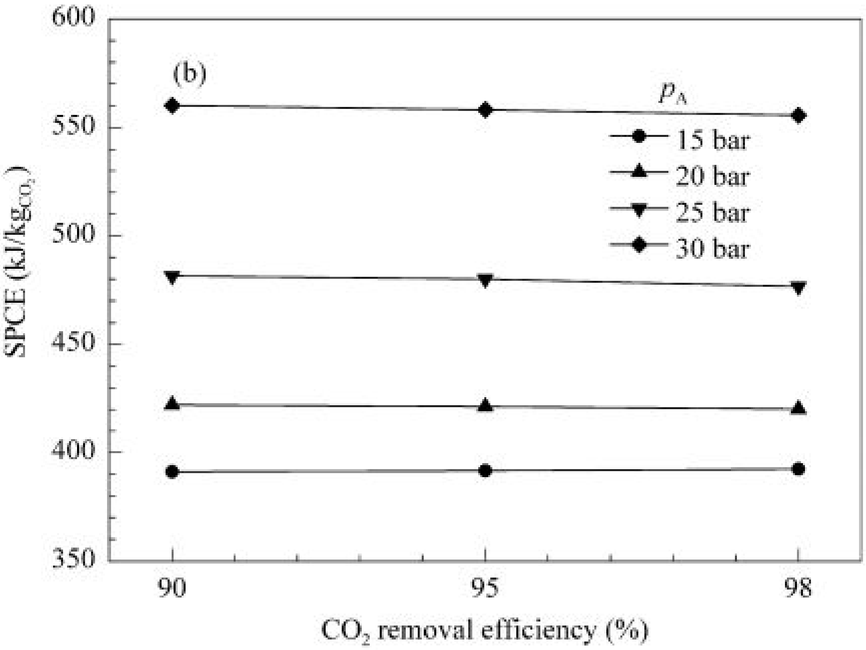


Figure 2.15 Specific power consumption excluding raw SNG & SNG compressions (Guo et al. 2012)

3.4.2 Adsorption

According to Warren et al. (1986): “In adsorption a solute is removed from either a liquid or gas through contact with a solid adsorbent, the surface of which has a special affinity for the solute.” Adsorption is a physicochemical surface phenomenon where substances atoms, ions or molecules in liquid or gaseous phase will attach to a surface of the solid adsorbent bed (Figure 2.16). (Rackley 2010) (Mirzaei et al. 2015) Adsorption can be classified as physical (adsorption enthalpy < 20 - 40 kJ/mol), chemical (adsorption enthalpy > 20 - 40 kJ/mol) or both (Shi et al. 2015). Classification between physical- and chemical adsorption is dependent on the nature of the surface phenomenon forces. Physical adsorption forces are mainly weak van der Waals forces whereas chemical adsorption has electron transfer equivalent to formation of chemical bond between substance and sorbent. The difference between these two types of adsorption can be understood by basis of the different surface forces. (Ruthven 1997) According to: Kohl & Nielsen (1997): “Adsorption can be based on chemical bond or physical attractive force.” The physicochemical forces holding adsorption together are not as strong as chemical bonds and that makes it easier for reverse the reaction to desorption. Therefore, the adsorption temperature requirement is lower than chemical adsorption where chemical bonds are stronger. (Kohl & Nielsen 1997)

Adsorption is a phenomenon that can be utilized for separation processes which is called selective concentration of one or more components (Kohl & Nielsen 1997). Adsorption occurs to a liquid- or mainly for gaseous substances and there are multiple regeneration technologies to neutralize the adsorbent. It can be used for the fractionation of different gas mixtures by using various selective adsorbents. (Mirzaei et al. 2015) Physical adsorption has a higher capacity than chemical due to multilayer formation. High adsorbent capacity has direct relation to adsorption costs (Ruthven 1997)

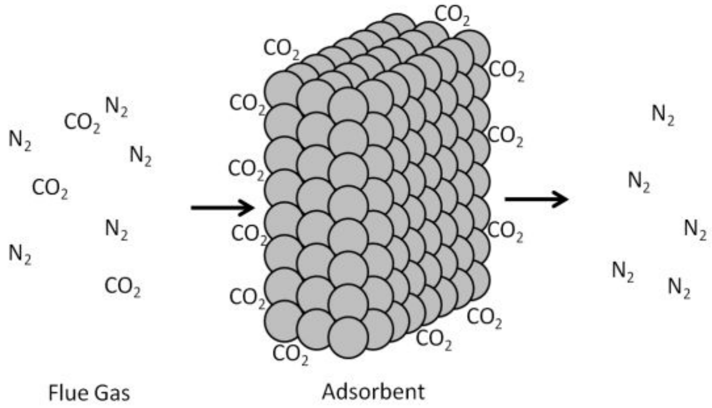


Figure 2.16 Illustration of CO_2 adsorption from N_2 containing flue gas (Rubin et al. 2010)

Surface of the substance on which the adsorption occurs is called adsorbent which adsorbs CO_2 from feed gas. Counter reaction of adsorption, desorption, is done by adjusting temperature, pressure or decreasing the partial pressure of the gaseous substance in gas mixture. (Kohl & Nielsen 1997) There can be more than one absorbent employed, which can increase the adsorption cycle time. Most important feature of adsorbent is its selectivity to adsorb desired components. Most adsorbents require SO2 removal from feed gas and feed gas cooling prior to adsorption (Pires et al. 2011) (Rackley 2010) Gas-phase adsorption is employed by large industrial purification or bulk separations for example petrochemical field. Gas-adsorption is often desired alternative separation method to the older distillation and absorption methods. (Ruthven 1997)

Physical adsorbents can be used from the ambient temperature up to 100 °C and are more utilized than chemical adsorbents that have higher adsorption temperature and capacity (Rackley 2010). Challenges for a physical sorbent like activated carbon and zeolites are low capture capacity with low CO_2 partial pressure (> 30 kPa), CO_2 selectivity and impurities effect on adsorption (Arunkumar et al. 2012). Physical adsorbents also suffer from poorer selectivity compared to chemical adsorbents (Shi et al. 2015). With high adsorption capacity, more CO_2 can be captured with less sorbent (Rackley 2010). Adsorption is an exothermic process, which is considered to be feasible in industrial scale.

Adsorption also presents lower regeneration energy demand and avoid some of the challenges of the liquid absorption. (Pires et al. 2011)

Adsorption process is done in cycles due to limited capacity and desorption reaction for clearing the adsorbent bed. Alternating adsorption process can be done by adjusting pressure and temperature for weakening the bonds for desorption and reducing the driving force for adsorption. (Mirzaei et al. 2015) Advantages for adsorption compared to absorption are wider operating temperature range and no liquid waste streams (Rackley 2010). For cost effective adsorption, the adsorbent regeneration must be energy efficient. Generally, adsorption has lower regeneration energy demand due to solid sorbents lack of water and looser forces compared to aqueous MEA regeneration. (Arunkumar et al. 2012)

Commercial adsorbents for gas-phase separation are in the form of pellets, beads or granular shape and have a diameter of few millimeters for larger contact area (Ruthven 1997). Solid adsorbents are seen as important field of development in CO_2 capture. There are adsorbents currently available for H_2 production in a form of PSA. (Rubin et al. 2010) Solid sorbents have longer lifetime when compared to chemical solvents. There is literature about novel sorbents, but new groundbreaking innovations are yet to be found. Current sorbents are used in cycles and can be applied to concentrated CO_2 streams. (Siriwardane et al. 2012) With some changes, solid sorbent adsorption could be adopted to effective CO_2 capture for low CO_2 streams. (Rubin et al. 2010)

However, there are some challenges with adsorbents. It is challenging for getting heat energy in and out from solid sorbents due to low heat capacity and poor heat transfer between gas-solid than in liquid-gas systems (Arunkumar et al. 2012) (Rubin et al. 2010). Advanced solid adsorbents can require additional equipment compared solvent absorption pumps. Also, resistance for attrition must be good for long-term usage. Research is mainly focusing on reducing the cost of CO_2 capture cost by durable sorbent designing and developing new sorbent materials. Low regeneration requirement and increasing the carrying capacity of CO_2 is essential for adsorption to be attractive. Faster reaction kinetics between adsorbent and CO_2 is preferred with small temperature and pressure changes. Lower the temperature and pressure, more cost effective is the process. High surface area of adsorbent is important and active contact area increases the reaction speed similarly as in absorption. (Rubin et al. 2010)

Solid sorbents

Solid sorbents are substances that can be potentially utilized in pre-combustion as well as post-combustion scenarios. Advantage for solid sorbent capture is their ability to be operated in high temperature compared to amine treatment. One major disadvantage for all solid sorbents is their handling compared to liquids. Handling can be a critical factor when choosing suitable capture technology and estimating operating costs in large scale. (Rubin et al. 2010) Many of the adsorbents are sensitive to impurities like NOx and SO_2 and vapor has a negative effect on adsorption when CO_2 is selectively adsorbed (Siriwardane et al. 2012). Adsorption with solid sorbents does not produce waste streams and sorbents can be disposed easily (Arunkumar et al. 2012). Solid sorbents that function near ambient pressure and temperature are interesting fields for research, because of easy regeneration (Rackley 2010).

Physical sorbents are mainly operated under 100 °C due to their weaker bonds compared to chemical sorbents. Physical sorbents capacity isn't as good as chemical sorbents, though they are more used. Chemical sorbents can operate in higher temperatures with higher adsorption capacity than physical and have potential to be applied to flue gas capture. Solid sorbents are divided to low- and high-temperature sorbents. (Arunkumar et al. 2012) Arunkumar et al. (2012) states that adsorption can be a promising option for traditional amine solvent absorption. Currently available solid sorbents can be seen in Appendix 3. Manufacturing and designing the selective sorbents for applications involves a manipulation of sorbent structure or sorbent chemistry to provide greater attractive forces for desired compounds over others. Sizing sorbent pores for example will control the access to the surface by molecular size. (Ruthven 1997)

With many sorbents available or approaching commercial status, there are a few criteria when selecting suitable sorbent for CO_2 capture (Arunkumar et al. 2012):

- Adsorption temperature and capacity
- High selectivity for CO_2 over other compounds
- Suitable adsorption kinetics under designed operating conditions
- Mechanical strength of adsorbent bed and sorbent particles
- Thermal- and chemical stability against impurities and temperature changes
- Low energy demand for sorbent regeneration
- Sorbent service lifetime and price

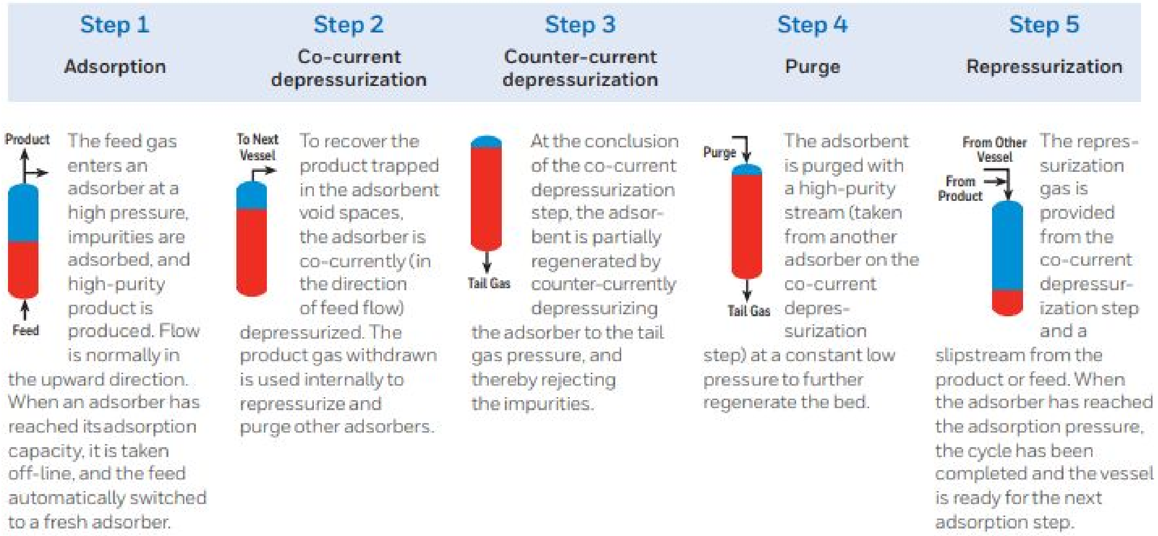
Generally, chemisorbents seem to have even greater potential than physical sorbents due to physical adsorbents low CO_2 adsorption capacity when CO_2 has low partial pressure. Novel polymer adsorbents with an amine coating, seem also to be potential chemisobents. Chemisorbents have typically stable structure during adsorption cycles and in theory, they have lower regeneration energy demand compared to solvent regeneration. Chemisorbents are not in commercial status and long-term reliability and potential need to further researched. (Arunkumar et al. 2012)

Following PSA & TSA technologies are classified as pre-combustion technologies by many research papers due to gasification applications. PSA & TSA are commercial technologies but applications for CO_2 capture are lacking, though their potential for flue gas treatment has been studied. PSA is used in refineries for SMR product H_2 purifying. They have large technical footprint and create parasitic load. Challenge is PSAs suitability for hot gas separation due the temperature of flue gas if not cooled. This is mainly why it is classified pre-combustion rather than post-combustion technology when heavy cooling and impurity removal is required.

Pressure swing adsorption

Pressure swing adsorption is common separation processes for gases and is applied in various industrial sectors (Bell et al. 2010). PSA utilizes selective bed that adsorbs components in a high pressure to catalyze adsorption in a cyclic process (Kohl & Nielsen 1997) (Honeywell 2016). Adsorption is done in so called vessels or packed columns. In PSA process, the temperature is constant, and CO_2 is adsorbed at high pressure. After the adsorption, desorption is done by reducing bed pressure. (Rackley 2010) PSA is intended to high concentrated CO_2 streams where amount of impurities is low, such as NG purification or SMR (Linnanen 2018). Since there is no need to heat or cool the adsorption vessel during the cycles, faster cycles are possible (Kohl & Nielsen 1997).

One or more components can be adsorbed at the same time using one or more adsorbents (Kohl & Nielsen 1997). In a cyclic process, half of the adsorption vessels are in adsorption stage and the other half in desorption stage. Cyclic process is presented in figure 2.17. Regeneration of saturated bed is done by pressure swing so that near vacuum conditions caused and process is swung between adsorption and desorption (Bell et al. 2010) Typically, desired components of feed gas are not adsorbed and are recovered as high purity product gas for further treatments (Honeywell 2016). Great advantage for adsorption and PSA is the solid adsorbent bed that can be reused numerous times and is easily regenerated. Adsorption process is less energy intensive than absorption methods and has less shortcomings when compared to absorption technologies that are available. (Mirzaei et al. 2015) Separated components are released or collected from the tail gas stream. PSA is cost-effective technical solution for gas component separation due to its simplicity, high performance in ambient conditions and high regeneration rate with adsorbents. (Bell et al. 2010)



Step 1
Adsorption

The feed gas enters an adsorber at a high pressure, impurities are adsorbed, and high-purity product is produced. Flow is normally in the upward direction. When an adsorber has reached its adsorption capacity, it is taken off-line, and the feed automatically switched to a fresh adsorber.

Step 2
Co-current depressurization

To recover the product trapped in the adsorbent void spaces, the adsorber is co-currently (in the direction of feed flow) depressurized. The product gas withdrawn is used internally to repressurize and purge other adsorbers.

Step 3
Counter-current depressurization

At the conclusion of the co-current depressurization step, the adsorbent is partially regenerated by counter-currently depressurizing the adsorber to the tail gas pressure, and thereby rejecting the impurities.

Step 4
Purge

The adsorbent is purged with a high-purity stream (taken from another adsorber on the co-current depressurization step) at a constant low pressure to further regenerate the bed.

Step 5
Repressurization

The repressurization gas is provided from the co-current depressurization step and a slipstream from the product or feed. When the adsorber has reached the adsorption pressure, the cycle has been completed and the vessel is ready for the next adsorption step.

Figure 2.17 PSA process (Honeywell 2016)

According to (Bell et al. 2010): “PSA technology is based on either equilibrium thermodynamics selectivity or kinetics selectivity.” Thermodynamic equilibrium selectivity depends on feed gases different concentrations at equilibrium state. PSA that utilizes equilibrium selectivity is strongly adsorptive for desired components of the feed gas and weakly adsorbed components flow through adsorbent bed with product gas stream. PSA based on kinetic selectivity is counting on different diffusion rates of gaseous molecules that are not in the equilibrium state in the system. So, it can be said that different diffusion rates determine the selectivity mechanism. For every PSA process, there are different kinds of operating specifications that provide the best conditions for adsorption. Optimization of adsorption bed size contact area and sorbent usage can increase adsorption effectiveness. PSA separation can be also a multistage process, where already separated product gas is fed to another adsorption vessel to increase product purity. (Bell et al. 2010)

PSA disadvantages are, cyclic process, limited bed size, low adsorption cycle times and shift stage time. Shift stage of process causes pressure changes and steady gas flow cannot be achieved without additional equipment. PSA is cost-effective when the feed gas has a high concentration of CO_2, but with low concentration the cost-effectiveness reduces notably. Despite the disadvantages, PSA, has a major role in gas separation due to its simplicity and easy integration potential to hybrid systems. (Bell et al. 2010) PSA equipment includes vacuum pumps and compressors which consume energy, but current PSA systems can be modified to reduce pressure losses during shifts and utilize adsorption pressure to re-pressurize another vessel (McLean 1994).

Many current available adsorbents have low selectivity and it means that higher concentrations of CO_2 in flue gas are required for more effective capture. Improving adsorption can be done by determining properties of feed mixture, such as molecular size & weight, polarity, pore size and spacing. Adsorbent contact area provides large area for components to attach. Components with smaller molecular size than CO_2 can diffuse into beds pores. Nitrogen for example has this ability and therefore total efficiency of adsorption decreases for every sequence and adsorption speed decreases. (Mirzaei et al. 2015)

PSA was compared to benchmark post combustion MEA absorption by Riboldi et al. (2017), both technologies met CO_2 separation targets 90 % capture rate and 95 % purity, and PSA displayed slightly lower energy penalty and larger technical footprint. PSA have potential in pre-combustion capture due to different temperature, pressure and CO_2 concentration. PSAs technical maturity leaves room for future improvements such as hot gas separation where its potential has been noted (Riboldi et al. 2017)

Temperature swing adsorption

TSA is also a simple separation process, which can be applied to gas mixtures where one or more components are selectively separated. In TSA, CO_2 is adsorbed from feed gas in ambient pressure and high temperature. Desorption is done by increasing temperature instead of pressure as in PSA. Also, TSA requires longer cycles time and larger equipment than PSA process due to poor heat transfer from gas to solid substance. (Rackley 2010) Adsorbent bed is the heart of the process and has the key effect on adsorption performance if the proper conditions are created (I&EC research 2016).

TSA regeneration is endothermic process and requires additional heat for regeneration of bed, which is provided by steam or direct purge of hot inert gas. TSA is more energy intensive than PSA and has become more interesting technology for refineries due to available low-grade thermal waste energy, that could be utilized in TSA regeneration. Also, flue gas temperature could be potential heat source. (I&EC research 2016)

High sorbent evaporation rates with chemisorbents and some physical sorbents has been concern that affects process and require precision. High evaporation of adsorbent means narrows operating temperature, especially with amine coated sorbents. Too high temperatures could result in non-effective adsorption and early release/regeneration of adsorbent. Key development for TSA capture is to search for better regeneration methods. There have been studies about utilizing captured CO_2 from desorption as a purge for regeneration. It could ensure CO_2 high purity assuming the adsorption-desorption conditions are maintained properly. Some amines, that are classified to chemisorbents tend to work better with TSA. (I&EC research 2016)

There have been promising results regarding the CO_2 capture from flue gas by utilizing combined PSA and TSA technology called PTSA. While PSA process is optimized, it is equally important to research new sorbents with high selectivity and high regenerability. Siriwardane et al. (2012) stated that PSA/TSA processes are ideal to be applied for CO_2 capture from gasification processes. Zeolites showed potential even with water vapor that has effect to process but can be deleted by increasing the temperature. Studied zeolites were able to capture CO_2 in high temperatures of 120 °C, however their adsorption capacity is notably higher in ambient temperature. (Siriwardane et al. 2012)

Sorption-enhanced reaction

Sorption enhanced reaction (SER) is a capture technology that can be applied to steam methane reforming. SER is an improved version of SMR, a new concept of fuel decarbonizing and CO_2 capture technology simultaneously that can convert light hydrocarbons to fuel grade H_2 (> 10 ppm CO). (Halabi 2011) (Zhang et al. 2014) When considering the current SMR process, there are multiple stages like reforming and water-gas shift (WGS) and operating parameters such as temperature and pressure. Driver for SER process is to combine all these process stages into a single step that can be obtained while increasing the H_2 yield by enhancing CH_4 conversion. (Romano et al. 2011) It is important to maximize the synergistic effects from partial processes. SER can be done in reforming stage (Equation 1), WGS stage (Equation 2) or simultaneously in combined reactor. SER-SMR process should be slightly exothermic when looked the stoichiometric ratios of reactants. Exothermic WGS reactions and carbonation reactions by calcium oxide CaO sorbent (Equations 3 - 6) for example can balance the endothermic reforming reactions and reduce operating temperature and energy demand. Main idea of SER is to shift the reaction thermodynamic equilibrium towards favorable H_2 production by capturing the forming CO_2. (Halabi 2011) SER can achieve high CH_4 conversion (> 80 %) and high purity of H_2 (> 95 %) (Johnsen 2006). Reforming, shift, CO2 removal and overall reactions for SER+SMR CaO adsorbent can be seen below from equations 3,4,5 & 6 by Lopez Ortiz & Harrison (2001)

$$CH4(g) + H2O(g) \rightleftharpoons CO(g) + 3H2(g) \tag{3}$$

$$CO(g) + H2O(g) \rightleftharpoons CO2(g) + H2(g) \tag{4}$$

$$CaO(s) + CO2(g) \rightleftharpoons CaCO3(s) \tag{5}$$

$$CH4(g) + 2H2O(g) + CaO(s) \rightleftharpoons 4H2(g) + CaCO3(s) \tag{6}$$

Capture of CO_2 during SMR process can be done from WGS reactors where CO is converted to H_2 and CO_2 in stages (Equation 2). Capture from WGS stage is called sorption enhanced water-gas shift SEWGS. In SEWGS, solid sorbent, membrane or both combined are used to capture CO_2 as it forms during WGS reaction under high pressure and temperature. Key technical challenges for SEWGS is to find suitable sorbent and membrane, which can reduce the amount of catalyst or even eliminate its need. (Yongqi et al. 2013) SER process is operated 4 to 20 bar range and around 500 °C. Proper process conditions can minimize the undesired intermediate reactions. Lower capital costs are achieved by better yield of H_2 and unnecessarily of additional purification process due to low concentrations of CO. (Halabi 2011) H_2 or CO_2 can be removed with collaboration of adsorbent and CO_2 or H_2 selective membrane. Product H_2 can be pure as much as 98 % and just ppm amounts of CO and CO_2, which means that product H_2 is suitable for some applications without purifying step (Harrison 2008).

SER and SEWGS processes require reactor where capture and sorbent regeneration are done. Hybrid reactors are fit for equilibrium limited conversions, where one product is removed, and the reaction is shifted towards the reaction products as in Le Chatelier's principle. Membranes permeable for H_2 can be also used for effecting SMR and shifting conversion reaction. Hybrid reactors result higher conversion than conventional ones and, in this case the operating conditions for temperature are around 500 °C while maintaining high conversion of CH_4. Lower operating conditions require cheaper materials for process equipment. (Oliveira 2009) There are potential advantages for SER in SMR process listed by Harrison (2008):

- Increased yield of high purity H_2
- Reduction of process temperature & replacement of expensive alloy steel materials
- Process simplification or possible elimination of H_2 purification
- Elimination of shift reactors
- Elimination of carbon deposition, slag and clogging in reforming reactor

For SMR, there are fixed bed reactor (tubes with catalyst) and auto thermal reactors available. SER process has various technical approaches as well and some are single reactor types that replace or modify reformer so that whole SMR process is done in a single step and WGS reactors are removed, or the WGS reactors are replaced by hybrid fixed bed reactors that boost WGS conversion while capture CO_2. Both types of processes should reduce or remove the need for additional H_2 purifying process and decrease CO volume. Fluidized bed reactor is one studied solution for reforming reactor that would be responsible for reforming and WGS reactions (Johnsen 2006). Fluidized bed has many advantages for SER process and most likely it is used for industrial applications as a circulating fluidized bed reactor (Figure 2.18). Circulating fluidized bed is utilized due to sorbent regeneration in bubbling regime. (Jakobsen & Halmøy 2009)

Traditional tubular reformer has numerous fixed bed reactor type tubes that are filled with catalyst. Fluidized bed would replace this fixed bed technique and provide better catalyst diffusion with smaller catalyst pellets. Also, heat transfer is better and expensive superalloy material doesn't have to be used. Effective heat transfer between bed particles and gas is done by circulation of these solids which work as heat carriers in fluidized bed. Fluidized beds are suitable solution for CH_4 oxidation and providing heat energy for endothermic reactions. (Johnsen 2006) There are two separate reactors in continuous fluidized SER process, joint reformer/carbonator where H_2 is produced and CO_2 absorbed and calciner where sorbent is regenerated. Also used catalysts can be oxidized. (Halabi 2011) SER process with fluidized bed- and fixed bed reactors have been demonstrated successfully with natural lime-based sorbents in laboratory-scale by Norwegian University of Science & Technology and Institute for Energy Technology. Continuous SER process must be demonstrated successfully for further possible up-scaling. (Romano et al. 2011)

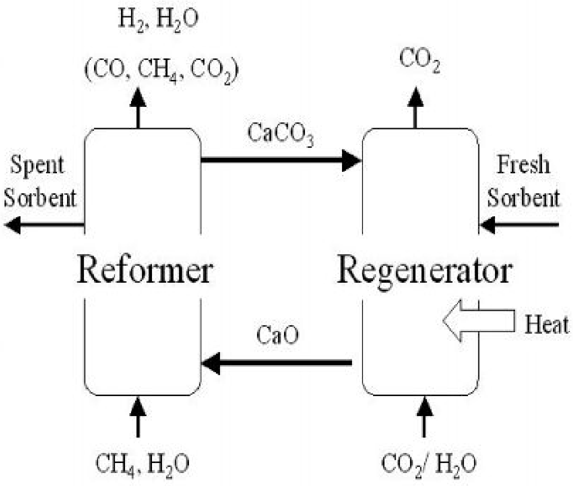


Figure 2.18 Fluidized bed with CaO sorbent (Johnsen 2006)

Second technical approach is fixed bed hybrid reactors that would replace the WGS reactors. H_2 would be purer after hybrid reactors than in traditional SMR before PSA and only H_2O is mixed with product H_2. Basically, it doesn't matter which of the products CO_2

or H_2 is removed. CO content in SE+SMR is a few ppm due to effective conversion with steam (Equation 2). (Oliveira 2009) According to Rout et al. (2015): "if CO_2 is removed in the SMR process as soon as it is formed, the reforming- and water-gas shift (WGS) reactions proceed beyond the conventional thermodynamic limitations, and consequently, more CH_4 is converted to H_2 and reaction temperature can be reduced." Product H_2 yield in different pressure can be seen in figure 2.19.

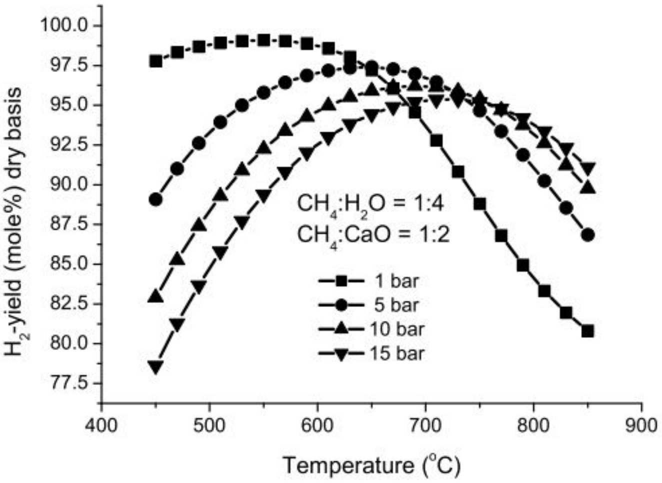


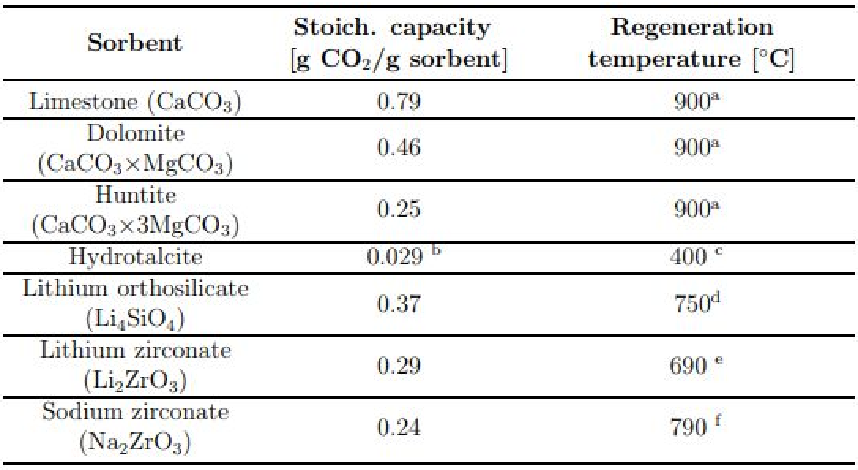
Figure 2.19 H_2 content as a function of temperature at different pressures (Johnsen 2006)

Original SER process patents were based on fluidized bed, but later research has been focusing on small-scale fixed bed reactors. Important factor in both types of reactors is the ratio between sorbent and catalyst. In this case, the WGS reactions are enhanced by CO_2 capture by fixed bed reactors that operate in cyclic principle. Fixed bed reactors are regenerated by pressure increase as in PSA. Fixed bed reactors aren't seen as applicable technology for industrial scale SER process although they are researched. Continuous regeneration and cyclic process are challenges and multiple reactor operating and synchronization creates large challenges. Also, sorbent capacity reduction in a closed reactor is an important factor and downtime between production and regeneration. (Johnsen 2006) Unlike the membrane enhancement for SMR capture, adsorption must have more columns that are operated to achieve and maintain continuous H_2 production (Oliveira 2009).

According to Oliveira (2009): “Literature dealing with hybrid reactor suitable for steam methane reforming report the use of membranes or sorbents to achieve the equilibrium shift towards the products.” Other stream leaving the reactors is the off gas if the H_2 is captured, it contains unconverted CH_4, CO and CO_2. CH_4 can be circulated back to conversion. H_2 is produced in low pressure conditions and its pressurization can add costs. (Oliveira 2009)

Currently, there are no sorbent that can meet all the requirements of SER process. Potential sorbents are studied and researched in literature. Sorbents are divided into natural and synthetic sorbents. Lime has the best capture capacity and highest regeneration temperature (Table 2.4). (Johnsen 2006) Sorbent is consumed during the process and conditions require that sorbent is easily regenerable and can be used number of cycles. This regeneration reaction can be done with pressure, temperature or both. Most of the SER research is focusing on sorbent durability in cyclic process. (Harrison 2008)

Table 2.4 Stoichiometric CO_2 capture capacities for different sorbents. (Johnsen 2006)



Sorbent	Stoich. capacity [g CO_2/g sorbent]	Regeneration temperature [°C]
Limestone ($CaCO_3$)	0.79	900[a]
Dolomite ($CaCO_3 \times MgCO_3$)	0.46	900[a]
Huntite ($CaCO_3 \times 3MgCO_3$)	0.25	900[a]
Hydrotalcite	0.029[b]	400[c]
Lithium orthosilicate (Li_4SiO_4)	0.37	750[d]
Lithium zirconate (Li_2ZrO_3)	0.29	690[e]
Sodium zirconate (Na_2ZrO_3)	0.24	790[f]

Johnsen (2006) set the following requirements for SER sorbents:

- High reaction rate and kinetics (450 - 650 °C)
- High CO_2 capture capacity
- Sorbents stability
    - Reversibility (adsorption/desorption)

    - Sorbent lifetime and cycle durability
    - Mechanical and thermal strength
- Small temperature gap between adsorption and regeneration
    - Lower energy consumption
    - Thermal shock resistance
- Low price and easy availability

CaO is widely used solid chemical and is also the most studied sorbent for CO_2 capture applications and for SER process. CaO has fast reaction kinetics in high temperatures of 500 - 700 °C. Similar temperature range can be found from gasification and SMR unit. CaO reaction equilibrium between carbonation and calcination can be seen in figure 2.20. CaO has also high capture capacity, easy availability and low material cost. (Clough et al. 2018) Other studied potential sorbents according to Clough et al. (2018) are hydrotalcites, Dolomites and MgO sorbents. Halabi (2011) states that SER reactions could be performed over mixture of sorbent and catalyst between as low as 400 - 500 °C.

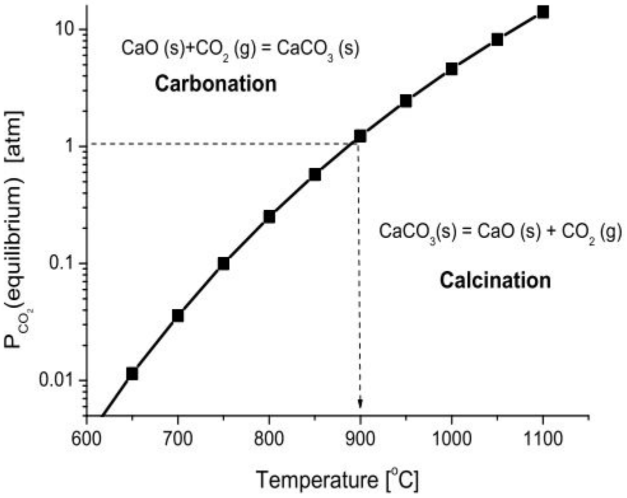


Figure 2.20 CaO equilibrium between temperature and pressure (Johnsen 2006)

Many sorbents such CaO tends to decay during the process and its CO_2 carrying capacity decrease during process, so fresh lime feed is needed. Sorbent decaying during multiple cycles results from thermal and reactive sintering. Much of the sorbent developing and testing is focusing on degradation challenge. (Clough et al. 2018) Overall outcome of SER+SMR process is defined by favorable thermodynamics of highly endothermic reforming reaction, fast reaction kinetics, effective capture of CO_2 and capacity of CO_2 capture in cyclic chemisorption (Zhang et al. 2014). SER is limited by mass transfer during particle diffusion of intermediate- and final products between catalyst and sorption sites. Combining the catalyst and sorbent into single component and substance is a keen interest for further research (Figures 2.21 & 2.22). This kind of single combined particle system can minimize the distance of diffusion and prevent dilution of intermediate products by bulk gas, which promotes the better mass transfer and conversion effectiveness. (Clough et al. 2018)

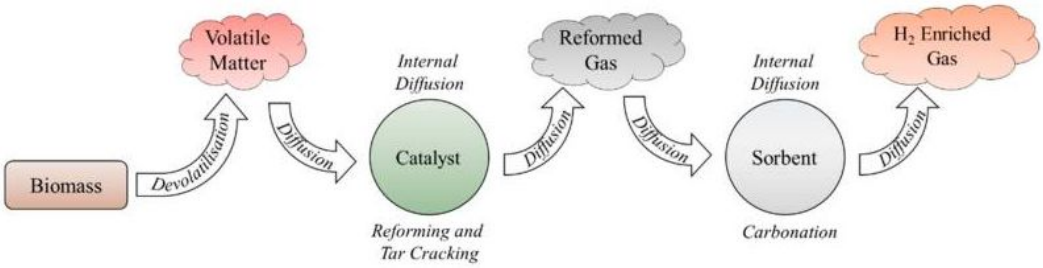


Figure 2.21 Diffusion pathway for typical SER process (Clough et al. 2018)

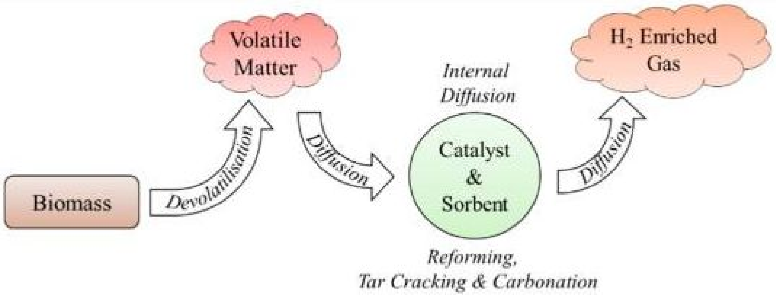


Figure 2.22 SER mechanism with single particle system (Clough et al. 2018)

3.4.3 Membranes

In gas or liquid absorption, membranes can be used to selectively filter the desired components (Mirzaei et al. 2015). Membranes are known for various filtration applications for example water treatment and laboratory usage. They can be also utilized in CO_2 capture with gas mixture filtration. Selective membrane film performs as a filter that allows desired components permeate through and blocks the other components. (Guozhao & Zhao 2017) Membrane filtration can involve numerous physical or chemical processes and is based on different permeability between components through thin film. (Kohl & Nielsen)

There are currently several kinds of membrane filtration technologies available, but CO_2 gas separation has attracted new research in the past few years (Guozhao & Zhao 2017). Components that pass the selective layer are called permeate and filtrations impurities as retentate. Although membranes are not the most effective separation method, they can be utilized with bulk separation operations, when just a large portion of specific components is separated. (Kohl & Nielsen 1997) Membranes are usually made from polymers and their most important parameters are selectivity and permeability. Permeability means the specific amount of gas that is captured through membrane. (Herzog et al. 2009) Membrane separation relies on differences in physical and/or chemical interaction with gases and membrane itself. Desired components can pass selective layer due to their size (kinetics) and/or affinity (thermodynamics). (Mirzaei et al. 2015)

Membranes can be applied for gas and liquid mixtures and be operated as continuous system (Guozhao & Zhao 2017). Membrane capture is done by contact between membrane film and CO_2 that is absorbed through the selective film due to permeability (Rubin et al. 2010). According to Mirzaei et al. (2015): “The membranes are compact, and they are not sensitive to flooding, entrainment, channeling, or foaming.” Desired components contact with membrane surface, dissolve to its surface and are transported through the film to other side. This phenomenon occurs due to so called concentration gradient, which is caused by the different partial pressure of the feed mixture components. (kohl & Nielsen 1997) Dissolution phenomenon through membrane layer is the key for separation but it is important to point out that if pressure on each side remain equal, separation is dependent on the components partial pressure. Performance of the membrane system is directly dependent on CO_2 partial pressure and is suggested feeds that have concentrations of 20 % or more. (Mirzaei et al. 2015)

Membranes don't usually achieve high separation rate and high concentration of CO_2 is desired in the feed gas. Membranes that are designed for gaseous compounds are usually sensitive for sulfur compounds and particle emissions. (Olajire 2010) Polymer based membranes have potential to capture CO_2 cost effectively, but the challenge lies with low partial pressure of CO_2. Low concentration of CO_2 in flue gas means that the amount of treated gas is large for small yield. (Yang et al. 2008) In order to obtain high, permeate gain and effective separation, feed gas flow is usually pressurized while product gas is connected to vacuum to achieve higher driving force for the separation. (Guozhao & Zhao 2017) Feed gas recirculation also enhances the separation, though the separated permeate can never be 100 % pure and some of the permeate is found from separation residues. (Rackley 2010) Membrane separation will be more effective when feed gas has over 20 % concentration of desired components (Mirzaei et al. 2015). Membrane technology can be combined with other separation technologies to work as a hybrid separation system (Kohl & Nielsen 1997).

Thin membrane film can be coated with some porous substrate to increase the thickness for better filtration force resistance and for better mechanical strength (Figure 2.23). Membrane film can have a thickness from nanometers to microns, and it is hard for the membrane film to resist the force of pressurization. Coated surface layer should not increase the resistance of feed flow due to large pores compared to membrane size. Coating the pores allows free flow of gas on both sides of separation. If the pores are too large, some cracking and peeling might occur during filtration in substrate part of filter. Additional interlayer with smaller pore size can be applied for smoother transition between layers. (Guozhao & Zhao 2017) Membranes can utilize porous and non-porous substrates and their size determines the particle size of the feed that is going to penetrate the selective layer (Rackley 2010).

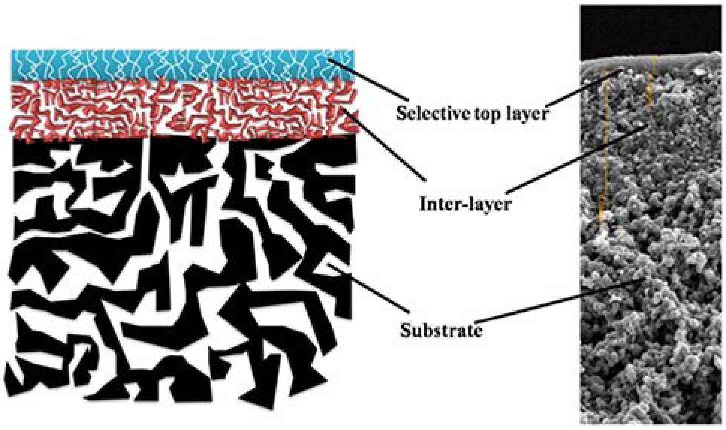


Figure 2.23. Membrane film with inter layer and coated substrate (Guozhao & Zhao 2017)

Membrane separation requires less equipment than other capture technologies. and are suitable for CO_2 separation and already utilized in NG purification due to their selectivity (Keskitalo 2013) (Baker & Lokhandwala 2008). Membranes can be applied to low concentrations and low gas volumes but impurities in feed gas mixture have negative effects in separation and permeate stream if not treated before membrane stage. (Rackley 2010) Membranes present suitable solution for bulk separations operations and if filtration criteria are not strict, they can offer economic and competitive solution without additives or steam load (Rubin et al. 2010). Also, membranes prefer pressurized processes. It is also critical to construct them into functional configuration (Yang et al. 2008).

Polyamides are most studied materials due to their chemical and physical resistance and good CO_2 permeability (Powell & Qiao 2006). Currently, membrane separation field is dominated by polymeric membranes (Yang et al. 2008). However, typical membranes like polymeric are not currently available solution for straight flue gas capture due to high temperature and the fact that membranes tend to work best with rich CO_2 gas streams. Flue gas should be treated for impurities and cooled before separation. (Keskitalo 2013) For the post-combustion technology, the selectivity of membrane for CO_2 must be over the N2 which is the main component of the flue gas. This permeability will determine the purity of separated CO_2 and the amount of the transported components through the membrane film given the process pressure difference. Also, the needed membrane surface area for capture can be determined by flue gas composition. (Rubin et al. 2010)

In membrane filtration, pressure difference must be created for effective separation and in large-scale, this might need a lot of energy (Yang et al. 2008). Most of the operating costs for membrane usage become from feed gas pressurization and replacement of membrane layers. There is also no fast decrease in separation rate, and it is a reliable method due to its simplicity and lack of additional solvents and process steps. Membranes can be left unattended and they inert, so they don't react with feed mixtures. Membranes are usually operated in a way that they remove desired percentage of desired components and can be adjusted by varying velocity of gas, volume flow and pressure. (Guozhao & Zhao 2017)

Membranes are an attractive low carbon emission separation technology. The continuous separation is preferred in industrial processes and it gives membranes advantage over cyclic systems. (Guozhao & Zhao 2017) Membrane CO_2 separation is researched topic and before adopting membranes widely, there are challenges to overcome such as design of the membrane gas separation units (IEAGHG 2010). Most of the studies done regarding the membranes are about liquid-liquid separation and only few for CO_2 capture (Guozhao & Zhao 2017). Membranes are very sensitive for high and medium temperatures and can even be destroyed easily. When applied to flue gas capture, temperature must be cooled under 100 °C.

Although, low gas separation of polymer-based membranes, they are cheap to manufacture. Some membranes with higher gas separation are polyamides. Membrane density can vary due to desired components and denser membranes are applied to gaseous compounds. Thick membrane structure causes lower gas fluxes than alternative structures for liquid separation. (Yang et al. 2008) There is currently a wide selection of membranes based on their physical and chemical properties and many show potentials for CO_2 capture applications (Guozhao & Zhao 2017). Generally, membranes suffer from the need for compression for creating the pressure difference for effective separation. Also, impure product stream and the fact that there are no commercial applications for CO_2 recovery from flue gas. Presence of fly ash in flue gas and components such as SOx, NOx, HCl and HF create complications for membrane separation. (CONCAWE 2011)

Membrane enhanced reaction

Reactors can be packed with membranes that enhance conversion reaction and remove CO_2 as in SER (Park 2004). Membranes cannot capture all the CO_2,but they can still enhance the conversion and be utilized in H_2 separation where reaction equilibrium is shifted also (Figure 2.24). (Johnsen 2006) The economy of membrane enhanced reforming depends on membrane permeability costs versus savings by eliminating WGS reactor and the PSA unit. High conversion reaction thermodynamics have led to efforts to eliminate constraints by the selective membrane enhancement so that the reaction equilibrium is shifted towards products at lower temperature. However, it must be recognized that H_2 produced with membranes is at low pressure and requires compression and available membrane flux is too low for applications. (Rostrup-Nielsen & Rostrup-Nielsen n.d.) Nazarkina and Kirichenko (2016) in their studies extracted pure H_2 from reforming reactor by applying selective palladium or its alloy-based membranes. These palladium-based membranes operated around 700 °C and resulted towards higher CH_4 conversion and pure H_2 was collected (Johnsen 2006). Also, one major technical challenge is membrane lifetime in SMR conditions, and it remains an important challenge to be solved. (Oliveira 2009) Membrane properties for CO_2 separation can be seen more in table 2.5.

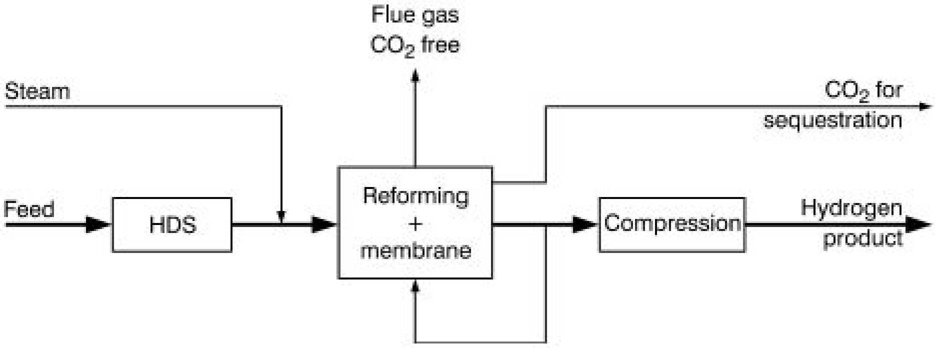


Figure 2.24. Simplified SMR membrane CO_2 sequestration flow chart (Rostrup-Nielsen & Rostrup-Nielsen n.d.)

Wu et al. (2015) in their research studied dual-enhanced SMR process in laboratory scale. In the study, simultaneous membrane separation and CO_2 sorption was tested (Figure 2.25). It was found that dual system reduced SMR process temperature down to 500 °C with NG conversion of 86,2 %. 0,6 product H_2 separation rate was achieved as well as 0,95 CO_2 sorption rate. With the same conditions, traditional conversion of NG achieved conversion rate of 52,1 % without reaction enhancement. Palladium membrane with electroless plating was used during tests. Fixed bed reactor system was used with Nano CaO sorbent and nickel oxide NiO and aluminum oxide Al2O3 catalysts (Figure 2.26). Experimental results demonstrated that lowered process temperature achieved 27,2 % higher conversion rate when reaction enhancement is applied at 600 °C with steam to CH_4 ratio of 4:1 and product H_2 was 98,1 % pure. (Wu et al. 2015)

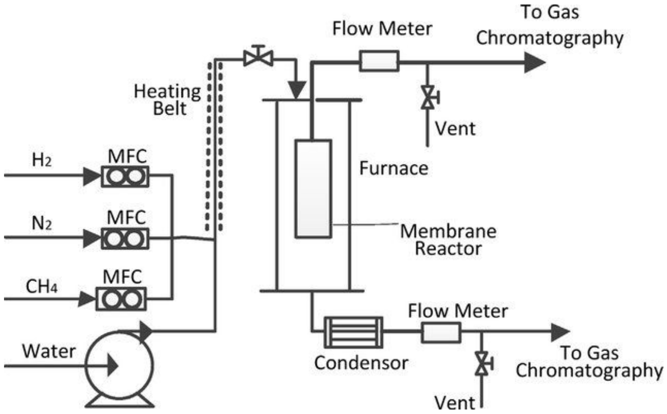


Figure 2.25. Dual-enhanced SMR process (Wu et al. 2015)

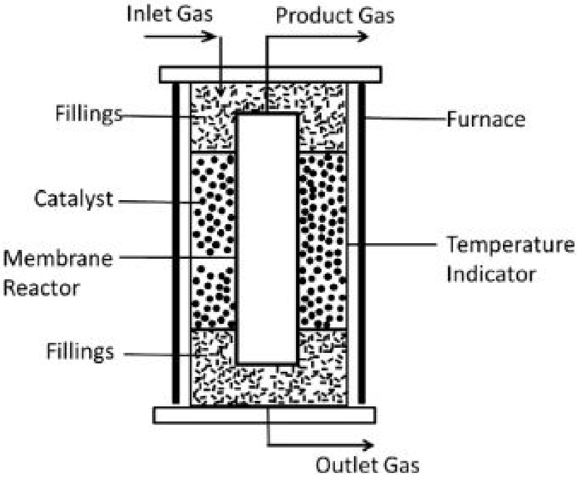
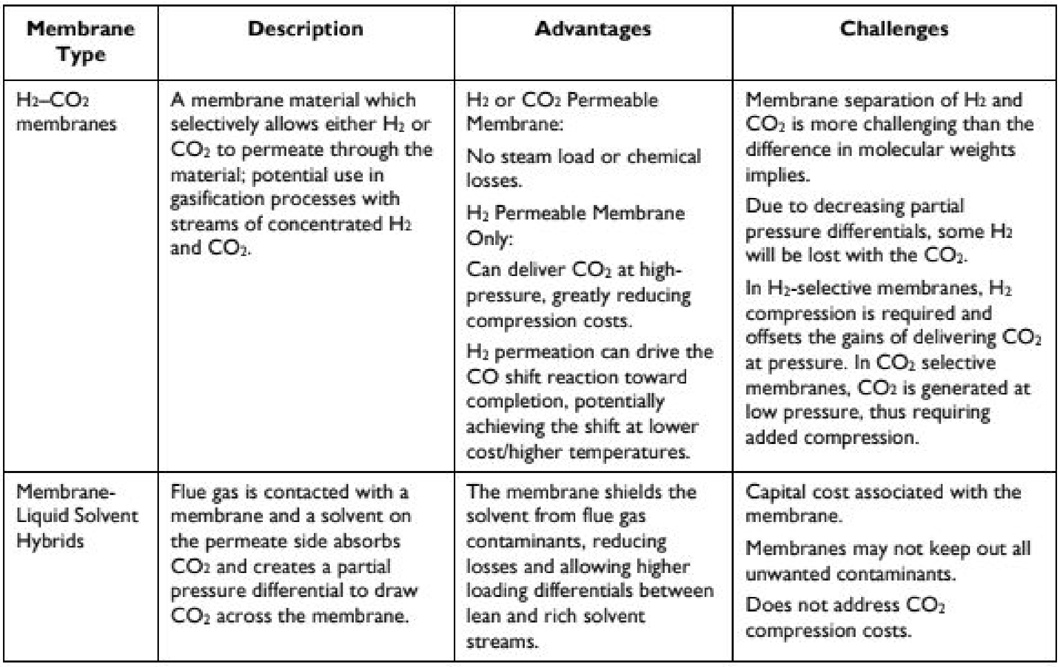


Figure 2.26 Membrane reactor illustration in dual-enhanced SMR process (Wu et al. 2015)

Table 2.5. Properties of pre-combustion membrane capture (Rubin et al. 2010)



Membrane Type	Description	Advantages	Challenges
H_2–CO_2 membranes	A membrane material which selectively allows either H_2 or CO_2 to permeate through the material; potential use in gasification processes with streams of concentrated H_2 and CO_2.	H_2 or CO_2 Permeable Membrane: No steam load or chemical losses. H_2 Permeable Membrane Only: Can deliver CO_2 at high-pressure, greatly reducing compression costs. H_2 permeation can drive the CO shift reaction toward completion, potentially achieving the shift at lower cost/higher temperatures.	Membrane separation of H_2 and CO_2 is more challenging than the difference in molecular weights implies. Due to decreasing partial pressure differentials, some H_2 will be lost with the CO_2. In H_2-selective membranes, H_2 compression is required and offsets the gains of delivering CO_2 at pressure. In CO_2 selective membranes, CO_2 is generated at low pressure, thus requiring added compression.
Membrane-Liquid Solvent Hybrids	Flue gas is contacted with a membrane and a solvent on the permeate side absorbs CO_2 and creates a partial pressure differential to draw CO_2 across the membrane.	The membrane shields the solvent from flue gas contaminants, reducing losses and allowing higher loading differentials between lean and rich solvent streams.	Capital cost associated with the membrane. Membranes may not keep out all unwanted contaminants. Does not address CO_2 compression costs.

3.4.4 Cryogenic

Cryogenic carbon capture (CCC) is based on low temperatures where substances thermodynamic and solidification properties are exploited based on condensation of components. CO_2 can be separated from NG or from flue gas, though more cooling is needed compared to purifying. (Hart & Gnanendran 2009) Industrial cryogenic technology is applied also to air separation unit (ASU). Cryogenic temperatures improve CO_2 & vapor removal, increase ASUs efficiency and decrease seasonal ambient pressure changes affect to the process. (Rackley 2010) Cryogenic separation or purification is done by cooling the gas stream and causing the components with low vapor pressure to condensate for easy removal. Separation itself is easy when condensated component or components are in liquid phase whereas others are in gaseous phase. With cryogenic capture, CO_2 is removed from gas stream after its condensation occurs. (Kohl & Nielsen 1997) Cryogenic capture is a special application that can be utilized for streams that have CO_2 concentration above 40 mol-%. Cryogenic process consists following operations; compression of feed gas, Cooling, Expansion and cold distillation of feed components. (Alexandre et al. n.d.)

CCC utilizes substances phase change to separate them from feed gas. In cryogenic process, feed mixture is cooled down to - 140 °C that causes CO_2 de-sublimation straight from gas to solid. Also, a sublimation phase change from solid to gas is used in the purification process. Solid CO_2 is separated easily from other gaseous components and pressurized which causes heat and melting of CO_2. When applying CCC, other pollutants can be separated as well as CO_2. If technology can remove more than one pollutant it is offsetting other treatment costs and lowers the price of flue gas treatment operations. Pollutant removal is based on the same method as CO_2 removal, cooling the feed gas stream and de-sublimation of pollutants in different temperatures. (SES Innovation 2008)

There are two ways to achieve cryogenic temperatures. Liquid nitrogen or other commercial cold substances can be used in cryogenic purification. Second and more widely used method is the compression-decompression sequence where gas stream is first compressed and cooled, and then decompressed causing the gas stream temperature to drop even more. Cryogenic method is tricky because CO_2 does not occur in liquid phase in ambient pressure so the process conditions must be arranged to be favorable for this chemical state transition from gas to liquid for easier transportation. (Rackley 2010) CO_2 can be separated from NG with cryogenic technology due to these components different sublimation points as in figure 2.27. CO_2 has sublimation point of -78,5 °C and CH4 has a melting point of -182 °C. (Hart & Gnanendran 2009) CO_2 separation from NG improves NG heating value and lowers its volume.

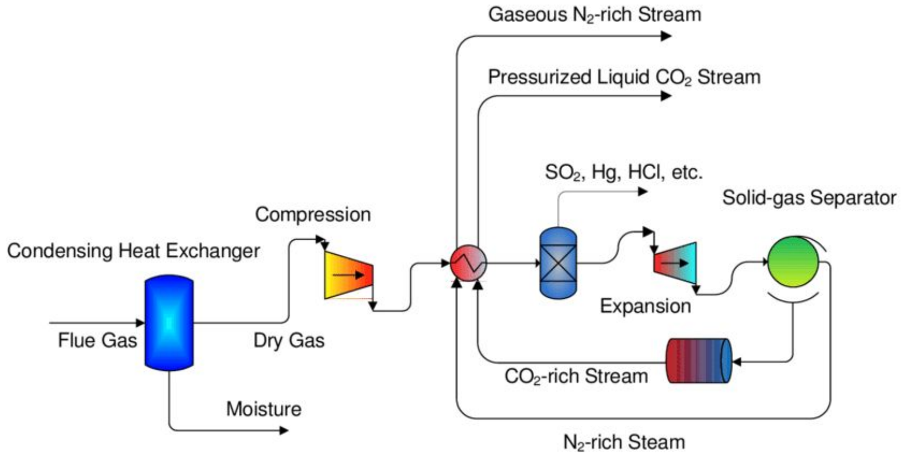


Figure 2.27 Cryogenic capture process (Baxter et al. 2009)

Applying CCC for post-combustion capture is challenging due to large volumes. Hot flue gases could be used effectively on heat exchanging so that low temperature flue gas is produced for cryogenic process and energy is not wasted. CCC is used mainly by chemical industry and gas purification operations. (Rackley 2010) Effective CCC could be done with almost half at the cost compared to current commercial capture technologies. CCC upside is the fact that it can be applied also to SOx, NOx and mercury removal at the same time with different temperatures to their own flows. With integration to power plant, CCC installation gives opportunities with flue gas energy and it can be utilized in various heating solutions and less waste heat is released. If the waste heat of flue gas stream can be harvested, it could boost the steam process and give better output for plant with the same initial investment. (SES Innovation 2008)

CCC can achieve 99 % CO_2 capture rate and cost less than 30 dollars per captured ton. When retrofitted to an existing power plant it has a parasitic load under 15 %. System equipment are scalable and can be installed for every size process without technical challenges or modifications. (SES Innovation 2008) CCC technology is limited for streams with high concentration of CO_2 for easier and economical separation and at least 40 %-mol is required or overall capture cost is driven up. Preferably, CO_2 concentration in the feed gas stream should be over 90 % for best function and that is why CCC is most utilized in purification processes rather than capture. (Ebner & Ritter 2009) CCC can be used to concentrate CO_2 to meet food quality standards for a variety of applications (Alexandre et al. n.n.). CCC technology is utilized globally in oil refineries in SMR process with PSA tail gas treatment. (Ebner & Ritter 2009)

According to SES Innovation (2008): “If the additional benefits of CCC are considered, other pollutant capture and possibility of power plant integration with waste heat utilization the total cost of capture is even lower than suggested.” Available capture technologies aren't economical and the latest amine treatment processes reach 69 \$/tCO_2. Compared to amine technology price in figure 2.28, CCC would cost approximately 35 \$/tCO_2 and if the additional benefits presented before are considered, price for captured ton of CO_2 with CCC reduces to 14 \$/tCO_2. (SES Innovation 2008) Main disadvantages of CCC are related to extreme process conditions of high pressure and very low temperatures and high-power consumption. Operating conditions are close to three times of CO_2 evaporation (- 56 °C and 5.2 bar). (Alexandre et al. n.d.) According to (SES Innovation 2008): “The parasitic load of the base CCC process with no plant integration is about 14 % compared to 28 % for amine absorption process.” Process cold products like solid CO_2 can be used for cooling the feed gas mixture and melting the solid CO_2 in the process. (SES Innovation 2008) Leung et al. (2014) states that cryogenic distillation at low temperature and high pressure consumes 600 - 660 kWh (2,16 - 2,38 GJ) t/CO_2 when recovered in liquid from. Currently, the three main available processes for cryogenic separation are Union Engineering's FlashCO_2, Air Liquide's CO_2-CPU and Fluor's CO_2LDSep^{SM} (Alexandre et al.)

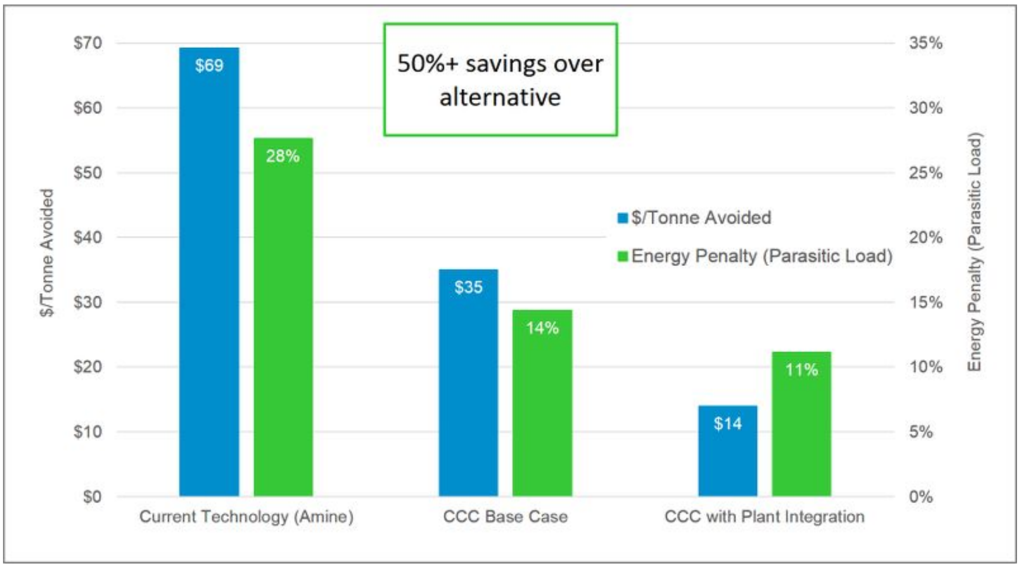


Figure 2.28 1st year CCC technology implementation costs and parasitic load (SES Innovation 2008)

3.5 Technology development

Most of the current R&D activities are focusing on cost reduction of capture technologies rather than just gaining higher capture efficiency. When higher capture efficiency is gained, typically costs will increase rather than decrease. Numerous research programs emphasize the need for capture technologies to be suitable for existing power plants. One critical challenge for capture technologies is the absence of significant markets globally. Novel capture technologies are in a difficult position, due to development and relation to political situation. (Rubin et al. 2010)

Key drivers for capture development are cost reduction, regeneration energy reduction and improving of technical designs (IEAGHG 2010). Many technologies are in research stage, laboratory stage or small-scale piloting (Teir et al. 2010). These technologies are at such an early stage that it is impossible to determine their potential, benefits or reliability in large scale. There are solid materials and solvents that show potential, but many challenges remain in scaling them to viable technology that could be commercialized. (Rubin et al. 2010) Commercialization of new technology is a long process and requires years of research and tests to determine the actual scaling potential. Figure 2.29 presents the situation of various capture technologies and their maturity level. Most researched post-combustion technologies are based on solid adsorbents, membrane technology and solvents that could replace current amines (Teir et al. 2009). More technologies under development can be seen in table 2.6. Novel technologies are attractive when they are not dependent on large volume of expensive chemicals and there should be a minimal amount of waste fractions from CO_2 separation (Carbon Management 2001).

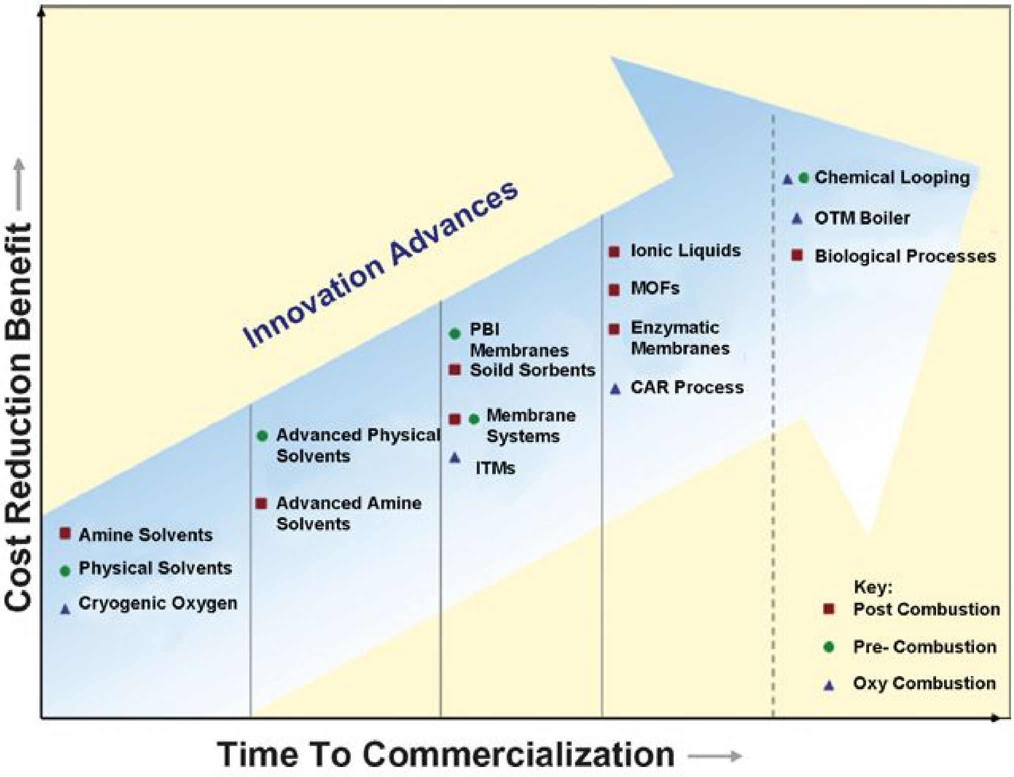
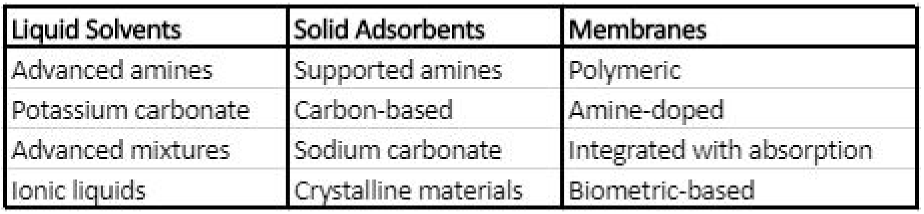


Figure 2.29 CO_2 capture technology maturity (Figueroa et al 2008)

Table 2.6 Capture technologies under development (Rubin et al. 2010)



Liquid Solvents	Solid Adsorbents	Membranes
Advanced amines	Supported amines	Polymeric
Potassium carbonate	Carbon-based	Amine-doped
Advanced mixtures	Sodium carbonate	Integrated with absorption
Ionic liquids	Crystalline materials	Biometric-based

Research has been mainly focusing on post-combustion capture, due to process dominance. Post combustion capture development is driven by separation of CO_2 with the lowest practical energy consumption. (Teir et al. 2009) Hybrid technologies are new approach for CO_2 capture and their objective is to combine the best features from two or more technologies to mitigate disadvantages of each other. Hybrid systems are driven by flaws of technologies and it is expected that if some hybrid systems reach the commercial status, capital costs could be high with the performance. (Rubin et al. 2010)

Development of physical solvents CO_2 carrying capacity could improve absorption-based capture. Weak bonds between CO_2 and solvent provides less energy intensive regeneration than chemical solvents. Higher capacity means higher capture rate in every cycle and easy stripping of CO_2 due to weak bonds. From these two properties, carrying capacity is the one more desired. Unlike for chemical solvents, pressure swing can be used for CO_2 stripping from physical solvent without the need of heat. There are novel amine-based solvents and promoters such as piperazine that can be added to improve the solvents CO_2 loading and thermal resistance. One practical problem with chemical solvents is their corrosivity properties. (Rubin et al. 2010)

Current solid sorbents are not well suited for flue gas capture due to low CO_2 capture capacity and presence of nitrogen (IEAGHG 2010) (Arunkumar et al. 2012). Novel sorbents are interesting field of research and adsorption can offer competitive technologies. New ultra-porous adsorbents are developed for effective CO_2 capture that have large contact area for adsorption. Available adsorbents require much energy for regeneration and capacity and reaction kinetics could be improved. Reason for solid sorbent research and interest is the fact that they don't produce liquid waste streams and have wider operating range compared to solvents. (Rackley 2010) Transferring heat into solid sorbent is challenging for regeneration due to slow heat transfer between gas-solid and low specific heat capacity of solid adsorbents. In temperature swing regeneration, it increases the desorption cycle. One potential solution is to utilize membranes in the surface of solid sorbents that allows heat transfer more efficiently between two sorbents in adsorption vessel if two sorbents are used. (Rubin et al. 2010)

Polymeric and ceramic membranes are been developed for capturing CO_2 from high temperature flue gas streams (Teir et al. 2010). Membranes could be applied to SMR- or IGCC process due to high pressure conditions, compared to post-combustion situation that requires additional energy for pressurization (Rubin et al. 2010). Post-combustion capture with membranes is in early development stage and according to IEAGHG (2010): “Membrane behavior could be improved by introducing the membrane gas absorption concept (membrane contactor with chemical solvent).” The future development of membranes for CO_2 capture depends on the success of solid sorbents and solvent absorption systems. (IEAGHG 2010) Some other innovative technologies are based on metal-organic materials, enzymatic selective membranes and biological process applications (Teir et al. 2010) (Teir et al. 2009).

Membrane- and cryogenic technologies are also potential options but their applications when considering refinery sources and volumes are not applicable. Hybrid technologies aren't either a solution due to technical immaturity as in case of sorption enhanced reaction, which could be a potential option in the future and with new SMR design rather than retrofitting to existing reformer unit. Current single stage membrane systems can only produce streams below specified purities. Cryogenic processes, among others, favour higher CO_2 concentrations in their feeds. Therefore, combining these technologies could prove viable. A single stage membrane system could be used to raise the CO_2 concentration to above 50 vol-%, followed by a cryogenic separation step.

3.5.1 Maturity of carbon capture and future prospects

Absorption-based technologies are the only applicable commercialized technologies in industrial scale if rapid CO_2 capture is required. Technical maturity of carbon capture is relatively low and there is room for development. Technical maturity variates between commercial technologies and novel technologies. Absorption based capture is a commercial technology and has a roughly estimated energy penalty of 30 % for power generation when employed. (Rochelle 2009) Also, PSA is commercial technology, but CO_2

selective applications have room for development. There is a wide range of technology options and almost infinite number of streams for capture. Cost of capture is hard to evaluate and should always be determined for specific technology and feed. Costs can vary a lot and they mainly give an idea, but values should be critically assessed. Some gathered capture costs from various sources can be seen from appendix 1 by Leeson et al. (2017).

Though the amine process is already widely used, substantial research and testing must be done for CO_2 selective post-combustion capture. Flue gas for example has low CO_2 content that affects equipment size and creates large technical footprint. Industrial capture was not designed for flue gas capture operations therefore, capture is mostly applied to sources that mostly meet the capture unit design objectives. (Carbon Management 2001) Amine treatment has been developed and modeled intensively resulting different configurations of the process. Heat integrated solutions and new reboilers are designed and new operation strategies are researched for energy decrease during regeneration. Reboiler in amine treatment is the main energy consumer and reboiler residence time has straight effect with total energy consumption of amine scrubbing. (Luis 2016) CO_2 separation from flue gas or other streams is relying on current absorption technology and applying it to large-scale is yet undemonstrated for refinery streams or scale. This will present technical challenges and major technical breakthroughs for absorption are required to achieve higher cost-effectiveness and technological attractiveness. (CONCAWE 2011) Also, reduction of capture equipment size, improving the reaction kinetics and intensifying the mass transfer between the capture agent and CO_2 are important topics for further research in operational and economical aspects (Carbon Management 2001).

4. Carbon footprint of selected technologies

In this final chapter, LCA is conducted to quantify and to determine the environmental impacts and carbon footprints (CFP) of the chosen technologies for refinery CO_2 capture. It is noted that LCA is specifically done for the capture part by using GaBi software and following the ISO-14040, ISO-14044 and ISO-14067 standard guidelines. GaBi used in this study has a professional license and been updated regularly.

Introduced SMR, FCC and process furnaces all present challenges for CO_2 capture and have different types of outlet gas streams. Also, they all have a large share and impact on refinery CO_2 balance. Potential source for effective CO_2 capture was determined to be the PSA unit tail gas. In the context of SMR, absorption-based capture could be applied to all three CO_2 sources, reformer flue gas, syngas or PSA tail gas. SMR unit PSA tail gas is the end of the line stream for CO_2 capture, which will reduce the capital costs compared to capture from intermediate processes. In the next subchapters, chosen technologies are presented and justified.

4.1 Carbon capture technology selection and justification

Selecting the suitable capture technology generally depends on the amount of CO_2 needed to be captured, CO_2 purity requirements, pressure, CO_2 partial pressure, impurities, retrofit and additional costs for power and steam if acquired from outside party. Also, employed technology's effects on sub-processes should be considered. Capture equipment have large technological footprint and retrofit planning must be done years prior to actual integration. Therefore capture equipment could only be installed during refinery stoppage that is done in a period of a few years due to effect on refineries revenue. Emission flows in refinery processes vary from tens to hundreds of tons per hour and suitable technologies should be scalable for these sources. In this study, requirements for chosen technologies were set to meet the quality requirements for a range of applications from appendix 2. Extent of purification depends on the volume- and the impurities in the feed gas. If the captured CO_2 is not purified to meet the application standards, corrosion of pipelines and equipment can occur as well as some unwanted side reactions with hydrocarbons (Abbas et al. 2013).

Each of the presented refinery CO_2 sources; FCC, SMR and process furnaces produce very different types of outlet gas streams and will require individual solutions for CO_2 capture. When selecting the most feasible source for capture, economical, technical and scalability factors are emphasized. All three sources produce large emission streams but due to high volume- and mass flow, low CO_2 concentration, low pressure and impurities, FCC and process furnaces are left out from further studies. Process furnaces and FCC provide variable flue gas streams and in their capture scenarios, mandatory cooling is required in order to ensure solvent function. When CO_2 content decreases from 12 to 4 %, capture cost can increase by 25 % (van Straelen et al. 2009). Lack of scaling is a critical factor when selecting technology because single source emitters that cannot produce at least 500 kt/CO_2 annually will drive the cost up as well. Desired and least costly CO_2 capture sources are the ones with high pressure & CO_2 concentration and low impurities. These attractive factors can be found from SMR unit, which emits on average 5 - 20 % or up to 50 % of refineries total CO_2 emissions annually (CONCAWE 2011) (Digne et al. 2014). According to CSFL (2018) demand for H_2 is growing, which in prospects makes the SMR unit desirable place for CO_2 capture in economic wise.

Process furnace capture scenario

Gas fired process furnaces produce dilute CO_2 flue gas with impurities and the amount of treated gas to capture a ton of CO_2 would be massive and expensive in cost wise. Process furnaces altogether are accountable for 45 - 55 % of refinery CO_2 emissions (Figure 1.1, page 12) according to CONCAWE (2011). Low CO_2 content and partial pressure require the use of alkanolamines and for such dilute and large volume source, the amount of solvent needed is massive and regeneration would be costly. Lots of low-pressure steam would be needed which creates a notable energy penalty. Also, impurities such as SO2 and

SO3 can be found from process furnaces flue gas (CONCAWE 2011). Variable feed stream is a challenge when optimizing capture process for one type of feed. Process furnaces are single point emitters that have a large share of total CO_2 emissions but without expensive rerouting to a combined stack, they aren't viable source for capture as multiple small sources. Capture cost from combined stack is around 3 - 4 times the current ETS price according to van Straelen et al. (2009).

Fluid catalytic cracker capture scenario

FCC is large single point CO_2 emitter, that produces flue gas type of outlet gas, which consists of CO_2, SO_3, NOx, nitrogen, CO, 1000 - 15 000 ppmv of SO_2 and some catalytic dust. FCC accounts for about 20 % of refinery total CO_2 emissions (CONCAWE 2011) (Digne et al. 2014). FCC outflow is quantitatively large and SOx removal prior to capture is required. Treatment for such volumes in two stages is expensive and size of the equipment would be massive. There are few studies about FCC CO_2 capture and none found on catalytic dust effects on capture agent, which should be carefully evaluated. There can be mechanical filters and electrostatic precipitators for the dust and particles, but there is always some wastage. CO_2 content could be increased by applying oxy-combustion to catalyst regeneration, which would require additional large ASU. Major concern with oxy-firing, would be the regeneration efficiency of the catalyst, though results by de Mello et al. (2009) did not indicate significant changes compared to normal operation. de Mello et al. (2009) also report that the cost of CO_2 avoided with oxy-firing technology is less than in the case of post combustion capture. Potential oxy-combustion could achieve more concentrated CO_2 FCC outlet gas and enable to combine SMR and FCC outlet streams to same capture unit. In that case, the refinery CO_2 balance could be affected significantly.

de Mello et al. (2009) estimated that FCC represents 40 - 45 % of total CO_2 emissions in typical refineries. CO_2 capture would be then essential to reduce refinery CO_2 emissions. Major problem for FCC CO_2 capture implementation is that it produces slightly more CO_2 than SMR unit, depending on the refinery complexity, but produces much larger volume in capture wise. SMR has an average of 15 % share in total refinery CO_2 emissions, but considerably lower volume to be treated with better capture properties that could result, lower capture cost per ton of CO_2 and per volume treated. It must be pointed out that refinery complexity can have a notable effect in SMR and FCC shares of CO_2 in total emissions due to higher grade refining, that requires more hydrogen and thus increases SMR CO_2 share. FCC is involved in many refining schemes and its operational importance cannot be emphasized enough, which means that the capture units reliability must be high and there can be no expensive stoppages or effects on primary cracking process.

Steam methane reformer capture justification

SMR is accountable for large amount of refinery total CO_2 emissions which total or partial capture could affect significantly for overall CO_2 balance. SMR provides rich CO_2 stream with low impurities, low O_2 and almost zero N_2. SMR is critical process for any refinery and it has an important role in emission balance. H_2 production is expected to increase in the future and European Commission in 2006 estimated H_2 demand to be 300 Mt in 2050, whereas Hydrogen Council estimated in 2017 it to be 550 Mt by 2050. This would imply that H_2 demand compared to 2015 values would increase by a factor of 5 to 10 due to oil refining and other clean fuel applications. According to Carbon Sequestration Leadership Forum (CSFL) member nations, there are currently at least six operations, where CO_2 is captured from H_2 production. Captured CO_2 amount per facility is around 1 Mt and those facilities are in the US, Canada, Japan and three in China. Increasing H_2 production creates an opportunity for SMR CO_2 capture and low emission H_2 production could be achievable.

Van straelen et al. (2010) estimated opportunities for a modern complex refinery post-combustion capture. It was concluded that one cost effective CO_2 source would be the SMR unit, where the cost was estimated to be about 30 €/tCO_2. SMR CO_2 rich raw syngas and PSA tail- gas are recommended sources for effective CO_2 capture. High pressured and CO_2 concentrated stream from SMR can be captured at lower cost compared to typical flue gas. (van Straelen et al. 2010) It must be emphasized that the real capture cost is always site- and process specific (Carbon Management 2001). PSA tail gas, unlike FCC and process furnace outlet gases, can be utilized as an energy source and is primarily used to fuel the steam reformer (SR). Tail gas/syngas capture reduces the tail gas volume, flow and increase its heating value.

When considering the SMR CO_2 capture options, SR flue gas consists of N_2, SOx, NOx, dust and only a fraction of CO_2, which means that a large amount of gas must be treated in order to capture less CO_2 when compared to syngas or tail gas. Flue gas capture is by far the most expensive solution and most of the CO_2 is released via raw syngas or PSA tail gas. Also, flue gas capture would require large absorber for CO_2 and lots of excess steam for solvent regeneration. Two-point capture in SMR unit can achieve 90 % overall capture rate, but as in many studies, SMR flue gas capture isn't considered practical or economical option if radical CO_2 reduction isn't needed. (Colloidi & Wheeler n.d.) Shahani & Kandziora (2014) pointed out that potentially in the future, CO_2 capture from SR flue gas could be applied, but first, technologies must reduce their costs compared to current state of the art solutions. Now, the best available large-scale technology are absorption-based.

Syngas would be attractive source for capture, and it has around 2 times the volumetric amount compared to tail gas with around 15 mol-% of CO_2 and H_2 component largely present (Colloidi & Wheeler n.d.). Syngas has a pressure of 20 bar prior to PSA unit before it is reduced to ambient pressure (Alexandre et al. n.d.). Syngas has notably lower CO_2 %-mol than tail gas and is preferably captured with MDEA amine solvent, which is used typically at 50 wt% aqueous mixture (Sheilan et al. 2015). Despite the large variety of amine solvents, MDEA does not react with acid gases so there is no corrosion problem. MDEA has high capacity of CO_2 loading and has low energy demand for regeneration compared to other amines. One drawback is the price of MDEA and the slow reaction kinetics, which can be improved by additive called activator. With activator, MDEA can achieve capture rate as high as 95 %. Raw syngas has potential for effective capture but presents technically a major challenge in implementation for most refineries. Capture unit retrofitting has not been considered in SMR unit design or building stages and there are usually other constraints such as lack of space as well. One large limitation lies with changing the configuration of the PSA unit, due to its altered PSA inlet stream after modification. When PSA inlet composition changes, it leads to major modification of PSA adsorbents their quantities and other process modifications. Therefore, capture is advised to be done after PSA unit so that reformer or PSA configuration does not have to go through a series of modifications. (Alexandre et al.)

In economic perspective from the two previous SMR CO_2 sources, flue gas capture would have substantially higher cost than syngas capture. There are hardly any technical barriers regarding the flue gas or syngas capture, but there are major challenges and limitations, regarding the retrofitting of capture unit. In theory, both options would result in higher cost than the current ETS price (Colloidi & Wheeler n.d.). This is why PSA tail gas is found to be the most attractive capture source due to its properties. Although PSA tail gas requires pressurization, after desorption, it is less expensive to compress the tail gas stream than treat 2- or 20- times larger volume. Compared to syngas or flue gas option, PSA tail gas has low water content, temperature and lowest volumetric flow. Low temperature eliminates the pre-cooling stage, solvent thermal degradation and simplifies capture process. PSA tail gas is slightly above atmospheric pressure after desorption sequence and has the following roughly estimated composition in table 3.1 by Turunen (2019).

When CO_2 is captured after SMR-PSA unit, it changes the composition of tail gas, which is the main fuel of SR. CO_2 removal from tail gas causes an increase in its heating value so less fuel is needed to fuel SR. New low CO_2 tail gas requires pre-heating and retrofitting new burners for combustion since the tail gas quality has changed and the low CO_2 tail gas has a tendency to form NOx when combusted. (Shahani & Kandziora 2014) (Colloidi & Wheeler n.d.) When CO_2 component is removed from PSA tail gas stream, investigation of tail gas compositions effects on SR furnace and the burners should be done. There can be some fluctuation in new tail gas stream due to capture unit.

According to Shahani & Kandziora (2014) amine solvents can only be applied to SMR unit's syngas or flue gas as seen in figure 2.4. Selexol and selective PSA are applied to CO_2 concentrated syngas and/or PSA tail gas. These three SMR streams differ in composition, pressure, temperature and CO_2 partial pressure, so different technologies must be used. PSA tail gas has high CO_2 partial pressure and concentration, which means that applicable commercial technologies are absorption with physical solvent or adsorption. There are however reports about MDEA solvent with chemical promoters applied to tail gas capture. Tail gas emits 55 % of SMR unit CO_2 and rest is emitted through reformer furnace, although tail gas is typically used to fuel the reformer and CO_2 is emitted through the chimney eventually. However, furnace flue gas with around 40 % of SMR total CO_2, will be in great significance environmentally, when more CO_2 reduction is required.

Two chosen technologies based on literature view for selected SMR-PSA tail gas capture and for LCA study are physical solvent absorption with selexol and selective PSA adsorption along with amine treatment as compared technology. Technologies are used to capture and concentrate PSA tail gas CO_2. Both selected technologies are mature and proven technologies, which are licensed by Honeywell. Adsorption can be also applied to already existing PSA unit by adding more vessels to the system with CO_2 selective adsorbents. It must be noted that although PSA is mature technology for gas separation, CO_2 selective adsorbents are still in development stage.

Selexol capture

Selexol capture is well established commercial technology for NG and syngas purification in gasification operations via physical absorption solvent. It is used to remove acidic components and its scalable and can be retrofitted. According to Alexandre et al. (n.d.) physical solvents can be used for absorption when CO_2 concentration is 15 - 40 %-mol and CO_2 partial pressure is high. These both criteria are fulfilled by the tail gas composition (Table 3.1, page 103). Cooling of the feed gas is essential and high pressure and CO_2 partial pressure are desired to enhance the solubility and solvent loading capacity (Mirzaei et al. 2015). Selexol has wide operating temperatures and tail gas has only a hint of H_2O that has higher solubility to selexol than CO_2. Selexol can be regenerated via pressure swing, heat or a combination of the two. Basically, selexol process requires energy for tail gas pressurization to 2 - 16 MPa and for refrigeration unit (Rackley 2010). Series of flash tanks are used to regenerate selexol by reducing the pressure in stages and to separate liquid and gas phases. Normally selexol and other physical solvents are applied to high pressure raw syngas after SMR unit but in the case of tail gas, pressurization must be done again to achieve the desired operating conditions for effective physical absorption. Selexol process can be enhanced by reducing system and solvent temperature close to 0 °C when CO_2 solubility into selexol increases whereas other impurities like higher hydrocarbons lose their solubility. CO_2 volume is larger than in typical flue gas due to lack of those two components and it enables faster reaction kinetics for the absorption. There is only a hint of O_2 and N_2 in the tail gas, which affects decreasingly to absorption column sizing. Selexol treatment is typically applied to syngas, but earlier presented technical challenges, amount of gas to be treated as well as CO_2 content and partial pressure are more favorable with the tail gas. There is a possibility to retrofit regenerator steam system that utilizes heat from raw syngas cooling to generate steam (Shahani & Kandziora 2014).

Selective pressure swing adsorption capture

In case of selective PSA capture, tail gas has a moderate temperature and high CO_2 concentration so that mandatory cooling or heating isn't needed, which enables short adsorption cycles due to desorption via pressure instead of heat. PSA allows efficient and simple CO_2 capture, that can be applied in two ways; 1) Adding CO_2 selective vessels into an existing PSA system where treated tail gas is adsorbed again or 2) constructing a whole new PSA unit with CO_2 selective adsorbents. PSA as mentioned, could be applied to raw syngas but the amount of treated gas would roughly double as determined so the tail gas option is better in cost wise. PSA is commercial technology, but CO_2 selective adsorbent research is lagging and effective adsorbents for industrial applications are needed. Advantage for PSA system is that only electrical energy is needed for the pressurization.

Alternative options

For the chosen SMR unit, there are new innovative ways to reduce CO_2 emissions radically that are worth a mention. First is the use renewable biogas feedstock in SMR, when H_2 production becomes a sink for CO_2 and part of the “carbon debt” is repaid. Second is adopting a new technology for H_2 production such as electrolysis. Electrolysis is used to split H_2O to H_2 and O_2 components by applying electricity and it is still in development stage. Both options present major challenges and are not yet considered viable options. Biogas demand for refinery scale SMR process would be massive and there should be ready infra for its transportation or production near the refinery. Electrolysis is extremely expensive and consumes lots of electricity and power input should be from a renewable source or it removes the purpose of the whole process. Electrolysis process follows the price of electricity, which is the most significant parameter that can be affected by temporal and spatial variation. Despite the current challenges, electrolysis has a potential to achieve emission free H_2 production.

4.2 Carbon footprint for selected technologies

In this subchapter, a consequential life cycle assessment is conducted to determine and evaluate the CFPs of chosen technologies, when capturing CO_2 from SMR-PSA unit tail gas. ISO-14044 states that consequential approach is a “system modelling approach in which activities in a product system are linked so that activities are included in the product system to the extent that they are expected to change as a consequence of a change in demand for the functional unit”. Modelling is done with the GaBi software and the study should follow the guidelines of ISO-14040, ISO-14044 and ISO-14067 standards. CFP is determined via ISO-14067 and its quantification is done in the LCA method, which utilizes ISO- 14040 & 14044 (SFS 2018). ISO-14040 covers the guidelines of the LCA framework and ISO-14044 gives more accurate guidelines and requirements for the LCA (SFS 2006 & 2018). Generally, goal of CFP study is to quantify the global warming impacts of the studied system by definition of GHG emissions (kg CO_2 eq) at all stages of the product system (SFS 2018). Unlike in ISO-14067, acquisition of raw materials, design, transport, delivery and end-of-life are excluded from this study due to lack of data, study universality and uncertainties of process specifics for the applied source.

Aim of the study is to perform CFP assessment and determine direct GHG emissions and impacts in CO_2 equivalent. With LCA results, sustainability and effectiveness of chosen technologies can be compared, assessed and captured net CO_2 can be calculated. There would be no point to utilize CO_2 capture, if the process itself emits more CO_2 than captures or isn't effective enough in order to make a difference in refinery scale. Also, cost-effectiveness must be emphasized due to price of ETS.

CFP is important when evaluating potential technologies and specially in case of aiming to reduce GHG emissions. CO_2 capture requires steam or electricity for operating and regeneration. This energy input has a major role when assessing the environmental impact of the process. In total, three different capture processes models are constructed to evaluate CO_2 captures environmental impacts along with capture agent production emission factors if valid data is found. Main interest is in the capture process itself and direct flows related to it. Outlined process in figure 3.1, where all main flows can be seen, serves as the system boundaries. This LCA study is divided into four sections in accordance with ISO-14040; 1) LCA goal and scope, 2) inventory analysis, 3) impact assessment and 4) results and interpretation.

4.2.1 Goal and scope

Goal of this LCA study is to determine the carbon footprint and emission profile of chosen technologies and their effectiveness to capture CO_2 based on their own environmental impacts. This study should address the lack of information about sustainability of typical refinery source capture with selected technologies. As in ISO-14067, this study is conducted to determine the system contribution to global warming by quantifying significant GHG emissions over the production life cycle. Only GHG emissions of CO_2

capture are under consideration due to the preliminary nature of this study to evaluate potential technologies to reduce CO_2 emissions and provide general information of refinery CO_2 capture sustainability and CFP. For specific refinery or process, further and more comprehensive studies are strongly recommended. Constructed models of selexol- and PSA processes are compared to amine (MEA) treatment models emission profile and environmental impacts. Amine treatment is used as comparison technology due to its technological maturity and wide adoption in sour gas treatment. MEA process is proven technology that can meet application specifications (Stewart et al. 2011). As noted in the theory part, amine treatment has high steam input and it is recognized that steam production compared to power production has a higher specific emission factor in selected Finnish processes from GaBi software.

This study can be used as a base tool to evaluate alternative technologies for SMR-PSA CO_2 capture and it should provide indicative results for scientific community and for refineries to support their decision making and further studies. This study is conducted due to the lack of comprehensive sustainability assessment of CO_2 capture technologies for refinery industry and due to ETS and EU rapid emission reduction targets for industrial sector. It is recognized that amines and MEA in this case are not suitable options for high concentrated tail gas capture although, MDEA is applied to syngas purification.

Functional unit

In this LCA study, functional unit for CFP quantification was set to 1 ton/CO_2 captured from PSA tail gas and all the flows are proportional to functional unit and presented in kilograms or GJ. CO_2 is just one component in the tail gas stream from which it is captured. Other components are listed later. Since this LCA study is done for technology and impact comparison, multiple energy input scenarios with variety of energy values are simulated. Each technology has a different energy consumption and multiple scenarios for capturing the same amount of CO_2. Results are gathered and presented as kg CO_2 eq/tCO_2 captured and net CO_2 captured by reducing the CFP from t/CO_2 captured.

Functions and system boundaries

System under study is CO_2 capture after refinery SMR-PSA unit. Studied system is constructed from theoretical processes and GaBi software is utilized to determine potential environmental impact of the systems for the comparison. Used capture process flow chart is simplified for LCA purposes and only main flows that have an environmental impacts are included. Systems follow a CO_2 “gate-to-gate” approach, where LCA is conducted for partial product system, where one-unit process is under study (Jiménez-González et al. 2000). Studied capture unit is directly after emission source and its assumed that there is no CO_2 escape prior to capture. The focus is on CO_2 capture and only relevant in- and outputs directly related to capture are considered, not for example compression and transport. Capture unit process includes two systems, process equipment that have electricity input and can be used for regeneration as well and steam input for solvent regeneration, though they are presented in single step in figure 3.1 flow chart. Product system description and boundaries can be seen in figure 3.1, where the processes outlined are included with the capture agent emission factors. Capture agents such as solvents and their additives can have a large impact on LCA modeling, when production and disposing are considered. (Teir et al. 2009) With chemical solvents, there is a valid concern regarding the capture process, where solvent leakages, losses, evaporation and other waste streams present serious environmental risk that must be managed. (IEAGHG 2010)

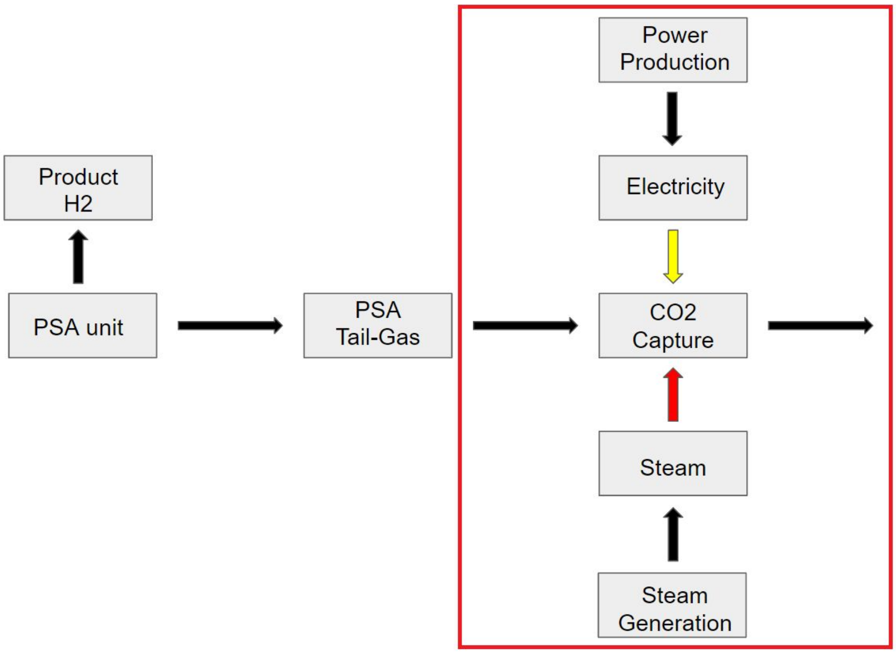


Figure 3.1. LCA system boundaries

In this study, captured CO_2 compression is excluded from the study along with dewatering because they are mandatory measures and have the same environmental impacts, regardless of the capture technology. Prior to utilization or storage, CO_2 must be compressed to a high pressure, where it liquefies and has a lower volume and easier properties for transport. SMR-PSA unit impacts from H_2/tail gas separation are also excluded, because SMR+PSA combination can already be found from most of the refineries and tail gas has a low-pressure so no compression is done prior to capture unit. Emissions from amine solvent initial input amount are excluded and only supplemented solvent emissions from production are considered. Transportation is excluded due to study universality and lack of specific refinery in question that would have its own properties such as location and transportation options. Also, end-of-life for CO2 is excluded due to different impacts of two options storage or utilization and the lack of infra and data. For these reasons It is more sensible to evaluate capture process first and then the whole life cycle if one decides to proceed. Due to focusing on specifically capture process, capture unit manufacturing emissions are also excluded.

CO_2 capture

Studied system consists of only a main process, CO_2 capture from the incoming PSA tail gas. In figure 3.1, capture process has a steam and electricity inputs, though not every technology or scenario utilizes the same energy inputs. In all the models, treated leftover tail gas is not included to study, because it is typically used to fuel the SR. However, energy value of the treated tail gas is calculated, but not linked to the capture energy input.

4.2.2 Life cycle inventory analysis

Life cycle inventory analysis (LCI) presents the collected data, calculations and assumptions for the LCA study. System boundaries limit the in -and outflows for the studied system. In LCA study, the goal of the study will define the quality requirements for the data and influence on the results. Used data, should be the type of information that is needed for decision making. Collected secondary data for the study is from public sources such as scientific papers, books and publications that can be found from references. Flows between unit processes present the different stages of a processing and can separate the impacts to a specific points and different unit processes, where most of the impacts are created. LCA is an effective tool for evaluating existing product systems or newly designed systems sustainability.

Data collection and quality

For this study, used secondary data is collected from public sources and are process specific. Collected data was qualified for general evaluation of capture technologies although some limitations were found. Some of the data is from scientific publications, which are measured results and based on literature or have conducted research related to capture processes and part of the data is based on evaluations made by an outside scientific party. Due to the nature of this thesis, public data fits for the purpose of this study and gives the coarse results so that further actions can be recommended, and the set goal can be achieved. Requirements for collected data were to be consistent and indicative due to the quantity of open source data. This thesis provides indicative information and basis for further studies to continue and focus on the smaller segment of refinery CO_2 capture.

The amount of energy needed for capture is essential, when analyzing the environmental impacts of the studied system. To determine the energy demand for capture agent regeneration, basic data was gathered from the theory chapter. All used data sources can be found from the references at the end. There was some variation and limitations regarding power consumption and reboiler duty data. Credible results could be achieved with multiple data points, but the lack of data causes some uncertainties, although results are indicative. Energy flows are based on theory chapter values and multiple scenarios are simulated to achieve more dispersed results and sensitivity of the results is studied by using various values. Only variables in this study are energy demand values for steam and electricity. GaBi software has an emission factor of 51,8 kg CO_2 eq/GJ for electricity grid mix and 74,5 kg CO_2 eq/GJ for steam produced from NG with 90 % efficiency. Steam and electricity could be produced as combined production of heat and power (CHP), but in case of refineries, electricity can be taken easily from the grid rather than producing it. Steam is used in many refining processes and it is mainly produced from low grade refinery gases in refinery plot.

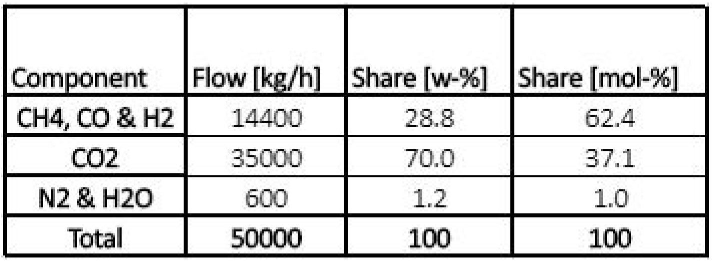
LCA models and their scenarios were constructed so that the used regeneration energy values variation effect on sustainability and CFP could be assessed and to get some comparison results and evaluate their sensitivity. Stripper column reboiler duty values for amine treatment are from several sources and highest value found was over two times the lowest value. One minor challenge was to found electricity consumption for process equipment such as pumps and fans for amine and selexol processes. Selexol and PSA technologies utilize electricity in their regeneration, but alternative scenarios for selexol process were made, where steam is applied with electricity for co-regeneration. General challenge is the sensitivity of the results that lies with regeneration energy, which is the most critical factor for capture process environmental impacts. Minor uncertainty is the power consumption for amine treatment equipment that is from a single source, though it has small impact on the results.

According to Young Guy et al. (n.d.) MEA solvent has an emission factor from its production of 3,4 kg CO_2 eq/kg. This factor should be considered with amine treatment impacts, but real impacts are hard to assess due to process specificities such as solvent evaporation, degradation (chemical/thermal/oxidative) or formation of intermediate products. During MEA degradation, ammonia is formed around 0,136 kg/tCO_2 captured and MEA is also evaporated by itself around 0,014 - 0,063 kg/tCO_2 captured. Solvent losses and general solvent loading deterioration requires that fresh MEA must be added around 0,5 - 3 kg/tCO_2 captured in power plant operations. (van der Giesen et al. 2017) 3 kg/tCO_2 captured MEA loss was assumed and its supplementation emissions are considered. There were no emission factors found for selexol solvent and PSA adsorbents.

Tail gas

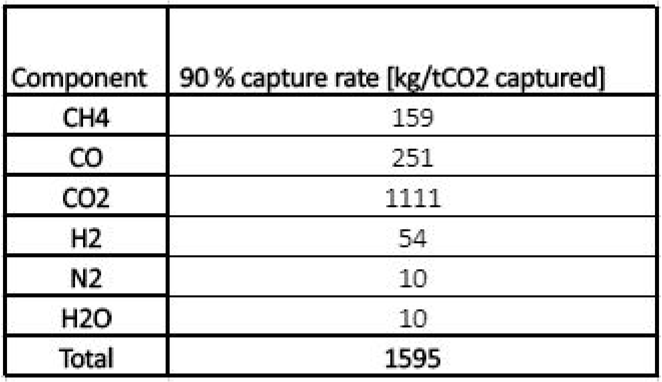
Tail gas is been divided into components in table 3.1, but allocation is not needed, because all the components are from the same single product system so all the impacts can be focused on one process. As the functional unit is set to 1 ton/CO_2 captured, the tail gas flow and components are normalized in relation to functional unit and 90 % capture rate, which means that roughly 1111 kg of CO_2 is needed to capture a ton of CO_2 at 90 % capture rate. Normalized tail gas components and their m-% and mol-% can be found in table 3.2. Used tail gas component mass shares are rounded for an easier calculation and modeling. it is noted that tail gas can have various compositions depending on the SMR unit design or feed.

Table 3.1. Assumed tail gas composition before capture unit (Turunen 2019)



Component	Flow [kg/h]	Share [w-%]	Share [mol-%]
CH4, CO & H2	14400	28.8	62.4
CO2	35000	70.0	37.1
N2 & H2O	600	1.2	1.0
Total	**50000**	**100**	**100**

Table 3.2. Normalized component mass flow kg/ tCO_2 captured at 90 % capture rate



Component	90 % capture rate [kg/tCO2 captured]
CH4	159
CO	251
CO2	1111
H2	54
N2	10
H2O	10
Total	**1595**

Assumptions

All three constructed models have the same functions, system boundaries and basic inflows for the capture unit as in figure 3.1. Tail gas composition form table 3.1 is assumed to be the same at every model and there is no CO_2 escape from SMR-PSA unit prior to capture. Also, 90 % capture rate is used in every model and the 10 % of tail gas CO_2 that is not captured, is not considered emission for capture process. 1595 kg of tail gas has a combustible components that have a higher heating value of 19 GJ/tCO_2 captured at given 90 % rate. Set 90 % capture rate is not in technical limits or in optimal economic point.

Carbon capture is a unit process, which involves a capture agent, gaseous feed mixture, energy input and process equipment for CO_2 separation. Ensuring data quality and accuracy for inventory analysis is challenging, when considering factors such as various process configurations, chemical reactions and refinery complexity for example. All these factors have an effect on the results and some assumptions had to be made to simplify the modeling and to leave unnecessary uncertainties out from the study. The purpose is to get indicative results about refinery CO2 capture sustainability and used secondary data quality only enables general sustainability evaluation. Following assumptions were made for the study and constructed models:

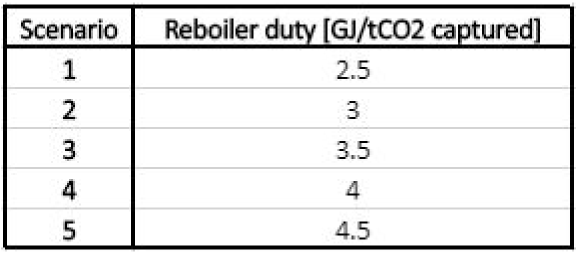
- Tail gas composition is the same in all models
- 90% capture rate in every model
- Complete absorption & adsorption
    - Exact amounts absorbed and released
    - No co-absorption of other components
- Complete heat transfer
- No solvent degradation
    - No emissions from the initial solvent input to the system
    - MEA loss of 3 kg/tCO_2 captured
- Steady operating conditions
    - Temperature
    - Pressure
    - No impurity effects on capture

Amine model

Constructed model of amine treatment (Appendix 6) has one mass input and two energy inputs. Mass flow to capture unit is the PSA tail gas from which a ton of CO_2 will be captured. Amine model utilizes steam for solvent regeneration and in total 5 scenarios with different steam inputs were constructed. Electricity consumption is constant in every amine model scenario and according to IPCC (2005) average electricity consumption per t/CO_2 captured is between 00.6 - 0.11 GJ. 0,11 GJ was used in this case. Also, 3 kg of solvent loss is assumed per t/CO_2 captured (Young Guy et al. n.d.)

Selected energy input values did not consider capture rate, even though in practice it depends on it. It is challenging to estimate amine treatment energy consumption for different feeds due to their volume, impurities, CO_2 concentration and partial pressure for example. Selected value range is based on the theory section and data sources can be found from list of references. Due to limited data, data quality and consistency, LCA model is done for 30 % MEA solvent for simplification. MEA is widely applied amine and there is data related to it and its consistency was found acceptable. MEA and amine solvents generally have different regeneration energy demands between solvents and different feeds. There are novel solvents developed and some additives and promoters can be used to improve their properties. Novel solvents have been reported to have regeneration energy demand in the range of 2,5 - 3 GJ/tCO_2 captured (IPCC 2005), whereas traditional amines can have up to 5,5 GJ/tCO_2 captured at 90 % + capture rate (Luis 2016). Therefore different scenarios were made to amine models and also to study the sensitivity of regeneration energy variation to CFP. Energy values for 5 different scenarios can be seen in table 3.3.

Table 3.3. Amine model reboiler duty scenarios



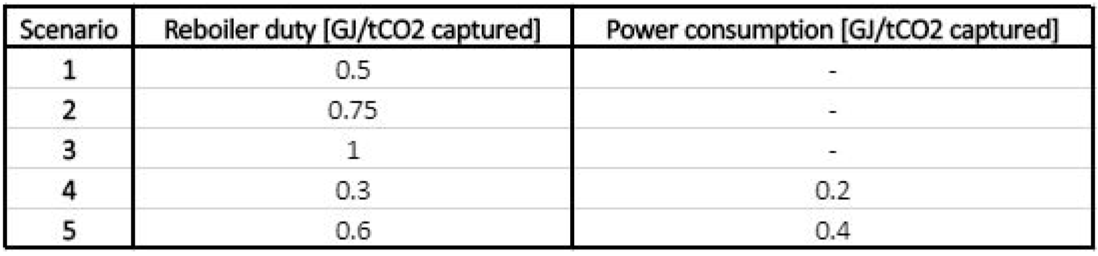
Scenario	Reboiler duty [GJ/tCO2 captured]
1	2.5
2	3
3	3.5
4	4
5	4.5

Selexol model

Selexol model was constructed similarly to amine treatment and the basic flow chart remains the same. Major difference to amine model is that selexol solvent is regenerated via pressure swing and not stripping. Physical solvents have strong relation to CO_2 partial pressure and in theory have potentially higher capacity than chemical solvents. Process operating conditions define the energy parameters and it is hard to estimate the real energy consumption. In selexol process, CO_2 is forced into solvent, which is typically operated in 2 - 16 MPa (CO_2 partial pressure > 70 bar) and 5 - 40 °C conditions (Rackley 2010) (Maroto-Valer 2010). Higher the pressure and lower the temperature equals better CO_2 solubility to solvent.

Selexol process can have various configurations due to regeneration alternatives but in this case, pressure swing was found best solution. 5 different scenarios are constructed for selexol model and all of them consume electricity, but scenarios 4 & 5 utilize also steam in co-regeneration for comparison reasons and to study CFP sensitiveness. Selexol model can be found in Appendix 7 and scenarios can be seen in table 3.4. Electricity in selexol process is consumed by compressor and refrigerator units. Series of flash tanks are utilized to separate liquid and gas phases when CO_2 rich solvent pressure is reduced in stages to separate CO_2. Two reference values for selexol CO_2 capture was found; 1) 566 - 1020 $kJ/kgCO_2$ (Guo et al. 2012) and 2) 189 $kJ/kgCO_2$ (Lemonidou 2017). Firstly presented value is the capture electricity consumption via pressure swing regeneration simulated Guo et al. (2012) and secondly presented value from Lemonidou (2017) is a reboiler duty energy demand when regeneration is done via heat.

Table 3.4. Selexol model reboiler duty & power demand scenarios



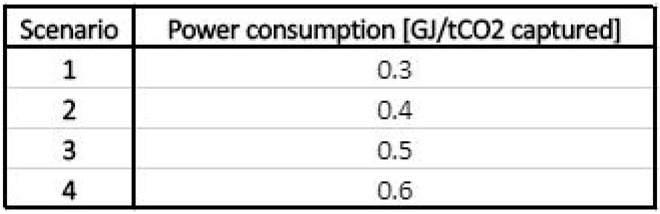
Scenario	Reboiler duty [GJ/tCO2 captured]	Power consumption [GJ/tCO2 captured]
1	0.5	-
2	0.75	-
3	1	-
4	0.3	0.2
5	0.6	0.4

PSA model

PSA technology differs from the two previous models from a technical point of view, although regeneration is done via pressure swing as in selexol process. Constructed PSA model (Appendix 8) is similar to the amine- and selexol models and the flow chart remains the same as well. PSA energy consumption is due for compressor that is used to pressurization and regeneration. Power consumption depends on the volume, temperature and composition of the feed gas. In case of PSA model, 4 different scenarios for evaluation of CO_2 capture and CFP sensitivity were made.

Used values in PSA scenarios are based on earlier presented value of 459 kJ/kgCO_2 captured, by Guo et al. (2012) and can be seen in table 3.5. That value was reported to be from CHP plant post-combustion capture, which means that true value could be lower for tail gas capture due to CO_2 concentration, volume and lack of combustion impurities. Data quality regarding the PSA regeneration energy values was found poor and lacking due to technological immaturity and similar usage. This model should give indicative results regarding the PSA CFP on different electricity demands.

Table 3.5. PSA model power consumption scenarios

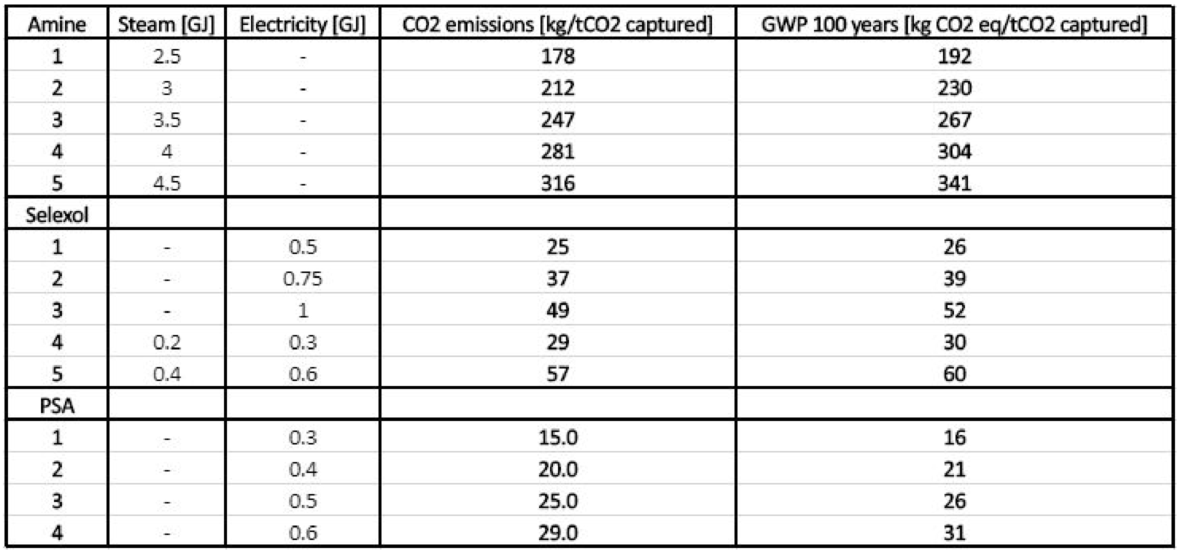


Scenario	Power consumption [GJ/tCO2 captured]
1	0.3
2	0.4
3	0.5
4	0.6

4.2.3 Impact assessment

According to ISO-14067 climate change can be indicated as a single impact category of “GWP 100 years”, which is used to quantify the global warming potential of all three constructed models. CML2001 – Jan.2016, Global Warming Potential (GWP 100 years) (excluding biogenic carbon) is quantified as kg CO_2 eq. By utilizing single impact category, weighting and normalization can be avoided, due to lack of need for selecting significant impact categories for the product system. In addition, capture agent emissions should be added to CFP results in order to determine technologies net CO_2 capture potential when all of their characteristic operating emissions are considered. GWP is a measure of how much heat specific GHG emission traps in the atmosphere during the time horizon relative to CO_2. In this case, 100 year's time horizon was selected, and results are characterized in relation to it. According to ISO-14067: “There is no scientific basis for choosing a 100-year time horizon compared to other time horizon”. But when considering that some gaseous emissions can absorb heat energy for a long time, contribution of GHG emissions to global warming will increase during that time horizon. GWPs and CO_2 emissions of constructed models are presented in table 3.6 below.

Table 3.6. LCA CO_2 emissions and GWP-100 values for different scenarios per t/CO_2 captured



Amine	Steam [GJ]	Electricity [GJ]	CO2 emissions [kg/tCO2 captured]	GWP 100 years [kg CO2 eq/tCO2 captured]
1	2.5	-	178	192
2	3	-	212	230
3	3.5	-	247	267
4	4	-	281	304
5	4.5	-	316	341
Selexol				
1	-	0.5	25	26
2	-	0.75	37	39
3	-	1	49	52
4	0.2	0.3	29	30
5	0.4	0.6	57	60
PSA				
1	-	0.3	15.0	16
2	-	0.4	20.0	21
3	-	0.5	25.0	26
4	-	0.6	29.0	31

4.2.4 Interpretation

This final sub-chapter will present results and discussion of the LCA study. Interpretation is the last phase of LCA in which the inventory analysis data and impact assessment results are evaluated, and most significant ones are identified. The results were categorized by the technology scenarios and characterized by category indicator and quantified. Every scenario is represented by value of GWP that identifies CFP in 100-year time period. Interpretation intends to report the LCA results clearly and sensitivity analysis will be conducted later.

Life cycle results

Based on the LCA modeling and impact assessment, it can be said that amine treatment has by far the highest GWP value. PSA and selexol processes rank well below amine treatments GWP values and have less variation due to pressure swing regeneration instead of stripping. Results are only valid for SMR units that use NG feed and have PSA unit for H_2 separation. Based on the findings, CFPs varies from 16 to 341 kg CO_2 eq/tCO_2 captured + 10,2 kg CO_2 eq/tCO_2 captured for amine treatment from MEA supplementation.

Variation between results is significant when considering that ton of CO_2 is captured from the same stream. CO_2 capture LCA results are only characterized by the impacts from heat and power inputs, because they were the only used factors in this study. As indicated, steam has higher specific emission factor per energy content than electricity and due to high steam consumption amine treatment causes highest environmental impact. It can be noticed from selexol scenarios (4 & 5), where steam is used for co-regeneration, the GWP values increase although the energy input stays in the same range as in the other scenarios.

Results seem to be consistent with the input data and relation between energy inputs and end results is correlative. It is found that results follow the given data as a linear pattern meaning that GWP value increases in the same relation as the input energy increases. This is due for single parameter change in the models and effects can be seen clearly. Steam has major impact on amine treatments CFP and amines generally require intensive stripping to release the CO_2. GWP 100 years results for the technologies and scenarios can be found in figure 3.2 below and captured net CO_2 is calculated into table 3.7 by using equation 7.

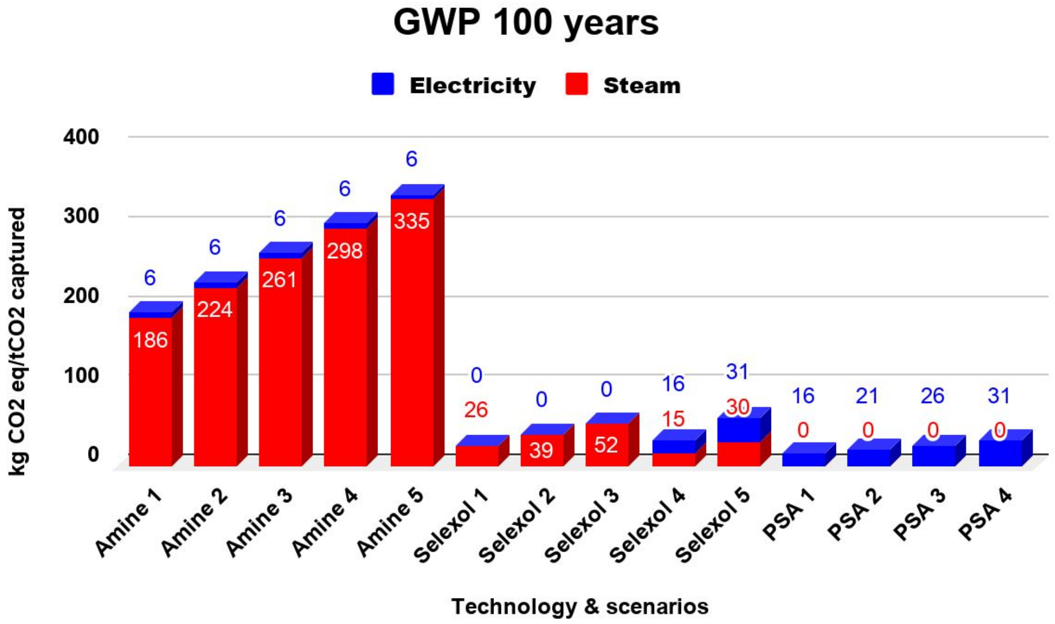
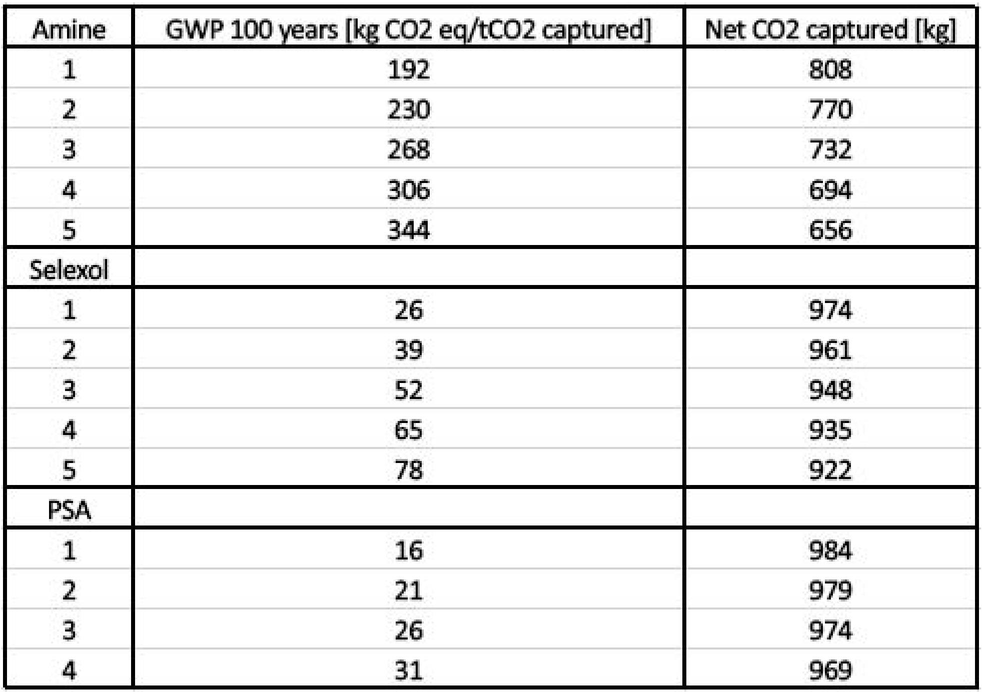


Figure 3.2. LCA results presented in diagram based on table 3.6

$$CO2\ captured_{net} = Captured\ CO2\ -\ Capture\ emissions \quad (7)$$

Table 3.7. Captured net CO_2 for different scenarios



Amine	GWP 100 years [kg CO2 eq/tCO2 captured]	Net CO2 captured [kg]
1	192	808
2	230	770
3	268	732
4	306	694
5	344	656
Selexol		
1	26	974
2	39	961
3	52	948
4	65	935
5	78	922
PSA		
1	16	984
2	21	979
3	26	974
4	31	969

According to table 3.7, every capture process can achieve CO_2 reduction by turning the SMR-PSA tail gas one step closer to a carbon neutral H_2 production. It must be noted that no technology can recover all the CO_2 from the tail gas and therefore, 111 kg of uncaptured CO_2 at given 90 % capture rate is emitted. This isn't considered when assessing capture CFP.

Sensitivity analysis for process parameters

In this sensitivity analysis, used steam and electricity process from GaBi database are simulated under different nationalities to identify the sensitivity of the obtained results. Sensitivity analysis is done by using 1 GJ energy value for both steam and electricity. Selected nationalities are US, China and EU-28 (average value on EU area). Tabled results can be seen in figure 3.3 below. Steam and electricity were selected for sensitivity analysis because they were the only two variables in selected technologies.

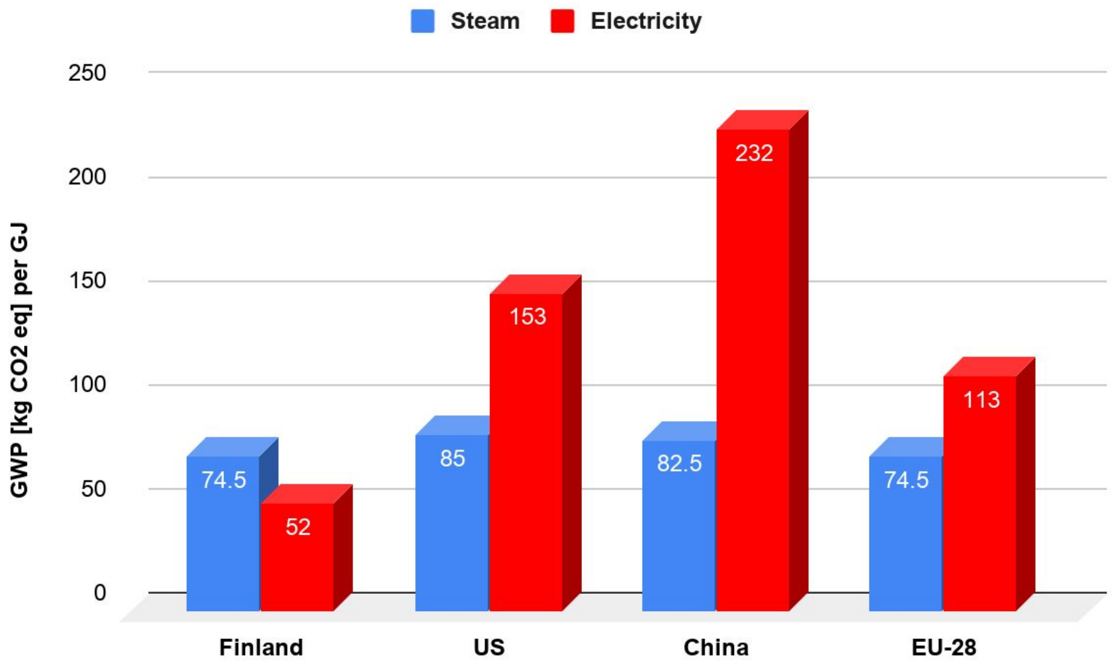


Figure 3.3. Sensitivity analysis for steam and electricity per GJ

It can be clearly noticed that used Finnish steam and electricity processes produce the lowest GWP impacts compared to others. Steam GWP impact variation was at highest around + 12 % compared to used Finnish value of 52 kg CO_2 eq/GJ, whereas electricity was almost 4 ½ times higher in case of China compared to used processes. This sensitivity analysis demonstrates that there are notable differences between countries electricity production. Used “grid mix” process for electricity is a sum of used power generation technologies in selected country. The US and China strongly depend and rely on fossil fuels such as coal and NG, which explains the results. In this case, if electricity process under different nationality would have been used, there would have been notable differences in captured net CO_2. It must be emphasized that Finland has low electricity GWP impact even when compared to EU-28 value, that is over 2 times greater.

Limitations and recommendations

Limitations and recommendations should always be considered when conducting LCA and CFP modeling based on ISO-14044 & 14067. In this study, there were some limitations that could have a negative impact on the results reliability. Also, prior listed assumptions had to be made for simplification of the study that can have an effect when comparing process in theory to practice. Carbon capture and storage is a production chain that covers emission source, CO_2 capture, compression, transport and sequestration or utilization. Only capture stage was considered and rest of the production chain were left out from system boundaries. Also, capture equipment manufacturing, and service were ruled out. Most limitations are data related and as recognized in the theory chapter, that carbon capture has low technical maturity which affects data availability. Due to limited data and technical maturity, this study provides indicative results that have certain margin of error as seen in sensitivity analysis before. Limited and low-quality data affected to scope and depth and caution is advised before making decisions based on this study.

It must be emphasized that the used processes from GaBi database for steam and electricity generation are provided by software and don't necessarily represent the actual case of the practical operation, which could be dependent on location, season, fuel and fuel prices for example. Energy parameters were based on the scientific literature and there were limited amount of data regarding the energy values for CO_2 capture/agent regeneration. This is why it's essential to create multiple scenarios to achieve dispersion in results by using various input values from different sources. Only few sources were found for selective PSA and selexol technologies, whereas amine values were constructed by the data from various sources. It is pointed out that given values for energy are from scientific journals and laboratory/piloting sized configurations that cannot produce exact data for large scale processes as simulated in this study.

Capture agent production and amounts have impacts and their evaporation if an open system is used. MEA can absorb CO_2 at highest rate mole-per-mole basis, whereas selexos is directly dependent on CO_2 partial pressure, pressure, concentration and temperature. Adsorbents in moderate temperatures usually have a long lifetime and the same amount can be used for large amount of treated CO_2. Adsorbents emission factor is preferably lower than solvents, which are consumed, evaporated, degraded or lose their activity.

There are currently available novel amine solvents that have chemical promoters and additives to improve solvent loading and reaction kinetics. These kinds of factors have an effect on capture sustainability and reboiler duties have been reduced with new stripper configurations so that 10-year-old data isn't necessarily valid anymore. Also, variation in feed streams can cause different outcomes in sustainability perspective and as seen, country specific energy production impacts should be evaluated case by case.

Life cycle assessment discussion

This LCA study was conducted to provide indicative results for oil refinery CO_2 capture from SMR unit PSA tail gas. CO_2 capture could become a necessity in the future and based on these results, selexol and PSA could be suitable technologies from a sustainability perspective. It was also found that based on amine solvent emission factor, capture agent impact on the results is minor, if only supplemented solvent is considered. Some assumptions were made to simplify the process modelling for the comparison. Due to limited data, study depth and scope were limited. Only one source of information was found for MEA emission factor, and it should be treated with caution. There was no data found regarding the selexol or selective adsorbents emissions from manufacturing that would increase their CFP results, that's why further research is recommended. As stated, limited data and technological immaturity enhances a concern that should be highlighted. Obtained results were anticipated and it was known beforehand that amine treatment is energy intensive technology. Capture technologies are only comparable when they are applied to the same stream. To ensure comparable results, the same feed stream has been used in every case.

In sensitivity analysis, it was found out that energy and electricity in particular have a huge impact on the results if this study or actual operation were to be carried out in other countries. Capture cost is affected by the actual net CO_2 captured, which will ultimately determine the potential and sustainability of the technology employed. Oil refineries usually have low-grade hydrocarbon streams that are used in energy generation due to low refining potential. Steam and electricity from this kind of energy generation is not represented in GaBi software. It was decided that “Steam from NG” at 90 % efficiency was close enough to refinery situation and NG is structurally closest one to used refinery gases chemical composition. As discussed in LCA models, CO_2 was captured at 90 % rate and 111 kg of CO_2 was let through uncaptured and wasn't considered capture process emission.

Steam and electricity inputs are in relation to feed gas volume and in some capture process, scaling upwards can have positive effects on sustainability and that's why large sources are desired. Feed gas must often have a mandatory cooling that could be used for energy recovery. Energy could be harvested instead of waste and low-grade steam or heat could be produced to heat boiler feed water for example. Also, refinery PSA tail gas compositions can vary, depending on the SMR feedstocks for example. As stated, NG (mainly CH_4) has the highest H_2 content relative to molecular weight compared to other higher hydrocarbons.

CO_2 concentration strongly effects on technology selection and also equipment sizing such as absorber. In amine treatment, absorber is the largest and most expensive equipment, which is affected by the dilute CO_2 stream that increases its size and requires large contact area for effective separation. Also, solvent flow is determined by the CO_2 concentration and feed gas flow. In the case of amine solvents, mixing ratio of solvents, typically around 30 %-wt, can influence on reboiler duty due to water heating during stripping. Equipment sizing and optimization in modern column configurations can achieve high capture rate and energy efficiency. In this study, selexol and amine solvent absorber configurations were “closed system” without any gas or solvent losses, where the treated gas is combusted instead of release. Tail gas has a hint of N_2 that is a typical flue gas component and has increasing effect on absorber sizing. Equipment and their operating conditions like temperature and pressure can have large impacts on sustainability and for example in selexol process, temperature strongly effects on refrigeration unit's energy input. Temperature also generally effects on solvent viscosity and in low temperatures, aqueous mixtures become denser. These kinds of thermodynamic phenomena have an effects and assumptions are used to simplify the modeling and calculations instead of managing large amounts of data.

Selective PSA capture can be perceived as a separate unit or an added module for refineries current PSA system. In case of modeling, this makes no difference, though retrofitting to an existing system can have some advantages and energy consumption can be estimated to remain the same, but the system construction impact is lower. New PSA system is costly, and it has a large technical footprint so addition of adsorption vessels to an existing system can be considered. CO_2 selective adsorbents can have different adsorption properties that can affect adsorbent loading, kinetics and cycle times. These factors have direct relation to energy consumption and technological suitability for given purpose.

Although, selexol- and PSA models were constructed in a way that electricity was primarily used for regeneration, both could be regenerated with heat as well. Low pressure steam could be applied to selexol process for stripper column reboiler and for PSA by changing its configuration to TSA. By applying heat to selexol regeneration, more complete regeneration is achieved with co-regeneration of pressure- and temperature swing. Temperature swing would increase the solvent temperature and refrigeration unit power demand. Usually, it is easier to utilize pressure swing with selexol process, because compressor is required anyway, and flash tanks are easier to operate.

PSA could be modified to be regenerable via heat but currently the adsorbent development is lagging and medium temperature adsorption applications for CO_2 capture are missing. PSA is more of a bulk separation technology and can remove a large share of CO_2 with reasonable purity. It also requires a high CO_2 concentration in the feed gas to achieve high purity product gas, which could be used as a purge for desorption and clearing the adsorbent bed. PSA for CO_2 separation has a development status and there is a lack of comprehensive data of adsorbent effectiveness in CO_2 removal and regeneration. If applied in refinery scale, PSA system would need a large amount of sorbent to handle the feed gas volumes and due to poor heat transfer between solid and gas substances, cycle times would be long. Thus, further research is needed for reduction of energy penalty, high capacity adsorbents and for sorbent impurity resistance.

5. Conclusions

There's been progress in CO_2 capture during the past decade and new research and technologies have surfaced due to the changes in situation of emission management and legislation. There are only a few LCA studies done on CO_2 capture and even fewer on refinery capture. It was found that new potential technologies are piloted, and traditional absorption-based technologies still dominate the field of acid gas treatment. Lack of incentives, political- and legislative framework are inhibiting the wide scale adoption and there haven't been demand on the markets for capture technologies so the development has been on hold or neglected. With the demand for capture technologies, market forces could shift towards their adoption and achieve GHG reduction.

ETS price is the dominant factor and decides when the capture can become economically feasible. EU 2020 targets are approaching, and applied measures are evaluated and new ones established for mitigating climate change. Corporate responsibility has an effect on actions against climate change in corporate level and inactivity could become costly in near future when mandatory measures are required.

There are currently commercial pre- and post-combustion capture installations in various scales applied for acid gas removal in industrial sector. Major disadvantage for CO_2 capture is its high operating costs and energy demand, that has a large contribution to the costs. Costs are also due for combustion-based capture installations, which produce dilute CO_2 flue gas. Carbon capture is widely researched topic and cost reduction is pursued. Many of the presented technologies are in development stage and haven't been established in large-scale, which is why cost estimates are indicative. Before commercialization, technology must be proven and demonstrated successfully.

Refineries are large stationary CO_2 emitters with large volume- and mass-flows, which require large-scale solutions. Major disadvantage for refineries is that they aren't one-point emitters but have scattered sources. Actions towards CO_2 reduction in refineries are inevitable and when rapid reduction of CO_2 emissions is under consideration, only commercialized scalable technologies should be considered. CO_2 capture will become potential option if economic and technical criteria are fulfilled. It was concluded that capture in modern refineries requires focusing on most concentrated and large volume emission sources that can have an effect on emission balance from which SMR-PSA tail gas was found to be most attractive and here are hardly any technical barriers associated with CO_2 capture in industrial scale H_2 production. FCC and process furnaces were left out from further studies due to their outlet gas stream volumes, mass flow, dilute CO_2, impurities and temperature, which would result substantially higher capture costs. Commercial selexol treatment was found to be most attractive technology for tail gas CO_2 capture.

Carbon capture in refinery surrounding is a complex process, which requires infrastructure around it to ensure continuous operation. Usually, modern refineries have already existing infrastructure and resources such as equipment, piping, tanks and means of transportation that could be utilized in capture production chain. There are factors to consider before selecting suitable technology for CO_2 capture such as differences in refinery complexity, location, crude quality and energy generation. Therefore, there is no universal capture solution that would be suitable for all refineries and any case study results wouldn't be valid when refinery configuration and location are changed for example. When selecting the suitable capture technology for refinery, not only CFP applies. Many processes are crucial and capture impacts on unit processes should be investigated. In SMR capture, only SR furnace operations are affected by change in tail gas composition. In the context of SMR, unit lifetime, retrofitting potential and energy efficiency should be considered as well.

In theory, retrofitted capture unit could utilize waste heat, electricity and other resources that are already found from refineries. Waste heat utilization could have a notable effects on capture CFP, but energy availability between refineries should be evaluated case-by-case basis. Steam generation impacts could be reduced by displacing it with low pressure excess steam that would be otherwise wasted. Regeneration via waste heat such as low-pressure steam for adsorption or absorption could be more sustainable than studied cases and an interesting field of research before ETS price increase or necessary CO_2 capture. Also, when steam and electricity are produced by using renewable fuels, environmental impacts are reduced, and it should be considered when determining the CFP.

In this study, technologies were compared based on the indicative results that suggest that selexol and PSA technologies have lower impacts than amine treatment. It was also found that capture agent emissions have a minor effect on technologies CFP when initial solvent input for system wasn't considered. When capture rate is increased, the absolute cost of capture increases as well although the price per captured CO_2 amount might reduce. The optimal rate must be found and if technologies could capture more of uncaptured excess CO_2 by increasing their own GWP value less than the amount of uncaptured CO_2, it would be favorable because otherwise the passing CO_2 is considered an emission. It is obvious that carbon capture in refinery as in any case should capture more CO_2 than emit it when considering process energy inputs and their environmental impacts. Also, some scale impact reduction is desired for process to be worthwhile.

There is a fundamental difference between net CO_2 captured that is relevant to the purpose of CO_2 capture and CO_2 captured that capture process have to accomplish. This has major effects on the needed resources and related costs regarding the capture processes and energy demand. In order to avoid the CO_2 generated by a facility, capture unit must be built which can capture more CO_2 than just amount wanted to be “avoided”. Overall captured amount could be reduced as a result of process optimisation and improvements in capture technologies. This captured net CO_2 could be used as indicator for technology comparison. Carbon capture would considerably increase refineries energy consumption because capture operation requires more resources to produce the same output of energy to end users. This will be a major challenge in the context of already limited energy reservoir and especially with fossil sources.

Energy management will become an important factor in environmental impacts, when refineries have to apply CO_2 capture, which highlights that the refinery complexity, feed gas composition, energy production, fuel, location and other characteristics that have a direct impact on CO_2 capture, operating requirements and GWP value. Capture process that could lead to permanent sequestration, CO_2 utilization with economical value or can be integrated into a closed loop without any CO_2 losses is the best system. This system model could reduce carbon emissions along with the use of virgin materials and production costs. This model is hopefully applied to SMR unit, which was found best source for CO_2 capture currently and for prospects.

Based on findings, carbon capture is a future solution due to its current stage, research of the novel technologies, ETS price and high operating costs. Further research is recommended along with other options to reduce emissions and improve efficiency. ETS price and competitor's actions should be monitored.

6. Summary

Although, there are a range of capture technologies, there aren't many viable solutions for large scale adoption, although technologies are heavily researched internationally. There is not any clear imminent winner technology and the lack of suitable applications or geological storages means that foreign storages must be considered, and global geopolitical and corporate negotiations need to take place to implement large-scale CCS. In many cases, significant factor regarding the viability and profitability of CO_2 capture is the ETS price for CO_2 and the cost of energy needed for operations. Also, it is noted that more efficient H_2 separation in SMR unit prior/alongside the capture could lead to better efficiency of SMR and capture units as well as profits. Hydrogen production is estimated to grow and actions towards CO_2 capture from H_2 production are advised.

Most popular actions and alternatives for CO_2 capture are improving energy efficiency of energy production, increasing the utilization of renewable energy sources and replacing fossil fuels by carbon neutral biomass or co-firing. There is always an option to wait and assess the need for capture while the ETS price reaches the point that capturing CO_2 becomes economical. Therefore, regulatory and political framework are needed to create incentives for CO_2 capture, storage and utilization.

Based on the results of this thesis, it can be concluded that for the implementation of SMR-PSA tail gas capture in refineries; 1) considerable increase in ETS values, 2) mandatory regulation of CO_2 capture or 3) major breakthrough is required to CO_2 capture succeed compared to current situation. Capture is still too expensive, technologically immature or challenging to retrofit. Only large stationary sources are considered when planning CO_2 capture. Multiple small source capture has been recognized to have notably higher cost than already expensive dilute CO_2 streams. From a sustainability perspective, it is extremely important that capture processes energy penalty incurred does not result in increased emissions. All in all, based on this master's thesis, it can be concluded from economic perspective that the integration of a CO_2 capture unit should be placed after the SMR-PSA unit if the ETS price allows the SMR combined with capture unit to operate above or near the economic breakpoint.

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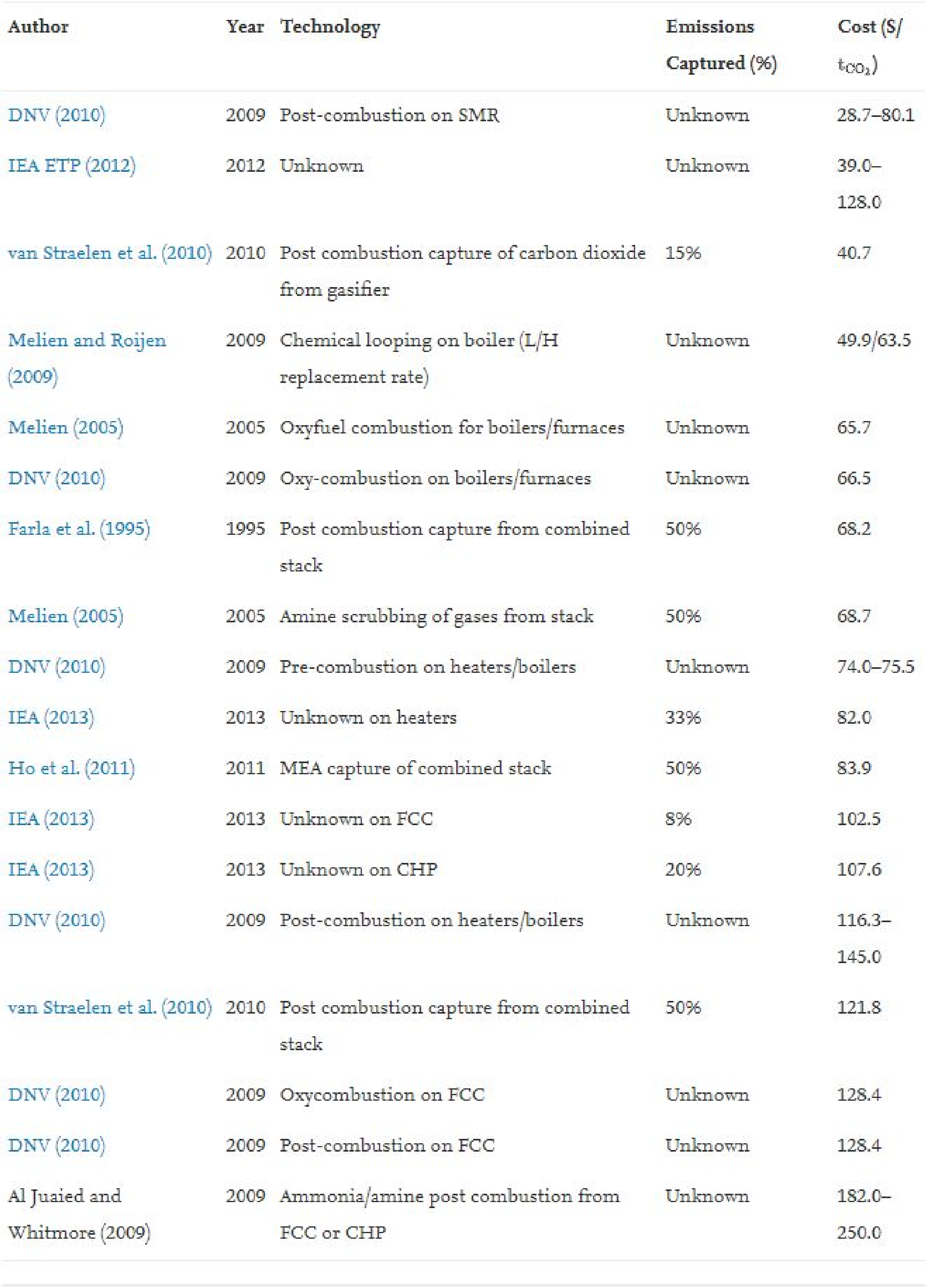
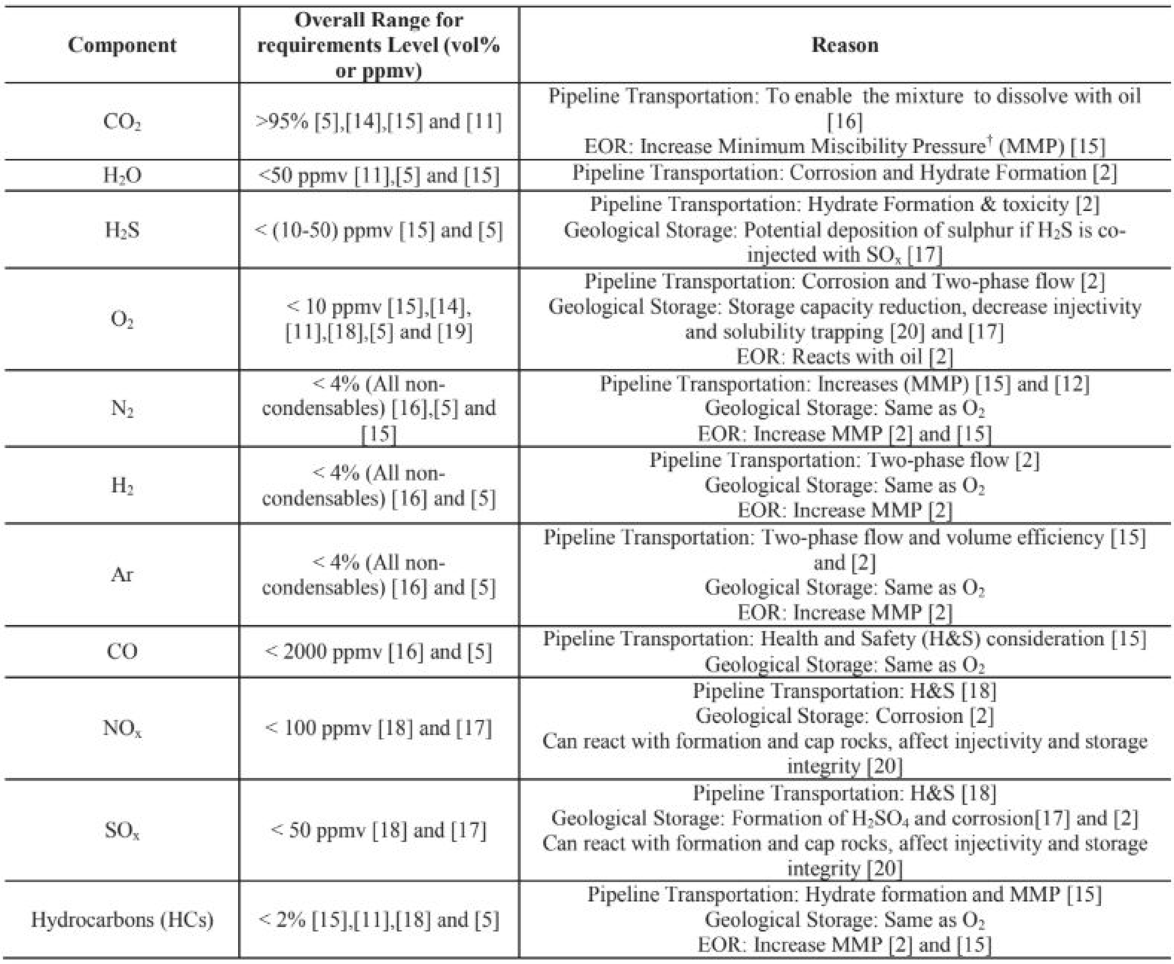
APPENDIX 1. Capture costs (Leeson et al. 2017)



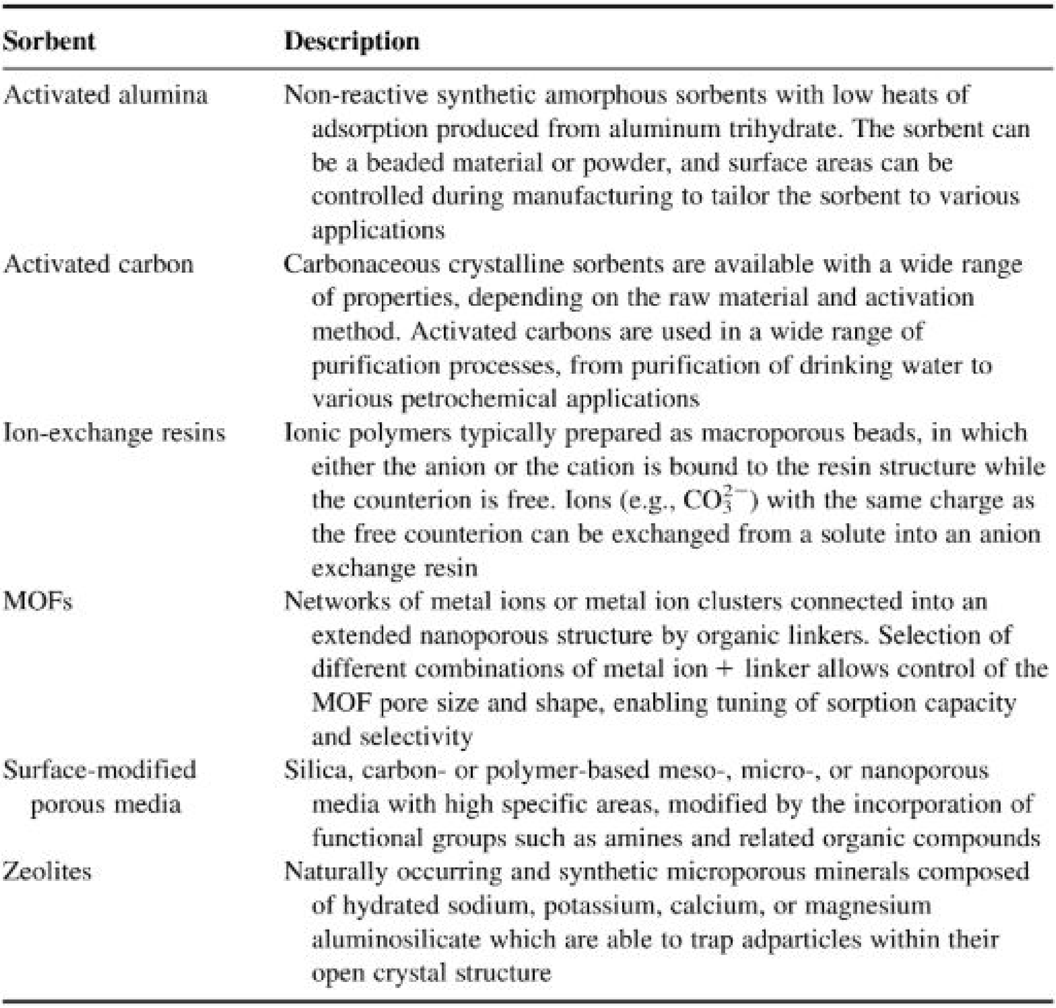
Author	Year	Technology	Emissions Captured (%)	Cost ($/$t_{CO_2}$)
DNV (2010)	2009	Post-combustion on SMR	Unknown	28.7–80.1
IEA ETP (2012)	2012	Unknown	Unknown	39.0–128.0
van Straelen et al. (2010)	2010	Post combustion capture of carbon dioxide from gasifier	15%	40.7
Melien and Roijen (2009)	2009	Chemical looping on boiler (L/H replacement rate)	Unknown	49.9/63.5
Melien (2005)	2005	Oxyfuel combustion for boilers/furnaces	Unknown	65.7
DNV (2010)	2009	Oxy-combustion on boilers/furnaces	Unknown	66.5
Farla et al. (1995)	1995	Post combustion capture from combined stack	50%	68.2
Melien (2005)	2005	Amine scrubbing of gases from stack	50%	68.7
DNV (2010)	2009	Pre-combustion on heaters/boilers	Unknown	74.0–75.5
IEA (2013)	2013	Unknown on heaters	33%	82.0
Ho et al. (2011)	2011	MEA capture of combined stack	50%	83.9
IEA (2013)	2013	Unknown on FCC	8%	102.5
IEA (2013)	2013	Unknown on CHP	20%	107.6
DNV (2010)	2009	Post-combustion on heaters/boilers	Unknown	116.3–145.0
van Straelen et al. (2010)	2010	Post combustion capture from combined stack	50%	121.8
DNV (2010)	2009	Oxycombustion on FCC	Unknown	128.4
DNV (2010)	2009	Post-combustion on FCC	Unknown	128.4
Al Juaied and Whitmore (2009)	2009	Ammonia/amine post combustion from FCC or CHP	Unknown	182.0–250.0

APPENDIX 2. CO2 quality requirements for range of applications (Abbas et al. 2013)

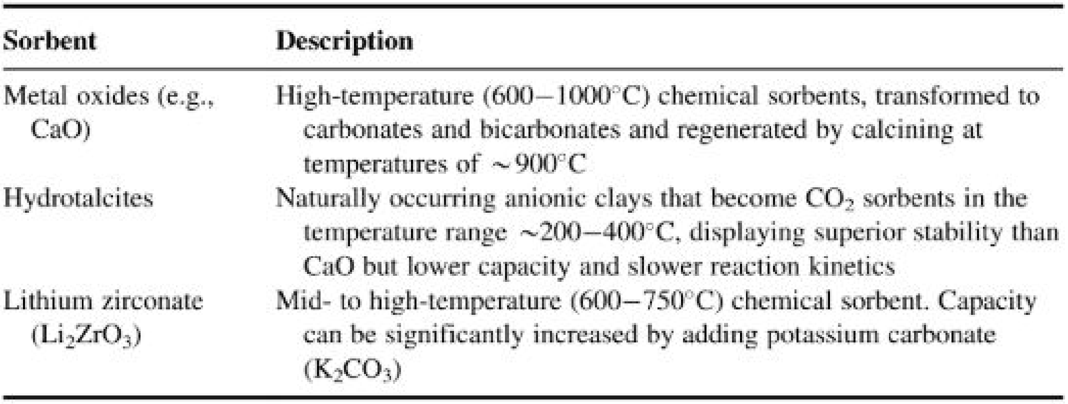


Component	Overall Range for requirements Level (vol% or ppmv)	Reason
CO_2	>95% [5],[14],[15] and [11]	Pipeline Transportation: To enable the mixture to dissolve with oil [16] EOR: Increase Minimum Miscibility Pressure[†] (MMP) [15]
H_2O	<50 ppmv [11],[5] and [15]	Pipeline Transportation: Corrosion and Hydrate Formation [2]
H_2S	< (10-50) ppmv [15] and [5]	Pipeline Transportation: Hydrate Formation & toxicity [2] Geological Storage: Potential deposition of sulphur if H_2S is co-injected with SO_x [17]
O_2	< 10 ppmv [15],[14], [11],[18],[5] and [19]	Pipeline Transportation: Corrosion and Two-phase flow [2] Geological Storage: Storage capacity reduction, decrease injectivity and solubility trapping [20] and [17] EOR: Reacts with oil [2]
N_2	< 4% (All non-condensables) [16],[5] and [15]	Pipeline Transportation: Increases (MMP) [15] and [12] Geological Storage: Same as O_2 EOR: Increase MMP [2] and [15]
H_2	< 4% (All non-condensables) [16] and [5]	Pipeline Transportation: Two-phase flow [2] Geological Storage: Same as O_2 EOR: Increase MMP [2]
Ar	< 4% (All non-condensables) [16] and [5]	Pipeline Transportation: Two-phase flow and volume efficiency [15] and [2] Geological Storage: Same as O_2 EOR: Increase MMP [2]
CO	< 2000 ppmv [16] and [5]	Pipeline Transportation: Health and Safety (H&S) consideration [15] Geological Storage: Same as O_2
NO_x	< 100 ppmv [18] and [17]	Pipeline Transportation: H&S [18] Geological Storage: Corrosion [2] Can react with formation and cap rocks, affect injectivity and storage integrity [20]
SO_x	< 50 ppmv [18] and [17]	Pipeline Transportation: H&S [18] Geological Storage: Formation of H_2SO_4 and corrosion[17] and [2] Can react with formation and cap rocks, affect injectivity and storage integrity [20]
Hydrocarbons (HCs)	< 2% [15],[11],[18] and [5]	Pipeline Transportation: Hydrate formation and MMP [15] Geological Storage: Same as O_2 EOR: Increase MMP [2] and [15]

APPENDIX 3. Low- and high temperature sorbents for CO2 adsorption (Rackley 2010)



Sorbent	Description
Activated alumina	Non-reactive synthetic amorphous sorbents with low heats of adsorption produced from aluminum trihydrate. The sorbent can be a beaded material or powder, and surface areas can be controlled during manufacturing to tailor the sorbent to various applications
Activated carbon	Carbonaceous crystalline sorbents are available with a wide range of properties, depending on the raw material and activation method. Activated carbons are used in a wide range of purification processes, from purification of drinking water to various petrochemical applications
Ion-exchange resins	Ionic polymers typically prepared as macroporous beads, in which either the anion or the cation is bound to the resin structure while the counterion is free. Ions (e.g., CO_3^{2-}) with the same charge as the free counterion can be exchanged from a solute into an anion exchange resin
MOFs	Networks of metal ions or metal ion clusters connected into an extended nanoporous structure by organic linkers. Selection of different combinations of metal ion + linker allows control of the MOF pore size and shape, enabling tuning of sorption capacity and selectivity
Surface-modified porous media	Silica, carbon- or polymer-based meso-, micro-, or nanoporous media with high specific areas, modified by the incorporation of functional groups such as amines and related organic compounds
Zeolites	Naturally occurring and synthetic microporous minerals composed of hydrated sodium, potassium, calcium, or magnesium aluminosilicate which are able to trap adparticles within their open crystal structure



Sorbent	Description
Metal oxides (e.g., CaO)	High-temperature (600−1000°C) chemical sorbents, transformed to carbonates and bicarbonates and regenerated by calcining at temperatures of ~900°C
Hydrotalcites	Naturally occurring anionic clays that become CO_2 sorbents in the temperature range ~200−400°C, displaying superior stability than CaO but lower capacity and slower reaction kinetics
Lithium zirconate (Li_2ZrO_3)	Mid- to high-temperature (600−750°C) chemical sorbent. Capacity can be significantly increased by adding potassium carbonate (K_2CO_3)

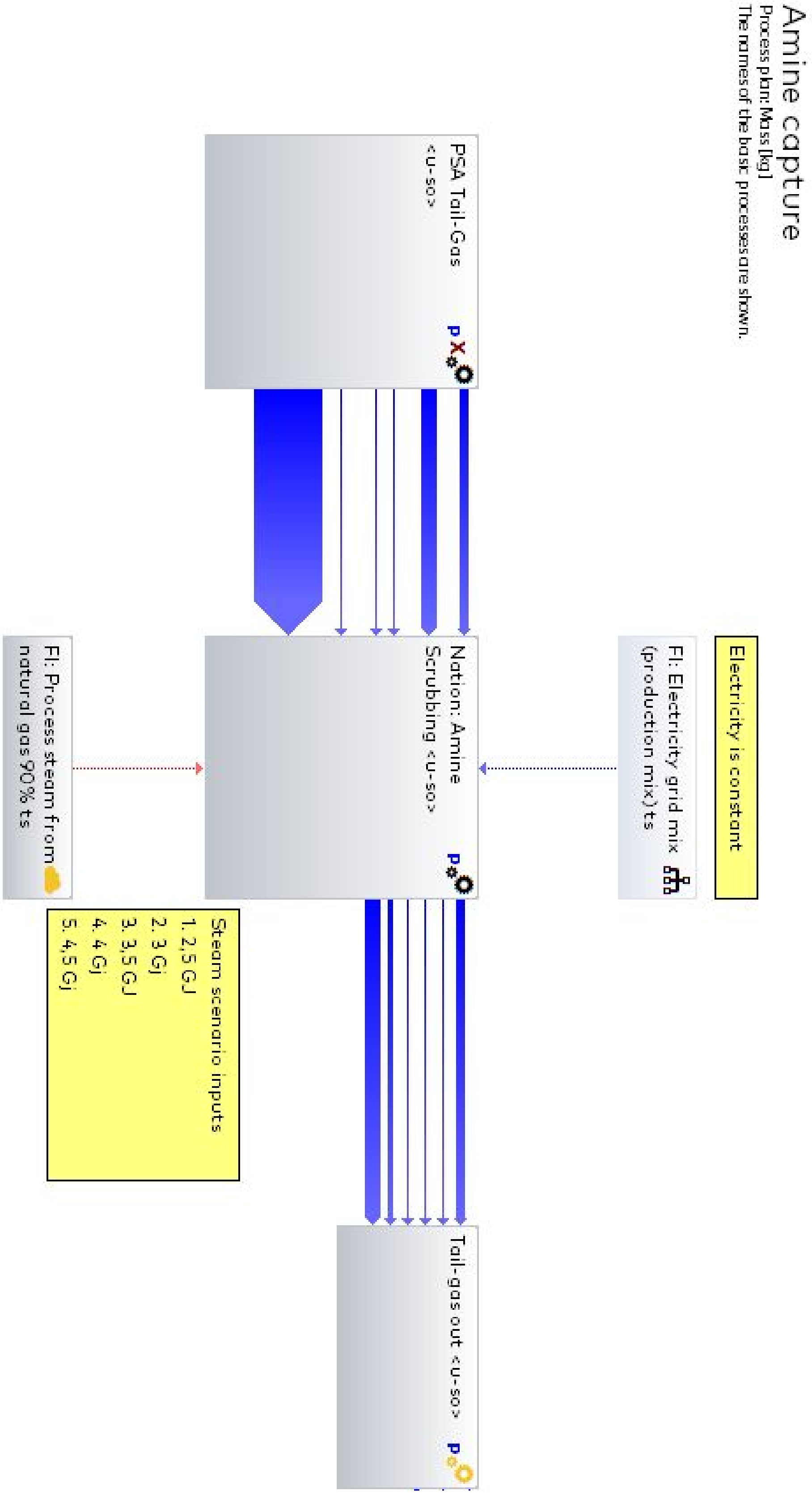
APPENDIX 4. Physical absorption advantages and disadvantages (Rackley 2010)

Absorption technology	Advantages	Disadvantages	RD&D focus areas
Physical absorption			
Fluor process (propylene carbonate)	Well-proven technology with 50+ years of commercial application High selectivity for CO_2 relative to methane Noncorrosive solvent Lower hydrocarbon losses and recycle gas compression requirement compared to Selexol	Low H_2S tolerance in feed gas stream Feed gas must be dehydrated due to high water solubility Irreversible reaction with CO_2 and water at 90°C precludes temperature swing regeneration	
Rectisol process (chilled methanol)	High selectivity for H_2S and CO_2 Able to remove many contaminants in a single process Low solvent cost Long-proven commercial application in gasification projects	High refrigeration energy cost	
Selexol process (dimethyl ethers of polyethylene glycol [DMEPG])	Well-proven technology with 30+ years of commercial application Chemically inert solvent not subject to degradation Nonaqueous solvent allows low-cost carbon steel plant construction	Feed gas must be dehydrated due to high water solubility Required high partial pressure of CO_2	

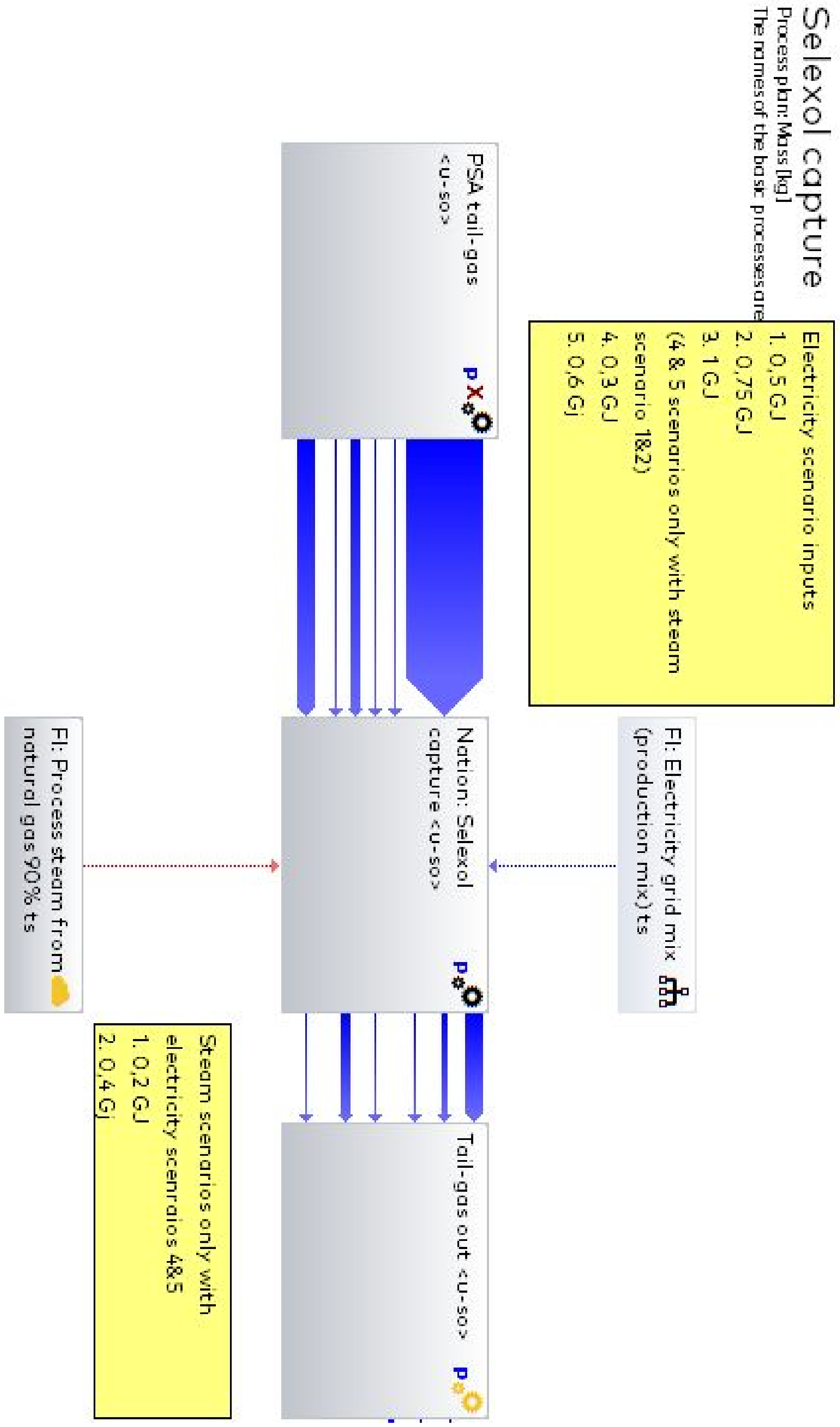
APPENDIX 5. Chemical absorption advantages and disadvantages (Rackley 2010)

Chemical absorption			
Amine systems (e.g., MEA)	Well-proven technology with extensive commercial application, leading to low capital costs Range of solvents have been developed	Low amine concentrations to resist corrosion limit loading capacity Low tolerance to SO_2, NO_x, and O_2 in flue gas	Identification of new amine-based solvents with lower heat of adsorption Improvements in energy integration with host plant
	Technical and economic benchmark for other solvent systems	High energy requirement for absorbent regeneration	Additives to improve system performance (e.g., to enable higher amine concentration)
			Engineering improvements to absorption and stripping towers to reduce energy requirements
Carbonate systems	Higher solvent loading capacity Lower regeneration energy requirement Low oxygen solubility, reducing corrosion	High cost of additives such as piperazine	Energy saving through improved tower packing and multistage stripping
			Catalysts or additives to improve CO_2 absorption rate and reduce stripping heat requirement
Dry sorbent systems	Potentially lower cost and heat requirement than amine systems	Mechanical complexity due to solids handling	Sorbent particle preparation and structure to maximize surface area and reduce particle attrition during fluidization and transport between reactors

APPENDIX 6. Amine treatment LCA model



APPENDIX 7. Selexol capture LCA model



APPENDIX 8. Selective PSA capture LCA model