



**NTNU – Trondheim**  
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# Options for Carbon Capture with Storage or Reuse in Waste Incineration Processes

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**MASTER THESIS**

for

Student Gina Plahte Helsing

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Options for Carbon Capture with Storage or Reuse in Waste Incineration Processes

*Alternative løsninger for CO<sub>2</sub> fangst med lagring eller gjenbruk i søppelforbrenningsanlegg***Background and objective**

Oslo Kommune (the Municipality of Oslo) has the goal of being among the most environmentally friendly cities in the world. As part of this vision, it is of interest to look at options for CO<sub>2</sub> capture with either storage or reuse of this carbon. Carbon Capture and Storage (CCS) is considered one of the most important ways to deal with the problem of global warming, and that reaching the maximum 2 degrees target is impossible without extensive use of CCS.

The energy recovery unit in Oslo (Energigjenvinningsenheten – EGE) has a total emission of 400 000 tons of CO<sub>2</sub> per year from their waste incineration plants delivering heat to district heating and some power to the grid. About 40-50% of this carbon emission has a fossil origin. The plant at Klemetsrud is responsible for 75% of these emissions.

The main objective of this Master thesis project is to suggest changes to the existing processing plant to provide for optimal CO<sub>2</sub> capture while preserving as much of the energy as possible.

**The following tasks are to be considered:**

1. Study process related conditions for the plant at Klemetsrud, and compare these with the requirements of existing technologies for CCS.
2. Make recommendations for possible installations and targets for carbon capture.
3. Establish a list of potential application areas for the captured CO<sub>2</sub> based on a literature survey, and indicate the specifications (CO<sub>2</sub> purity, etc.) for each of these applications.
4. In summary, the following are the expected deliverables from this Master thesis project:
  - i) A technical evaluation of the different available technologies for carbon capture.
  - ii) Potential projects for changing the process with respect to optimal CO<sub>2</sub> capture, while preserving as much of the energy as possible.
  - iii) A report on possible application areas for the captured CO<sub>2</sub>.

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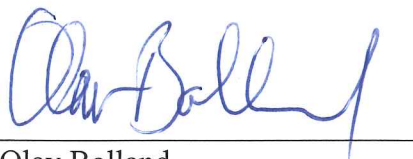
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- Work to be done in lab (Water power lab, Fluids engineering lab, Thermal engineering lab)  
 Field work

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## Preface

This report, *Options for Carbon Capture with Storage or Reuse in Waste Incineration Processes*, was written as the Master's Thesis of Gina Plahte Helsing. The thesis was produced at the Department of Energy and Process Engineering at the Norwegian University of Science and Technology in Trondheim, Norway. This study was commissioned by Energigjenvinningsetaten in Oslo (EGE) and the resulting report was written as the final work of a 5-year Master of Science Degree.

The aim of the work was to present the CCS technologies currently available and to evaluate the applicability of the relevant capture technologies at Klemetsrud waste incineration plant.

The author of this report is hopeful that this work may assist EGE in their evaluation process by giving a brief introduction to the subject and by highlighting the degree of applicability of the technologies presented. The hope is that this thesis may act as a small contribution in the battle against climate change.

I would like to thank my supervisor, Truls Gundersen, for helpful meetings when I needed guidance and for letting me work independently when I did not. I would also like to thank EGE for making this thesis possible.



## Abstract

Motivated by the ascertain need for climate mitigation, more than 100 countries have endorsed the goal of reducing their emissions. The maximum of a two degree rise is emphasised but despite this, fossil fuels are predicted to remain the main source of energy in Europe in the foreseeable future. By applying carbon capture technology, we can combat climate change whilst enabling the continued use of fossil fuels.

Carbon Capture and Storage (CCS) technology is predicted to be the most important low cost technology for CO<sub>2</sub> capture. By applying capture technology on plants utilising biomass, negative CO<sub>2</sub> emissions are achievable, which will thus deprive the atmosphere of CO<sub>2</sub>, and Klemetsrud waste incineration plant is one such plant. Though transport and storage of the recovered CO<sub>2</sub> are equally important in CCS projects, capture technology has been the main area of focus in this work.

This report presents the available CCS technologies and makes a recommendation as to which CO<sub>2</sub> capture technology is best suited for Klemetsrud. Klemetsrud represents a flue gas point source with a CO<sub>2</sub> concentration of 11,5 vol% at atmospheric pressure. Due to these limiting factors, as well as being a retrofit project, post-combustion capture using amines was evaluated to be the best suited technology. Different amines and relating processes were evaluated based on the energy penalty they will impose on the incineration plant and the maturity of the technology. In general, amine based technologies are associated with large energy penalties, but through extensive and proper integration and choosing the right process, an acceptable efficiency is achievable.

Amines have been utilised in the process of removing CO<sub>2</sub> for decades, and is therefore regarded as a mature technology. MEA is the most common amine, but less energy intensive processes using hindered amines are also commercialised. The world's first commercially scaled power plant is utilising the Cansolv process, which uses a proprietary hindered amine.

Basted on a literature study, energy saving capture processes and changes to the incineration and capture plant were suggested to achieve a higher efficiency. The most promising retrofit of the incineration plant is implementing oxygen enriched combustion. This technology is not mature and was therefore not recommended for EGE at this point, but in combination with post-combustion capture it is emphasised that this technology has great potential.

Transport on a large scale is usually carried out by ship or pipelines. There is no such network in Norway, and transport is therefore predicted to be carried out by rail or road tankers, and is therefore not discussed in detail. Utilisation and permanent storage of the recovered CO<sub>2</sub> is discussed based on the emission reduction effect. An attractive way of utilising CO<sub>2</sub> while at the same time ensuring permanent storage in Norway is through Enhanced Oil Recovery (EOR). CO<sub>2</sub> specifications have been listed for the main areas of CO<sub>2</sub> application.



## Sammendrag

Motivert av den ubestridte nødvendigheten av økt klimatiltak, har over 100 land samlet seg om et felles mål om å redusere klimagassutslipp. Det er lagt stor vekt på å holde temperaturøkningen under 2 °C, men på tross av dette viser prognoser at fossilt brensel fortsatt kommer til å være den viktigste energikilden i Europa i fremtiden. Ved å bruke CO<sub>2</sub> fangende teknologi kan vi redusere klimaendringene, samtidig som vi kan fortsette å bruke fossilt brensel.

Karbonfangst og -lagring (CCS) er sett på som den potensielt viktigste lavkostteknologien for å fange CO<sub>2</sub>. Ved å anvende fangstteknologi på prosesser som utnytter biomasse, kan et negativt CO<sub>2</sub> regnskap oppnås, som da vil fjerne CO<sub>2</sub> fra atmosfæren. Klemetsrud er et anlegg som har potensial til å oppnå dette. Selv om transport og lagring av CO<sub>2</sub> er like viktige aspekter når et CCS prosjekt skal kartlegges, er fangstteknologien det som har blitt sterkest vektlagt i denne oppgaven.

Denne rapporten presenterer de tilgjengelige CCS teknologiene og kommer med en anbefaling om hvilken fangstteknologi som er best egnet for Klemetsrud. Klemetsrud representerer en punktkilde av eksos med CO<sub>2</sub> konsentrasjon på 11,5vol% og atmosfærisk trykk. På grunn av disse begrensende faktorene, samt at Klemetsrud er et retrofit prosjekt, ble det konkludert med at det er mest aktuelt å fange CO<sub>2</sub> direkte fra røykgassen ved hjelp av aminbasert teknologi. Forskjellige typer aminer og relaterte prosesser ble evaluert basert på grad av effektivitetsreduksjonen implementeringen påfører, samt grad av modenhet på teknologien. Aminbasert teknologi er assosiert med høy energistraff, men gjennom nøye og omfattende prosessintegrasjon og ved å velge riktig prosess, vil det være mulig å oppnå overkommelige effekter.

Aminer har blitt brukt for å fjerne CO<sub>2</sub> i flere tiår, og er derfor ansett for å være en moden teknologi. MEA er den mest brukte typen amin, men det finnes også kommersialiserte hindrede aminer som brukes i mindre energikrevende prosesser. Verdens første kraftverk i kommersiell skala er utstyrt med fangstteknologi som benytter seg av Cansolv-prosessen som bruker en proprietær hindret amin.

Basert på et litteraturstudie ble implementering av energibesparende fangstprosesser og tilpasninger av forbrenningsanlegget foreslått for å oppnå en høyere effektivitet. Oksygenberiket forbrenning er en av de mest lovende endringene. Selv om denne teknologien ikke er moden, og derfor ikke anbefalt for EGE, er det vektlagt at denne forbrenningsmetoden har stort potensiale i kombinasjon med annen fangstteknologi.

Transport av CO<sub>2</sub> i stor skala blir som regel utført ved hjelp av skip eller rørledninger. Det er ikke tilrettelagt for den typen transport i Norge, og det er antatt at transport derfor vil foregå hovedsakelig via tog eller tankbiler, og er derfor ikke nøye diskutert. Utnyttning og permanent lagring av CO<sub>2</sub> er diskutert med tanke på deres utslippsreducerende effekt. En attraktiv måte å lagre CO<sub>2</sub> på i Norge som i tillegg vil føre til permanent lagring, er ved merutvinning av olje (EOR). CO<sub>2</sub> spesifikasjoner for de største bruksområdene er beskrevet.

## Acronyms and abbreviations

°C	Degrees centigrade, measure of temperature
ASU	Air separation unit
CCGT	Combined cycle gas turbine
CCS	Carbon capture and storage
CCSU	Carbon capture, storage and utilisation
DNV	Det Norske Veritas
ECBM	Enhanced coal bed methane recovery
E.g.	Exempli gratia
EGE	Energigjenvinningsetaten
EGR	Enhanced gas recovery
EOR	Enhanced oil recovery
g	Gram
GHG	Greenhouse gas
GWh	Gigawatt hour
h	Hour
IEA	International Energy Agency
IEAGHG	International Energy Agency Greenhouse Gas R&D Programme
IFFCO	Indian Farmer's Fertilizer Cooperative
IPPC	Intergovernmental Panel on Climate Change
K	Kelvin, measure of temperature
KA1	Klemetsrud waste incineration line 1
KA2	Klemetsrud waste incineration line 2
KA3	Klemetsrud waste incineration line 3
km	Kilometres
KM/ALC	Kerr-McGee/ABB Lummus
LSIP	Large scale integrated CCS project
m	Metre
mbar	Millibar
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MFO	Metal organic framework

mg	Miligram
MSW	Municipal solid waste
Mtpa	Million tonne per annum
N.A.	Not available
n/a	Not available
Nm <sup>3</sup>	Normal cubic meter (at standard conditions)
p	Pressure
ppm	Parts per million
ppmv	Parts per million on a volumetric basis
R	Universal gas constant
R&D	Research and Development
SNG	Synthetic natural gas
SP	Setpoint
Syngas	Synthesis gas
T	Temperature (Celsius)
t	Tonne (metric)
tpa	Tonne per annum
tpd	Tonne per day
V	Volume
Vol%	Volume percent
v/v	Volume fraction
Wt%	Weight percent
WtE	Waste-to-energy
w/w	Mass fraction
Yr	Year
$\chi$	Mole fraction

## Nomenclature, subscripts and chemical symbols

### Parameters

E	Energy	[W]
$\dot{m}$	Mass flowrate	[kg/h]
$\dot{m}C_p$	Heat capacity rate	[W]
M	Molar mass	[g/mole]
n	Number of moles	[mole]
$\dot{n}$	Molar flow rate	[moles/s]

### Subscripts

el	Electricity
FG	Flue gas
th	Thermal

### Chemical Symbols

Ar	Argon
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
N <sub>2</sub>	Nitrogen
NO <sub>x</sub>	Nitrogen oxide
O <sub>2</sub>	Oxygen
SO <sub>x</sub>	Sulphur oxide
SO <sub>2</sub>	Sulphur dioxide



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# 1 Introduction

## 1.1 Motive and objective

The motive for this thesis is the necessity of climate mitigation. There is an overall consensus that the threat global warming imposes on the climate has to be taken seriously. In a report published by the Intergovernmental Panel on Climate Change (2005), the U.S. government emphasize the importance of a maximum of 2 °C rise, relative to preindustrial levels to prevent fatal damage to the environment. Sharing this concern, more than 100 countries have endorsed the goal of climate mitigation, Norway being one of them. (GCCSI, 2013)

Power generation is the single largest source of CO<sub>2</sub> emissions, and reducing this is thus an important step towards changing the trend of an increasing CO<sub>2</sub> level in the atmosphere (Wang et al., 2011). However, fossil fuel fired power plants play an important role in meeting the globally increasing energy demand which, according to McKinsey's prognostics, will nearly double from 2005 to 2030 (McKinsey, 2008). They predict that fossil fuels will cover approximately 60% of the energy demand in Europe, which necessitates the application of carbon capture technology to combat climate change.

CCS is predicted to be the most important low cost technology to capture CO<sub>2</sub>. (McKinsey, 2008) Norway has decades of experience with CO<sub>2</sub> separation from the petroleum industry, and this knowledge is applicable in the development of CCS technology, which puts Norway in a leading position within CCS in Europe. (GCCSI, 2013)

Despite being available for many years, CCS technology has not been widely deployed. The main reasons for the slow break through is the high costs and energy penalty related to the implementation. Applying CCS technology will either increase the fuel consumption of the power plant or reduce the energy output, either way reducing the energy supply efficiency of the plant. This is mainly due to the energy intensive CO<sub>2</sub> separation process. It is therefore important to choose the CCS technology best suited for the relevant process and ensure proper integration with the process plant to minimise the imposed energy penalty.

The Municipal of Oslo has a goal of being amongst the most environmental friendly cities in the world. Oslo's waste-to-energy agency, Energigjenvinningsetaten (EGE), is a division within the Municipal of Oslo, and is thus imposed the same vision. The main objective of this thesis is to determine which technology that is best suited for EGE's own waste incineration plants in Oslo, for optimal CO<sub>2</sub> capture, whilst preserving as much energy as possible. The evaluation is based on the criteria provided by EGE, as listed in Chapter 1.3.

### 1.1.1 EGE

Energigjenvinningsetaten, from now on referred to as EGE, are governed by Oslo's Department of Culture Affair and Business. They own and operate two waste incineration plants, two optical sorting plants and a biogas plant. They are also responsible for the strategic planning of renewable energy projects in the Oslo region. (Oslos byrådsavdeling for kultur og næring, 2014)

The two waste incineration plants have a combined waste capacity of 410 000 tonne per year, and a thermal output of 850 GWh, which covers almost half of Oslo's district heating demand. The largest plant, Klemetsrud waste incineration plant, from now on referred to as Klemetsrud, also produce 160 GWh of electricity per annum, enough to cover the electricity demand of all the schools in Oslo.

The sorting plant located next to the second incineration plant was opened in 2009, and is the world's largest sorting system with a capacity of 100 000 tpa of waste. In 2012, the second sorting plant was opened next to the incineration plant at Klemetsrud, and has a capacity of sorting 50 000 tpa of waste.

The optical sorting plants separate green and blue bags from the rest of the waste. Rolls of green and blue bags are provided to the citizens of Oslo so that they can colour code their sorted waste. Green bags are filled with organic waste and are transported to the biogas plant for further processing. The blue bags are filled with plastics and are shipped to Germany for recycling. The rest of the waste is transported to the nearby incineration plant for combustion.

The biogas plant treats the organic waste received in the green bags, and converts it into bio methane and bio fertiliser. The plant has two digesters, and is one of Europe's most modern organic waste processing plants. The annual waste capacity of the plant is

50 000 tonne, enough to supply 135 busses with fuel, either as compressed biogas or as liquefied biogas. One of the bi-products of the conversion process is up to 90 000 tpa of bio fertiliser, corresponding to the demand of 100 medium sized farms. (Melbye et al., 2014)

### 1.1.2 Climate mitigation through bio-CCS

Negative CO<sub>2</sub> emissions can be achieved by applying CCS technology on a process utilising biomass. As biomass is assumed to be carbon neutral, capturing and permanently storing CO<sub>2</sub> from such a source will deprive the atmosphere of CO<sub>2</sub>. The CCS technology involved in such a process is often referred to as bio-CCS technology. (Arasto et al., 2014)

### 1.1.3 References to relevant publications

Flue gas characteristics are more or less determined by the combustion process, and the CO<sub>2</sub> separation process design is dependent on the flue gas characteristics, such as composition and pressure. This means that the applicability of a capture technology is not solely determined by the type of industrial process it is being applied to, although there are certain correlations. Knowledge through experiments and experience is therefor applicable across different industries. (Al-Fattah et al., 2012)

The main focus of CCS application within the power sector has been on coal-fired power plants, as these are the single largest contributors of anthropogenic CO<sub>2</sub>, after oil. Biomass fuels produce equal or slightly higher quantities of CO<sub>2</sub> than bituminous coal, and the CO<sub>2</sub> concentration of the two flue gas streams are thus very similar (IPPC, 2005). The data collected and knowledge gained from CCS coal-fired power plants are thus representable for bio-CCS plants. (Tang et al., 2013).

A preliminary study conducted by Zeman (2010) showed that implementing CCS technology with a MSW incineration plant have the potential of being a low cost source of CO<sub>2</sub> reductions. Several other studies states that CHP in combination with CCS has the potential of outstanding efficiency performance compared to any other CCS implementations. (Arasto et al., 2014) This is mainly due to the heat integration possibilities when applying post combustion-capture.

In 2013, Tang et al. published a study evaluating the possibility of implementing CCS technology with a MSW in China. A lifecycle analysis was conducted and the paper concluded that oxyfuel combustion gave better efficiency than MEA. This study confirms the stated, that in most cases it is more attractive to capture CO<sub>2</sub> from point sources with high CO<sub>2</sub> concentrations. (Berstad et al., 2014)

Many of the studies conducted have not taken into account the possibility of utilising excess heat through district heating. The integration between the capture plant and the process plant will thus not exploit its full potential.

## 1.2 Risk assessment

There has neither been any laboratory work nor excursions related to this thesis. It has thus been regarded as unnecessary to perform a risk assessment.

## 1.3 Scope and outline

The scope of this thesis is to introduce and evaluate CCS technology, and discuss their applicability to Klemetsrud waste incineration plant, based on the criteria listed below, as provided by EGE.

- Mature technology
- Low energy penalty
- Retrofit application

Different ways to store the recovered CO<sub>2</sub> will be discussed and transport will be briefly mentioned. Globally, it is most common to transport CO<sub>2</sub> via pipelines, where the infrastructure has to be solved on a national level. This paper will therefore not go into details on the subject.

There are concerns regarding undesirable emissions due to degradation of some liquid solvents. (Yang et al., 2008; Davison, 2007) It was decided that that was beyond the scope of this project but it should be a part of a future evaluation process.

A chapter describing the method of work was evaluated as being unnecessary. The evaluation is based on previous studies and data collected from pilot plants.

Documentation provided by EGE's internal database provided most of the details on



Klemetsrudanlegget. The other data collected was retrieved through publications accessed through NTNU's licences.

## 1.4 Overview

In Chapter 1, the thesis is presented and the company that commissioned this project is introduced. Chapter 2 gives a short introduction to the waste incineration plant at Klemetsrud, including relevant flue gas data and boiler safety measures. An overview of CO<sub>2</sub> capture routes are given in Chapter 3. In Chapter 4, the applicability of the different technologies to Klemetsrud MSW incineration plant is evaluated. Chapter 5 investigates the performance of the retrofit plant for both post-combustion capture and oxyfuel combustion technology implementation. In chapter 6, measures for increasing the efficiency of both the capture and the process plant are presented and based on these findings and previous argumentation, a capture technology is suggested. Transport is briefly introduced in Chapter 7 and in Chapter 8, CO<sub>2</sub> storage and utilisation are presented and discussed based on their climate mitigation potential.



## 2 Klemetsrud waste incineration plant

Documents from EGE's internal database provided most of the data and parameters for Klemetsrud incineration plant, and will not be referred to in the text, as they are irretrievable for the public. Some of the documents were outdated and their home page was then used as supplement, as listed in the list of references.

### 2.1 Introduction

Every year, EGE prevent 260 000 tonne of CO<sub>2</sub> reaching the atmosphere by their production of "green" energy and recycling of plastics. Klemetsrud receives municipal solid waste (MSW) from households and industries in the Oslo region. The annual production is 590 GWh of heat and 160 GWh of electricity generated by steam turbines and four gas turbines. The steam turbines run on the steam produced by the plant and the gas turbines run on landfill gas provided by Grønmo Landfill. The plant has three incineration lines, KA1, KA2 and KA3, combusting respectively 10, 10 and 20 tonne of waste per hour.

The combusted waste provides an energy input of 745 GWh, which is utilised through direct combustion. The annual amount of CO<sub>2</sub> emitted from Klemetsrud is calculated by EGE to be 300 000 tonne. 40-50 % is assumed to be of fossil origin, which implies fossil CO<sub>2</sub> emissions of 120 000-150 000 tpa. Motivated by the vision of the Municipal of Oslo to protect the environment, CCS technology is considered implemented into Klemetsrudanlegget to further reduce the emissions.

EGE has a theoretical potential to reduce their emissions by of 300 000 tonne of CO<sub>2</sub> per year (Mikkelsen, 2014). Klemetsrud will then partly fall into the definition of a bio-CCS project. By assuming the environmental impact of the carbon emitted from non-fossil originated waste is negligible, it would result in negative carbon emissions as they can capture up to 150 000 – 180 000 tonne of bio-carbon in addition to the fossil carbon. To obtain this, a capture rate of 100% is necessary, which is not economically feasible.

A capture rate of 80-95% depending on technology is feasible and would result in an annual reduction of 240 000-285 000 tonne of emitted CO<sub>2</sub>, as indicated in Table 2-1. Although applying CCS technology will result in lower emissions, it will also result in a decrease in heat and electricity production. The impact will vary with the type of capture technology applied and the degree of plant integration (Romeo, 2008).

The main data of importance, from Klemetsrud, is presented in Chapter 2.4, which gives the basis for the evaluation.

Table 2-1: Annual CO<sub>2</sub> capture potential at Klemetsrud

	Amount of CO <sub>2</sub> captured annually [tpa]
95% captured CO <sub>2</sub>	285 000
90% captured CO <sub>2</sub>	270 000
85% captured CO <sub>2</sub>	255 000
80% captured CO <sub>2</sub>	240 000

## 2.2 The incineration process

The main components of the incineration lines are:

- The grate (Horizontal grate)
- The boiler (Steam boiler)
- The external Eco system (Hot water)
- Bag filter (with active coal to remove dust)
- Scrubber (2 steps (acidic and basic), removes HCl and SO<sub>2</sub>)
- Control system

Figure 2-1 shows where the components are located within the plant, and the numbers on the figure correspond to the names listed below (EGE, 2012).

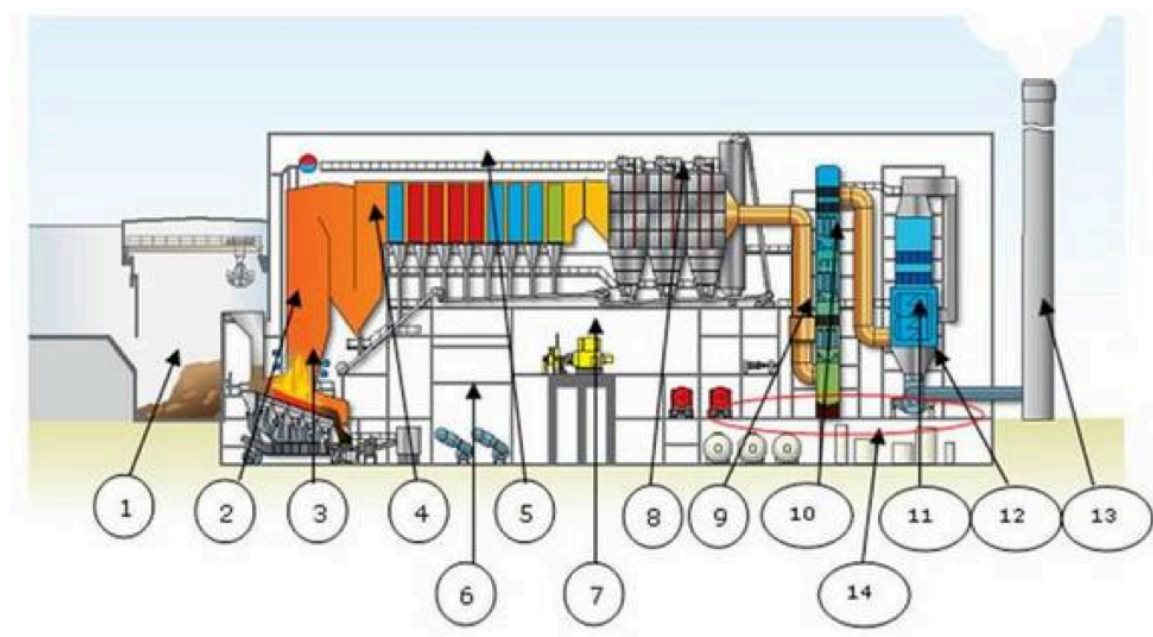


Figure 2-1: Main components of Klemetsrud's waste incineration lines (EGE, 2012)

1. Waste pit
2. Boiler
3. Grate
4. Boiler vertical stretch
5. Boiler horizontal stretch (Heat recovery: super heater, evaporator, and economizer)
6. Primary and secondary air fans
7. Turbine (electricity production)
8. Electro filter (removing particulates from the flue gas)
9. Economizer (heat recovery)
10. Multistep scrubber (removes SO<sub>2</sub>, HCl, dioxins and metals)
11. Selective catalytic reduction (removes NO<sub>x</sub>)
12. Flue gas fan
13. Stack
14. Water treatment system

The waste that is left on the conveyer after passing through the optical sorting system is transported into a waste pit located inside the incineration plant. A large crane lifts the waste from the pit into the feed hopper, which leads the waste into the furnace and onto the grate. The grate consists of many movable rods, connected to multiple shafts. The shafts are moving independently of each other, resulting in a “walking floor”-movement. This movement increases circulation and spreading of the waste, and moves the mass through the furnace. The grate is designed in 5 different sections where each section represents a specific combustion zone. Details on the combustion zones are provided in the project work of Helsing (2014). The waste stays in each zone for as long as required, before being pushed into the next zone by the moving floor. The run-through time is 30-60 minutes, depending on the quality of the waste. The temperature inside the furnace is normally 1000 -1100 °C. The annual operating time for each line is approximately 8150 hours.

A descriptive drawing of the boiler is shown in Figure 2-2. It illustrates how the flue gas is routed from the combustion chamber to the flue gas filters. In the furnace, the dominant heat transfer is by radiation, but from the horizontal stretch and onwards, convection dominates and is where most of the heat transfer occurs. In the horizontal stretch, the flue gas passes through five sets of pipelines system connected by a drum, known as the economizer, evaporator and super heater. Water circulates within the pipelines, and heat from the flue gas is transferred to the water, producing hot water and steam. Most of the hot water is delivered to Hafslund’s distinct heating network,

whilst some of it is used to heat the primary and secondary air in the combustion stage. The steam is sent through steam turbines for electricity production, but the heat supply to the district heating has priority over the electricity production.

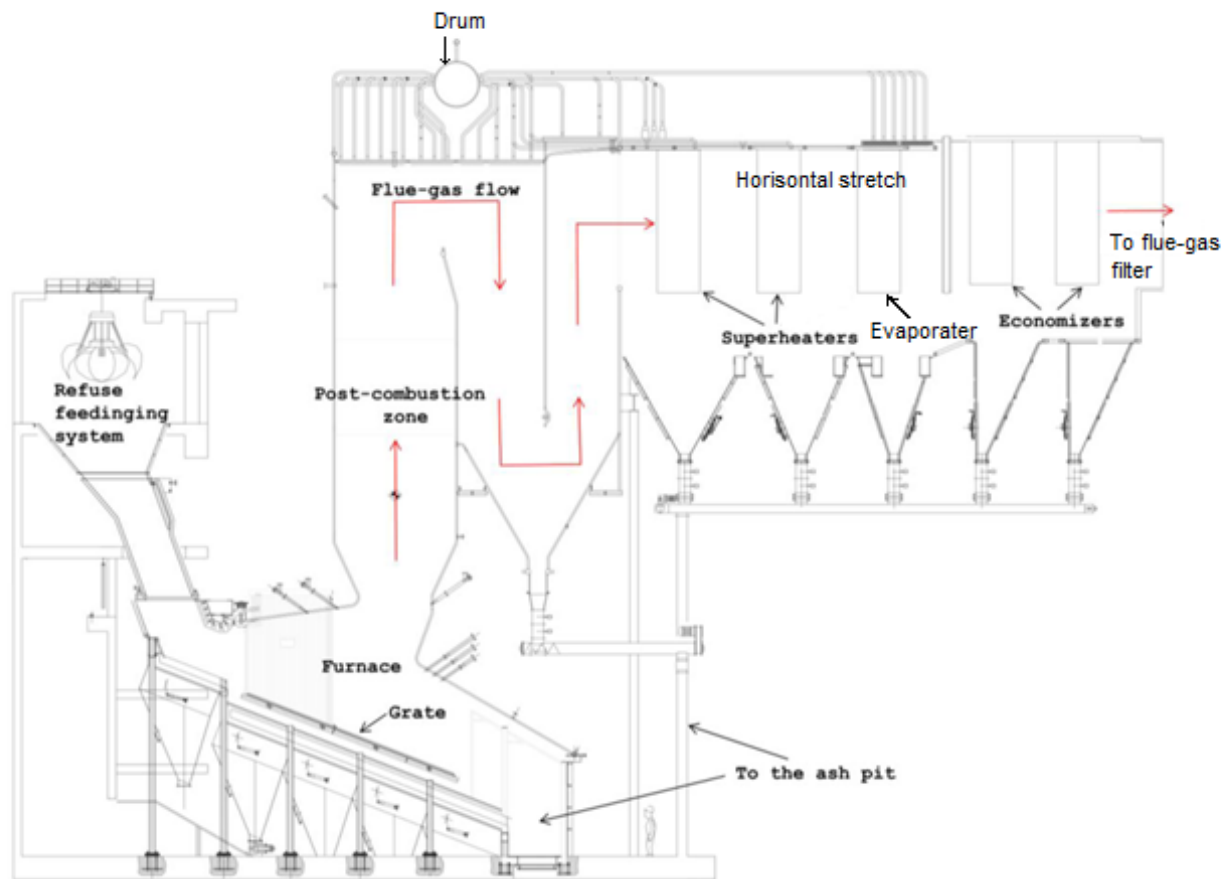


Figure 2-2: The flue gas path through the boiler (Rinaldi, Najafi, 2013)

### 2.3 Boiler safety measures

**Pressure:** The pressure in the boiler is below atmospheric to prevent backfiring in the feed hopper and waste pit, and to route the flue gas to the stack. The lower pressure is created by flue gas fans, located after the flue gas filter and at the foot of the stack, as shown in Figure 2-1 (#12). It is therefore important that all the openings to ambient pressure are sealed when the incineration line is operating.

**Temperature:** The optimal heating value of the waste is 10-12 MJ/kg, and the temperature in the furnace should not exceed 1300 °C. The temperature cannot be too high as it could damage the materials. Water is sprayed into the furnace to control the

temperature if the upper limit is reached. If the temperature is too low, the combustion will be incomplete and harmful emissions may be emitted into the atmosphere. Downstream equipment may not work properly either, as they are designed for a given temperature range. It is therefore imposed by law that the flue gas in the combustion chamber has to hold at least 850 °C, for 2 seconds. This is the case for all waste incineration plants in EU, and is stated by Directive 2000/76/EC of the European Parliament (EU, 2011).

The flue gas filter can only withstand temperatures up to 220 °C, so the exhaust gas has to be cooled, even when there is heat surplus in the district heating network. After the water has recovered the heat from the flue gas, it is vented to the air. This is especially common during the summer when the heat demand is low.

## 2.4 Main data of importance for Klemetsrudanlegget

Key numbers from 2014 are presented in Table 2-2 (Mikkelsen, 2014). The plant is operating at a near full load at all times. The mass flow of waste into the boiler is set, and a reduction in plant efficiency will thus result in a reduced power output rather than an increase in fuel consumption.

Table 2-2: Key numbers 2014, Klemetsrud

	Value
Waste combusted [tpa]	291 145
Waste energy density [MWh/t]	2,56
Theoretic energy from waste [GWh]	745
Utilised energy from waste [GWh]	706
Energy sold [GWh]	643
Heat utilisation [%]	91,1
Thermal efficiency [%]	86,3

### Flue gas parameters

In June 2014, the molar flow of the flue gas was measured during normal operation, and the values obtained are therefore assumed presentable as a basis for all calculations. The values are presented in Table 2-3.

Table 2-3: Flue gas parameters, Klemetsrud

	Measured molar flow [Nm <sup>3</sup> /h, wet]
KA1/KA2	68 500
KA3	131 300
Total*	199 800

\*Total molar flow, assuming the flow of KA2 is equal to KA1

The composition of the flue gases of KA1/KA2 and KA3 is presented in Table 2-4 and 2-5 respectively, before being released through the stack. There is a large variation in the data, and the average values are thus hard to determine. The concentration of CO, SO<sub>2</sub>, and NO<sub>x</sub> are so small that they are assumed to not have an impact on the volumetric flow rate of the flue gas, and are therefore given in ppmv.

Table 2-4: Composition of the flue gas emitted by KA1/KA2

	Average value	Range
CO <sub>2</sub> * [vol%]	11,5	-
H <sub>2</sub> O [vol %]	11-14	10-24
O <sub>2</sub> [vol %]	6,4	6-7
N <sub>2</sub> ** [vol %]	67,5-70,5	-
CO [ppmv]	9,0-16,4	-
SO <sub>2</sub> [ppmv]	3,4	1,13-23,4
NO <sub>x</sub> [ppmv]	79	78,8-129

\*CO<sub>2</sub> concentrations were provided on a molar basis and a conversion to volumetric fraction was conducted. The calculations are shown in Appendix A.

\*\*Calculated. Assuming components not mentioned in the table are negligible.



Table 2-5: Composition of the flue gas emitted by KA3

	Average value	Range
CO <sub>2</sub> * [vol%]	11,5	-
H <sub>2</sub> O [vol %]	15-16	15-16
O <sub>2</sub> [vol %]	10-13	7,5-17
N <sub>2</sub> ** [vol %]	58,9-62,9	-
CO [ppmv]	2,5	-
SO <sub>2</sub> [ppmv]	1,21	1,21-5,48
NO <sub>x</sub> [ppmv]	10,4	10,4-188

\*CO<sub>2</sub> concentrations were provided on a molar basis and a conversion to volumetric fraction was conducted. The calculations are shown in Appendix A.

\*\*Calculated. Assuming components not mentioned in the table are negligible.

### **Flue gas temperature**

There are no sensors measuring the temperature of the flue gas when it enters the stack. To get an indication of the temperature, there are two temperature sensors of relevance, one placed upstream of the bag/electro filter, and the other one placed in the chimney, 40 meters above ground. EGE used these two temperatures to calculate the temperature of the flue gas when it enters the stack. The resulting temperatures are listed in Table 2-6.

Table 2-6: Flue gas parameters from concession related measurements, 19 June 2014

	Average value	Range
Pressure [mbar]		989-997
Temperature before entering filter [°C]		165-175
Temperature entering stack * [°C]	160	
Temperature in stock [°C]	85***	62-87**

\* Calculated by EGE

\*\*Sensors are placed 40 m above ground

\*\*\* (EGE, 2012)



## 3 Introduction to CO<sub>2</sub> capture technology

### 3.1 History

The first carbon capture technology was patented in 1930 by Robert Roger Bottoms, and was developed for the petroleum industry (Bottoms, 1930). The patent was on a scrubber using amine solvent to remove sour gases from other gases or gas mixtures. At that time, it was common to use alkaline carbonates, such as sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) to remove CO<sub>2</sub>. By employing the new solvent the solubility and absorption capacity of CO<sub>2</sub> was increased, and less solvent and energy was required in the process. (Bottoms, 1930)

The absorption CCS technology commercially available today is very similar to that invented by R. R. Bottoms. The key feature of an adsorbing column and a regenerative column is the same, as well as an amine-based solvent. The main difference is in the design of the column and the properties of the solvent. When it was first invented, the inside of the column was filled with trays, whilst today it is most common to use packed materials. The solvents being developed today have a higher load factor and require less heat for regeneration.

### 3.2 Capture technology overview

Carbon capture technology has the ability to separate CO<sub>2</sub> from other constituents of a stream. All capture processes require energy supplied either as electricity, heat, flow energy of the stream, or a combination of these, depending on the technology. The capture technology is utilised in combination with other processes where CO<sub>2</sub> is found at higher concentration, e.g. a point source such as a flue gas stream of a power plant.

When applying CCS technology in a process plant, it is desirable to find a capture technology that requires energy in a form that can be provided by the plant for optimal integration. For an industrial plant with high waste heat production, it is feasible to apply a capture technology that will mainly require heat, as this will have a smaller impact on the process plant. For a plant producing electricity that is not connected to the grid, it is desirable to implement a capture technology that can utilise the excess electricity.

The trade-off between electricity and heat requirements means that each capture technology has to be evaluated based on the available energy in the process plant and its

operating parameters. CCS technologies are divided into groups, where each group provides certain advantages for different types of process plants. Other constraints, such as water and fuel availability, may also influence the decision.

### 3.2.1 Three different capture routs

Carbon separation technologies are divided into three main categories, categorized by the carbon capture route. The three categories are; post-combustion capture, pre-combustion capture and oxyfuel combustion. The respective flow diagrams are presented in Figure 3-1. Though there are three main capture routs, there are many different technologies within each category. In Table 3-1, an overview of the current and future technologies is presented. As indicated by the table, there are some technologies commercially available, and many more are under development. A lot will happen within the foreseeable future, as many of these will be commercialised. The most promising technologies will thus be presented in later chapters despite some not being on the level of maturity requested by EGE.

Table 3-1: An overview of current and future technology (IEA, 2008)

Capture method	Post-combustion decarbonisation CO <sub>2</sub> /N <sub>2</sub>		Pre-combustion decarbonisation CO <sub>2</sub> /H <sub>2</sub>		Oxyfuel conversion O <sub>2</sub> /N <sub>2</sub>	
	Current	Future	Current	Future	Current	Future
Principles of separation						
Membranes	Polymeric	Ceramic facilitated transport Carbon molecular sieve	Polymeric	Ceramic Palladium Reactors Contactors	Polymeric	Ion-transport facilitated transport
Solvents / Absorption	Chemical solvents	Improved process design Improved solvents Novel contacting equipment	Chemical solvents Physical solvents	Improved process design Improved solvents Novel contacting equipment	NA	Bio-mimetic solvents
Cryogenic	Liquefaction	Hybrid process Anti-sublimation	Liquefaction	Hybrid process	Distillation	Improved distillation
Solid Sorbents	Zeolites Activated carbon	Carbonates Carbon based solvents	Zeolites Activated carbon Alumina	Dolomites Hydrotalcites Zirconates	Zeolites Activated carbon	Carbonates Hydrotalcites Silicates
Biotechnology		Algae production		High pressure		Bio-mimetic

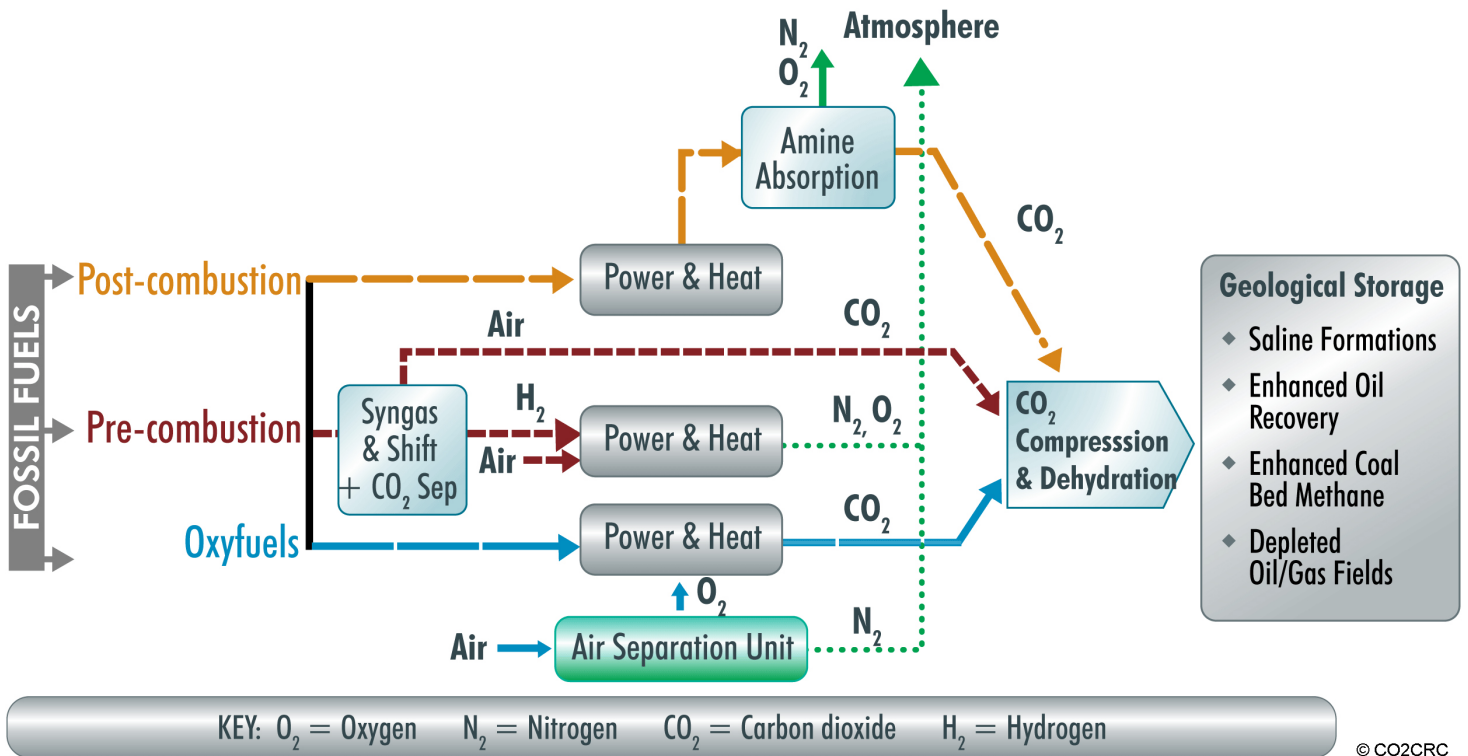


Figure 3-1: Flow diagram of post- pre- and oxyfuel combustion capture (CO2CRC, 2002)

### Post-combustion

Post combustion capture is applied as an end-of-pipe installation where the CO<sub>2</sub> is separated from the other flue gas constituents. As the CO<sub>2</sub> separation and capture occurs downstream of the process plant, no significant modifications to the plant are required (Al-Fattah et al., 2012). Hence, these are the most common capture technologies used in retrofit projects (GCCSI, 2015). See Appendix B for technology distribution for LSIPs.

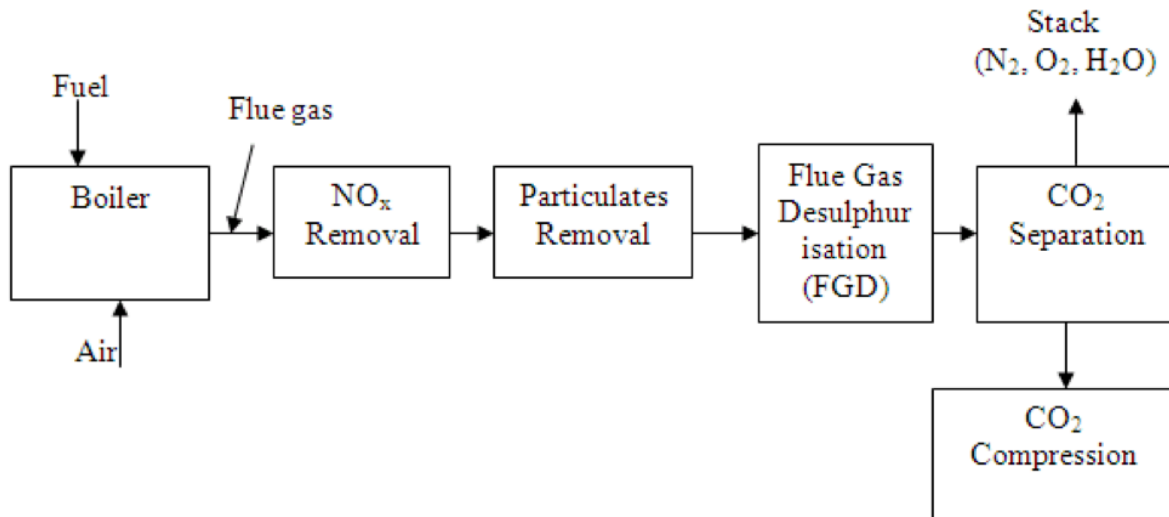


Figure 3-2: Post-combustion capture block flow diagram (Al-Abbas, Naser)

Post-combustion capture is usually performed at low CO<sub>2</sub> concentrations, typically 3%-15% and the product is a relatively pure stream of CO<sub>2</sub>. As indicated in Figure 3-2, the capture of CO<sub>2</sub> is done by routing the flue gas through separation equipment. The equipment has the ability to selectively let some flue gas constituents pass through, resulting in a stream consisting mainly of H<sub>2</sub>O, N<sub>2</sub> and O<sub>2</sub> being emitted through the stack, while a pure stream CO<sub>2</sub> can be sent to compression. Many different technologies can be employed, including absorption, adsorption, cryogenics and membranes. These will all be presented and evaluated in Chapter 4.1.

As an end-of-pipe technology, post-combustion capture has certain advantages.

- Retrofit: The possibility to implement the technology into an already existing process plant
- Increased operational flexibility: It is easy to switch between capture and non-capture modes

The technology is suitable for many types of industries because the separation is happening downstream of the industrial process. Post-combustion capture is regarded as the best available option mainly due to its retrofit ability to existing power plants, high CO<sub>2</sub> selectivity and high maturity (Abu-Zahra, 2013). Despite being the most widely deployed technology, there are some drawbacks related to the technology. In order to separate CO<sub>2</sub> from the flue gas, all the flue gas has to be processed. The small partial pressure of CO<sub>2</sub> and the large volumes of gas, result in large equipment size and high capital costs (Olajire, 2010). To remove small concentrations of CO<sub>2</sub> from a flue gas, the solvent must have a high selectivity and must bind strongly to the CO<sub>2</sub>. The heat requirement for regeneration is thus high, and is the main reason for the high energy penalty imposed on the process plant.

## Pre-combustion capture

The primary fuel, most commonly natural gas or coal, is processed in a reactor to produce a gas mixture mainly comprising CO and H<sub>2</sub>. The gas, often referred to as synthesis gas or syngas, can then either be further processed or utilised in a Combined Cycle Gas Turbine (CCGT) to produce electricity and heat, as shown in Figure 3-3 (Al-Fattah et al., 2012). The key feature of this process is to remove carbon from the fuel prior to combustion. In the process “hydrogen production with CO<sub>2</sub> removal”, the basic steps have been in use for more than 50 years.

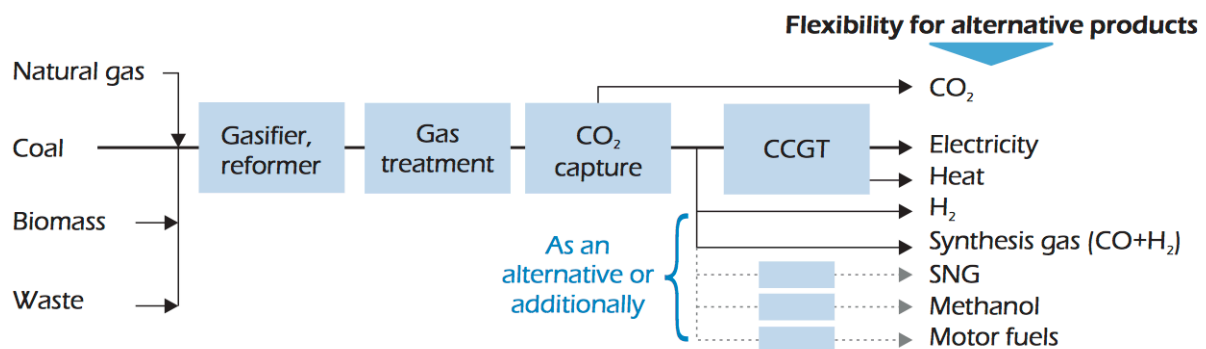
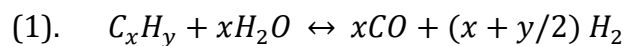


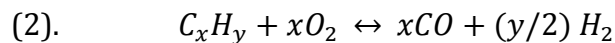
Figure 3-3: Pre-combustion capture block flow diagram (IEA, 2008)

In the reactor, syngas is produced by gasification, partial oxidation or steam reforming. Steam reforming is achieved by adding steam to the primary fuel, as described by Equation 1. Partial oxidation is obtained by adding O<sub>2</sub> to the primary fuel, where the primary fuel is a gas, as shown by Equation 2. When the primary fuel is a solid, the same process is referred to as gasification.

Steam reforming:

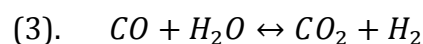


Partial oxidation/gasification:



In both conversion routes, a catalyst may be applied to enhance the water-gas shift reaction described by Equation 3, to accelerate the reaction between CO and H<sub>2</sub>O to produce more H<sub>2</sub> and CO<sub>2</sub>. (Kanniche et al., 2010)

Water Gas Shift Reaction:



CO<sub>2</sub> can then be separated and removed. As the partial pressure of CO<sub>2</sub> is higher than in a conventional flue gas stream, the process equipment can be smaller, and cheaper technologies can be applied than for post-combustion capture. The energy required in the separation process is also lower due to the lower binding energy required between the solvent and the CO<sub>2</sub>.

One of the main advantages of gasification is the possibility to utilise low-grade fuels, such as MSW, sawdust and agricultural waste as these fuels may be cheaper (Cormos, 2014). The main drawback of this process is that it cannot easily be implemented into an existing plant. As the process is very complex, it is best suited for new plants.

According to IPCC (2005), pre-combustion capture has predictively two main areas of application. The first area of application is in production of the carbon free fuel, hydrogen. Secondly, the capture process can be used to reduce the carbon content of a fuel. Through gasification, low H:C ratio fuels can be converted into liquid Fischer-Tropsch fuels or other fuels with higher H:C ratio. This is especially attractive in critically polluted areas, such as in large cities. (IPPC, 2005)

**Oxyfuel combustion**

Oxyfuel combustion is the combustion of a fuel in pure oxygen. O<sub>2</sub> is separated from the ambient air and is injected into a sealed environment, where the combustion occurs. The resulting fuel gas will then consist mainly of CO<sub>2</sub> and H<sub>2</sub>O, which can easily be separated by cooling the mixture enough to condense the water (Mathieu, 2010). Oxyfuel combustion has been used in the industry for several years, e.g. in welding and in glass furnaces to increase the temperature and to improve the energy efficiency of the process. (Al-Fattah et. al, 2012)

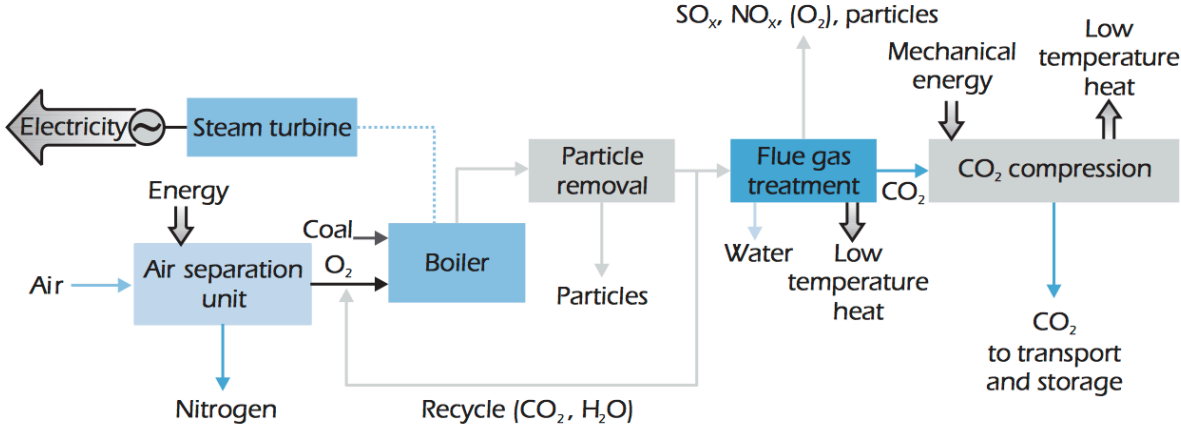


Figure 3-4: Block flow diagram of oxyfuel combustion in a coal-fired boiler with flue gas recycling (IEA, 2008)



Removing the nitrogen prior to combustion has two main effects on the properties of flue gas stream:

- Higher CO<sub>2</sub> partial pressure: N<sub>2</sub> will no longer dilute the other constituents of the flue gas, and the partial pressure of CO<sub>2</sub> in the flue gas is thus increased significantly
- Higher temperature: Nitrogen does not participate in the oxidation of the fuel. Removing the N<sub>2</sub> will thus reduce the  $\dot{m}C_p$  of the stream, and therefore increase the temperature of the combustion and the resulting flue gas
- Enhanced combustion
- Reduced flue gas losses

Oxyfuel combustion is only applicable to combustion processes occurring in sealed environments, such as in boilers. This is to prevent N<sub>2</sub> from reaching the combustion zone or diluting the flue gas. Combustion in 95-99% O<sub>2</sub> results in a flue gas stream consisting of 90-95% CO<sub>2</sub> on a dry basis. Other components present in the flue gas are water vapour, noble gases, SO<sub>x</sub>, NO<sub>x</sub>, as well as other impurities.

From a technical point of view, utilising this technology in boiler application is feasible for both retrofit and new industrial plants. Cooled flue gas can be recycled back into the boiler to limit the temperature increase, as shown in Figure 3-4. For gas-turbine-based combined cycle application, oxyfuel combustion is only possible for new plants specifically designed for this purpose (Al-Fattah et. al, 2012). In the case of retrofitting a boiler, the main changes to the existing plant would be installing an air separation unit, and making the materials close to the combustion zone withstand the increased temperatures. Flue gas recycling is often installed to control the temperature and to increase the volumetric flow through boiler.

This technology enhances combustion and may increase the overall plant efficiency. The large drawback of this type of installation is the energy intensive air separation process required.

### 3.3 Maturity of CCS technology

As previously mentioned, absorption technology has been commercially available for decades, but for the technology to be applicable for power plants, a large scale up is required. Large scale integrated CCS projects, LSIPs, are projects involving plants that are large enough to be representative for commercial involving capture,

These are projects aimed at simulating CCS plants on a commercial level, hence involving CO<sub>2</sub> capture, transport and storage.

By reviewing these types of project, important information and experiences can be collected and learned from. LSIPs are thus an important step towards successfully implementing CCS plants on a commercialized and economically viable level.

Definition of LSIPs (GCCSI, 2015):

CCS projects that are large enough to be representative for commercial evaluation.

Minimum scale:

- 800 000 tonne of CO<sub>2</sub> per annum for coal-based power plants
- 400 000 tonne of CO<sub>2</sub> per annum for other emissions-intensive industrial facilities

This corresponds to the minimum amount of CO<sub>2</sub> emitted from a typical commercial-scaled industrial facility. Per definition, Klemetsrud is not a large scale project, as the annual CO<sub>2</sub> emission is equal to 300 000 tpa. The CCS project will thus be categorised as a pilot plant project.

As of March 2014, there are 55 large-scale CCS projects, LSIPs, worldwide, either in the planning, construction or operating phase. The combined capture capacity of these plants is 107 Mtpa (GCCSI, 2015). As of today, 13 of the 55 LSIPs are operational, and another 9 projects in the construction stage. These 22 projects have a combined capture capacity of 40 Mtpa. Within the power sector, the world's first large-scale integrated CCS plant opened in 2014. The plant, Boundary Dam, is coal-fired and utilises post-combustion capture technology. A chemical absorption process using the proprietary amine DC-103 is applied. The capture plant has a CO<sub>2</sub> capture capacity of 1 Mtpa. See Appendix C for plant details and Appendix B for technologic distribution of the LSIPs within the power sector.

## 4 CCS applicability to Klemetsrud

When evaluating the different capture technologies, certain criteria have been provided by EGE:

- Applicable in a retrofit project
- Mature technology
- Low efficiency penalty

Efficiency penalty is a way of measuring the impact of a process implementation, defined as the percentage decrease in net power plant efficiency due to the implementation. This measuring tool, in combination with an evaluation of technical applicability, performance and maturity, is used in this chapter to evaluate the feasibility of the different capture technologies.

Capture technology performance and applicability varies with the composition and CO<sub>2</sub> partial pressure of the gas to be treated. There are ways to increase the CO<sub>2</sub> partial pressure of a flue gas, such as compression or enriched oxygen combustion. Compression is not regarded as a viable option, as this would be very energy consuming and could not be justified by reduced downstream energy consumption. Enriched oxygen combustion on the other hand, has a great potential when being combined with post-combustion technology. The technology is not mature and will thus not be regarded as a currently viable option for Klemetsrud, but it is emphasised that this technology may be attractive at a later stage. A process that utilises this technology is the SYNCOM process, which will be briefly discussed in Chapter 6.3 as a means to increase the efficiency of the incineration plant, and more thoroughly presented in Appendix H. As a result of this argumentation, the applicability of post-combustion technology is based on the point source flue gas at atmospheric pressure, as presented in Chapter 2.4.

### 4.1 Post-combustion capture technology

Figure 4-1 shows an overview of the classifications of the main separation techniques available for post combustion capture. Several comparative studies show that chemical absorption is currently the preferred method, mainly due to the maturity of the technology (Abu-Zahra et al., 2013). As indicated by Figure 4-1, microbial and algal systems can be utilised as a CO<sub>2</sub> capture technology. The technology has only been tested in lab scale and the required upscaling is far from viable at the moment (Jacob et al.,

2015) These systems have a better performance in tempered environments, so due to the level of maturity and the climatic performance, microbial and algal systems are not discussed in this report.

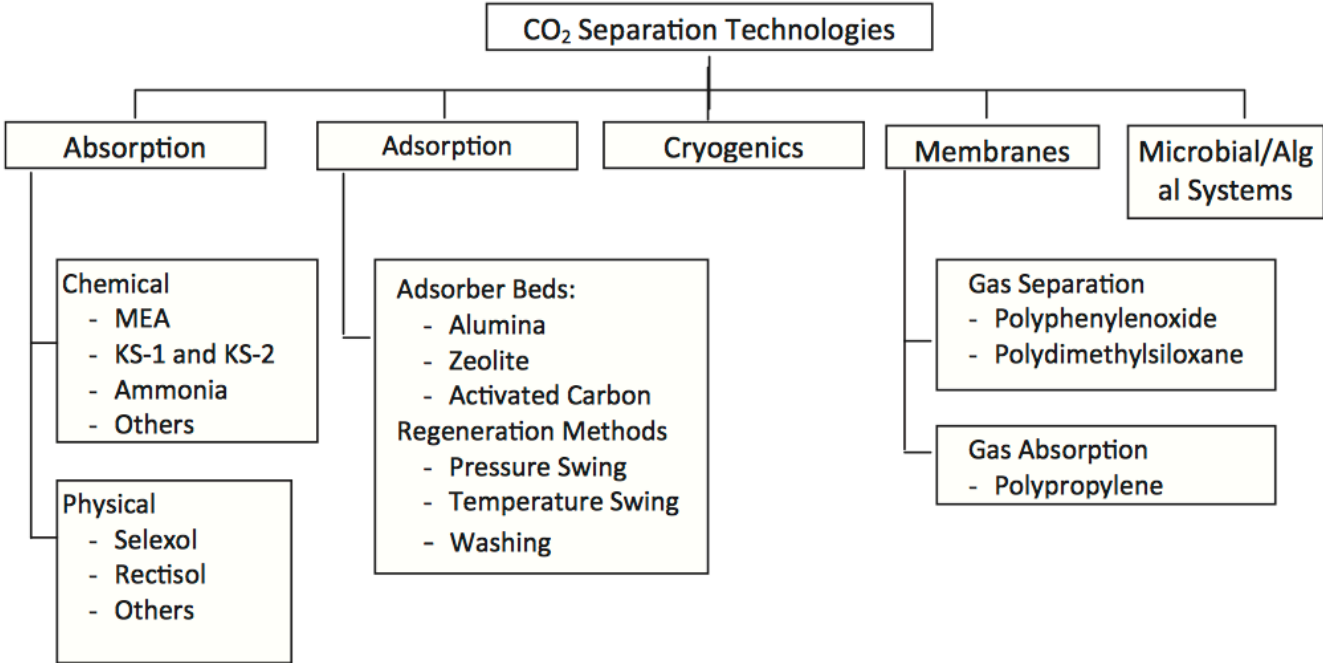


Figure 4-1: Process technologies for post-combustion capture (Wang et al., 2011)

4.1.1 Absorption

Separation via absorption is utilising the difference in solubility of constitutes in a media called the solvent. The technologies comprise two main steps, the first being routing the gas through a solvent so that the favoured constituent, CO<sub>2</sub>, will preferentially be absorbed. This takes place in the absorber. The second step takes place in the stripper, where the saturated solvent is heated and the CO<sub>2</sub> is boiled of. This process is called regeneration. Absorption is enhances at low temperature and high pressure, as this increases the CO<sub>2</sub> loading capacity of the solvent, as illustrated in Figure 4-2 and 4-3. Regeneration is conducted at high temperature and low pressure when the loading capacity is low (Desideri, 2010). The evaporated CO<sub>2</sub> can then be collected at the top of the stripper, and transported to a storage facility or utilisation unit. Further processing, such as scrubbing or compressions is often required prior to transport. A generic process flow diagram of CO<sub>2</sub> separation with absorption is shown in Figure 4-4. The solvents are categorised by the way they bind to the CO<sub>2</sub>, the two groups being chemical and physical solvents. In chemical absorption, the solvent reacts with the CO<sub>2</sub>, resulting

in strong covalent bonds. In physical absorption, the solvent binds to the CO<sub>2</sub> mainly due to the weaker Van der Waals forces (Pinto et al., 2014).

The loading capacity of a chemical solvent increases with increasing partial pressure of CO<sub>2</sub> until a maximum pressure is reached. When the saturation limit is reached for amines, and the absorption capacity will stagnate. Physical solvents, on the other hand, will have a linear capacity increase beyond this pressure (Kanniche et al., 2010). Figure 4-2 illustrates this relation of the loading characteristics, where the circulation rate of the solvent is proportional to the loading capacity difference between the rich and the lean solvent, marked as  $\Delta_{ph}$  and  $\Delta_{ch}$  for the physical and chemical solvent, respectively. The red linear line illustrates the loading capacity of a physical solvent versus the partial pressure of CO<sub>2</sub>. The blue line illustrates the same for a chemical solvent.

Figure 4-2 shows a generic case, where the ability remove CO<sub>2</sub> is almost twice as high for the physical solvent than for the chemical solvent, per mole of solvent. This is due to the physical solvent having a much lower loading capacity at CO<sub>2</sub> partial pressure B, whilst having only slightly lower loading capacity than the chemical solvent at CO<sub>2</sub> partial pressure A. The physical solvent can then release more CO<sub>2</sub> in the regeneration process, and a lower solvent circulation rate is required to remove the same amounts of CO<sub>2</sub>.

If the CO<sub>2</sub> partial pressure A is further increased, the chemical solvent will reach its saturation limit. This is illustrated in Figure 4-2 by the red line becoming very steep, with an almost infinite slope. Lower loading capacity means that a higher solvent mass flow is necessary to remove the same amount of CO<sub>2</sub>. This implies an increase in electricity consumption due to the increased pumping force.

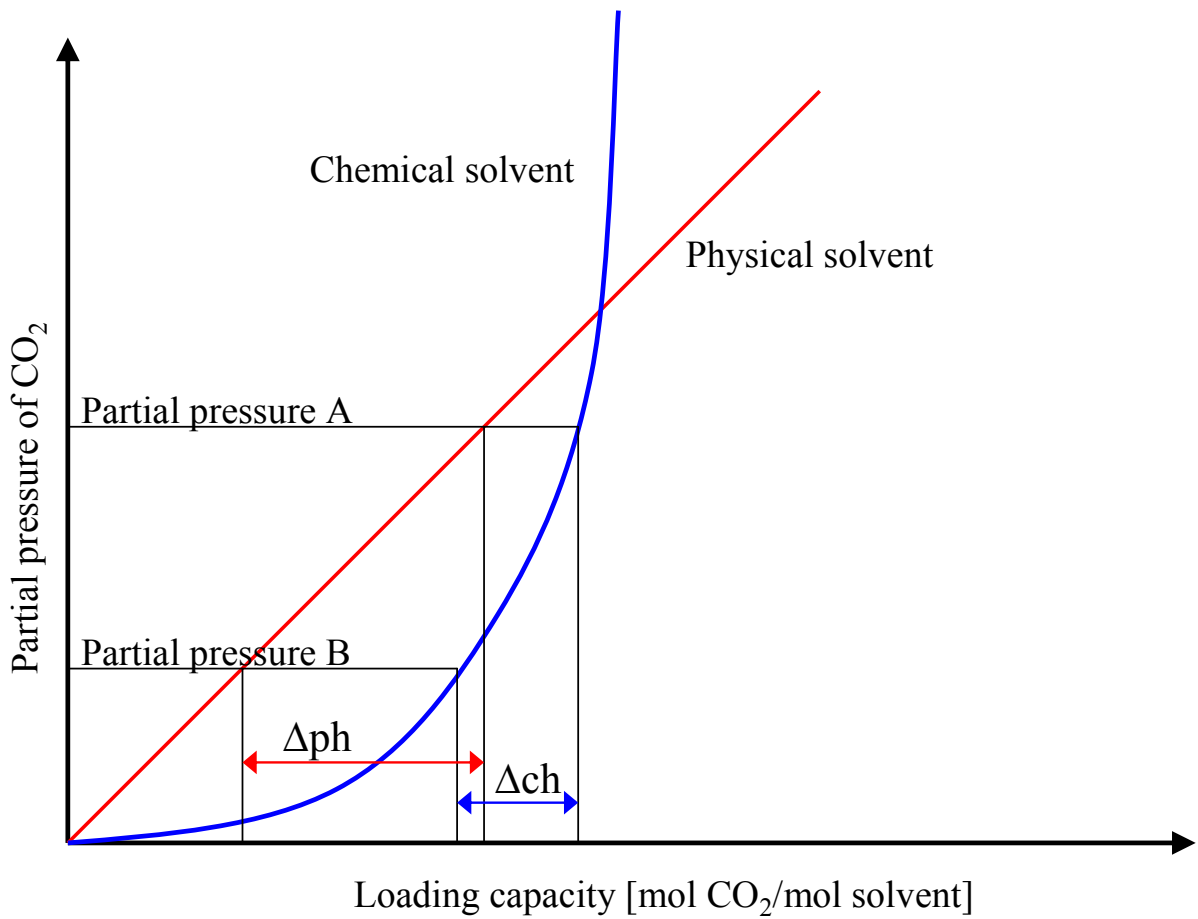


Figure 4-2: Loading capacity as a function of pressure and solvent type (Bolland, 2015)

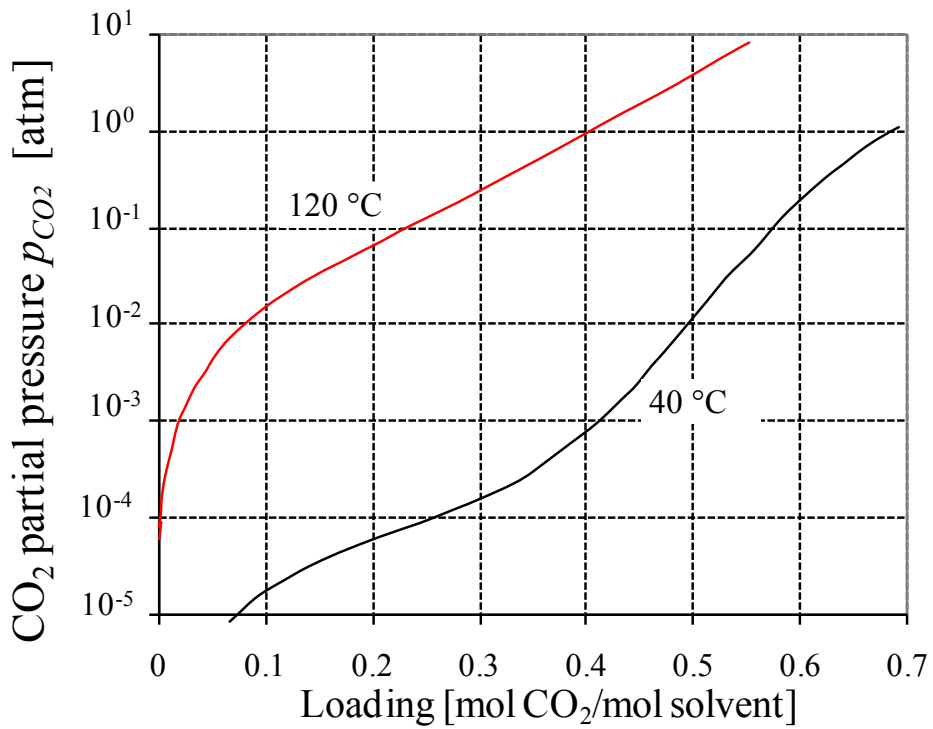


Figure 4-3: Solubility as a function of temperature (Bolland, 2015)

The flue gas at Klemetsrud has a pressure slightly below atmospheric. A generic process flow diagram for absorption with a liquid solvent at atmospheric pressure is shown in Figure 4-3. To prevent solvent degradation, the flue gas is cooled before entering the absorber. The process requires large amounts of heat, provided as steam in the reboiler, and a smaller amount of electricity consumed by the flue gas fans and solvent circulation pumps.

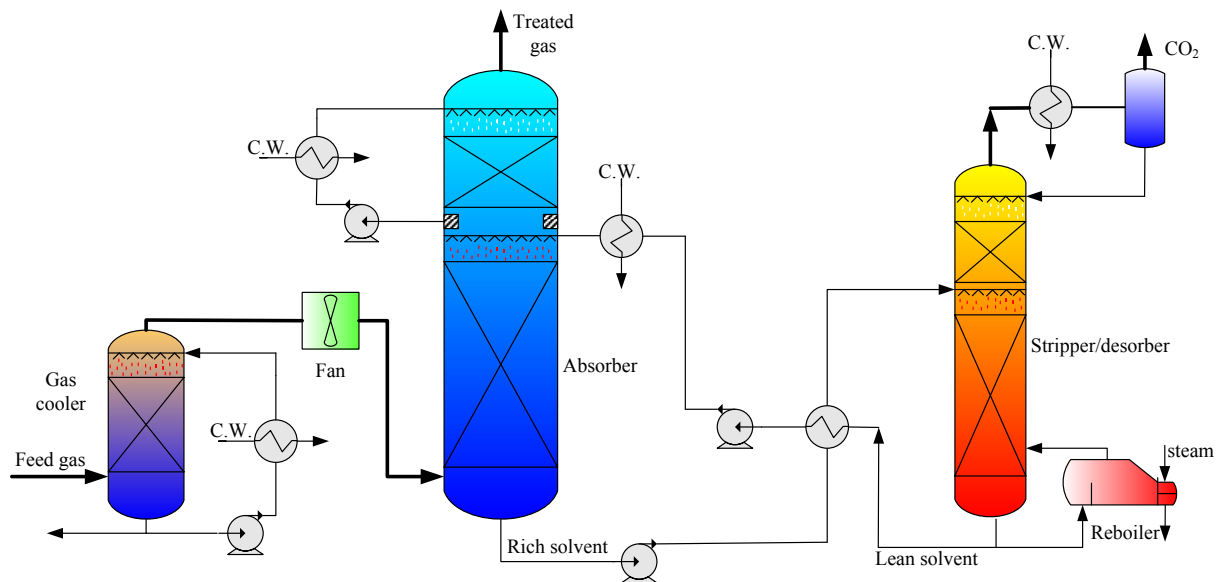


Figure 4-4: Generic low-pressure absorption process (Bolland, 2015)

### **Physical absorption**

The process involves physical absorption of CO<sub>2</sub> into a solvent. The dominating binding force is the Val der Waal forces, which are fairly weak compared to the covalent bonds created in a chemical reaction. The Val der Waals forces are so weak that the absorbed CO<sub>2</sub> will be desorbed by either reducing the pressure or by increasing temperature in the column, as described in Appendix F (Pinto et al., 2014). The drawback is that an efficient absorption process requires high CO<sub>2</sub> partial pressure, and for flue gas treatment systems this often necessitates compression of the flue gas stream. According to IEA, physical absorption is not economical for streams with CO<sub>2</sub> partial pressures lower than 15 %, which excludes this technology for Klemetsrud (Pinto et al., 2014).

### **Selexol**

Selexol is a process where the solvent, a proprietary mix of dimethyl ethers and polyethylene glycol (DEPG), absorbs CO<sub>2</sub> at a relatively high pressure.

Pro: No water is needed

Con: The sorbent has higher viscosity than water, resulting in an increased need for pumping force (Smit et al., 2014)

## Rectisol

Rectisol uses an organic non-proprietary solvent, typically methanol, which is cheap and easily available (NETL, 2015). CO<sub>2</sub> capture is conducted at high pressures and very low temperatures, typically between -62 °C and -40 °C (Smit et al., 2014).

Pro: Cheap and easily available solvent

Con: Low capture temperature which necessitates expensive (stainless steel) refrigerated vessels (Smit et al., 2014)

## Chemical absorption

The solvent will react with the CO<sub>2</sub> to form a strong bond in an exothermic reaction. The covalent bonds will not be broken by solely reducing the pressure, so the temperature has to be increased as well. Typical operating conditions for absorbers and strippers are presented in Table 4-1.

Table 4-1: Typical operating conditions for an absorber and a stripper (Cottrell et al., 2009; Pinto et al., 2014; IPCC, 2005)

	Temperature range [°C]	Pressure range [bar]
Absorber	40-60	1-1,5
Stripper	100-140*	1 -4*

\*Some solvents are capable of being regenerated at much higher pressures and temperatures

The thermal heating required for regeneration is significant and is most likely provided as low-pressure steam generated from the turbine of the power plant (Cottrell et al., 2009). To minimise the energy penalty caused by the extraction, the steam extracted should be at a temperature as close as possible to the regeneration temperature.

The regeneration process can be divided into three energy intensive process steps (Davidson, 2007):

- Heating the solution to the boiling point
- Boiling of the CO<sub>2</sub>, i.e. breaking the chemical bond between the CO<sub>2</sub> and the solvent
- Production of the steam to establish the operational partial pressure for CO<sub>2</sub> required for stripping. The steam will also act as a stripping gas

To achieve higher pressures in the stripper for enhanced desorption, multistep compression can be applied. There is a trade-off between pressure increase and steam



consumption, as indicated by the absorption characteristics indicated by Figure 4-2 and 4-3. A flow diagram of a multi-pressure stripping cycle with vapour recompression is shown in Figure 4-4.

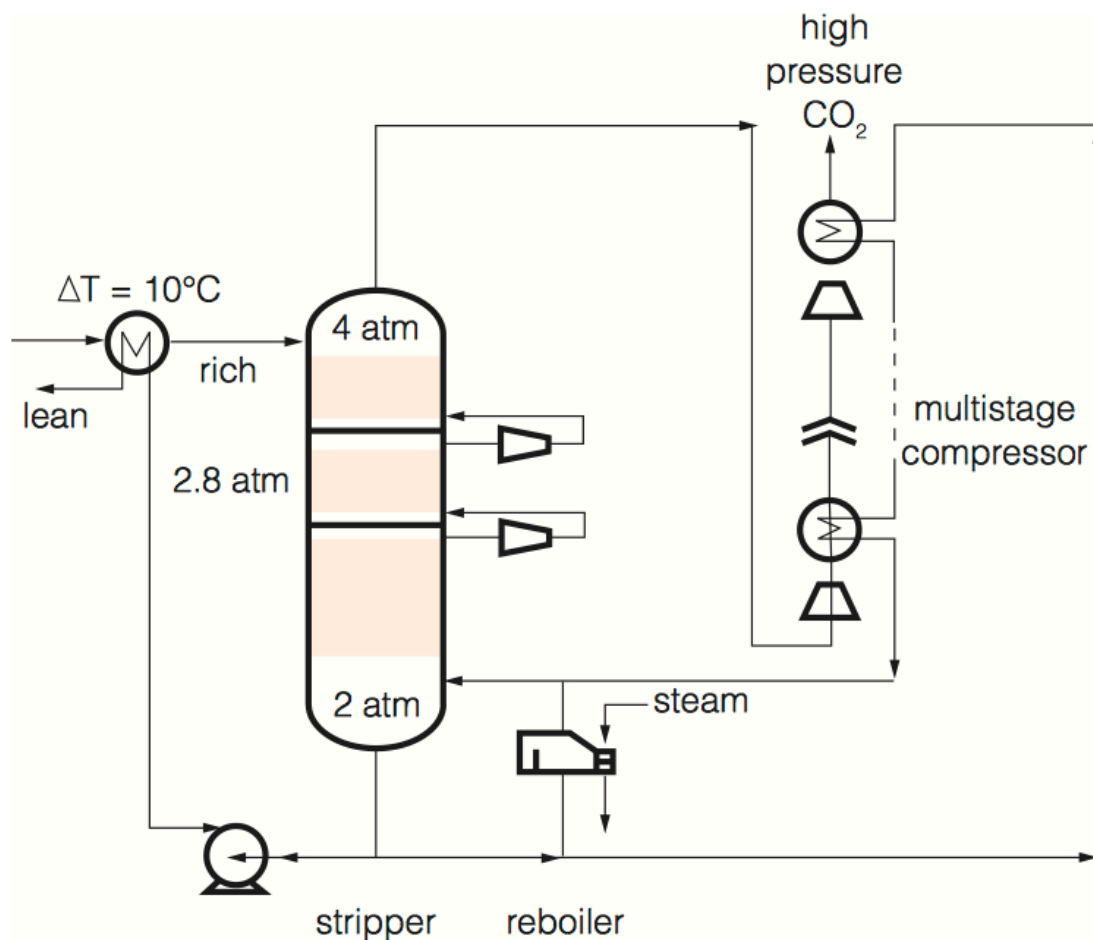


Figure 4-5: A flow diagram of a multi-pressure stripping cycle (Davidson, 2007)

### **Typical types of chemical solvents**

As indicated by Figure 4-1, there are many types of chemical solvents, but variations of amines are the only types commercialised. Out of the amines, MEA, DC-103 and KS-1 are the types preferred in CCS application and are therefore discussed more thoroughly than the others.

### **Amines**

Amines are compound derivatives of ammonia, and is currently the most common technology used in CO<sub>2</sub> capture (Pinto, 2014). The types of amines being used as solvents are categorized as either simple alkanolamines or sterically hindered amines. Within the category of simple alkanolamines, there are three groups of amines, named by the number of functional groups (R-groups) in the molecule. The R-groups are alkane

groups, such as CH<sub>3</sub>, and the number and type of R-groups will influence the properties of the amine (Smit et al., 2014).

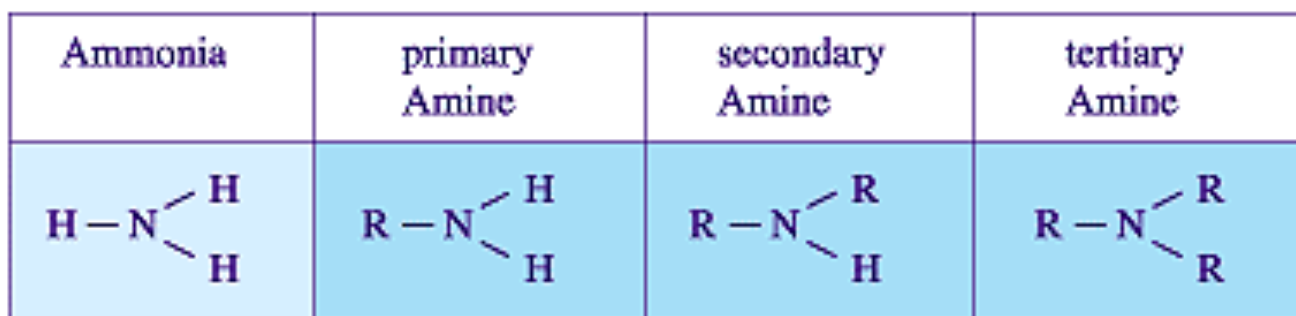


Figure 4-6: Primary, secondary and tertiary amines (U.S.Amines, 2015)

Primary amines will rapidly react with CO<sub>2</sub> to form carbamates. Primary and secondary amines will also partially be hydrolysed to form bicarbonates. The maximum loading capacity lies therefore in the range of 0,5-1 moles of CO<sub>2</sub> per mole of amine (Smit et al., 2014). The formation of carbamates is not possible for tertiary amines due to the additional R-group preventing this reaction, as indicated in Figure 4-6. Thus, tertiary amines facilitate CO<sub>2</sub> hydrolysis resulting in a maximum loading capacity of 1, albeit having a lower reactivity rate with CO<sub>2</sub> compared to primary amines (Smit et al., 2014). The heat of reaction is lower for the formation of bicarbonates than that of carbamates, and the heat requirements for regeneration are thus lower as well. A kinetic absorption activator, such as piperazine or MEA can be added to increase the rate of reaction (Kanniche et al., 2010). Likewise, tertiary amines, such as MDEA, are often blended with primary or secondary amines to reduce the cost of regeneration (Wang et al., 2011). Sterically hindered amines are specially designed to reduce the regeneration costs. They have the reaction rate similar to that of a primary amine, but as for tertiary amines, they do not produce carbamates, resulting in a higher CO<sub>2</sub> loading factor of 1 (Udesideri, 2010). Current commercial plants for CO<sub>2</sub> recovery are either using the primary amine MEA, or one of the sterically hindered amines DC-103 and KS-1. See Appendix C and D for references.

**Table 4-2: Properties of primary, secondary, tertiary and sterically hindered amines (Smit et al., 2014; Al-Fattah et al., 2012)**

Type of amine	Examples	Pros	Cons
Primary	Monoethanolamine (MEA) Diglycoamine (DGA)	High reactivity with CO <sub>2</sub>	Very reactive to other impurities Sensitive to degradation Corrosive High regeneration energy required
Secondary	Diethanolamine (DEA) Diisopropanolamine (DIPA)	Lower energy requirements than primary amines Less sensitive to degradation	Less reactive than primary amines to CO <sub>2</sub> Problematic applicability to flue gas with low CO <sub>2</sub> partial pressure
Tertiary	Methyldiethanolamine (MDEA) Triethanolamine (TEA)	Low degradation Low heat requirements	Low reactivity Problematic applicability to flue gas with low CO <sub>2</sub> partial pressure
Sterically hindered amines	KS-1 KS-2 KS-3 DC-103	Very low heat requirements Not corrosive High loading factor	More expensive Not as mature as the other amines

### Enzymes

In the human body, the enzyme carbonic anhydrase catalyses the reaction of CO<sub>2</sub> and water to bicarbonate, and the same process is copied to produce a solvent. The use of enzymes in carbon capture is not commercialised, because it does not work in the required temperature range and concentration due to unstable properties at these conditions.

### Ionic liquids

Depending on the type of ion, ionic liquids can be either chemical or physical solvents. Ionic liquids consist solely of ions, making the very little volatile (Smit et al., 2014). By

mixing ionic liquids, a tailored solvent can be created possessing desired properties of both chemical and physical solvents (Pinto, 2014). The loading capacity of CO<sub>2</sub> has been reported to be 0,75 for several ionic liquids (Huang, R  ther, 2009). As indicated by Figure 4-7, ionic liquids are not assumed to be commercialised for quite some time and are therefore not regarded as a feasible choice for EGE.

According to Kanniche et al. (2010), the following applies for absorption:

**Table 4-3: Absorption technology pressure range (Kanniche et al., 2010)**

Pressure range [bar]	Most appropriate solvent	Process type
< 1	MEA	Chemical
≥ 1	Tertiary amines, e.g. MDEA	Chemical
> 8 *	Will vary	Physical

\* 8 bar is the higher limit of which chemical solvents are applicable, but lower pressures may be feasible for physical solvents

Most flue gas point sources will have a CO<sub>2</sub> partial pressure of less than 8 bar. According to Kanniche et al. (2010), chemical absorption is thus most appropriate, which corresponds well with the trend in the industry. As of today almost all commercial processes for capturing CO<sub>2</sub> use liquid alkaline solutions, such as amines (Wang et al., 2011).

#### 4.1.2 Adsorption

Adsorption is a physical process where a gas or liquid attaches to a solid surface. The flue gas is sent through a material that selectively takes up CO<sub>2</sub> and binds to the surface of the material referred to as the sorbent. When the material is saturated, it must be regenerated. As for physical absorption, this can be done by either reducing the pressure or increasing the temperature in the column, where both operations result in a release of the adsorbed CO<sub>2</sub>. Physical sorbents do not give rise to corrosion, as some solvents do. Depending on the type of bed, the desorption process is either performed by changing the conditions in the absorber (which will then become a stripper) or by transporting the sorbent into a separate stripper unit. These processes are described in more detail in Appendix F. Some of the sorbents commonly applied in CO<sub>2</sub> capture are activated carbon, alumina, metallic oxides and zeolites (Wang et al., 2011).

It has been stated that current adsorption systems may not be suitable for flue gas treatment in large-scale power plants. This is mainly due to the generally poor

selectivity of the sorbents and low loading capacity (Wang et al., 2011). These undesirable abilities necessitate pre-treatment of the flue gas stream, e.g. to increasing CO<sub>2</sub> concentration and remove water. Zeolite for instance, has a high affinity for water vapour. Application of some sorbents will therefore require extensive distillation of the flue gas before entering the bed. As indicated by Figure 4-7, this technology is not yet mature for post-combustion capture and is thus not regarded as a suitable technology for Klemetsrud.

#### 4.1.3 Cryogenic distillation

Cryogenics separates CO<sub>2</sub> from the flue gas stream by condensation. This occurs at very low temperatures, and the process is therefore best suited for streams with high CO<sub>2</sub> partial pressures. The high costs of refrigeration makes this option mainly used in oxyfuel combustion capture (Pinto et al., 2014). See Chapter 4.3.1 for technical description.

#### 4.1.4 Membranes

Through selectivity provided by the membrane, separation of gases occurs due to differences in partial pressures on each side of the membrane (Pinto et al., 2014). See Chapter 4.3.2 for technical description. For an incineration plant, the flue gas is approximately at ambient pressure, and compressing the flue gas would be very expensive due to the large quanta. This is why current membrane technology has a reputation of not being very efficient for this application (Smit et al., 2014). Also, low selectivity is often a problem, and multistage separation is then required to produce a sufficiently pure stream of CO<sub>2</sub>. This results in extra operating and capital costs due to the need of several membranes and high energy penalty due to the recompression in-between each membrane stage (Pinto, 2014). Based on the arguments listed above, current membrane technology does not possess the qualifications required by a post-combustion technology for optimal performance at Klemetsrud.

#### 4.1.5 Metal organic frameworks

Metal organic frameworks (MFOs) are porous crystals consisting of metal ions. MFO-177, has been reported to have the largest CO<sub>2</sub> loading capacity of all porous materials investigated of 147,4 wt% (Davidson, 2010). The technology has low regeneration

energy requirements, good thermal stability, high tolerance to contaminants and high attrition resistance. The technology has a large potential, but as indicated by Figure 4-7, it not predicted to become available in a commercial scale for quite some time. The drawbacks of MFOs is that high pressures are required for optimal utilisation and that the gas has to be dried upstream of the process, as water will reduce the loading capacity (Davidson, 2010).

4.1.6 Maturity

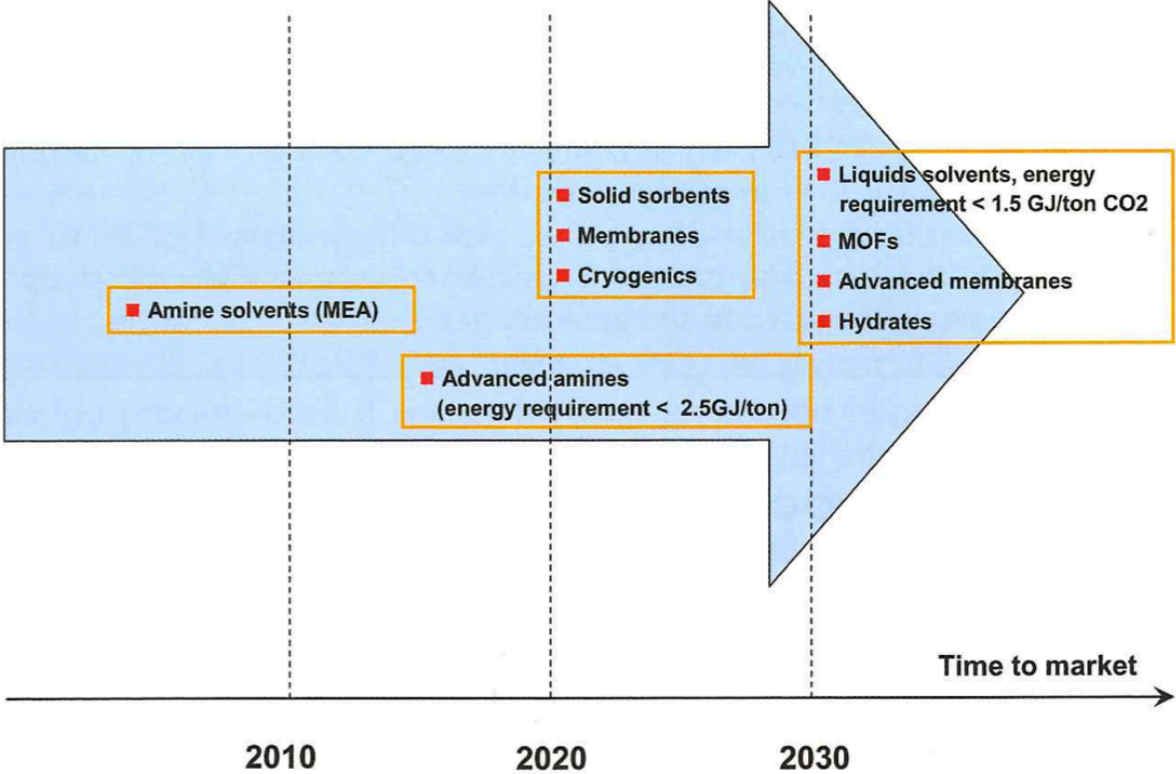


Figure 4-7: Time-to-market for post-combustion technologies (Al-Fattah et al., 2012)

As previously mentioned, amines are the most mature CO<sub>2</sub> capture technology, and the first LSIP within the power sector, utilises the proprietary amine DC-103. Figure 4-7 indicates the predicted time-to-market prospective for post-combustion technology. According to the figure, varieties of advanced amines are under commercialisation, which agrees with the literature (Desideri, 2010). The proprietary sterically hindered amine KS-1 is already on the market and others have been thoroughly tested in pilot plants (Fluor, 2004; Kanodo et al., 2013).

## 4.2 Pre-combustion capture technology

At Klemetsrud, the primary fuel would be MSW, which is a solid, and the appropriate conversion route would therefore be through gasification. For the MSW to be suited for gasification, pre-treatment is crucial. Figure 4-8 shows a generic box flow diagram of a MSW pre-treatment system, indicating the most important steps prior to the gasification process (Zafar, 2009). As indicated by Figure 4-8, metals, glass and plastics have to be removed prior to MSW preparation. MSW preparation may involve sorting, shredding, grinding, blending with other materials, drying and/or pelletization.

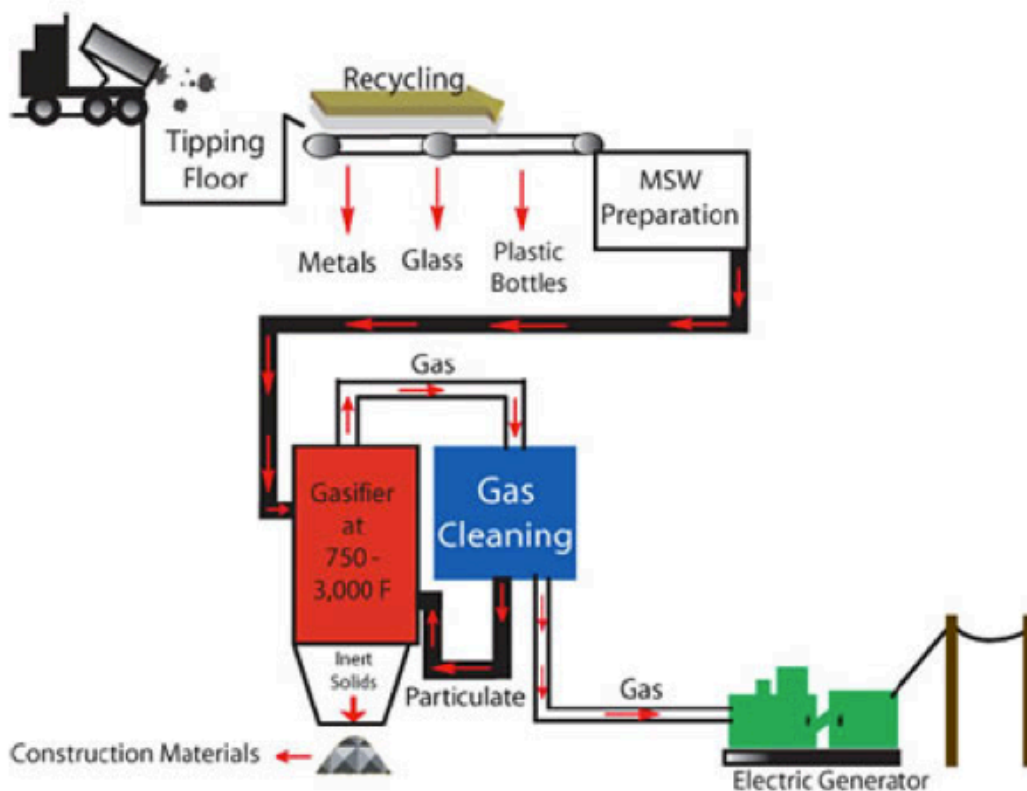


Figure 4-8: MSW pre-treatment and gasification process overview (Zafar, 2009)

### Pros:

- Easier CO<sub>2</sub> separation process due to the higher partial pressure of CO<sub>2</sub>
- Allows efficient and uniform combustion of low grade fuels

### Cons:

- Gasification requires extensive waste processing
- Cannot be easily implemented into an existing plant

Gasification of the waste would result in large changes to Klemetsrud. The product of the gasification process is hydrogen, which it is not viable to utilise in the production of heat and electricity and the retrofit project would be very costly as expensive equipment and extensive modifications to existing installations are necessary. As discussed in Project Work (Helsing, 2014), hydrogen has a higher market value as a transport fuel than as a fuel in heat production. Gasification technology is mature but there are currently no commercial plants combining heat and hydrogen production in operation (Kanniche et al., 2010). Based on the criteria listed at the beginning of this chapter, pre-combustion capture is not applicable at Klemetsrud.

### 4.3 Oxyfuel combustion technology

Many studies show that oxyfuel combustion with flue gas recycling is more attractive than conventional combustion. This is mainly due to the potential of increased combustion efficiency, low NO<sub>x</sub> emissions and easy CO<sub>2</sub> recovery (Lai et al., 2011).

In a preliminary study performed by Tang et al. (2013), the feasibility of implementing CCS technology into an existing MSW incineration plant in China was investigated. The study shows that CO<sub>2</sub> capture by oxyfuel combustion gives better results in both energy consumption and environmental impact when compared to MEA technology (Tang et al., 2013).

A techno-economic study by Sing et al. (2003) evaluated the viability of retrofitting a coal-fired power plant. The study concluded that oxyfuel combustion is more attractive than MEA scrubbing. According to the calculations, amine solvents have to perform 50% better than MEA to be competitive with oxyfuel combustion with flue gas recycling (Singh et al., 2003).

Despite being a technology with a high electricity demand, as well as not being mature as a CO<sub>2</sub> capture technology, the technology will be presented in this chapter as many studies conclusively rates this as the best capture technology for MSW incineration plants.



**Pros:**

- Applicable in large-scale boilers and retrofit projects (IEA, 2008)
- Easy CO<sub>2</sub> separation by condensing and removing water vapour. A boiler temperature similar to in conventional combustion is obtained by recycling 60%-80% of the flue gas back to the boiler (Tang et al., 2013)
- Low SO<sub>x</sub> and NO<sub>x</sub> emissions compared to post-combustion capture (IEA, 2008)
- Increased boiler efficiency (Tang et al., 2013)

**Cons:**

- ASU is not sufficiently efficient. Electricity is required in the cryogenic distillation of air, and heat integration to recover the energy demand is thus not an option (Mathieu, 2010)
- Reduced power supply efficiency (Tang et al., 2013)
- Retrofitting requires changes to the incineration plant
- A minimum purity of 95% is required to keep CO<sub>2</sub> at monophasic conditions when compressed (Al-Fattah et al., 2012). Therefore, if a higher purity than what the plant can provide is required for safe transport or storage, a CO<sub>2</sub> purification plant is needed. The plant that removes impurities such as O<sub>2</sub>, N<sub>2</sub>, Ar, SO<sub>2</sub> and NO<sub>x</sub> operates at approximately -55 °C which implies an increased efficiency penalty (Mathieu, 2010)
- In oxyfuel boilers, air may leak in, as the pressure is kept below atmospheric. As air ingresses into the boiler, the purity of the recovered CO<sub>2</sub> stream is reduced, increasing the probability of the need for a CO<sub>2</sub> purification plant (Mathieu, 2010)

As previously mentioned, separating the air is the critical process step in oxyfuel combustion. Published literature anticipates that the ASU requires approximately 60 % of the total energy requirements of the carbon capture process (Davison, 2007; Singh et al., 2003). It is therefore important to apply the separation technology best suited for the relevant application. In the next section, the following air separation technologies are presented:

- Cryogenic distillation
- Polymeric membrane
- Oxygen transport membranes
- Adsorption
- Chemical looping

### 4.3.1 Cryogenic distillation

The most common air separation technology is using air cryogenic distillation in an air separation unit (ASU). The technology has been used in the steel and refinery industry for a century, and the largest ASU plants currently produce 4000 tpd of  $O_2$  (Kluiters et al., 2010). The main process equipment in an ASU is the distillation column.  $N_2$ , the most volatile component of the air, leaves at the top of the column, and the less volatile  $O_2$  is collected at the bottom (Kluiters et al., 2010). Ar has a volatility in-between  $N_2$  and  $O_2$ , and the process of separating Ar from  $O_2$  is very energy intensive. The purity of the produced oxygen rich stream is decided by the column design and the number of stages. Figure 4-9 shows a process flow diagram of a 2 stage ASU using cryogenic distillation.

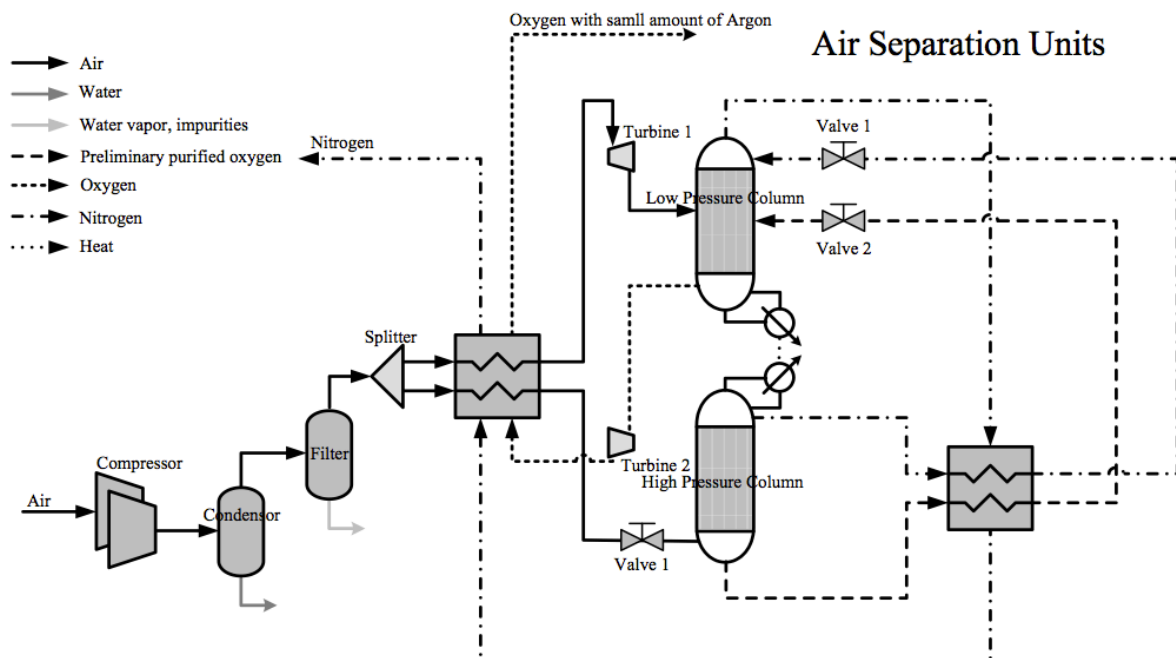


Figure 4-9: Process flow diagram of a 2 stage ASU (Hu, 2011)

### 4.3.2 Polymeric membranes

A membrane has the ability to separate two gases by only letting specific components of the gas pass through the membrane due to a difference in selectivity. The selectivity is the ratio of the permeabilities of the gases to be separated and is a property of the membrane (Smith, Klosek, 2001). The constituent given the highest permeability will penetrate the membrane and is referred to as the permeate. The rest of the gas, called the retentate, will not pass through. A membrane can then be designed so that  $O_2$  passes through easier than  $N_2$ . There is a pressure drop over the membrane, which is the main

driving force of the separation process (Smit et al., 2014). A thin selective layer made of a composite polymer is bonded to a thicker, non-selective, low-cost layer to provide mechanical strength to the membrane (Leung et al., 2014). Polymeric membranes are usually limited to the production of oxygen-enriched air, with an oxygen purity of 25-50%. This is not enough to facilitate oxyfuel combustion, and new technologies such as oxygen transport membranes are thus of great interest (Smith, Klosek, 2001).

### 4.3.3 Oxygen transport membranes

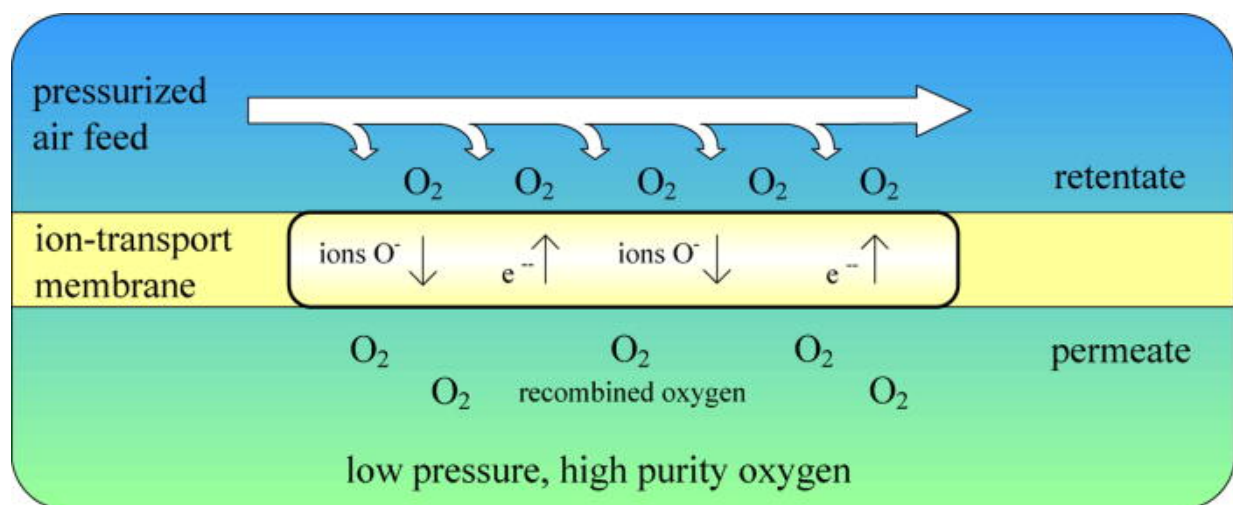


Figure 4-10: Oxygen Transport Membrane (Gambini, Vellini, 2012)

Oxygen transport membranes (OTMs), also referred to as oxygen selective membranes (OSM), ion transport membranes (ITMs), mixed conducting membrane (MCM) or mixed ionic electronic conducting membranes (MIECs), are regarded as the most promising oxygen separation technology under development, and produces a stream of pure  $O_2$  (Kluiters, 2010). The current generation of OTMs operates at high temperatures and feed side pressures in the range of 700-1000 °C and 5-40 bar, respectively (Kluiters, 2010). This necessitates the need for compression and heating on the feed side of the membrane, implying a high efficiency penalty. There are several ways to reduce the penalty, and the most important ones are listed below (Kluiters, 2010).

- As there is heat and high pressure remaining in the  $N_2$ -rich retentate flow, the energy in this stream should be recovered
- The heat released in the combustion zone as well as the heat from the retentate flow can be utilised to heat the feed stream through heat integration

As indicated in Figure 4-13, these membranes are still in the developing phase. Based on the performance and level of maturity, OTMs are currently not a potential technology for Klemetsrud.

#### 4.3.4 Adsorption

As mentioned in Chapter 4.1.2, separation by adsorption is based on the ability of a material to preferentially adsorb a component of a mixture. Adsorption is more attractive in air separation than in CO<sub>2</sub> separation due to the higher partial pressure of N<sub>2</sub>, which is the component to be adsorbed. See Appendix F for more details.

Zeolite is a common solid sorbent, where the separation abilities are caused by a non-uniform electric field existing in the void spaces of the material. N<sub>2</sub> is more polarizable than O<sub>2</sub> and Ar, and is thus more strongly adsorbed (Smith, Klosek, 2001). As shown in Figure 4-11, air is filtered and pressurized before entering the adsorbing bed, marked as 'zeolite bed A'. As N<sub>2</sub> is retained, an O<sub>2</sub> rich stream leaves at the top of the column with a typical purity within the range of 93-95%.

As the capture process in a power plant has to be continuous, it is necessary to have at least two vessels. As shown in Figure 4-11, 'zeolite bed A' can operate in capture mode while the other one, 'zeolite bed B', operates in regeneration mode. Multiple beds can be employed to permit energy recovery during bed switching.

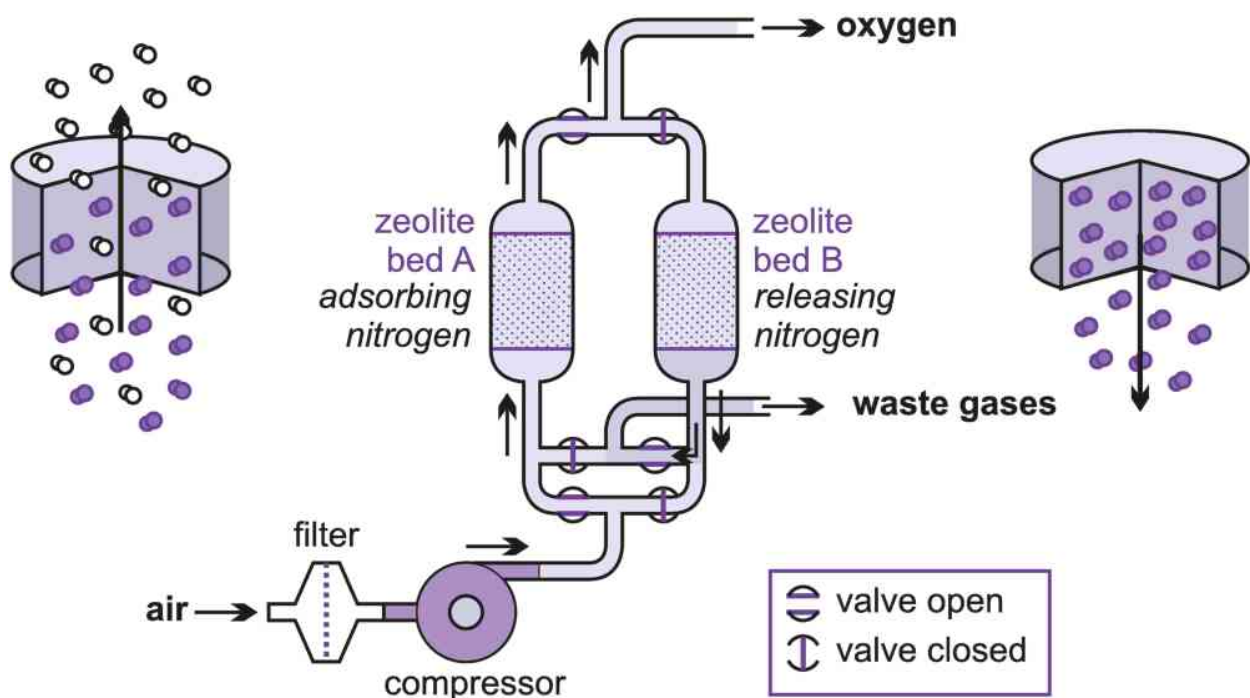


Figure 4-11: Zeolite process overview (TUY, 2013)

## Chemical-looping

Chemical-looping may be used as an air separation technology in combination with oxyfuel-combustion. The combustion process is then referred to as chemical-looping combustion, where the fuel is being oxidized without the direct use of oxygen (Anthony, 2010). The two main process steps of this combustion are separated into two separate reactors; a fuel reactor and an air reactor. A typical sketch of a metal oxide looping cycle is shown in Figure 4-12.

In the air reactor, some of the  $O_2$  from the air oxidizes the oxygen carrier. The oxygen carrier, which is usually a metal, is then transported to the fuel reactor where the combustion occurs. When the oxygen has reacted with the fuel, the oxygen carrier is returned to the air reactor, which forms a closed loop operating at temperatures in the range of 800-1200 °C (Smith et al., 2014; Anthony, 2010). The flue gas properties are similar to that of direct combustion in pure oxygen, consisting mainly of  $H_2O$  and  $CO_2$ . The water can then be condensed, and the  $CO_2$  can be collected. This technology is still in the under development but studies shows that this type of combustion results in low energy penalty and no  $NO_x$  formation (Smith et al., 2014).

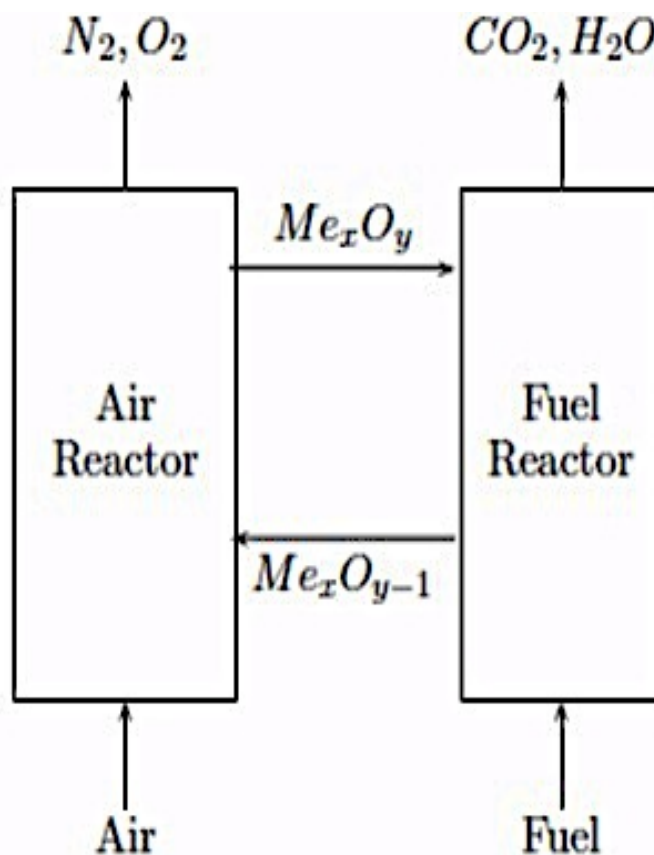


Figure 4-12: Chemical-looping combustion (Ramachandran)

### 4.3.5 Maturity

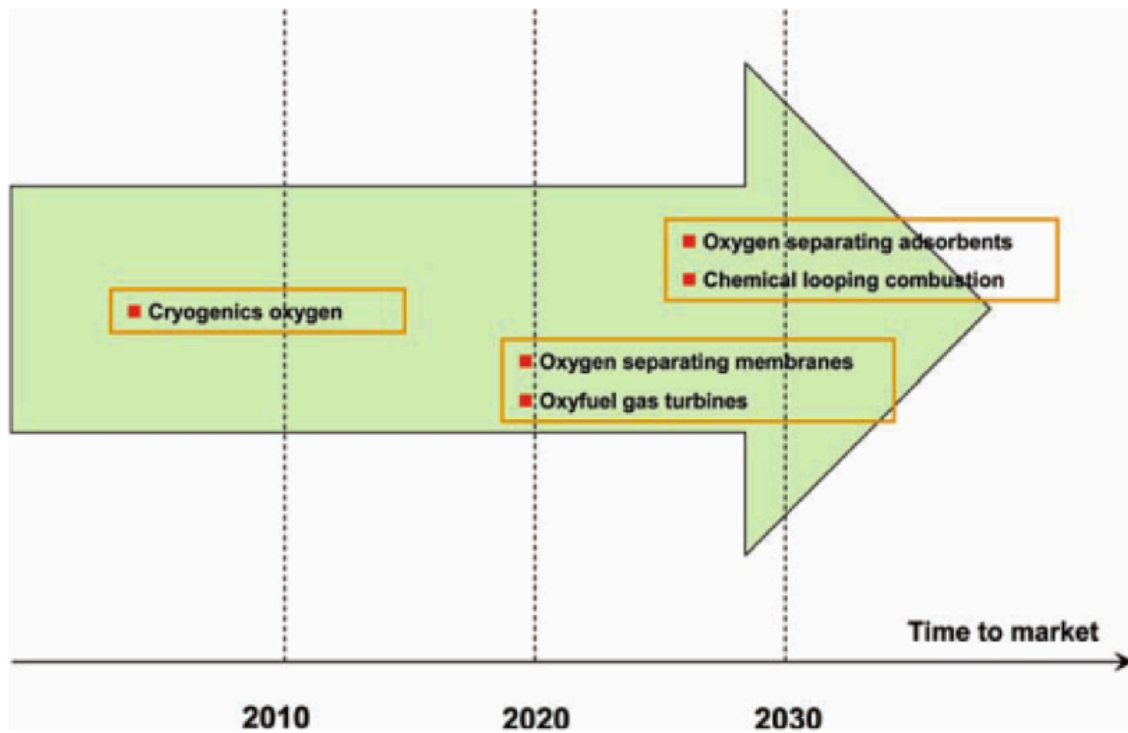


Figure 4-13: Time-to-market for oxyfuel technology (Al-Fattah et al., 2012)

As indicated by Figure 4-13, cryogenic air separation is the only technology currently available at a commercial scale that can provide the required oxygen purity.

## 4.4 Discussion

From the argumentation presented in this chapter, it is clear that post-combustion capture using amines is the most relevant technology based on the level of maturity. Oxyfuel combustion is by many regarded as the most efficient way to utilise MSW in combination with CCS. Several studies emphasise the low energy penalty when comparing to post-combustion technology. Despite not being commercialised as a capture technology, all the process steps involved are separately regarded as proven. Amines and oxyfuel combustion are thus the technologies to be further evaluated in Chapter 5.

## 5 Retrofit performance

### 5.1 Post-combustion capture using amines

As shown in Figure 4-4, flue gas is cooled and contacted counter-currently with a lean amine solution. CO<sub>2</sub> is absorbed by the solvent and the remaining gas exits the top of the absorber. Before being vented to the atmosphere, the gas is water washed to remove traces of solvent. Due to the reaction between the CO<sub>2</sub> and amine being exothermic, the lean amine is gradually heated as it absorbs CO<sub>2</sub>. When the saturated solvent reaches the bottom of the absorber it is and pumped to the stripper for regeneration. The rich solvent is heated by the lean solvent exiting the stripper by a heat exchanger before entering the stripper, as shown in Figure 4-4. The heated rich amine enters the top of the stripper, and is regenerated as it moves towards the bottom of the column. This occurs at elevated temperatures and reduced pressures to enhance desorption. Heat is supplied as steam in the reboiler, and is the major contributor to the energy penalty imposed on the plant. The regenerated solvent is then pumped via the heat exchanger, back to the absorber. Impurities, such as heat stable salts, are accumulated in the reclaimer unit and purged from the system when necessary (Pinto et al., 2014).

Absorption performance with amines is mainly affected by (Al-Fattah et al., 2012):

- Required regeneration energy
- Solvent losses (mainly due to degradation and volatilization of solvent)
- Corrosion induced by amine solution

Applying a technology that requires heat rather than electricity is very attractive for Klemetsrud as extensive heat integration is possible due to the plant's ability to utilise low grade heat. Especially during the summer when there is a heat surplus in the district heating network, it is desirable to utilise the heat that would otherwise have been vented to the atmosphere. Another important feature of the amine capture plant is the ability to be switched off when full load is necessary to cover peak load requirements in the district heating network (Kärki et al., 2013).

Today, the two most commonly used technologies in post-combustion plants are the two MEA processes Kerr-McGee/ABB Lummus Crest and FluorDaniel/Dow Chemical, developed during the 1970's and 80's (IPCC, 2005). A third commercialised process, the Mitsubishi-Kansai process, was developed in the 1990's and requires less heat for regeneration, and has low amine losses and degradation by utilising the sterically hindered amine, KS-1 (Desideri, 2010).

As shown in Appendix B, 4 out of the 5 scheduled retrofit LSIP's utilise amines in their capture technology. This includes the first power plant with CCS on a commercial scale, Boundary Dam, which is equipped with Cansolv's integrated SO<sub>2</sub>-CO<sub>2</sub> capture technology. Amines are thus by far the most mature capture technology, although quite expensive due to the high regeneration energy demand. As previously mentioned, Klemetsrud is per definition not a LSIP, and smaller capture plant may thus be representable for EGE's application. KS-1 has been commercialised on a scale similar to that of Klemetsrud, and the experience is thus applicable.

### 5.1.1 Commercialised MEA absorption processes

#### **Kerr-McGee/ABB Lummus Crest, the KM/ALC process**

The solvent of the Kerr-McGee/ABB Lummus (KM/ALC) process is an aqueous solution of MEA, with 15-20 wt% MEA (Desideri, 2010). The process tolerates O<sub>2</sub> and a limited amount of SO<sub>2</sub> in the flue gas. The first plant to utilise the Kerr McGee technology was built in 1978 in California, with a CO<sub>2</sub> production rate of 800 tpd (Desideri, 2010). The plant is fired with coal, coke and natural gas.

#### **FluorDaniel/Dow Chemical, the ECOAMINE Process**

In 1989, the Fluor Daniel Ecoamine process was released. The MEA-based process uses a solvent of an aqueous solution with inhibited 30 wt% MEA. The inhibitors are added to increase the solvents tolerance of O<sub>2</sub> and NO<sub>x</sub> and to prevent steel corrosion due to the high concentrations of MEA (Desideri, 2010). The inhibitors are activated by O<sub>2</sub>, and a minimum concentration of 1,5 vol% is desirable to maintain inhibitor activity (Chapel et al., 1999).

The largest plant utilising this technology was built in 1982 in Texas, and is currently producing 1200 tpd of CO<sub>2</sub>. The technology was originally developed for enhanced oil recovery (EOR) and there were more than 20 plants utilizing this technology in 2010 (Desideri, 2010). The process cannot reduce gases containing CO, H<sub>2</sub>, H<sub>2</sub>S, and O<sub>2</sub> content of more than 1 vol%, hence these components have to be removed upstream of the MEA-process. The technology can process gasses containing NO<sub>x</sub>, SO<sub>x</sub> after SO<sub>2</sub> removal, and can recover 85-95% of the CO<sub>2</sub> in the flue gas. The CO<sub>2</sub> produced has a purity up to 99,95%, which is high enough to qualify for CO<sub>2</sub> delivery to the food industry, urea production and enhanced oil recovery (Desideri, 2010). The flue gas has to be cooled to the water dew point of 50 °C before entering the absorber to reach the allowable water content and to prevent solvent degradation (Chapel et al., 1999).



### 5.1.2 Commercialised sterically hindered amine absorption processes

#### Kansai Electric Power Cooperation/ Mitsubishi Heavy Industries, the KM-CDR process

The result of this collaboration is the sterically hindered amines KS-1, KS-2 and KS-3, where KS-1 is the only one that has been commercialised. The heat of reaction for KS-1 is 20% lower than that of MEA (Rameshini). As KS-1 is regenerated at a lower temperature than MEA, has a lower heat of reaction and a higher loading capacity the heat requirements are significantly lower, as indicated in Figure 5-1. There are currently 10 commercial plants are utilising this technology, where two are briefly presented in Appendix D.

The first commercial plant to utilise the KM-CDR process was a steam reforming plant producing urea, built in Malaysia in 1999. The solvent, KS-1, is used in the process of capturing 160 tpd of CO<sub>2</sub> (Smit et al., 2014). This process has a larger difference between the lean and rich solvent's CO<sub>2</sub> loading capacity than the two other amine processes technologies mentioned, and the solvent circulation rate can therefore be lower (Desideri, 2010). The regeneration temperature is approximately 110 °C and solvent degradation, corrosiveness and amine losses are minimal without the use of inhibitors. (IPCC, 2005)

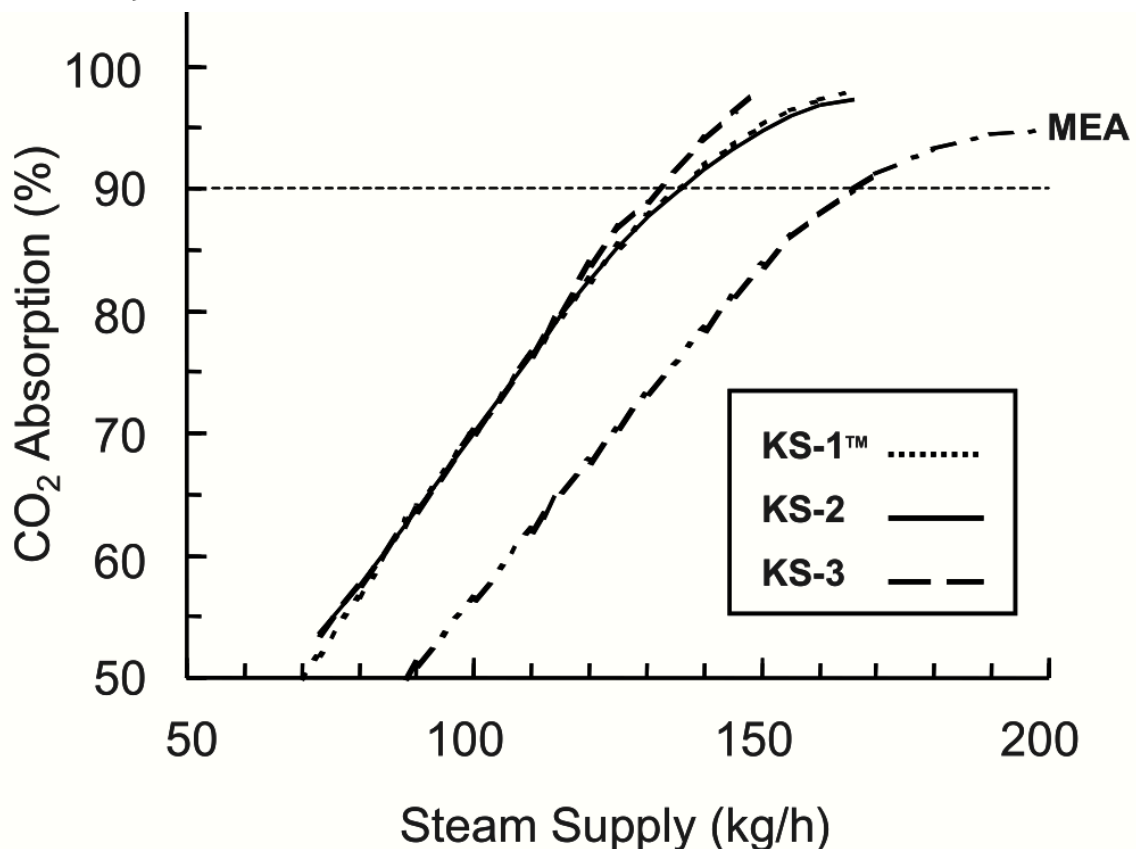


Figure 5-1: Absorption capacity and steam supply of KS-1, KS-2, KS-3 and MEA (Kanodo et al., 2013)

## Shell, the Cansolv process

The world's first commercial CCS power plant commissioned was Boundary Dam, a coal-fired, electricity producing power plant. The plant is equipped with Cansolv's integrated SO<sub>2</sub>-CO<sub>2</sub> capture technology, which can reversibly absorb SO<sub>2</sub>, NO<sub>2</sub> and CO<sub>2</sub> (Rameshini). A description of the power plant can be found in Appendix C. The Cansolv process utilises the proprietary solvent DC-103, consisting of 50 wt% amine and 50 wt% water. The heat of reaction is 40% less than that of MEA, although the reaction rate is comparable (Abu-Zahara et al., 2013). 80% of the heat used for in the SO<sub>2</sub> stripper is recovered and used in the CO<sub>2</sub> stripper (Cansolv, 2015).

### 5.1.3 Comparison between commercialised amine processes

According to IPCC and Shell, the allowable concentrations of SO<sub>2</sub> and NO<sub>2</sub> in a flue gas are as presented in Table 5-1 (Fluor, 2004; IPCC, 2005; Shell).

Table 5-1: NO<sub>2</sub> and SO<sub>2</sub> tolerances of several amine processes

	SO <sub>2</sub> [ppmv]	NO <sub>2</sub> [ppmv]
ECOAMINE	< 10	< 20
KM-CDR	< 1	
MEA	< 10	
Cansolv*	< 4 200	

\*The process comprise an integrated SO<sub>2</sub>-CO<sub>2</sub> scrubber

### ECOAMINE+ vs. KM-CDR

In a study performed by Fluor on behalf of IEAGHG, a comparison was done between KM-CDR and Fluor's own Ecoamine+. Ecoamine+ is an improved version of Ecoamine that is offered on a commercial scale by FluorDaniel/Dow Chemical, but is yet to be deployed in a commercial scale. The study was based on a coal-fired and a natural gas-fired power plant, and it shows that the energy penalty is significantly lower for the KM-CDR process, as both heat and power consumption was reduced. For both plants utilising this process, the heat requirement was lower because KS-1 was used rather than MEA. The power consumption was lower because the pressure drop over the absorber is less, so the flue gas fans consumes less power. The pressure drop is lower due to the column design. The resulting efficiency penalties are presented in Figure 5-2, where KM-CDR is labelled as MHI, and Ecoamine+ is labelled as Fluor. The energy penalties due to compression are similar for a specific type of plant, as the two capture processes produce CO<sub>2</sub> streams with similar pressures. As the scope of this thesis is to

evaluate capture technologies based on their energy requirements and imposed energy penalties, the KM-CDR process shows a better performance than Ecoamine+ and thus Ecoamine as well. The coal-fired power plant evaluated in the study was only producing electricity, and the energy penalties would therefore have been lower for a CHP plant for both processes.

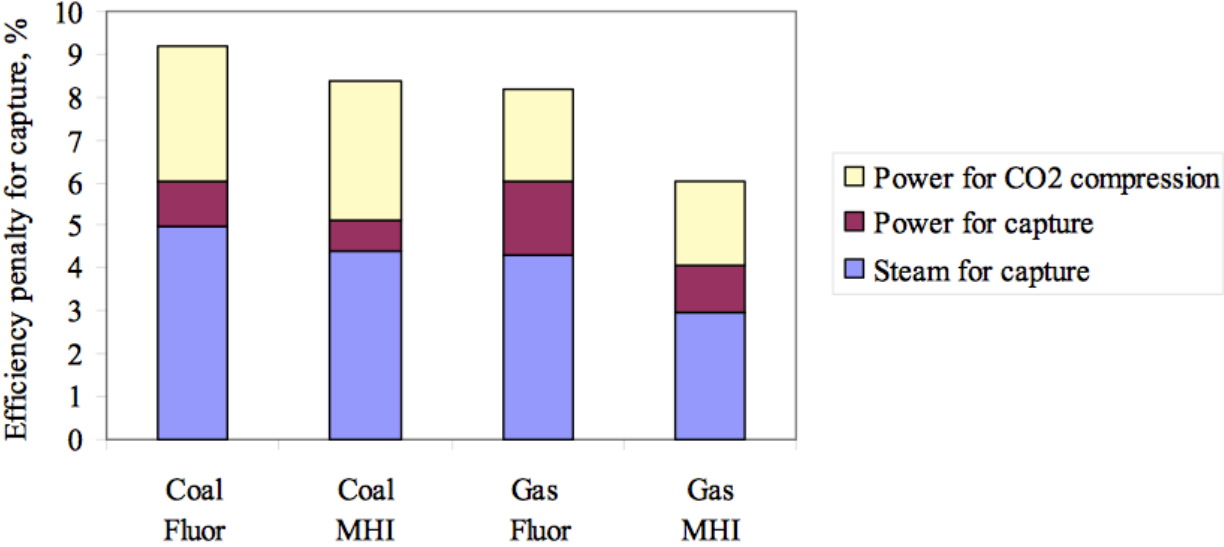


Figure 5-2: Efficiency penalty for ECOAMINE+ and KM-CDR (Fluor, 2004)

In the same study, Fluor made a multifactorial comparison between the three amine processes KM/ALC, KM-CDR, Ecoamine+. The result is shown in Table 5-2, where the processes are labelled Kerr McGee, KS-1 and EFG Plus, respectively. The study was conducted in 2004, and may therefore not be fully up to date on ‘commercial experience’. The notes are referring to the method of comparison, and are listen in Appendix G. As the study is performed on behalf of IEAGHG and published in their name, this source is assumed to be objective.

Table 5-2: Multifactorial Comparison of Commercial Amine Scrubbing Technologies (Fluor, 2004)

FACTOR	NOTES	KS-1	EFG Plus (MEA)	Kerr McGee (MEA)
		(MHI)	(FLUOR)	(ABB Lummus Global)
Gas pretreatment to lower SO <sub>2</sub> / NO <sub>2</sub> required?	1	yes	yes	yes
Scaleable to commercial power plant sizes	2	yes	yes	yes
Energy use	3	Lowest	Close to KS-1	highest
Capex	4	Close to Fluor	lowest	highest
Opex	5	High	High	High
Solvent cost	6	High	Low	Lowest
Commercial Experience	7	1 plant	>20 plants	3 plants
Coal based plants built	8	none	none	Yes; all 3 plants are coal based
Process Development programmes ?	9	Yes	Yes	?
Market position?	10	modest	modest	lower

### The resulting retrofit requirements for Klemetsrud

#### **Flue gas pretreatment**

The flue gas produced at Klemetsrud holds a temperature of 160 °C when entering the stack. The flue gas will therefore have to be reduced before entering the absorber to prevent solvent degradation. NO<sub>2</sub> and SO<sub>x</sub> will react with the amines to form heat stable salts that will reduce the absorption capacity (IPCC, 2005). The reaction is irreversible, resulting in solvent loss. It is therefore important to remove NO<sub>2</sub> and SO<sub>x</sub> prior to absorption, as indicated by Table 5-2. The amount of SO<sub>2</sub> to be removed is determined by the economic trade-off between the cost of removal and the cost of the solvent loss.

Klemetsrud is currently equipped with both NO<sub>x</sub> and SO<sub>2</sub> scrubbing equipment. In the flue gas, NO<sub>x</sub> are assumed to comprise a maximum of 15% NO<sub>2</sub>. NO<sub>2</sub> is thus not a limiting factor in the applicability of amine technology. SO<sub>2</sub> on the other hand, will influence the performance of the system as average concentrations up to 3,4 vol% have been documented, but in all processes except the KM-CDR process, this level is regarded as acceptable. To apply the KM-CDR process, an upgrade of the existing scrubber or an additional flue gas pre-treatment process is thus advisable.

### **Steam cycle**

As data for the steam cycle at Klemetsrud was irretrievable, a literature study is conducted and the efficiency increasing measures found in the literature are presented in Chapter 6.1. The steam provided in the reboiler will be extracted from the low pressure part of the steam cycle. It is therefore reason to assume that changes have to be made to the steam turbine, as the volumetric flow through the turbine will be drastically decreased.

#### **5.1.4 Amines evaluated based on the criteria provided by EGE**

**Applicability to retrofit projects:** Amines are by many claimed to be the best option in retrofit projects because it is installed as an end-of-pipe technology.

**Maturity:** The technology is mature. The first large-scale power plant is in operation, and an amine solution was the choice of capture technology.

**Efficiency penalty:** The penalty will depend on the overall efficiency of the plant, degree of integration and operating parameters. Minimising the efficiency penalty is possible through extensive heat integration and choosing the right solvent, as will be discussed in Chapter 6.1.

## **5.2 Oxyfuel Combustion**

N<sub>2</sub> is removed in an air separation process, currently performed by cryogenic distillation in an ASU. Combustion in pure O<sub>2</sub> is preferred from a thermodynamic point of view, but the air separation process would be extremely costly mainly due to the presence of the inert gas Argon (Al-Fattah et al., 2012). Studies show that an oxygen purity of 95 mol% is optimal based on the trade-off between the cost of producing higher-purity O<sub>2</sub> and the cost of separating the CO<sub>2</sub>, when using an ASU (Davison, 2007).

To produce the amount of O<sub>2</sub> consumed in a commercial scaled plant at a purity of 95% and at a low pressure of 1,7 bar, the electricity required by the ASU is approximately

200-250 kWh per tonne of O<sub>2</sub> (Mathieu, 2010). The main consumers of the electricity are the compressors operating at 5-6 bar. According to Mathieu (2010), this results in an efficiency penalty equal to 10-14%, which is similar to that of an amine based post-combustion capture process.

Combustion of MSW is performed at sub-atmospheric pressure to prevent backfire in the duct and waste pit and to route the flue gas to the stack. Some N<sub>2</sub> may thus leak into the boiler, which will reduce the purity of the CO<sub>2</sub>. Preliminary studies on oxyfuel coal-fired power plants with flue gas recycling have assumed that the amount of infiltrated air into the boiler is approximately 1% of the total amount of air combusted (Singh et al., 2003).

According to S. M. Al-Fattah et al., implementing current cryogenic technology into a coal-fired power plant will result in an efficiency penalty of 7-11%, a little less than what was predicted by Mathieu (2010). This will reduce the electricity generation of the plant by 15-25%, and is similar to what one can expect from a post-combustion capture implementation (Al-Fattah, 2012).

The energy analysis performed by Tang et al. on an electricity producing MSW incineration plant concluded with the following. Implementing oxyfuel combustion technology into an MSW power plant will increase the boiler efficiency by 6,9 %, but reduce the power supply efficiency by 12,6%. The reason for the increased efficiency is the reduced thermal loss of flue gas. Although increased efficiency results in a higher electricity production, the electricity required by the ASU is a lot more than what is gained, resulting in an overall reduction in power supply capacity.

For a coal-fired power plant, this results in an efficiency penalty of 7-9%. The corresponding penalty for a MEA process is said to be in the range of 10- 14 %. The study performed by Tang et al. gave a power supply efficiency penalty of 12,6% and 14,7% for oxyfuel and MEA implementation, respectively. The implementation has a larger effect on MSW plants because the power supply efficiency is lower than for a coal-fired power plant. Few studies take into consideration the possibility of utilising waste heat in the production of district heating, which is the main area of interest for EGE. The calculated efficiency penalties will therefore not be fully representable for Klemetsrud. At Klemetsrud, the waste heat from the stripper can be utilised in the production of district heating, as mentioned in Chapter 5.1.

### 5.2.1 Oxyfuel combustion evaluated based on the criteria provided by EGE

**Applicability to retrofit projects:** The boiler at Klemetsrud can withstand temperatures up to 1300 °C. If flue gas recycling is installed and a high recycling rate is used, this should be sufficient to maintain an acceptable temperature.

**Maturity:** The air separation technology is mature, but it has never been combined with power production. The technology is thus not said to be proven. Few studies have been conducted on MSW power plants, but coal-fired power plants have been investigated and the knowledge and experience gained is to a large extent applicable in MSW incineration plants.

**Efficiency penalty:** The penalty is mostly calculated based on electricity producing coal-fired power plants. The heat integration will be poorer than for a CHP plant, and the overall efficiency penalty will therefore be lower than suggested by the literature. The energy requirements of the capture plant are mainly covered by electricity and heat integration is thus not as efficient as if the energy was supplied as heat.

As of today, this technology is not viable for EGE mainly due to the level of maturity. Although all the components of the technology are proven, oxyfuel combustion in a MSW plant has never been tested and is thus not proven when combined. An alternative solution that has received increased attention within the field of MSW incineration combustion research is oxygen enriched combustion. This technology will enhance combustion and has the potential of utilising air separation technology that results in a lower energy penalty, as the O<sub>2</sub> purity requirements are lower. The implementation is further discussed in Chapter 6.3.





## 6 Efficiency increasing measures

To minimise the efficiency penalty due to the implementation of the capture plant, it is important to review and optimise both the capture plant and the retrofit plant. Based in a literature study, energy increasing measures for both plants will be discussed in this chapter. Amine based solvents are the only capture technologies applicable at Klemetsrud and are therefore the only ones to be evaluated.

### 6.1 Power plant

To improve the efficiency of the plant, it is important to review all aspects of the capture process, including improvements of the solvent, extensive integration between the capture and power plant, and optimisation. The benefit of each step is illustrated in Figure 6-1. By choosing a more efficient solvent, such as a hindered amine (e.g. AMP) instead of MEA, the graph is shifted to the right with a starting point below the original, indicating a reduction in efficiency penalty.

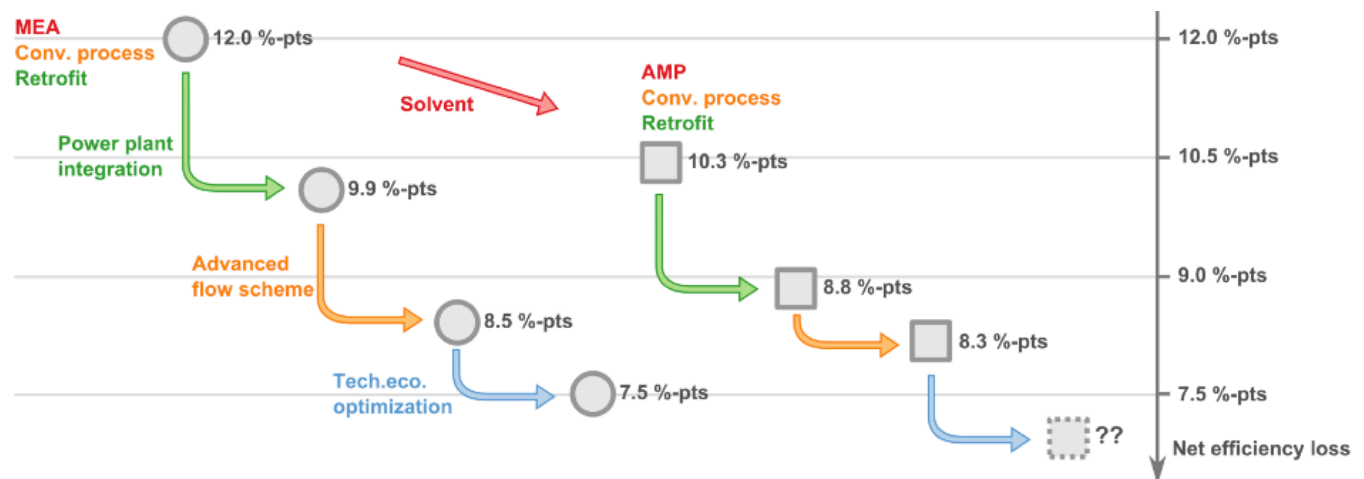


Figure 6-1: Means of reducing the energy penalty as a result of CCS implementation (Singh, 2013)

#### **Choosing the right solvent**

There is often a trade off between maturity and efficiency penalty. The most mature solvent, MEA has been on the market the longest, and is thus most mature. Newer solvents have proved to require less heat for regeneration, but as the product is more modern, the level of maturity is lower. This is a choice that EGE have to make when deciding on which technology to apply. As discussed in Chapter 5.2, a MSW incineration plant with MEA-technology will suffer an energy penalty of approximately 14,7 %, a little higher than indicated in Figure 6-1. The steam supplied in the reboiler accounts for approximately 50% of the energy penalty imposed, and it thus of great interest to find the solvent that has the lowest heat requirements and acceptable performance for the given application (Fluor, 2004).

## **Integration**

The capture plant can be thoroughly integrated into the incineration plant. This will further reduce the energy penalty caused by the capture plant. According to Singh (2013), there are some key areas of important that should receive extra attention when integrating a capture plant on a coal-fired power plant. The main issues listed below are to some extent relevant for Klemetsrud as well, and should be investigated in detail by EGE.

- How the power plant performance is affected by the steam requirements, electricity duty and operational flexibility of the capture plant
- The possibility of incorporating process integration to an existing CO<sub>2</sub> capture plant
- Site specific issues, such as availability of space to additional pipe work, water requirements, and ambient conditions

## **Steam extraction**

Studies show that to obtain optimal performance, it is optimal to extract saturated steam midway through the low-pressure section of the steam turbine. According to Romeo (2008), the pressure should be 1,8-2.8 bar, using the lowest possible steam quality available to fit the reboiler requirements. Most steam turbines do not have extraction at this point, especially not in a retrofit-case. Different approaches have been analysed for existing coal-fired power plants, and some of them are presented below.

A novel strategy to reduce efficiency losses is to extract steam from an IP/LP crossover pipe, and routing it through a new auxiliary turbine. A study confirming the theory was based on a 500 MW<sub>el</sub> coal-fired power plant retrofitted for post-combustion capture of CO<sub>2</sub> using MEA. According to the researcher C. Alie, integration was performed at this location because the steam extracted will have a sufficient quality, given that a maximum stripper temperature of 125 °C (Romeo, 2008). The physical configuration of the turbine may allow a large steam extraction at this location.

During the retrofit of the LSIP Boundary Dam, a new turbine was installed to optimise performance. According to IPCC (2005), the modifications can be limited by using small backpressure steam turbines using medium pressure steam to drive the feed water pumps and flue gas fans in the capture plant. A generic process flow diagram of a boiler turbine plant with CO<sub>2</sub> recovery is shown in Figure 6-2. The assumed extraction point is at the turbine labelled as PL-1 turbine.

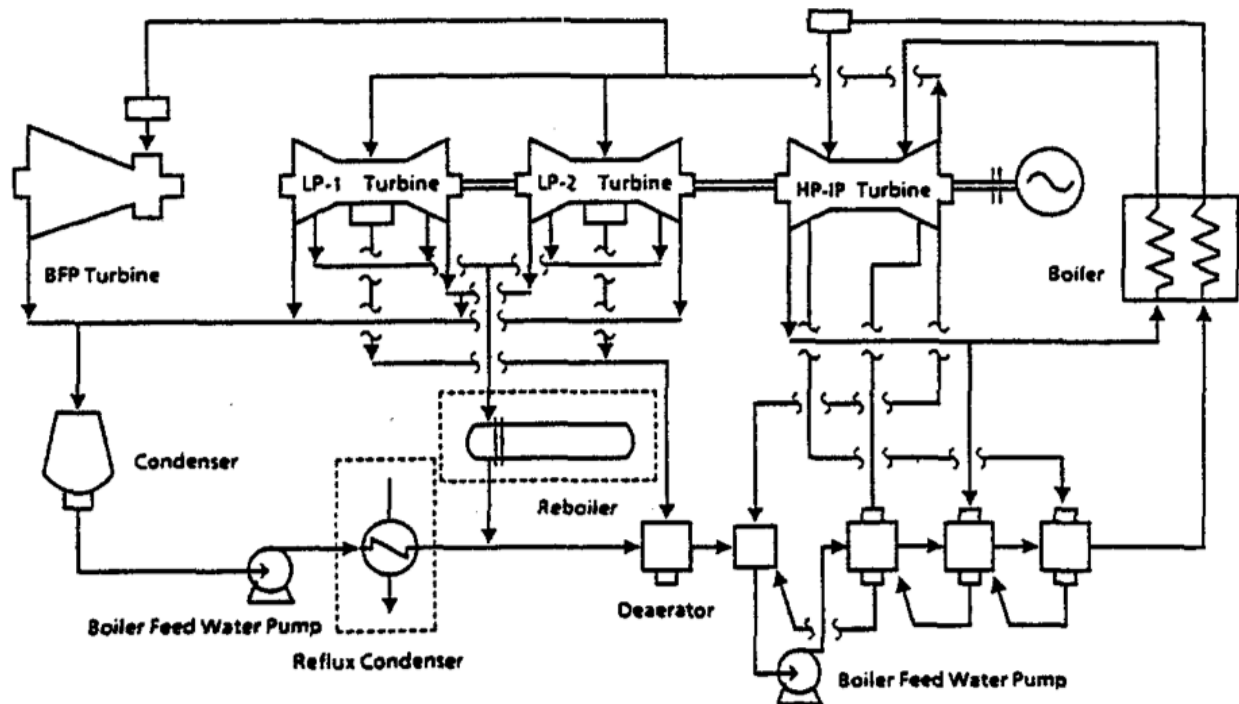


Figure 6-2: Boiler turbine power plant CO<sub>2</sub> recovery steam system (Mimura, 1997)

### Heat recovery

The flue gas must hold a minimum temperature to prevent water from condensing in the stack. Before entering the absorber, the flue gas is cooled to the water dew point of approximately 50°C. As the condensed water is removed, the lower flue gas temperature is allowed through the stack. The heat can be recovered and utilised, thus potentially increasing the efficiency of the plant.

### Techno-economic optimisation

Optimising the processes will result in a further reduction in efficiency penalties. From an energy point of view, it is important to optimise the heat transfer between the streams. Extensive heat integration between the capture and the process plant will be perused and changes to the existing heat flow patterns should be considered. An evaluation tool, such as Pinch Point Analysis should be utilised to obtain optimal heat flow patterns between the streams.

## 6.2 Capture plant

To obtain energy savings, improvements to the capture plant as suggested by MHI are listed below (Iijima et al, 2011).

- Lower the temperature in the absorber. This will increase the CO<sub>2</sub> loading capacity of the rich solvent
- Reducing the circulation rate of the solvent, which will reduce the absorbent heat loss and thus also the amount of heat required for regeneration
- Lowering the temperature at the top of the regenerator. This will reduce the heat loss to the CO<sub>2</sub> reflux cooler

These efficiency increasing designs are applied in three commercial KM-CDR capture plants, two in India and one in Abu Dhabi (Iijima et al., 2011). See Appendix D for plant details and process flow diagram of the improved process.

During the design of the first LSIP within the power sector, special energy saving technologies were applied in the Cansolv process, some of which are listed below (Shaw, 2009).

- The vapour leaving the lean amine can be recompressed (from 1-1,25 to 2-2,5 bar) and re injected into the reboiler. This technology, called Lean flash mechanical vapour compression line-up, can reduce the steam consumption by 33%. If condensate line up is applied as well, a further reduction of 5% is achievable, resulting in an over all steam reduction of 38%
- A thermal reclaimer unit can be installed to achieve a 99,75 % solvent recovery rate. To maximise the recovery, the unit is operated at 190-200 °C

When amines react with CO<sub>2</sub>, heat is generated as a result of the reaction being exothermic. The temperature in the absorber will thus rise towards the bottom of the column where the solvent is saturated. The increase in temperature will cause the equilibrium to shift and less CO<sub>2</sub> to be absorbed as the loading capacity is reduced, as indicated in Figure 4-3 (Stoffregen et al., 2014). Intercooling may therefore be applied to prevent the resulting reduction in performance. An intercooler can be installed in-between the stages in the absorber to maintain a low and constant temperature for optimal performance. The heat removed can be used somewhere else in the plant. An example of this is Linde's patented gravity-driven interstage cooler. As it is gravity-driven, it does not require a circulation pump, and most of the energy can thus be recovered.

### 6.3 Future improvements

#### **The SYNCOM Process**

As discussed previously, oxyfuel combustion has the benefit of producing a flue gas with a higher CO<sub>2</sub> partial pressure. It has been proved that by elevating the O<sub>2</sub> concentration in the combustion zone, combustion is enhanced. An example of such a process is the SYNCOM process, where oxygen enriched air is supplied in combustion zone 2 and 3. Some of the positive effects of oxyfuel combustion are obtained, while keeping the O<sub>2</sub> requirements at a minimum. The implementation is not as extensive as oxyfuel combustion and it has been utilised in several test plants. See Appendix H for plant and process details. Through test plants, oxygen-enrichment of the primary air has proved to have the following effects (Gohlke, Busch, 2001):

- Reduction of flue gas flow, resulting in a higher partial pressure of CO<sub>2</sub>
- A significant reductions of organic pollution in the flue gas at the boiler
- Increased sintering of bottom ash and decreased amounts of fly ash
- Increase of the fuel bed temperature (1200°C has been documented)
- Increased boiler efficiency

A waste incineration plant in Coburg in Germany was equipped with the SYMCOM process. The plant has two incineration lines, each with a capacity of 7 t/h, which corresponds to 70 % of KA1/KA2, and 20% of the total capacity of Klemetsrud. The process was implemented into one of the waste incineration lines, while the other line was operating as normal, facilitating a good basis for comparison. Primary air oxygen concentrations of 29% and 31% in combustion zone 2 and 3, respectively, gave a 39% reduction in volumetric flow rate of the flue gas (Gohlke, Busch, 2001). For Klemetsrud, this would result in a flue gas flow rate of 121 878 Nm<sup>3</sup>/h and a flue gas CO<sub>2</sub> concentration of 18,9 %. Assuming that a linear scale-up is presentable for the oxygen consumption, the excess oxygen requirements of Klemetsrud would be

$$\Delta \dot{n} = 1300 \text{ Nm}^3/\text{h} * \left(\frac{100}{20}\right) = 6500 \text{ Nm}^3/\text{h}$$

, which corresponds to a mass flow rate of 9285 kg/h or 222,8 t/d of pure O<sub>2</sub>. It is emphasised that this is the amount used to enrich ambient air, and the 21% we can exempt from ambient air must also be taken into account when calculating the total amount of O<sub>2</sub> injected into the boiler.

According to Tang et al. (2013), if Klemetsrud were to apply oxyfuel combustion, an ASU power demand of 0,38- 0,40 kWh per Nm<sup>3</sup> of O<sub>2</sub> produced is a reasonable assumption. The O<sub>2</sub> production rate will be lower than in the case of oxyfuel combustion, but the power consumption of the ASU is assumed to be similar. Taking the losses into account, a power consumption of 0,42 kWh/Nm<sup>3</sup> may be assumed (Tang et al., 2013). For Klemetsrud, this would result in a power consumption of

$$\begin{aligned} \frac{W_{ASU}}{yr} &= \Delta \dot{n} * \frac{\dot{W}}{\Delta \dot{n}} * t \\ &= 6500 \text{ Nm}^3/\text{h} * 0,42 \text{ kWh/Nm}^3 * 8150 \text{ h/yr} \\ &= 22,25 \text{ GWh/yr} \end{aligned}$$

, which corresponds to 14% of the electricity production. The resulting power supply efficiency reduction will depend on the degree of integration and should be calculated by EGE to provide a basis for evaluation.

The fuel bed temperature was increased from 1065°C to 1200 °C, which is below 1300°C and is thus acceptable for Klemetsrud. By combining oxygen enriched combustion with CCS technology, less energy intensive capture technologies can be applied. The process equipment can be smaller as the gas stream to be processed is significantly reduced. Technologies that were previously regarded as not feasible may now be applicable. According to Pinto et al. (2014), physical absorption may be such a technology.

As of today, to control a too high combustion temperature, water is sprayed on the waste. This will reduce the temperature, but it will also reduce the efficiency of the system by increasing flue gas losses. By installing a flue gas recycling system, the temperature can be controlled without decreasing the efficiency. If the SYNCOM process were to be implemented into the plant, flue gas recycling would be implemented as a part of the process, and the resulting increase in efficiency should be taken into consideration during the evaluation process.

### **SYNCOM-Plus**

SYNCOM-Plus is a process to further improve the bottom ash quality, and is an add-on to the SYNCOM process. SYNCOM-Plus is installed downstream of the boiler and will increase boiler efficiency by utilising waste heat and thus reducing losses through to stack and reduce the amount of boiler ash disposed at landfill (Martin et al., 2015). See Appendix I for details.

## 7 Conclusion

It has been stated that MEA technology has to be improved by 50% to compete with oxyfuel combustion (Singh et al., 2003). Though having a bad reputation, most of the literature and scientific studies on post-combustion capture has been performed on coal-fired power plants, many producing only electricity. Heat recovery is not as beneficial for these power plants as it would be for a CHP plant, as CHP plants can utilise recovered low grade heat from the capture plant. A study performed by Kärki et al. (2013) showed that the most feasible CCS solution is achieved if the heat from the capture plant can be utilised in the production of district heating.

If the capture plant were to be implemented tomorrow, post-combustion by chemical absorption using a solution of inhibited 30 wt% MEA solution as the solvent, would have been the preferred technology. This is based on the criteria provided by EGE where maturity is the most conclusive argument. Despite being associated with high efficiency penalty, implementing MEA into a CHP plant with extensive heat integration, an acceptable production efficiency is achievable. If upscaling or change of solvent is desirable, choosing MEA will not exclude this at a later stage. MEA degradation is a well-known drawback but it is somewhat justified by being the cheapest amine (Rochelle, 2009). At Klemetsrud, the SO<sub>2</sub> concentration in the flue gas is at an acceptably low level, and additional scrubber equipment is thus not needed.

The Cansolv process and the KM-CDR process are also a very relevant processes for Klemetsrud. Both processes utilises hindered amines to reduce the heat requirements of the process. They are both commercialised, though the Cansolv process is the only one that has been applied in a power plant. The Cansolv process utilises an integrated SO<sub>2</sub>-CO<sub>2</sub> removal unit, which is not feasible for Klemetsrud as the plant is already equipped with an SO<sub>2</sub> scrubber. It is possible to only apply the CO<sub>2</sub> removal unit, but the process would not be as proven, and the low penalties as a result of the extensive heat integration between the SO<sub>2</sub>-CO<sub>2</sub> removal processes would not be obtainable. If the KM-CDR process is to be applied, an upgrade of the SO<sub>2</sub> scrubber is necessary as it is advised that the concentration should not exceed 1 vol%.

In a longer perspective, oxygen enriched combustion and oxyfuel combustion should be further investigated. Oxygen enrichment of the primary air will reduce the volumetric flow rate of the flue gas, thus increasing the CO<sub>2</sub> partial pressure. When combining this with post-combustion capture technology, smaller equipment size can be used. As the partial pressure of CO<sub>2</sub> if increased, less energy intensive separation technologies can be

applied, which will reduce the energy penalty imposed by the capture plant. The required purity of O<sub>2</sub> is fairly low, and more suitable technologies for heat integration, such as polymeric membranes, may be applied. Flue gas recycling will be installed to control the temperature and to maintain the desired volumetric flow through the boiler, which eliminates the need for water spraying the waste when the temperature in the furnace is too high. This will further increase the efficiency of the process.

Oxyfuel combustion has been estimated to be the most efficient way of combusting MSW. The increased combustion efficiency does not currently compensate for the immaturity of the technology. The efficiency penalties are still too high, and several studies have concluded that the plant efficiency would be the same as when utilising MEA. Breakthroughs in air separation technology will have a huge impact on the electricity demand of capture plant, and the predicted development of the technology is therefore important to take into account when considering oxyfuel combustion (Singh et al., 2003).



## 8 Transport

CO<sub>2</sub> can be transported by pipelines, marine tankers, rail and road tankers. Prior to transport, it is necessary to compress and/or cool the CO<sub>2</sub> to reduce the volume of the gas to make the transport more efficient. At atmospheric pressure, CO<sub>2</sub> can only exist in either gas or solid phase, as shown in Figure 8-1. Liquefaction is achieved by cooling the CO<sub>2</sub> to a temperature between its triple point (-56,4 °C) and its critical point (32 °C), and compressing to the corresponding liquefaction pressure. In Figure 8-1, the CO<sub>2</sub> phase envelope is shown, and the optimal operation of CO<sub>2</sub> pipelines and ships are indicated as recommended by DNV (2012).

At distances up to 1 000 km, pipelines are regarded as the most viable option of transportation when large volumes of CO<sub>2</sub> are to be transported over a long period of time (IPCC, 2005). Transporting substances by pipelines are widely deployed, and the technology used is very mature. Several commercial CCS projects, such as Sleipner, Snøhvit, In Salah and Weyburn, use onshore and offshore pipelines to transport CO<sub>2</sub>. The transportation of CO<sub>2</sub> is not too different from transportation of petroleum gases, and established oil and gas pipeline networks can therefore be reused (Leung et al., 2014).

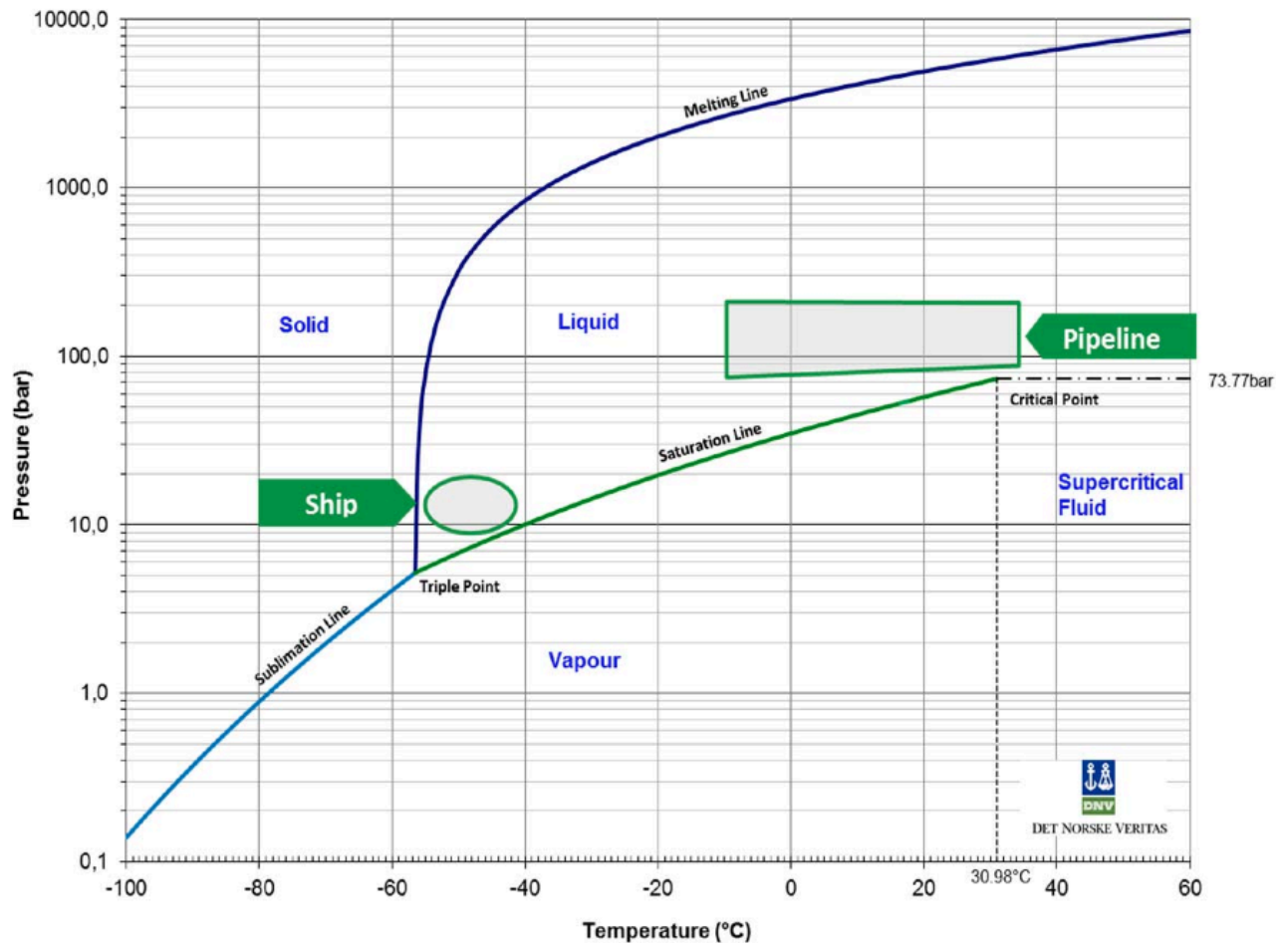


Figure 8-1: CO<sub>2</sub> phase envelope, indicating the optimal pressures and temperatures for transport (DNV, 2012)

Offshore shipping by CO<sub>2</sub> takers is assumed to be economically competitive as the investment costs of offshore pipelines are high (Leung, 2014). It will also add flexibility to the project. The existing CO<sub>2</sub> carriers are semi-refrigerated systems, where the CO<sub>2</sub> is cooled and pressurized to ensure transport in the liquid phase (IPPC, 2005).

In Norway, rail and road tankers are the most common ways to transport CO<sub>2</sub>, as there is no pipeline network established. The Norwegian CO<sub>2</sub> merchant market is therefore highly regional (Johnsen, 2008). As when transported by ship, the CO<sub>2</sub> is compressed and cooled to enhance liquefaction for a more efficient transport.

## 9 Carbon dioxide storage

### 9.1 Permanent storage

Permanent storage is when CO<sub>2</sub> is verifiably retained under ground or used as feed stock in a material that will not degrade over time. The CO<sub>2</sub> is thus ideally kept from entering the atmosphere for all time. At present, the most developed and promising method of CO<sub>2</sub> storage is by injection into geological formations (Bouzalakos, Maroto-Valer, 2010; IPCC, 2005). The three main types of suggested underground storage sites are as follows:

- Deep saline aquifers
- Depleted oil and gas reservoirs
- Deep unmineable coal seams

In Norway, geological storage is only available offshore, as the crystalline mainland does not possess the necessary properties to facilitate safe storage (Höllner, Viebahn, 2011). Deep saline aquifers and depleted oil and gas reservoirs offer the largest storage potential in Norway (Halland, Riis, 2014). Experience gained from existing commercial operations such as Sleipner, Snøhvit and In Salah has proven that geological storage in saline aquifers is technically feasible (Eiken et al., 2011).

At the Sleipner Vest field, CO<sub>2</sub> has been injected safely at a rate of 1 Mtpa of CO<sub>2</sub> into a saline aquifer called the Utsira Formation for more than 17 years (Lindeberg et al., 2009; Michael et al., 2010) The Utsira Formation is by many regarded as the most potential CO<sub>2</sub> sink in Europe, with its suitable permeability and porosity. Depending on whether conservative or optimistic predications are made, the anticipated storage capacity is in the range of 1-600 Gt of CO<sub>2</sub> (Höllner, Viebahn, 2011). A study based on both static volume estimates and reservoir simulation of injection shows a cost effective storage potential of 20-60 Gt of CO<sub>2</sub> (Lindeberg et al., 2009).

To maintain an acceptable low pressure in the saline aquifer during injection, saline water is correspondingly produced. In countries that suffer from water shortage, the saline water is processed, as it is regarded as a desirable product. The recovered CO<sub>2</sub> is then utilised to produce a product and the CCS technology will fall into the definition of CCUS, which is discussed in Chapter 9.2. In the process, now referred to as enhanced water recovery (EWR), the water can be desalinated and used for drinking, agriculture or industrial purposes (Li et al., 2014). This is not a viable option in Norway as there is

no water shortage. EWR is therefore not regarded as a CCUS technology in a Norwegian context.

**9.2 Why utilisation?**

IEA (2009) predict that CCS has to account for 20% of the reduction in GHG emissions within 2050 to prevent a 2 °C rise of the atmosphere. In CCS, the carbon is considered a waste, which it is bothersome to get rid of. In many industries CO<sub>2</sub> is an asset, and the concept associated with converting CO<sub>2</sub> into commercially valuable products or as a mean of producing such a product is referred to as carbon capture, storage and utilisation (CCSU) has emerged. Through utilisation we will get a shift in focus from the disposal of an inconvenient by-product towards production of a profitable product (IEA, 2014). There are many ways to utilise CO<sub>2</sub>, and the main areas of application are presented in Figure 9-1.

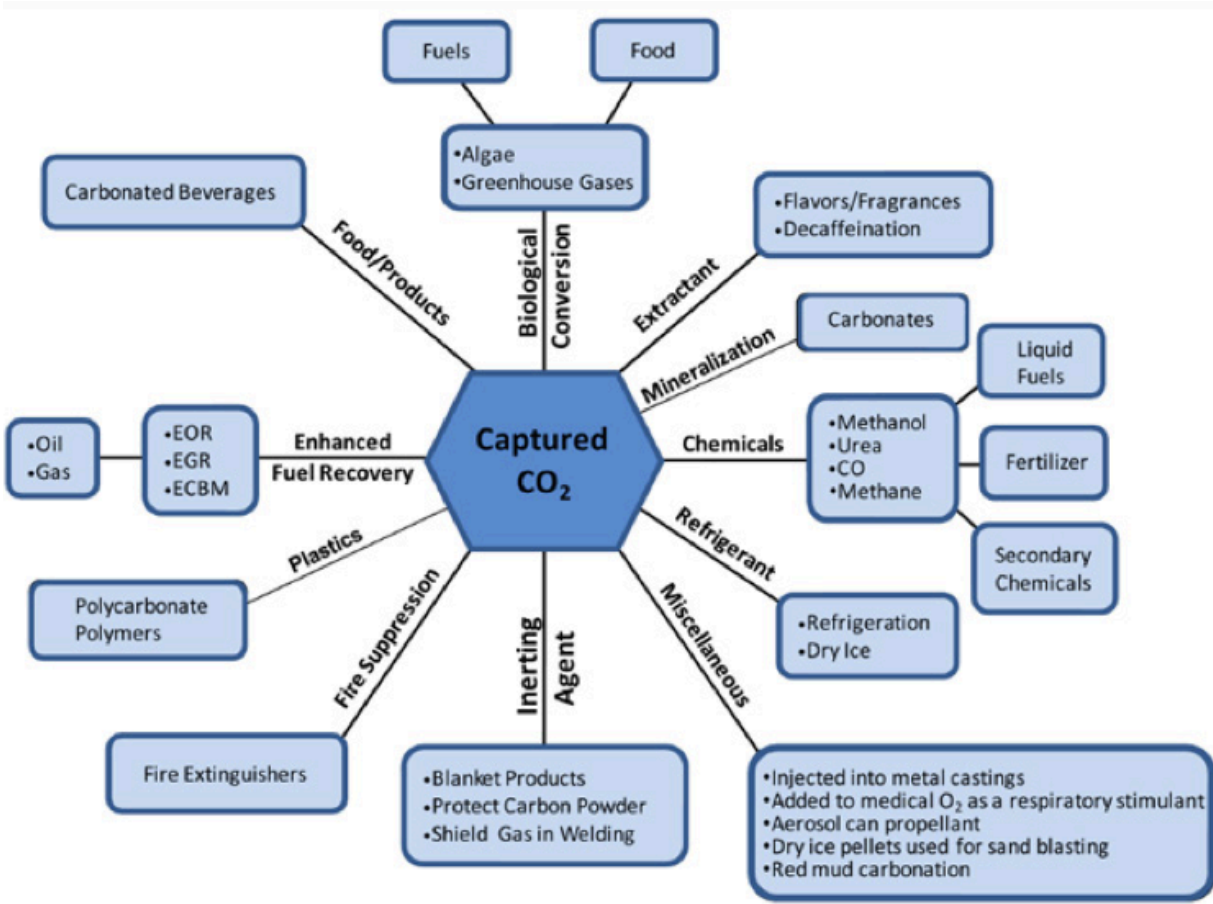


Figure 9-1: CO<sub>2</sub> utilisation overview (SCOT project, 2015)

CCSU will not directly contribute to reduce carbon emissions as long as the storage facility is not permanent. Figure 9-2 illustrates how utilising the carbon may lead to

subsequent emissions. The boxed texts in the figure denote a process, while the unboxed texts denote stocks of carbon.

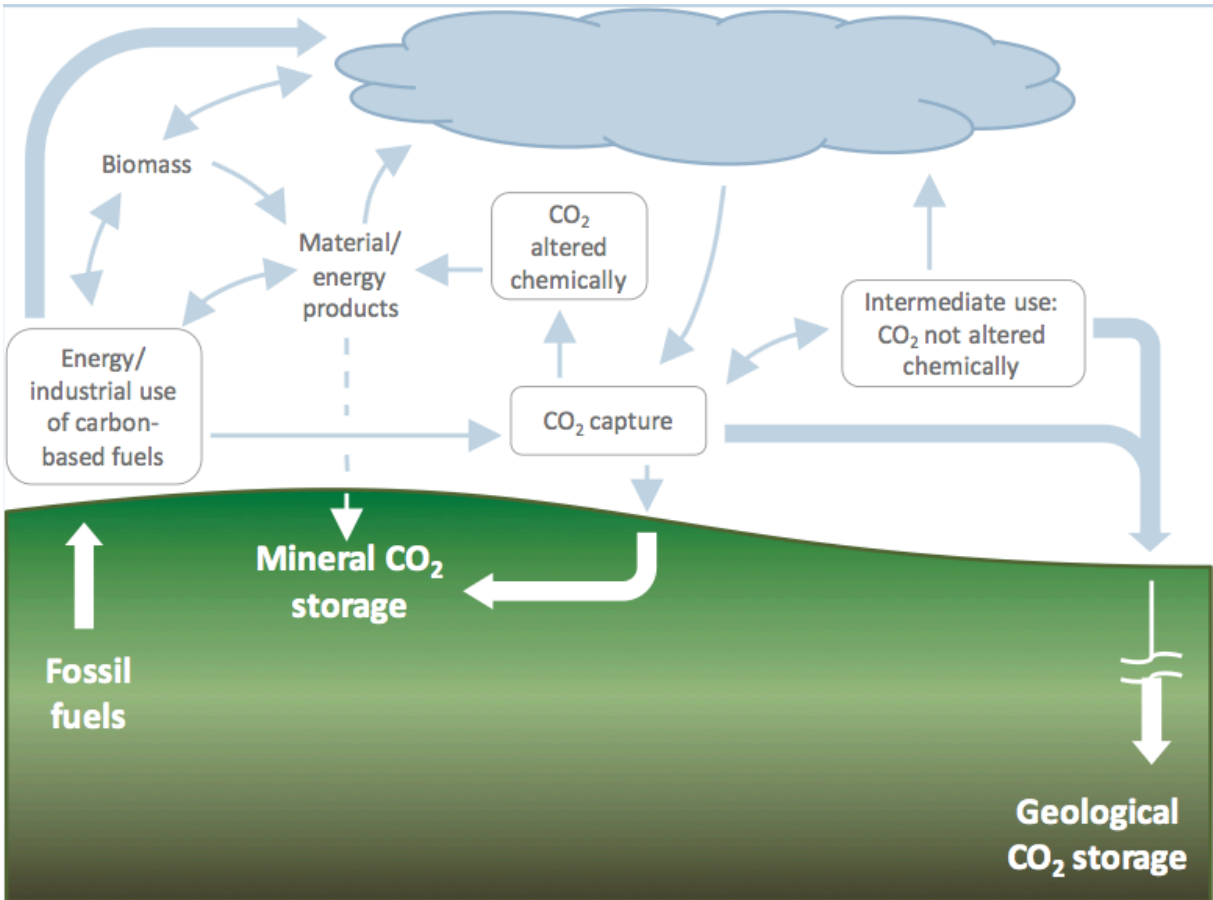


Figure 9-2: How CCSU may lead to subsequent emissions (IEA, 2014)

It is therefore a broad consensus that CCSU must involve permanent storage to qualify as a climate mitigation technology (IEA, 2014; ZEP, 2013). However, it has been argued that utilisation may lead to an indirect reduction in GHG emissions by making CCS projects profitable, and thus contribute by obtaining valuable data and experience. This way, utilising the recovered CO<sub>2</sub> provides a long-term benefit by providing secure revenue for other CCS projects by reducing future costs of CCS. Hence, CCSU will have an indirect positive environmental effect by accelerating the deployment and technological development of CCS (IEA, 2014). Another argument is that CCSU can reduce emissions by producing a product that can replace products of fossil origin. An example of such a product is biofuels produced through biological conversion as shown in Figure 9-1.

Due to the large variety in climate mitigation potential of the storage and utilisation options, IEA have made a classification system where areas of utilisation are classified as

Type A or Type B, depending in their emission reduction benefit (IEA, 2014). The definitions of the two types are presented in Table 9-1.

**Table 9-1: Definition of the two types of utilisation classifications, Type A and Type B (IEA, 2014)**

Type	Summary	Examples
A. Utilisation that leads to permanent storage of the CO <sub>2</sub>	<p>Through the production and use of commercial goods with CO<sub>2</sub> as an industrial input, the carbon is effectively prevented from reaching the atmosphere as a greenhouse gas.</p> <p>The expected level of CO<sub>2</sub> emissions reduction could be comparable to or greater than that from geological storage of CO<sub>2</sub> if the processes or products of CO<sub>2</sub> utilisation displace alternatives that have larger carbon footprints, assuming equal upstream emissions from both systems. For example, oil from CO<sub>2</sub>-EOR being used in place of transport fuels with a lower emissions profile.</p>	<p>Enhanced extraction of geological resources, including oil, gas and potentially water, whilst ensuring the effective retention of CO<sub>2</sub> in the subsurface.</p> <p>Manufacture of construction materials or long-lived polymers for which normal use and the regulatory environment ensure very low risks of the CO<sub>2</sub> being emitted.</p>
B. Utilisation that leads to subsequent emission of CO <sub>2</sub>	<p>Through the production and normal use of commercial goods with CO<sub>2</sub> as an industrial input, the carbon is not prevented from reaching the atmosphere as a greenhouse gas.</p> <p>CO<sub>2</sub> reductions of varying levels could accrue depending on the fossil fuel feedstock that CO<sub>2</sub> use displaces and/or the fossil fuel that the use of the commercial good substitutes.</p>	<p>Manufacture of fuels, plastics, polymers, agricultural inputs, foods and fine chemicals.</p> <p>Enhanced extraction of geological resources that do not ensure the effective retention of CO<sub>2</sub> in the subsurface.</p>

**9.2.1 Type A**

From a climate point of view, it is most attractive to focus on Type A, where the utilisation processes leads to permanent storage of the recovered CO<sub>2</sub>. In combination with the most relevant storage sites, saline aquifers, depleted petroleum wells and unmineable coal seams, it is possible to use the injected CO<sub>2</sub> to enhance mineral extraction through the scenarios listed below (IEA, 2014):

- Enhanced oil recovery (EOR)
- Enhanced gas recovery (EGR)
- Enhanced coal bed methane recovery (ECBM)
- CO<sub>2</sub> as a fraccing fluid

**Enhanced oil recovery (EOR)**

In EOR, CO<sub>2</sub> is injected into an oil reservoir to increase the driving forces of the reservoir to enhance recovery. EOR is the single largest consumer of the global CO<sub>2</sub> consumption, exceeding 70 Mtpa. It is by far the most advanced CCUS technology, and has been practised for decades in a large scale (IEA, 2014). It is estimated that 80% of all oil reservoirs might be suitable for CO<sub>2</sub> injection (Bouzalakos, Maroto-Valer, 2010). A typical EOR process and its related processes are shown in Figure 9-3.

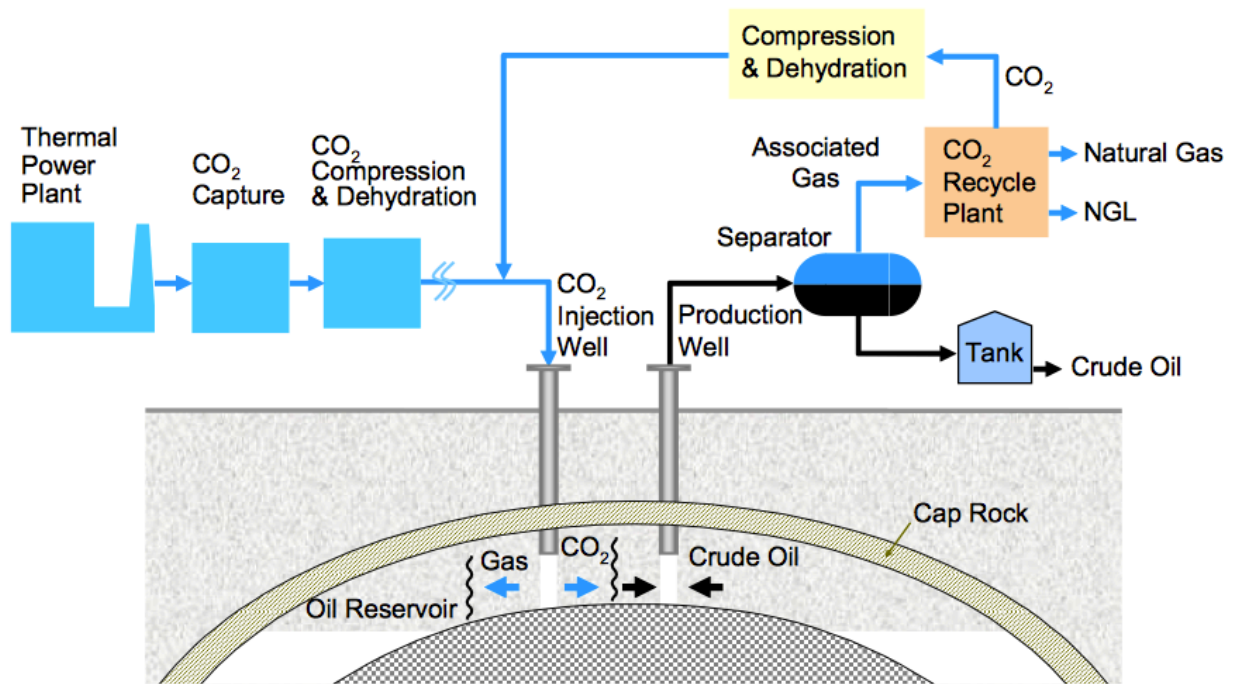


Figure 9-3: Enhanced Oil Recovery process overview (MHI, 2010)

### Enhanced gas recovery (EGR)

EGR is based on the same principle as EOR, but gas is produced instead of oil. Gas reservoirs have a larger storage potential than oil reservoirs at depletion, due to their large size and recovery factor, ranging from 80 to 90%.

### Enhanced coal bed methane recovery (ECBM)

CO<sub>2</sub> is injected into unmineable coal beds, which will increase the pressure in the coal bed. The methane adsorbed by the coal will then be desorbed and the bed will thus start to produce methane. Deep unmineable coal seams have been estimated to have the smallest storage potential out of the underground storage sites, and ECBM is still an immature technology (Ogden, Johnson, 2010).

### CO<sub>2</sub> as a fracturing fluid

The main focus of this operation is to extract hydrocarbons in tight reservoirs that requires fracturing to produce. It is not common as there are uncertainties related to possible water contamination and leakages.

### 9.2.2 Type B

Although Type B utilisation does not qualify as a climate mitigation technology, it may be indirectly beneficial by means of:

- Adding significant economic value to CCS projects
- Accelerating the deployment of CCS technology by providing knowledge, experience and social acceptance
- Substituting the captured CO<sub>2</sub> for fossil derived product

Utilisation that leads to subsequent emissions of CO<sub>2</sub>, as presented in Figure 9-1:

- Conversion to a fuel, such as methanol or bio-oil
- Chemical feedstock for synthesise chemicals
- Raw material in the production of building materials though mineralisation
- Plastics
- Refrigerant, such as dry ice and refrigeration fluid
- Enhance productivity in greenhouses

#### **Renewable methanol**

Methanol is produced by mixing the recovered CO<sub>2</sub> with hydrogen. Methanol may directly replace fossil fuels, and will thus directly contribute to a reduction in CO<sub>2</sub> emissions (SCOT project, 2013)

#### **Biofixation**

Microorganisms use CO<sub>2</sub> for cell growth and can CO<sub>2</sub> therefore be used in microalgal farming. CO<sub>2</sub> can then be converted into biofuel (Bouzalakos, Maroto-Valer, 2010). Algae are recognized by EU as the most promising method for bio-fuels production and industrial capture of CO<sub>2</sub> (CORDIS, 2013). The process is not economically viable yet, but there is a lot of research activity in this field.

#### **Chemical feedstock**

Urea is a product of CO<sub>2</sub> and synthetic ammonia, and is used as a fertiliser. Other chemical products can be produced through catalytic conversion such as syngas (H<sub>2</sub>+CO) via drying reforming of CH<sub>4</sub> with CO<sub>2</sub> and pharmaceutical chemicals (Wang et al., 2011).

#### **Mineralisation**

Mineralisation is an exothermic reaction where magnesium or calcium is converted to carbonates (SCOT, 2013). The product is stable and can be used as a building material.



## **Polymers**

CO<sub>2</sub> can be used as a feedstock to produce plastics, and may then replace other energy and emission intensive feedstocks (BMBF, 2014). This is not done at a commercial scale, but pilot plants do exist.

## **Dry ice**

The principal use for solid CO<sub>2</sub> is refrigeration of food, such as ice cream and meat (Johnsen, 2008). At atmospheric pressure, CO<sub>2</sub> goes directly from solid to gas state at a temperature of -79°C, and is thus suitable for rapid freezing of foods (IPPC, 2005).

## **Enhanced productivity in greenhouses**

Pure CO<sub>2</sub> is injected into greenhouses to enhance the productivity and growth of plants. This is very common in Europe due to the cold climate (MHI, 2010).

## **Other areas of application**

- Replace sandblasting when removing paint. (Reduces costs as there is no need to no clean up or material to dispose)
- To enhance brittleness in materials. (E.g. blended with molded rubber to beak of flash)
- Several areas of application in hospitals, laboratories and airplanes
- Bottled gas for draught beer

## **9.3 Limiting characteristics**

There are no current specifications for required CO<sub>2</sub> purity for neither transport nor geological storage, however several guidelines and recommended practises do exist. Pipeline operators have made their own pipeline specifications to prevent corrosion and to enhance safe transport. The recommendations for transportation in steel pipes and geological storage, made by the National Energy Technology Laboratory for the U.S. government, are presented in Table 9-4. Future regulations and purity requirements are assumed to be more strict for pipeline transportation than for geological storage, especially for the components that may cause corrosion, such as SO<sub>x</sub>, NO<sub>x</sub> and H<sub>2</sub>O (Porter et al., 2015). Current recommendations can therefore be assumed to be within the acceptable values for CO<sub>2</sub> used in geological storage.

There is an international standard, the ISO 13623 'Pipeline Transportation System', covering the design, materials, construction, operation, maintenance and abandonment of pipelines that are used in transportation of petroleum and natural gas streams. This is

the overruling standard, but many countries, including Norway, operate under their own preliminary pipeline standards. According to DNV (2012), the requirements of CO<sub>2</sub> pipelines and the operating parameters are assumed to be incorporated into this standard.

### Type A

There are no widely used standards for the purity of CO<sub>2</sub> that is to be stored in geological formations. There are recommended guidelines but in the end, the purity of the CO<sub>2</sub> is project specific. Table 9-2 shows an overview of CO<sub>2</sub> specifications from Kinder Morgan and the pipeline specifications for Weyburn and Sleipner. These specifications are based on CO<sub>2</sub> retrieved for pre-combustion capture and SO<sub>x</sub> and NO<sub>x</sub> specifications are thus not emphasised, as they would have been for post-combustion capture (Visser et al., 2008).

Table 9-2: CO<sub>2</sub> stream specifications for Kinder Morgan, Weyburn and Sleipner (Visser et al., 2008)

	Kinder Morgan	Weyburn	Sleipner
<b>Type of Project</b>	EOR	EOR	
CO <sub>2</sub> [vol%]	95%	96%	93-96%
CH <sub>4</sub> [ppm]		0,7	
C <sub>2</sub> H <sub>6</sub> [ppm]			
C <sub>3+</sub> [ppm]			
Total hydrocarbons [ppm]	< 5%	2,3%	0,5-0,2%
H <sub>2</sub> [ppm]			
CO [ppm]		1000	
N <sub>2</sub> [ppm]	< 4%	<300	
Other inerts [ppm]			
Total inerts [ppm]			Non-condesable gases (N <sub>2</sub> , H <sub>2</sub> , Ar): 3-5%*
O <sub>2</sub> [ppm]	10	<50	
H <sub>2</sub> S [ppm]	10-200	9000	Up to 150
SO <sub>x</sub> [ppm]			
Total sulphur [ppm]			
H <sub>2</sub> O [ppm]	30 lbs/MMcf**	<20	Saturated
Hg [ppm]			
Other [ppm]			
Glycol [ppm]	0,3 gal/MMcf		
Methanol [ppm]			
Selexol [ppm]			
Anime [ppm]			

\*The non-condensable gas content is not expected to increase above 3% during normal operation, even though 5% non-condensable is stated as design basis

\*\*1 lbs/MMcf=21,8ppm

1 ppm =0,0001 %=10<sup>-6</sup>

## Geological storage, guidelines supplied by DYNAMIS

The maximum concentrations provided in Table 9-3 are guidelines provided by the DYNAMIS European project for CO<sub>2</sub> that is to be stored underground. The method of transport is assumed to be pipelines, and all limitations may thus not apply if other means of transportation are to be used.

Table 9-3: CO<sub>2</sub> stream purity guidelines provided by DYNAMIS (Visser et al., 2008)

	Concentration	Limitation
H <sub>2</sub> O [ppm]	500	Design and operational considerations
H <sub>2</sub> S [ppm]	200	Health and safety considerations
CO [ppm]	2000	Health and safety considerations
CH <sub>4</sub> [vol%]	Aquifer < 4, EOR < 2	As proposed in ENCAP project
N <sub>2</sub> [vol%]	< 4 (all non-condensable gasses)	As proposed in ENCAP project
Ar [vol%]	< 4 (all non-condensable gasses)	As proposed in ENCAP project
H <sub>2</sub> [vol%]	< 4 (all non-condensable gasses)	Further reduction in H <sub>2</sub> recommended, because of its energy content
CO <sub>2</sub> [vol%]	> 95,5	Balance with other compounds in CO <sub>2</sub>

A report prepared for the United States Department of Energy lists the recommended maximum amounts of impurities in a CO<sub>2</sub> stream that is destined for EOR and saline reservoir for CCUS. The recommendations presented in Table 9-2, 9-3 and 9-4 shows moderate variations and confirms that CO<sub>2</sub> stream specifications are project specific, as previously stated. It is noted that all values are within the literature range presented in Table 9-4.

If post-combustion capture technology is utilised, it is important to take into consideration what levels of solvent that will cause damage to downstream CCUS equipment, but that is beyond the scope of this work.

Table 9-4: CO<sub>2</sub> stream composition and recommended limits provided by the U.S. Department of Energy (Herron, Myles, 2013)

Component	Unit (Max unless Otherwise noted)	Carbon Steel Pipeline		Enhanced Oil Recovery		Saline Reservoir Sequestration		Saline Reservoir CO <sub>2</sub> & H <sub>2</sub> S Co-sequestration	
		Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature
CO <sub>2</sub>	vol% (Min)	95	90-99.8	95	90-99.8	95	90-99.8	95	20 – 99.8
H <sub>2</sub> O	ppm <sub>v</sub>	500	20 - 650	500	20 - 650	500	20 - 650	500	20 - 650
N <sub>2</sub>	vol%	4	0.01 - 7	1	0.01 - 2	4	0.01 - 7	4	0.01 – 7
O <sub>2</sub>	vol%	0.001	0.001 – 4	0.001	0.001– 1.3	0.001	0.001– 4	0.001	0.001 – 4
Ar	vol%	4	0.01 – 4	1	0.01 – 1	4	0.01 – 4	4	0.01 – 4
CH <sub>4</sub>	vol%	4	0.01 – 4	1	0.01 – 2	4	0.01 – 4	4	0.01 – 4
H <sub>2</sub>	vol%	4	0.01 - 4	1	0.01 – 1	4	0.01 – 4	4	0.02 – 4
CO	ppm <sub>v</sub>	35	10 - 5000	35	10 - 5000	35	10 - 5000	35	10 - 5000
H <sub>2</sub> S	vol%	0.01	0.002 – 1.3	0.01	0.002 – 1.3	0.01	0.002 – 1.3	75	10 - 77
SO <sub>2</sub>	ppm <sub>v</sub>	100	10 - 50000	100	10 - 50000	100	10 - 50000	50	10 - 100
NO <sub>x</sub>	ppm <sub>v</sub>	100	20 - 2500	100	20 - 2500	100	20 - 2500	100	20 - 2500

Component	Unit (Max unless Otherwise noted)	Carbon Steel Pipeline		Enhanced Oil Recovery		Saline Reservoir Sequestration		Saline Reservoir CO <sub>2</sub> & H <sub>2</sub> S Co-sequestration	
		Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature
NH <sub>3</sub>	ppm <sub>v</sub>	50	0 - 50	50	0 - 50	50	0 - 50	50	0 - 50
COS	ppm <sub>v</sub>	trace	trace	5	0 - 5	trace	trace	trace	trace
C <sub>2</sub> H <sub>6</sub>	vol%	1	0 - 1	1	0 - 1	1	0 - 1	1	0 - 1
C <sub>3</sub> +	vol%	<1	0 - 1	<1	0 - 1	<1	0 - 1	<1	0 - 1
Part.	ppm <sub>v</sub>	1	0 - 1	1	0 - 1	1	0 - 1	1	0 - 1
HCl	ppm <sub>v</sub>	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*
HF	ppm <sub>v</sub>	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*
HCN	ppm <sub>v</sub>	trace	trace	trace	trace	trace	trace	trace	trace
Hg	ppm <sub>v</sub>	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*
Glycol	ppb <sub>v</sub>	46	0 - 174	46	0 - 174	46	0 - 174	46	0 - 174
MEA	ppm <sub>v</sub>	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*
Selexol	ppm <sub>v</sub>	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*	N.I.*

\* Not enough information is available to determine the maximum allowable amount

## *Type B*

The merchant CO<sub>2</sub> market is limited in Norway, and the quality of the CO<sub>2</sub> is often project specific. According to EIGA, liquid CO<sub>2</sub> is usually transported to the production site by rail or road tankers, or directly from the CO<sub>2</sub> production site and transport or compression may therefore lead to certain restrictions. For CO<sub>2</sub> to be used in the food sector, there are strict rules, which are listed below. There are special cases where the specifications are based on the area of application of the product, rather than the product itself. For example, there are no special requirements for dry ice to be used in non-food applications (Lorenzi et al., 2008), but when the dry ice is to be used in direct contact with food it is categorized as a food processing aid, hence the criteria for supplying the food and beverage industry applies.

### **Food sector**

The food sector covers the following categories (Girardon et al., 2011):

- Food additives
- Food processing aids
- Food ingredients

Strict quality standards are imposed on suppliers of CO<sub>2</sub> to the food and beverage industry. The product requirements listed in Table 9-5 have to be met, and the plant has to qualify as a supply plant. The qualification standards that have to be met are described in the European food and beverage legislations, such as Regulation 852/2004 on the Hygiene of Foodstuffs, Regulation 178/2002, Regulation 1935/2004 on materials and articles intended to come into contact with food, European Directive 2008/84/EC specific purity criteria on food additives other than colours and sweeteners, and European Regulation 1333/2008 on Food Additives (Lorenzi et al., 2008). EU safety regulations also require a food safety risk assessment and traceability of the product.

Table 9-5: EIGA limiting characteristics for CO<sub>2</sub> to be used in foods and beverages (Lorenzi et al., 2008)

Component	Concentration
<b>Assay</b>	≥ 99,9 v/v
<b>Moisture</b>	≤ 50 ppm v/v (≤ 20 ppm w/w)
<b>Ammonia</b>	≤ 2,5 ppm v/v
<b>Oxygen</b>	≤ 30 ppm v/v
<b>Oxides of Nitrogen (NO/NO<sub>2</sub>)</b>	≤ 2,5 ppm v/v
<b>Non-volatile residue (particulates)</b>	≤ 10 ppm v/v
<b>Non-volatile hydrocarbons (oil and grease)</b>	≤ 5 ppm v/v
<b>Phosphine*</b>	≤ 0,3 ppm v/v
<b>Total volatile hydrocarbon (calculated as methane)</b>	≤ 50 ppm v/v of which ≤ 20 ppm v/v non-methane hydrocarbons
<b>Acetaldehyde</b>	≤ 0,2 ppm v/v
<b>Benzene</b>	≤ 0,02 ppm v/v
<b>Carbon Monoxide</b>	≤ 10 ppm v/v
<b>Methanol</b>	≤ 10 ppm v/v
<b>Hydrogen Cyanide**</b>	≤ 0,5 ppm v/v
<b>Total Sulphur (as S)***</b>	≤ 0,1 ppm v/v
<b>Taste and Odour in Water</b>	No foreign taste or odour

\* Analysis necessary only for phosphate rock source

\*\* Analysis necessary only for carbon dioxide from coal gasification source

\*\*\* If the total sulphur content exceeds 0,1 ppm v/v as sulphur then the species must be determined separately and the following limits apply:

Carbonyl Sulphide	≤ 0,1 ppm v/v
Hydrogen Sulphide	≤ 0,1 ppm v/v
Sulphur Dioxide	≤ 1,0 ppm v/v

Where assay is the purity of the gas and v/v and w/w are volume and weight fraction, respectively.





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## Appendix A –Flue gas calculations

Table A-1: Flue gas trace composition

$n_{CO_2}$	225 g/Nm <sup>3</sup> flue gas
$n_{CO,KA1}$	11,3 mg/Nm <sup>3</sup> flue gas
$n_{CO,KA2}$	20,2 mg/Nm <sup>3</sup> flue gas
$n_{CO,KA3}$	3,00 mg/Nm <sup>3</sup> flue gas
$n_{SO_2,KA1}$	3,22 mg/Nm <sup>3</sup> flue gas
$n_{SO_2,KA2}$	9,74 mg/Nm <sup>3</sup> flue gas
$n_{SO_2,KA3}$	3,46 mg/Nm <sup>3</sup> flue gas
$n_{NO_x,KA1}$	112 mg/Nm <sup>3</sup> flue gas
$n_{NO_x,KA2}$	111 mg/Nm <sup>3</sup> flue gas
$n_{NO_x,KA3}$	14,7 mg/Nm <sup>3</sup> flue gas

$$1 \text{ ppm} = 0,0001\% = 10^{-6}$$

Calculating the quantity of CO<sub>2</sub>:

$$M_{CO_2} = 44,00 \text{ g/mole}$$

Assuming ideal gas:

$$n = \frac{pV}{RT}$$

At standard conditions:

$$1 \text{ Nm}^3 = \frac{101\,325 \text{ Pa} * 1 \text{ m}^3}{8,314472 \text{ J/moleK} * 273,15 \text{ K}} = 44,64 \text{ mole}$$

$$\chi_{CO_2} = \frac{V_{CO_2}}{V_{fg}} = \frac{n_{CO_2}}{n_{fg}} = \frac{225 \text{ g/Nm}^3}{44,64 \text{ mole/Nm}^3 * 44 \text{ g/mole}} = 0,115$$

The average concentration of CO<sub>2</sub> in the flue gas has been calculated to be 11,5%.

The same procedure was followed to calculate volumetric fraction of CO, SO<sub>2</sub> and NO<sub>x</sub>.

$$M_{CO} = 28,0 \text{ g/mole}$$

$$M_{SO_2} = 64,1 \text{ g/mole}$$

$$M_{NO_x} = 31,6 \text{ g/mole, assuming that NO}_x \text{ consists of 10\% NO}_2 \text{ and 90\% NO}$$

Table A-2: Flue gas NO<sub>x</sub> and SO<sub>2</sub> content

	SO <sub>2</sub>	NO <sub>x</sub>
KA1	1,125	79,6
KA2	3,40	78,8
KA3	1,21	10,4



## Appendix B –LSIPs technology overview

Table B-1: LSIPs technology overview matrix (GCCSI, 2015)

	Pre - comb	Post - comb	Oxy-fuel	n/a	New	Retrofit	n/a	Amine, MEA	Advanced amine	Rectisol	Shift reactor	Cryogenic	Inorg. Chem.	Selexol	n/a
Coal	8	6	2	1	12	3	2	6	1	4		3		1	2
Coal & Biomass	1	1	1		2	1		1			1	1			
Natural gas		2			1	1		1					1		
New	9	4	2					4		4	1	3	1	1	1
Retrofit		4	1					4				1			
n/a		1		1					1						1
Amine	1	7			4	4									
Advanced amine		1					1								
Rectisol	4				4										
Shift reactor	1				1										
Cryogenic	1		3		3	1									
Inorganic chem. abs		1			1										
Selexol	1				1										
n/a	1			1	1		1								

As indicated by Table B-1, each capture route utilises different capture processes, where the most common are as follows:

Post-combustion capture: Amines

Pre-combustion capture: Rectisol

Oxyfuel Combustion: Cryogenic distillation



## Appendix C –LSIPs power plant reference projects

According to MIT (2015), there is currently one large CCS power plant in operation with, two under construction and nineteen in the planning phase.

Table C-1: LSIPs within the power sector, operating or soon-to-be commissioned plants (MIT, 2015)

Project Name	Leader	Location	Feed-stock	Size [MW]	Capture process	CO <sub>2</sub> fate	Status
Boundary Dam	SaskPower	Saskatchewan, Canada	Coal	110 net 139 gross	Post	EOR	Operational
Kemper Country	Southern	Mississippi, USA	Coal	582 net	Pre	EOR	Under construction
WA Parish Petra Nova	NRG Energy	Texas, USA	Coal	250	Post	EOR	Under construction

Post=Post-combustion capture, Pre= Pre-combustion capture, EOR= Enhanced oil recovery

### **Kemper and Petra Nova**

The CO<sub>2</sub> capture plant at Kemper Country Energy Facility is expected to commence within the end of 2015 (GCCSI, 2014). The plant will have a CO<sub>2</sub> capture capacity of 3 Mtpa and a capture rate of 65% (MIT, 2015). The construction of WA Parish Petra Nova started in July 2014, and is planned to start operate in 2016. The CO<sub>2</sub> capture capacity of the plant will be 1,4 Mtpa.

### **Boundary Dam**

Boundary Dam is the first, and so far only, commercially scaled power plant with CO<sub>2</sub> capture in operation. The capture plant was installed on an already existing coal fired power plant and was opened in 2013. The plant is equipped with Cansolv's integrated SO<sub>2</sub>-CO<sub>2</sub> capture technology, which is a post-combustion capture technology using the regenerative amine DC-103 (Rameshini). Figure C-1 shows a process flow diagram of the capture plant. According to Cansolv, the proprietary amine formulations require 40% less regeneration heat, compared to conventional MEA solutions. The plant has a capture capacity of 170 tpd of CO<sub>2</sub>, but due to boiler limitations, the daily capture rate is 120 tonne of CO<sub>2</sub>. At normal operation the average capture rate is 91%, however, a capture rate of 98% is achievable. This adds up to over 1 Mtpa of CO<sub>2</sub> (Stéphenne, 2014).

During the test period of the plant, the average CO<sub>2</sub> concentration of the flue gas entering the absorber was measured to be 9,1 vol%. After the absorber, the average concentration was reduced to 0,85 vol%. This implies a 91% capture rate, and the average purity of the captured CO<sub>2</sub> was measured to be 99,8%. Data from the warranty test run of the plant are presented in Table C-2.

**Table C-2: Boundary Dam capture performance (Singh, Stéphenne, 2014)**

	Average	Standard deviation	Comment
CO <sub>2</sub> capture rate [%]	91		
CO <sub>2</sub> purity [%]	99,8	0,18	
Steam consumption [kg/h]	4 700	191	
Average stripping factor [kg steam/kg CO <sub>2</sub> captured]	1,05	0,06	Corresponds to an average energy requirement of 2,33 GJ/ton of CO <sub>2</sub> captured
Average amine recovery [%]	99,75		A maximum of 99,8% was achieved

Most of the captured CO<sub>2</sub> is transported in a 66 km pipeline to a nearby oil field where the CO<sub>2</sub> is used for EOR (MIT, 2015). The total cost of installing CCS on the existing coal fired power plant was \$1.3 billion. Of that, \$500 was spent on retrofitting the power plant. SaskPower are predicts a reduction in capital costs of 20-30% on their next installation. Amines are used to capture both SO<sub>2</sub> and CO<sub>2</sub>, and selective heat integration reduces the capture plant's steam requirements.



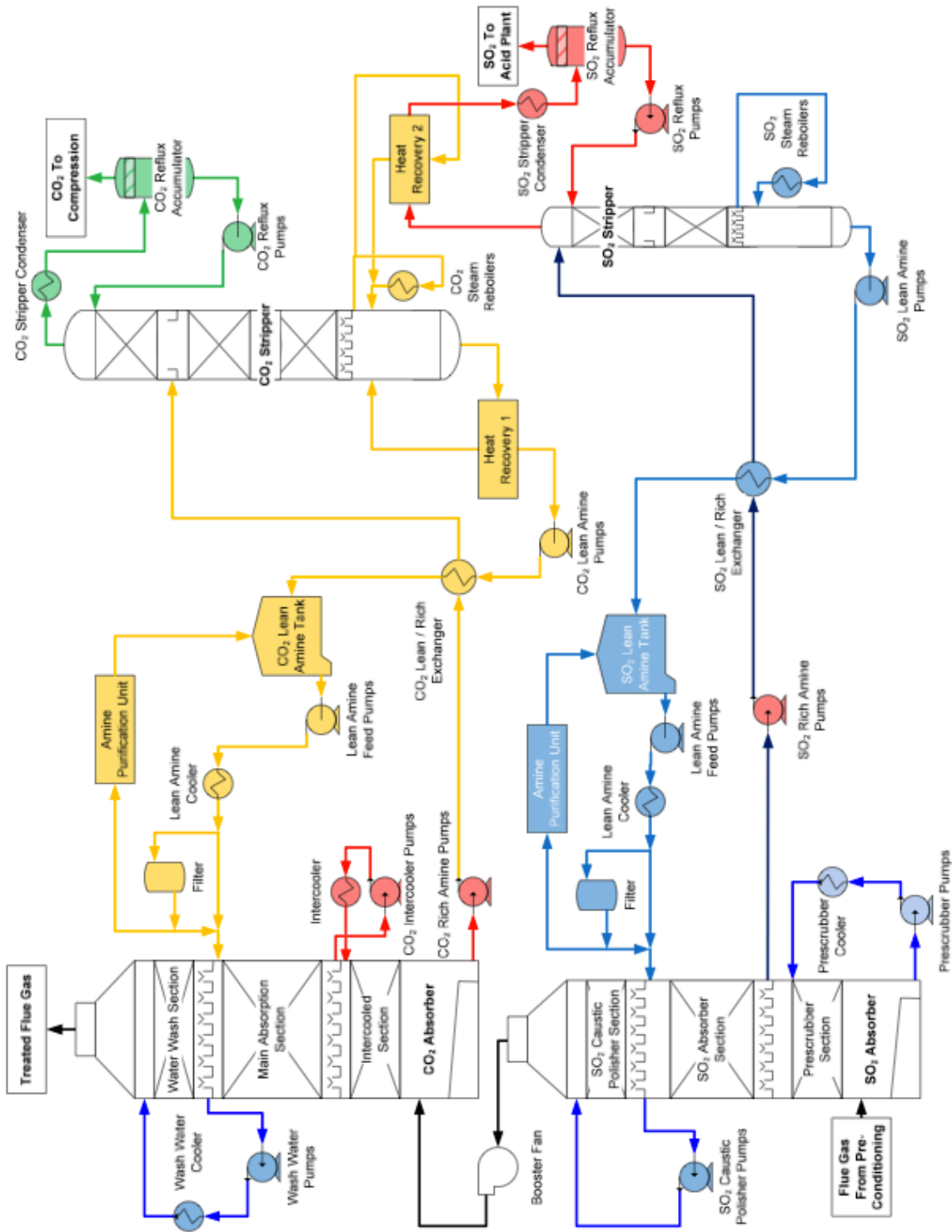


Figure C-1: Process flow diagram of Boundary Dam(Singh, Stéphenne, 2014)



## Appendix D –KM-CDR commercial CCS projects

### Indian Farmer’s Fertiliser Cooperative (IFFC), India

Aonla and Phulpur CO<sub>2</sub> recovery plants are capturing CO<sub>2</sub> from a natural gas fired reformer and are located in India. The CO<sub>2</sub> capture plant is utilising the improved KM-CDR Process and the recovered CO<sub>2</sub> is used as a feedstock in the production of urea. The main data of the capture plants is presented in Table D-1. The difference between the conventional KM-CDR process and the improved process is partly listed in Chapter 6.2. A process flow diagram of the improved capture plant is shown in Figure D-1.

Table D-1: Key data on Aonla and Phulpur capture plant utilising the KM-CDR process (Iijima et al., 2011)

	Aonla	Phulpur
Flue gas CO <sub>2</sub> concentration [%]	8,1	8,2
Flue gas flow rate [Nm <sup>3</sup> /h]	132 000	129 000
CO <sub>2</sub> recovery volume [tpd]	450	450
Flue gas NO <sub>x</sub> concentration [ppmv]	254	257
Flue gas SO <sub>2</sub> concentration [ppmv]	6	6
CO <sub>2</sub> recovery rate [%]	90	90
CO <sub>2</sub> purity [%]	99,9	99,9

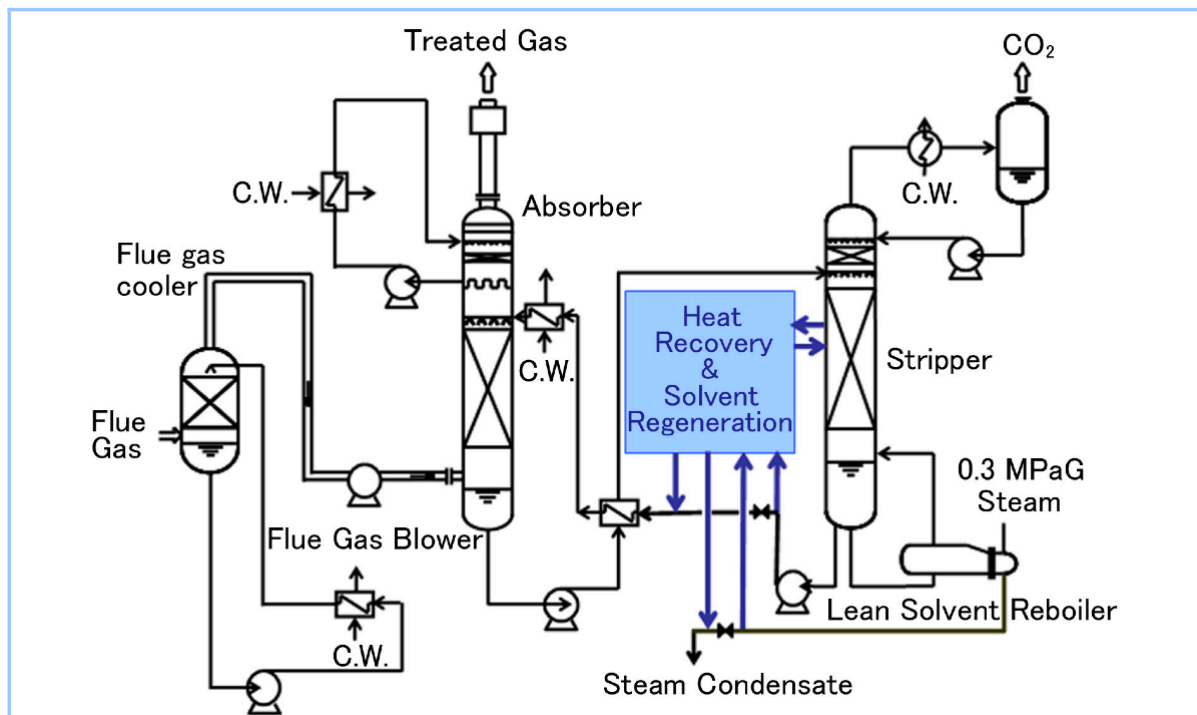


Figure D-1: Process flow diagram of the energy saving regeneration system (Iijima et al., 2011)



## Appendix E –CCSU: SAGA MSW incineration plant

The CO<sub>2</sub> capture plant was implemented in 2013 and captures 10-20 kg of CO<sub>2</sub> per day (Toshiba, 2014). The post combustion capture system is integrated into the existing MSW incineration plant of Saga City in Japan. Saga City are planning to utilise the CO<sub>2</sub> captured to enhance crop cultivation and growing algae. According to Toshiba, the CO<sub>2</sub> captured has a purity rate of over 99%.

Key data of Saga CCSU plant:

- Post-combustion capture
- Capture capacity: 20 kg/day
- Chemical absorption, amine based solvent
- Utilisation: Crop cultivation and algae culture



## Appendix F –Regeneration by pressure and/or temperature swing

An absorption and adsorption processes can be divided into two sub process steps, referred to as absorption/adsorption and regeneration, as discussed in Chapter 4.3.4 and 4.1.2. To promote these processes, a sorbent can be utilised in three different types of beds:

**Fixed bed:** A column filled with a bed material preferentially absorbing/adsorbing CO<sub>2</sub>. When the sorbent is saturated, regeneration is enhanced by changing the conditions in the column.

**Simulated moving bed:** Inside the column there is a rotating valve so that the location of the flue gas inlet steam changes. Hence, the absorbing/adsorbing and regenerative section changes even though the bed material is still.

**Fluidized bed:** The bed material circulates and can therefore be regenerated in a continuous process. It is therefore only need for one column, albeit the process is more complicated than for fixed bed adsorption. The sorbent is usually some kind of powder (Smit et al., 2014).

The most widely used bed type is the fixed bed, requiring the simplest process equipment. When the bed material is saturated, the feed stream is switched to a fresh vessel, and the vessel with the saturated bed material can be switched into regeneration mode, as indicated in. Regeneration can be accomplished in three ways, as described below.

**Temperature swing adsorption (TSA):** A bed material having a higher load capacity at lower temperatures are used. When the bed material is saturated, regeneration is needed before capturing carbon can continue. To regenerate the bed material, the temperature is increased. This will decrease the loading capacity and the absorbed/adsorbed constitute will be released and a stream of e.g. CO<sub>2</sub> can be collected at the top of the column. When the bed material has reached equilibrium, the temperature is decreased and the working capacity is increased. The bed material is now regenerated and a new cycle is started. This process is a batch process, where the column alternately acts as an absorber/adsorber and a stripper. At a power plant, the CO<sub>2</sub> capture or O<sub>2</sub> production process should be a continuous process, and it is therefore necessary to have at least two columns to have simultaneous absorption/adsorption and regeneration (Basile et al., 2010).

**Pressure swing adsorption (PSA):** Absorptive/adsorptive materials preferentially absorbing/adsorbing a constitute at high partial pressure are used. In air separation this this constitute would be N<sub>2</sub>. To regenerate the bed, the partial pressure of N<sub>2</sub> is lowered, often by adding a purging gas that contains minimal amounts of N<sub>2</sub>. The bed material

will be oversaturated, and  $N_2$  will be desorbed. The generative column operates at near-ambient temperatures (Elkamel et al., 2010).

**Vacuum swing adsorption(VSA):** Absorption/adsorption takes place at atmospheric pressure, while the sorbent is regenerated at partial pressures well below ambient, usually in the range of 200- 20 mbar.

TSA is associated with slow adsorption and desorption rate and is thus not used in air separation. Changing the pressure rather than the temperature results in with faster cycle time and simplified operation (Smith, Klosek, 2001). In PSA, when the pressure increases, co-absorbed  $O_2$  is enhanced reducing the performance of the process. PSA is thus limited to a maximum production of 15 t/d. VSA is the preferred method and are commercially available at a production rate up to 120 t/d (Eriksson, Kirros, 2014). Changing both the pressure and the temperature can be applied to obtain a less energy demanding regeneration process.



## Appendix G –Notes to Table 5-2

**Note 1:-** All of the processes will require pretreatment of raw flue gas, particularly those derived from coal fired plant since these are likely to contain, in particular, high levels of SO<sub>2</sub> and NO<sub>2</sub> which will be neutralised by the amine to form heat stable salts. MEA processes usually have a solvent reclaiming system to assist in solvent recovery but any heat stable salts have to be purged from the system and constitute loss.

**Note 2:-** There are many examples in the chemical and petroleum refinery industries where there are larger equipment sizes than those which will be needed in commercial power plant post combustion scrubbing units. There are also cases where the scale up factors in going from one generation of plant to the next have been larger than those anticipated in post combustion amine scrubbing commercialisation. Scale up is not therefore seen as a potential problem.

**Note 3:-** Energy use has been substantially reduced in the latest evolution of MEA scrubbing plants such that they are now competitive with KS-1 which remains the gold standard for low energy consumption. Development work continues with MHI developing KS-2 and KS-3 amines which are expected to have lower consumptions than KS-1 (as low as 670 kgcals/kg of CO<sub>2</sub>). FLUOR are also developing new alkanolamine systems, based on MEA which are expected to

lower the energy consumption of the EFG + process still further. It is not yet known what the asymptotic limits will be for further generations of technology. If a commercial market develops for post combustion removal processes, then there will be an intensification of research in the area of new and improved amine formulations from all technology developers and suppliers.

**Note 4:-** The FLUOR EFG+ plus process probably has the lowest capital cost. However caution is required in interpreting this statement since detailed comparisons are required to establish this. There are no published studies which report comparisons (of all three processes in the same study) done with estimates of the required accuracy and based on installation at a specific highly defined site. Published study work done to date has not produced sufficient detailed design and estimating data to allow this question to be answered.

**Notes 5 & 6:-** All amine scrubbing processes when applied to post combustion carbon dioxide recovery have high operating costs. The principal elements are capital charges and energy costs. MEA processes have an advantage in that the amines they use are cheap commodity chemicals whereas KS-1 solvent is a speciality formulation of high cost and limited availability. It is unlikely that amine scrubbing costs will achieve dramatic reductions (they already represent mature technology).

**Notes 7 & 8:-** There is limited operating experience with the MHI KS-1 process. The single commercial plant operates on a stream with very low oxygen concentrations (0.87%) and there are, therefore, outstanding questions on the long term stability of KS-1 solvent operating in a commercial environment with oxygen concentrations of 4-12% which is the probable range of power plant flue gas. FLUOR has the greatest amount of commercial experience and has long term operational experience of plant on gas turbine exhausts. The Kerr McGee MEA process is the only one of the three processes which has operated on plants with coal derived flue gases although both MHI and FLUOR have done detailed paper studies of plants for use on coal derived streams. None of the processes have been applied to large scale commercial power plants of any type.

**Notes 9&10:-** MHI have active laboratory and pilot plant programmes in place for the development of their amine technology. FLUOR have theoretical and contract research programmes in place and still have access to the operating experience being gathered on the Bellingham plant. None of the technology developers have pilot plants operating on slip streams from coal or gas turbine fuelled power plants.



## Appendix H –The SYNCOM process

Excess air has a positive effect on the combustion efficiency, albeit reducing energy efficiency (Tsiliyannis, 2014). This is due the increased  $\dot{m}C_p$  of the air stream and the increase of losses through the stack. Reducing the excess air is thus a way of increasing the boiler efficiency as well as increasing the CO<sub>2</sub> partial pressure in the flue gas. In combination, these are the key benefits of combining the SYNCOM process with post-combustion capture technology.

SYNCOM is a shortening for synthetic combustion and was developed by MARTIN GmbH, and is based on combustion in oxygen enriched air (Koralewska, 2009). The oxygen enriched air is supplied as primary air of combustion zone 2 and 3. This will provide a good balance between combustion efficiency and excess O<sub>2</sub> requirements. Enriching the primary air with O<sub>2</sub> results in many benefits, such as:

- Reduction in volumetric flow of the flue resulting in a higher partial pressure of CO<sub>2</sub>
- A significant reductions of organic pollution in the flue gas
- Increased sintering of bottom ash and decreased amounts of fly ash
- Fuel bed temperature increase to 1200 °C

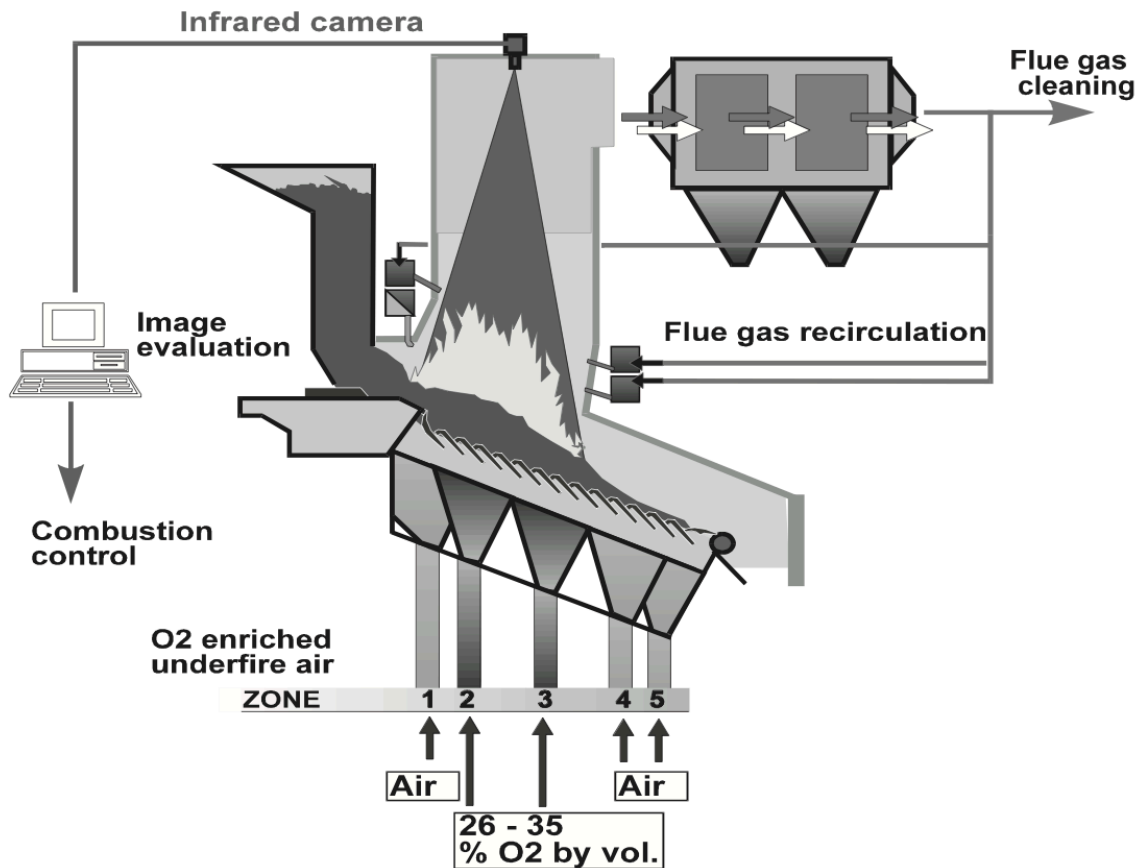
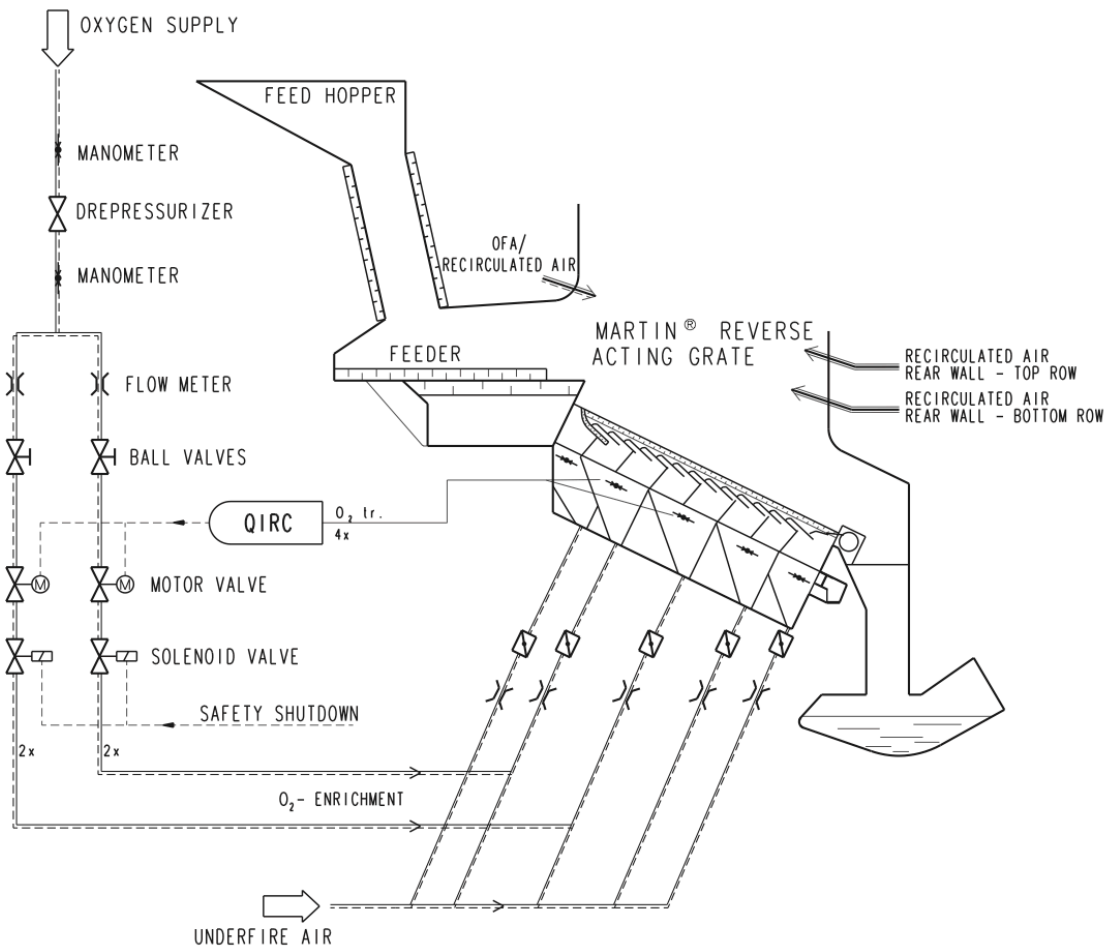


Figure H-1: The components of the SYNCOM process (Gohlke, Busch, 2001)

At Coburg WtE plant in Germany, comprising two incineration lines, a CCS demonstration plant is implemented. The demonstration plant was implemented into the second waste incineration line, while the other line was operating as normal, facilitating a good basis for comparison. Each of the two lines has a mass flow rate of 7 t/h. The retrofit of incineration line 2 involved installing a flue gas recycling system to control the combustion temperature and installing an infrared camera to measure the temperature. Based on the data collected from the infrared camera, optimal oxygen purity (SP up to 32%) and flue gas recycling rate is controlled by a control system. The pilot plant was supplied with pure O<sub>2</sub> instead of installing air separation technology due to the implementation not being permanent. Pure O<sub>2</sub> is added to the primary air supply of combustion zone 2 and 3, as indicated in Figure H-2. The main drawback of oxygen enriched combustion is the expensive implementation of an air separation unit, which is assumed to be the main reason for this process not being widely deployed (Gollan, Kleper). The excess O<sub>2</sub> consumption of the test plant was 1300 Nm<sup>3</sup>/h, and the supply flow diagram is shown in Figure H-2.



**Figure H-2: Oxygen supply of the SYNCOM process (Gohlke, Busch, 2001)**

All result presented are based on tests carried out over a one-week period.

An oxygen concentration in zone 2 and 3 of 29% and 31%, respectively, gave the following results:

- 39% reduction in volumetric flue gas flow (26 400 Nm<sup>3</sup>/h vs. 43 400 Nm<sup>3</sup>/h)
- Boiler efficiency was increased by 7% (relative)
- More intense and uniform combustion was achieved
- 42% reduction in CO emissions (11 mg/Nm<sup>3</sup> vs. 19 mg/Nm<sup>3</sup>)
- 13% increase in fuel bed temperature (1200°C vs. 1065°C)
- 22% reduction in production of fly ash (including boiler ash)
- Increased stability in steam production (deviation of 0,7 t/h vs. 1,1 t/h, respectively 3% and 5%)
- Reduced amounts of organic by-products in the bottom ash and flue gas



## Appendix I – SYNCOM-Plus

SYNCOM-Plus is a process to further improve bottom ash quality, and is an add-on to the SYNCOM process. SYNCOM-Plus is installed downstream of the boiler and will increase boiler efficiency by utilising low-grade waste heat and therefore presumably reduce losses through to stack and reduce the amount of boiler ash disposed at landfill (Martin et al., 2015). An energy distribution chart from a pilot plant is shown in Figure I-3.

Bottom ash accounts for the largest mass flow of the waste input. By applying the SYNCOM process, the increased bed temperature enhances bottom ash sintering but there will still be particles that are not fully oxidised. By adding a separation unit, granulate can be removed and the fine fractions and sludge can be recycled back into the boiler for complete combustion and further sintering, as indicated in Figure I-1 (Martin et al., 2015). The process in using a wet-mechanical treatment system and recycling, as indicated in Figure I-2.

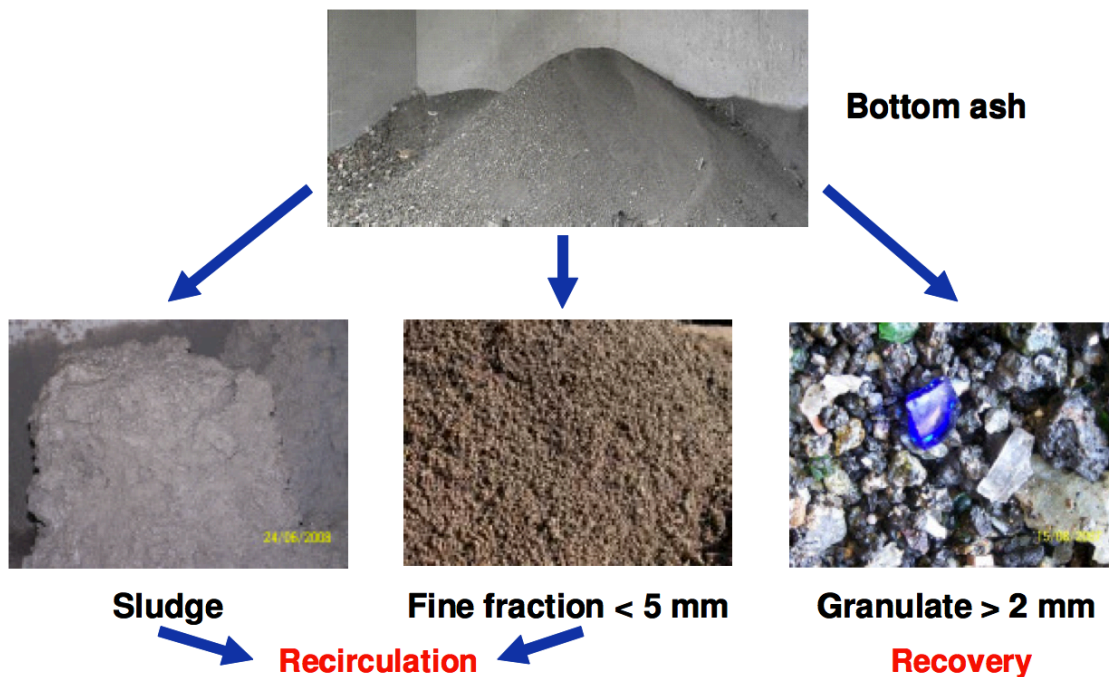


Figure I-1: Material flow of separated bottom ash in Arnoldstein SYNCOM WtE plant (Koralewska, 2009)

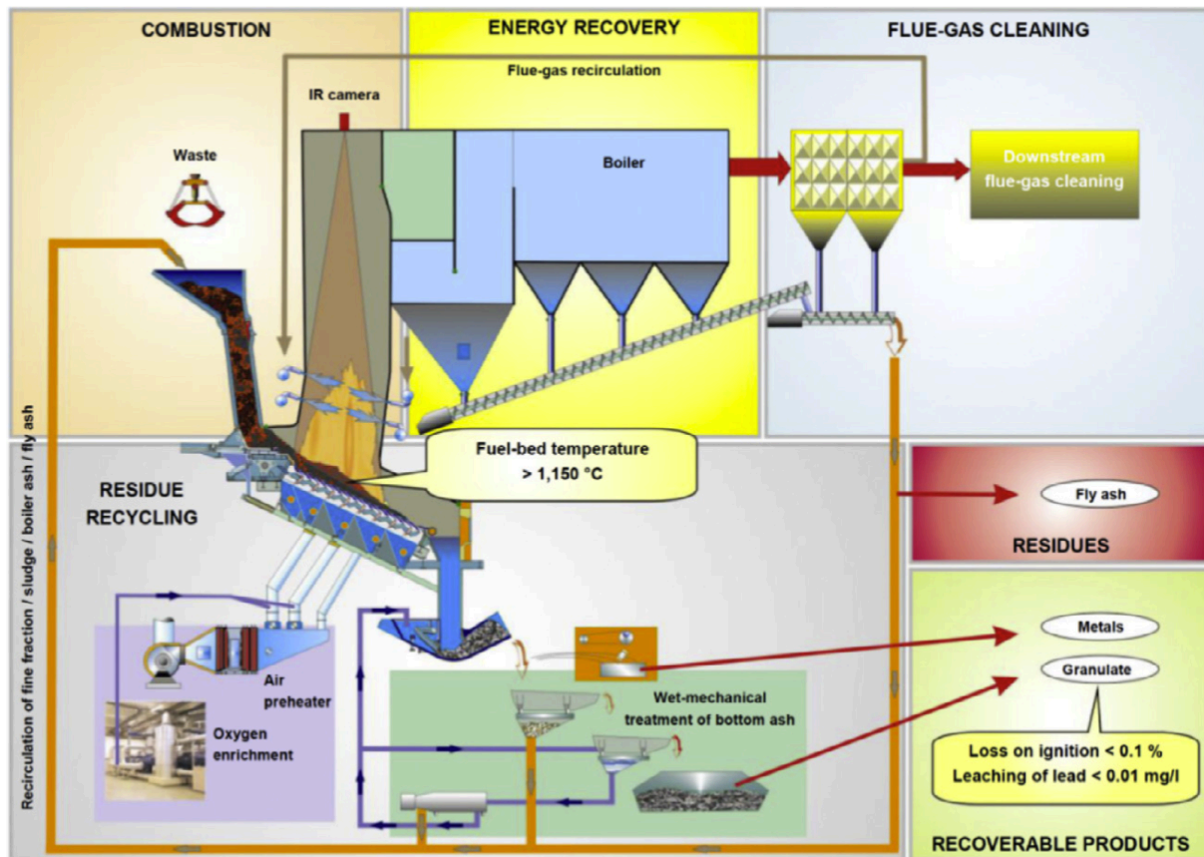


Figure I-2: Process overview of the SYNCOM process (Martin et al., 2015)

The process was implemented in the large-scale pilot plant, Arnoldstein, and the following results were achieved:

- 6,5 % (428, 180, 58 kg/h of respectively fine fraction, sludge and boiler ash) of the hourly waste input was recycled
- Optimized granulate quality with optional recovery
- No significant accumulation of fine fractions in the resulting bottom ash was detected
- The implementation of the SYNCOM-Plus process had no significant effect on neither the combustion parameters (Steam, bed temperature, etc.) nor the flue gas quality
- Continuous and stable operation
- Increased boiler efficiency due to the utilisation of waste-heat

The plant is smaller than Klemetsrud with a waste throughput of 10 700 kg/h, which is slightly higher than KA1 and KA2 but less than KA3. The mass flow through the plant is shown in Figure I-4. An overview of the energy distribution in the SYNCOM-Plus WtE plant Arnoldstein is shown given in Figure I-3. The effect of the waste heat utilisation will not have the same degree of efficiency increasing effect, as much of the waste heat is already utilised in the production of district heating.



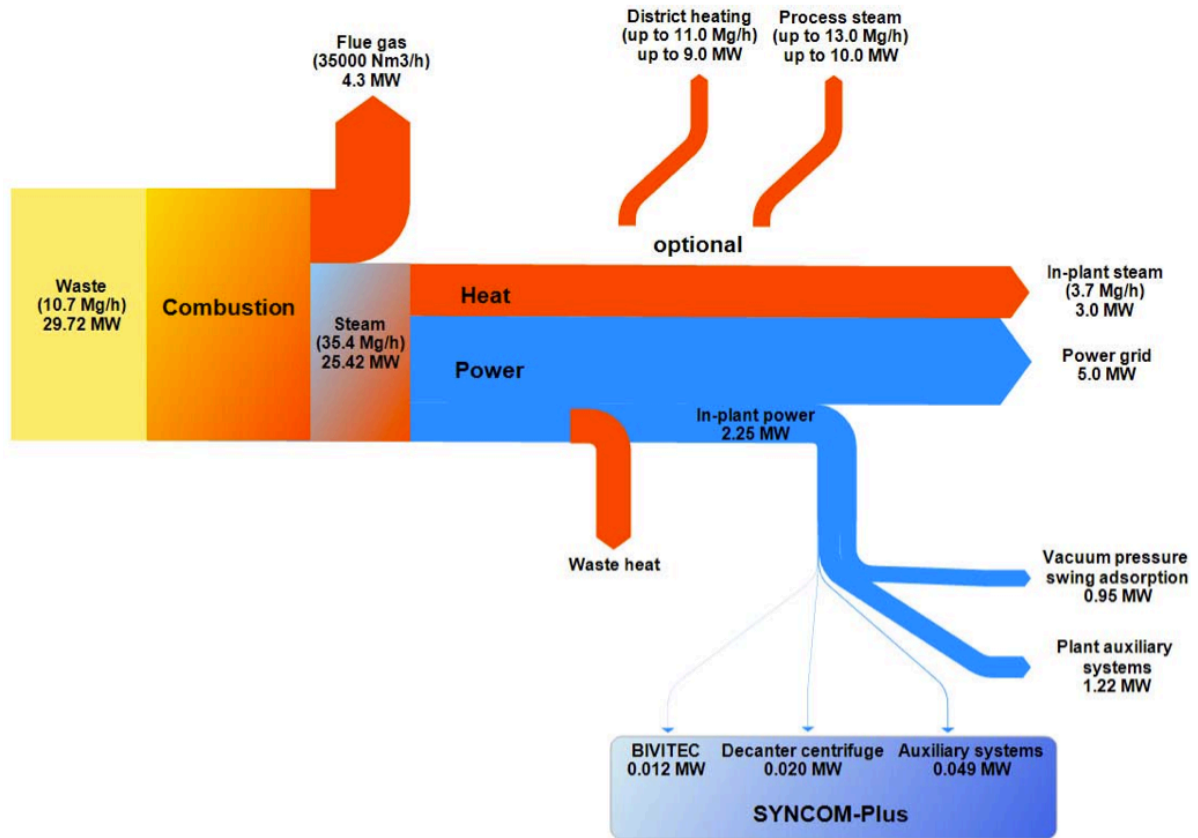


Figure I-3: Energy distribution in the SYNCOM-Plus plant Arnoldstein (Koralewska, 2009)

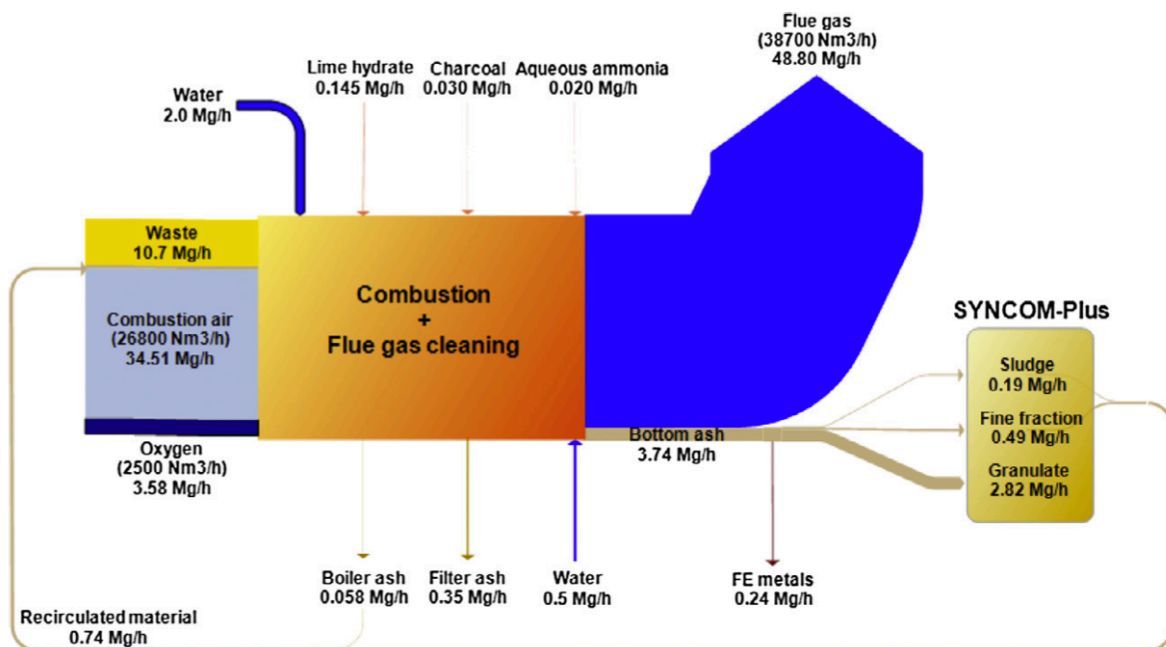


Figure I-4: Mass flow in the SYNCOM-Plus plant Arnoldstein (Koralewska, 2009)