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Conditioning of CO2 coming from a CO2 capture process for transport and storage purposes

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Master of Science in Energy and Environment
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Problem Description

CO2 capture, transport and storage in connection with power production is one of the most important technologies for limiting CO2 emissions to the atmosphere in the world today. CO2 capture involves a need to use energy. There are several principles for CO2 capture, and the different methods result in a CO2 rich effluent stream with different contents of other gases. Particularly so-called oxy-combustion plants will give a considerable dilution of CO2 with other gases.

Compression of CO2 has been suggested to a pressure of 100-150 bar. This relies on pressure loss during transport and depth of storage. Separation of CO2 from the other gases may be done in connection with the compression of CO2.

Assignment given: 20. January 2009
Supervisor: Olav Bolland, EPT

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Institutt for energi- og prosessteknikk

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MASTEROPPGAVE

for

Stud.techn. Vegard Bilsbak

Våren 2009

Kondisjonering av CO_2 for transport- og lagringsformål fra kilde med CO_2-fangst

Conditioning of CO_2 coming from a CO_2 capture process for transport and storage purposes

Bakgrunn

CO_2-fangst, -transport og –lagring i forbindelse med kraftproduksjon er på verdensbasis en av de viktigste teknologiene for å begrense utslippet av CO_2 til atmosfæren. CO_2-fangst innebærer behov for å bruke energi. Det finnes flere prinsipper for CO_2-fangst, og de ulike metodene gir en CO_2-rik strøm med ulik andel av andre gasser. Det er spesielt såkalte oxy-combustion anlegg som gir en betydleig uttynning av CO_2 med andre gasser.

Kompresjon av CO_2 har blitt foreslått til et trykk på 100-150 bar. Dette er avhengig av trykktap i transport og dybde ved lagring. Separasjonen av CO_2 fra den andre gassene kan gjøres i forbindelse med kompresjon av CO_2.

Mål

Målet med oppgaven er å finne kompresjon- og separasjonsprosesser for CO_2 fra et CO_2 fangstanlegg som tilfredsstiller krav til CO_2-renhet, trykk og temperatur, og som er energieffektiv.

Oppgaven bearbeides ut fra følgende punkter

1. Litteraturstudie for å finne krav til CO_2 i forbindelse med transport i rør eller skip, og lagring i akviferer eller for EOR.
2. Litteraturstudie for å finne aktuelle gassammensetninger fra prosesser med "CO_2-fangst", dvs. hvilke andre gasser enn CO_2 finnes, og eventuell forekomst av metaller og salter.
3. Litteraturstudie for å finne aktuelle separasjonsmetoder for gassammensetninger fra punkt 2.
4. Med utgangspunkt i et sett med valgte gassammensetninger skal design av egnet prosess utføres, hvor en ønsket CO_2-renhet, trykk og temperatur oppnås.
5. De foreslåtte prosessene fra punkt 4 skal modelleres og simulering skal utføres i et egnet verktøy. I simuleringen skal krav til CO_2-renhet og eventuelt andel av spesifikke gasser brukes som parametere i simuleringen. Energieffektivitet som kriterium for design av prosess skal vektlegges.

" - "

Senest 14 dager etter utlevering av oppgaven skal kandidaten levere/sende instituttet en detaljert fremdrift- og evt. forsøksplan for oppgaven til evaluering og evt. diskusjon med faglig ansvarlig/

veiledere. Detaljer ved evt. utførelse av dataprogrammer skal avtales nærmere i samråd med faglig ansvarlig.

Besvarelsen redigeres mest mulig som en forskningsrapport med et sammendrag både på norsk og engelsk, konklusjon, litteraturliste, innholdsfortegnelse etc. Ved utarbeidelsen av teksten skal kandidaten legge vekt på å gjøre teksten oversiktlig og velskrevet. Med henblikk på lesning av besvarelsen er det viktig at de nødvendige henvisninger for korresponderende steder i tekst, tabeller og figurer anføres på begge steder. Ved bedømmelsen legges det stor vekt på at resultatene er grundig bearbeidet, at de oppstilles tabellarisk og/eller grafisk på en oversiktlig måte, og at de er diskutert utførlig.

Alle benyttede kilder, også muntlige opplysninger, skal oppgis på fullstendig måte. (For tidsskrifter og bøker oppgis forfatter, tittel, årgang, sidetall og evt. figurnummer.)

Det forutsettes at kandidaten tar initiativ til og holder nødvendig kontakt med faglærer og veileder(e). Kandidaten skal rette seg etter de reglementer og retningslinjer som gjelder ved alle (andre) fagmiljøer som kandidaten har kontakt med gjennom sin utførelse av oppgaven, samt etter eventuelle pålegg fra Institutt for energi- og prosessteknikk.
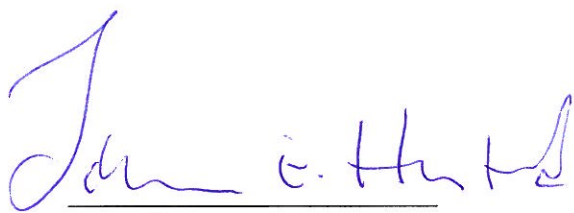
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Ett -1 komplett eksemplar av originalbesvarelsen av oppgaven skal innleveres til samme adressat som den ble utlevert fra. (Det skal medfølge et konsentrert sammendrag på maks. en maskinskrevet side med dobbel linjeavstand med forfatternavn og oppgavetittel for evt. referering i tidsskrifter).
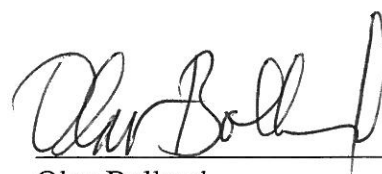Til Instituttet innleveres to - 2 komplette, kopier av besvarelsen. Ytterligere kopier til evt. medveiledere/oppgavegivere skal avtales med, og evt. leveres direkte til, de respektive.
Til instituttet innleveres også en komplett kopi (inkl. konsentrerte sammendrag) på CD-ROM i Word-format eller tilsvarende.

Institutt for energi og prosessteknikk, 12. januar 2009

Johan Hustad
Instituttleder

Olav Bolland
Faglig ansvarlig/veileder

Preface

When I am know finishing this work I would like to thank my guidance counsellor Olav Bolland. I will also like to thank all others who have helped me, especially my fellow students. I have experienced a lot of frustration along the way mostly due to computer problems. In that regard I will also like to thank Eugen Uthaug for helping me out reinstalling Pro/II.

Trondheim juni 2009

Vegard Bilsbak

Summary

A conditioning process for CO_2 captured from a power plant is considered for pre combustion, post combustion and oxy combustion using both coal and natural gas as fuel. Relevant compositions for the captured CO_2 along with recommendations applying to transport by pipeline or ship, has been found in the literature. Methods for removal of unwanted substances by separation or other means have also been described. With a basis in the gathered data, the CO_2 conditioning process has been simulated using Pro/II. The processes have been optimized to give the lowest required energy input obtainable. The simulation data has been gathered to evaluate the implications of meeting a certain quality recommendation.

The results show that energy penalty, in terms of power plant efficiency, connected to purifying CO_2 from pre and post combustion capture is low. The need for purification equipment is also low, reducing the need for increased investments. Oxy combustion processes also show low energy penalties due to CO_2 conditioning. The relative increase from obtaining a quality suited for basic underground storage and a quality suited for liquefaction is smaller than for pre and post combustion. For liquefaction of oxy combustion derived CO_2 from burning coal, the calculated power plant efficiency is only 0.1 percent lower than for post combustion, which has the highest efficiency. The limitations for oxy combustion processes have in this work been found to be the equipment needed for purification. Low pressures to obtain the required qualities will also result in large dimensions for the equipment.

For drying of captured CO_2, TEG performs less efficiently for oxy combustion than for the other capture methods. Combined effects of solubility of water in TEG and CO_2 enhance the drying effect at high partial pressures of CO_2.

For pre combustion using coal as fuel, capturing H_2S and CO_2 combined is advantageous over separate capture given that selective catalytic oxidation of H_2S is commercialized.

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Nomenclature

Abbreviations:

ATR	Auto thermal reforming
CCS	Carbon capture and storage
EIGA	European industrial gases association
EPRI	Electric power research institute
HRSG	Heat recovery steam generator
IEA	International energy agency
IEA GHG	International energy agency greenhouse gas programme
IGCC	Integrated gasification combined cycle
MMP	Minimum miscible pressure
MSA	Molecular sieve
PMG	Platinum metal group
ppm	Parts per million
SCR	Selective catalytic reduction
SMR	Steam methane reforming
SNCR	Non catalytic selective reduction
TEG	Triethylene glycol
VLE	Vapour-liquid equilibrium

1. Introduction

Ever since global climate change became an issue, a lot of work has been done on how to carry out carbon capture and storage or CCS. The thought has been to target large point sources of CO_2 emissions, and by capturing the CO_2, stabilize the concentration of CO_2 in the atmosphere. A majority of this work has been directed towards developing new concepts for electric power plants utilizing fossil fuel, the challenge being minimizing the energy penalty for capturing carbon. Most of these concepts are based on a combined cycle power plant where the fossil fuel is combusted and expanded through a gas turbine, and the heat in the turbine exhaust is used to produce steam for expansion in a steam turbine. The challenges related to the capture of CO_2 apply to the gas turbine since it is the combustion of fossil fuel that produces CO_2. Further, there have been three main areas of focus wherein the different concepts are categorized. The different areas are called pre combustion, post combustion and oxy combustion.

In pre combustion technology the idea is to capture the carbon from the fuel prior to combusting it. Ideally this will result in no CO_2 in the turbine exhaust. The capture is achieved by reforming the fossil fuel. The effluent gas from the reforming process will contain mainly CO_2, CO and H_2. The CO_2 is then removed by absorption, adsorption or the use of selective membranes. A syngas consisting of H_2 and CO can then be combusted and expanded in a turbine. The main challenge compared to using conventional gas turbines, is that the combustion temperature will be much higher when this syngas is combusted compared to combusting natural gas or gasified coal.

The area that is closest to realization technologically is post combustion. Power plants with post combustion capture uses technology already available today regarding turbines. The main difference from a conventional combined cycle is that the flue gas is lead through a contact column prior to being released to the atmosphere. In this column, the CO_2 is, for most of the concepts, absorbed using amines. From the absorption column, the amine, now rich in CO_2, is sent to a second column where it is reclaimed by boiling the CO_2 off.

Technology characterized as oxy combustion (or oxy fuel) deals with the carbon problem by modifying how the combustion is carried out. In conventional power plants the fuel is combusted using air which is about 79 percent nitrogen. The flue gas will thus mainly be made up of nitrogen and the concentration of CO_2 will be relatively low (around three percent for natural gas and 15 percent for coal). As a consequence, the partial pressure of CO_2 is low giving very large dimensions for an installation based on post combustion capture. The answer to this problem from an oxy combustion point of view is to combust the fossil fuel with oxygen only, giving mainly CO_2 and steam in the flue gas. As for pre combustion this calls for a development in turbine technology since the combustion temperature will rise when nitrogen is not present to absorb heat from the combustion. The solution, which creates the main challenge, is to reduce the temperature either by recycling CO_2, or by adding steam.

The widely adapted abbreviation for the technology to reduce CO_2 emissions, CCS, leaves out one important step namely transport. The CO_2 leaving the different capture processes will usually have a pressure close to atmospheric depending on the process. Geographically it will also in most cases be far from a suitable storage site. The CO_2 therefore has to be compressed and transported through a pipeline or liquefied and transported by ship. Both pipeline and ship transportation has been practiced for CO_2 for a number of years. Pipeline transportation has

been utilized mainly for reinjection of CO_2 to extend the extraction from an oil or gas reservoir, and ship transportation mainly in connection with the food industry.

For storage of CO_2 captured from energy production, two main alternatives have been pointed out. The first is storage in aquifers, which are underground geological formations of water-bearing rock or sand. Some of the largest aquifers are found underneath the seabed. The second is to utilize the CO_2 to increase the pressure in reservoirs to prolong extraction of oil and/or gas. When the reservoir is depleted, it is closed off to permanently store the CO_2. The latter concept is called enhanced oil recovery or EOR for short.

Depending on the type of transportation and storage, different demands regarding the quality of the CO_2, which is to be transported and stored, arises. From a transportation point of view, there are three main concerns which are influenced by the quality of the transported fluid. The first is corrosion of metal in pipelines, storage tanks or tanks aboard ships. CO_2 alone is not corrosive to metals, but if CO_2 is dissolved in water, carbonic acid will form. The amount of acid formed is dependent on the partial pressure of CO_2 above the solution. If water precipitates in a stream of mainly CO_2 at relatively high pressures and there is oxygen present, the result may be considerable damage to pipelines or tanks. When fossil fuels are combusted, other substances which are acidic in solution with water may also be formed. It is therefore important to limit the possibilities that water will precipitate from the CO_2 and also limit the concentrations of potentially acidic substances.

The second concern regarding the transport is energy efficiency. This ultimately comes down to the energy penalty of compressing or liquefying a mixture that contains substances that are not CO_2 in addition to the CO_2 itself. There will be a trade off because increasing the purity of the CO_2 requires a higher energy input, but on the other hand it lowers the energy required for compression after the purification. If substances more volatile than CO_2 are present in the effluent from the capture process, the increased CO_2 purity of the mixture will increase the temperature and lower the pressure required for liquefaction. For ship transport this is essential but it will also lower the energy required for pipeline transport since the last part of compression can be done by pumps rather than by gas compressors. If the captured CO_2-stream is transported in a liquid state, the density of the mixture will decrease considerably with increasing concentrations of relevant volatiles. This is due to the fact that the density of the liquid CO_2 will be much larger than that of the volatiles at the same state [1]. Hence the CO_2 transport capacity will decrease.

The third main concern is health and safety regarding humans affected by an emission following a rupture of a pipe or a tank. CO_2 has some toxic effects related to increased blood acidity, but the main concern in case of a rupture is CO_2 acting as an asphyxiant displacing oxygen. As for the concern of corrosion, there may be other substances present in the mixture that can cause problems. Typical products of combustion like nitrogen oxides (NO_x) or carbon monoxide (CO) are known to be toxic. The content of toxic substances must be kept at levels that will not result in lethal concentrations in air in close proximity to an emission from a rupture.

When it comes to the permanent storage of the captured CO_2 in depleted reservoirs or aquifers, there are still some uncertainties regarding if the CO_2 will escape or not. Research is being done to make sure, as far as possible, CO_2 actually can be stored safely. Assuming that the CO_2 stays in place, it is important that none of the components in the captured CO_2 engage in reactions that might compromise the aquifer or reservoir's ability to hold the CO_2.

If the captured CO_2 is to be used in EOR, some other considerations must be made. The best performance is achieved if the CO_2 dissolves in the oil, reducing its viscosity and displacing it. The lowest pressure at a given condition which this process occurs is called the minimum miscible pressure or MMP. This pressure is increased by volatile components potentially in the CO_2-mixture. An increase in the MMP lowers the potential of enhanced recovery and might exceed the maximum operational pressure for a given reservoir, making it unsuited for EOR altogether [1]. Another concern regarding EOR is the oxygen content of the CO_2 used. Oxygen might react exothermally with the oil increasing the temperature above the upper limit for the injection point. If the oil is oxidized it will also become harder to extract and refine [1].

The goal of this work has been to find out what implications a given form of transport and storage will have on the process of conditioning the CO_2. The considered processes include all three capture technology approaches and both natural gas and coal as energy source. To be able to develop models for simulation, it is necessary to establish possible compositions and conditions for the captured CO_2 from power plants using the different technologies. It is also necessary to find recommendations for specification of quality demands for the processed CO_2. A search through the literature has been done to acquire the necessary data.

2. Literature review

2.1. Pre combustion capture

There has been written many scientific papers on pre combustion technology, but not a lot of them define the quality of the captured CO_2. In the case of coal power plants using pre combustion, the papers found all dealt with IGCC's (Integrated Gasification Combined Cycle). The compositions that are used in this work come from a report by the International energy agency, IEA [2]. In this report IGCC power plants with technology from Shell and Texaco are compared both economically and performance wise. In an IGCC, the sour gases produced are both hydrogen sulphide (H_2S) and carbon dioxide. Both Technology providers have alternatives with combined capture of the sour gases as well as separate capture.

The cases chosen are the two cases from Shell with the highest efficiency and the lowest specific investment cost, one with combined capture of CO_2 and H_2S and one with separate capture of the two. Capturing CO_2 and H_2S as separate streams requires more energy and equipment, and the case with separate capture, from now on abbreviated C1b, has an efficiency 0.5 percentage points lower and a specific investment cost 7.7 percent higher than the case with combined capture, from now on abbreviated C1a. Both cases capture 85 % of the CO_2 produced from the coal. Case C1a uses an amine absorption process called aMDEA (activated methyldiethanolamine) and C1b uses the Selexol process which is based on the use of a mixture of dimethyl ethers of polyethylene glycol. Conditions for the captured stream are given to be 0.8 bar and 49°C for case C1a. For case C1b the captured CO_2 is in three different streams at different conditions which are not specified. Without further information the same conditions as those for C1a is used. The compositions are shown in Table 2-1.

Table 2-1: Composition pre combustion, coal

Component:	C1a:	C1b:
CO_2	92,17 %	97,69 %
CO	0,03 %	0,19 %
H_2O	6,56 %	0,28 %
H_2	0,72 %	1,74 %
N_2	0,03 %	0,06 %
Ar	0,00 %	0,03 %
H_2S	0,49 %	0,01 %

The case selected for pre combustion technology with the use of natural gas, comes from a paper published by the Dynamis project related to Sintef energy research [3]. The paper considers three cases of methane reforming to produce the hydrogen to be combusted in the gas turbine. Of the three, one is utilizing steam methane reforming (SMR), one an oxygen blown auto thermal reformer (ATR) and one an air blown auto thermal reformer. The case selected is the one using an air blown ATR, from now on abbreviated NG1. As for case C1b, the aMDEA process (simulated in HYSYS) is used to capture 96 % of the CO_2 produced from the natural gas. The conditions of the captured stream is 1 bar and 45°C. The composition is shown in Table 2-2.

Table 2-2: Composition pre combustion, natural gas

Component:	NG1:
CO_2	90,2 %
CO	8,8 ppm
H_2O	9,6 %
H_2	0,11
CH_4	16 ppm
N_2	532 ppm
MDEA	9,6 ppm
MEA	140 ppm

2.2. Post combustion capture

In post combustion capture technology, the most common form of capturing CO_2 is by using an amine absorption process. The flue gas exiting the gas turbine is contacted with the amine solution in one column, and the amine is regenerated boiling off the CO_2 in another column. The selected composition for the case of CO_2 captured from power plants using coal, from now on abbreviated C2, is taken from a paper in a journal titled "Carbon dioxide capture for storage in deep geological formations" [4]. The conditions for the CO_2-rich stream are not specified, but it is mentioned that the regenerating column is typically operating at 150-175 kPa. The pressure is therefore set to 1.5 bar. Based on another source [5] the temperature is set to 37.8°C and the overall CO_2 capture rate to 85 %. The composition is shown in Table 2-3.

Table 2-3: Composition post combustion, coal

Component:	C2:
CO_2	93,2 %
H_2O	6,5 %
N_2	0,17 %
O_2	0,01 %
Ar	Trace
SO_2	Trace
SO_3	Trace
NO_x	Trace
HC	Trace
Me	Trace[1]

[1] Depending on the fuel process

Since the oxygen concentration of 0.01 % equal to 100 ppm (parts per million) is stated, the concentrations simply given as "trace" is further assumed to be at least one order of magnitude smaller. The total sum of the concentrations equal 99.88 %. In the implementation of the composition, the concentrations will be scaled up so that the total sum is 100 %.

The case of post combustion capture from a natural gas combined cycle power plant, from now on abbreviated NG2, is taken from an IEA Greenhouse gas R&D programme report [5]. In this case the amine process used is the vendor Fluor's process Econamine FG+. Pressure and temperature of the captured CO_2-rich stream is 1.48 bar and 37.8°C respectively, and the overall CO_2 capture rate is 85 %. The composition is shown in Table 2-4.

Table 2-4: Composition post combustion, natural gas

Component:	NG2:
CO_2	95,5 %
H_2O	4,48 %
N_2	167,84 ppm

2.3. Oxy combustion

In oxy combustion the CO_2 is not really captured, but by recirculating CO_2 in order to keep the temperature in the gas turbine from getting to high, the concentration of CO_2 in the flue gas is increased a lot compared to a conventional combustion process. To be able to supply the oxygen needed, a power plant using oxy combustion has to separate oxygen from air. The solution realizable at the present time is an air separation unit (ASU). An ASU uses cryogenic technology to separate oxygen from air hence it is an energy demanding unit. To limit the energy consumption, oxygen is normally produced with a purity of 95 percent. This purity is in a report from the IEA Greenhouse House gas R&D programme [6], found to be an optimum in connection to air in-leakage. Oxy combustion concepts using other less energy intensive ways of supplying oxygen exists, but are farther from commercialization at this point.

Apparently, papers on power plants burning coal in oxy combustion mode supplied with flue gas compositions, seems to outnumber any other configuration. The compositions however vary according to how the oxygen is supplied, the purity of the oxygen and air in-leakage. The composition chosen, taken from the aforementioned IEA GHG report [6], is based on a power plant using an ASU to produce oxygen with a purity of 95 percent. The total air in-leakage is 0.03 kg air per kg flue gas. Exiting from the HRSG the temperature is 111°C and the pressure is 1.02 bar. The flue gas is scrubbed to remove particulate and cooled before part of the CO_2 is recycled and the rest enters the purification process. The resulting composition for this case, from now on abbreviated C3, is shown in Table 2-5.

Table 2-5: Composition oxy combustion, coal

Component:	C3:
CO_2	71,46 %
H_2O	5,62 %
N_2	14,34 %
O_2	5,88 %
Ar	2,31 %
SO_2	0,35 %
NO	0,04 %
NO_2	0,001 %

The final composition from an oxy combustion plant burning natural gas, is taken from a report written at NTNU [7]. The flue gas composition for this case, from now on abbreviated NG3, is the result of oxy combustion of natural gas containing 0.25 percent hydrogen sulphide (H_2S). Temperature is given to be 130°C and the pressure is atmospheric (1.01 bar). The composition is shown in Table 2-6. Components in concentrations less than 1 ppm in the original composition are left out of the flue gas entering the compression and purification section.

Table 2-6: Composition oxy combustion, natural gas

Composition:	NG3:
CO_2	75,07 %
H_2O	15,03 %
N_2	3,16 %
O_2	1,88 %
Ar	4,83 %
SO_2	0,0163 %
H_2SO_4	0,00101 %
NO	0,0125 %

2.4. Quality recommendations pipeline

In the literature there are different recommendations for what quality needs to be achieved in order to store the CO_2. Some are based on experience from existing CO_2 pipelines, and others are developed specifically for capture from energy production with more focus on health and safety regulations. In 2005 the ENCAP project (Enhanced capture of CO_2), founded by the EU, published their recommendations covering three different scenarios for transport and storage [8]. The first scenario, called design case, covers the removal of major impurities for transport in pipelines at 100-150 bar and temperatures down to 0°C, following storage in a geological formation. The second scenario, EOR case, has stricter limits especially concerning water and sulphuric components. In addition, limits for the oxygen content have been included to prevent exothermic reactions at the storage site. As for the design case, transport is considered to be pipeline at 100-150 bar pressure and storage, like the name of the case implies, combined with EOR. The last scenario called the severe limit case, has recommendations based on ship transport combined with EOR and handling at places with strict HSE regulations (health, safety and environment). Compared to the EOR case, limits for water has been reduced significantly as well as the limits for components regarded as toxic. Recommendations for all the cases are shown in Table 2-7.

Table 2-7: ENCAP WP 1.1 Guidelines for concerned gases

Component:	Design case:	EOR case:	Severe limit case:
CO_2	> 90 %	> 90 %	> 95 %
H_2O	< 500 ppm	< 50 ppm	< 5 ppm
SO_2	From MB[1]	< 50 ppm	< 5 ppm
NO	From MB	From MB	< 5 ppm
H_2S	< 1,5 %	< 50 ppm	< 5 ppm
CO	Inerts lump	Inerts lump	< 5 ppm
Inerts lump	< 4 %	< 4 %	< 4 %
O_2	Inerts lump	100 ppm	100 ppm
HCN	From MB	From MB	5 ppm
COS	From MB	< 50 ppm	5 ppm
Mercaptans	From MB	< 50 ppm	10 ppm
NH_3	From MB	From MB	From MB
Hg	From MB	From MB	From MB

[1]Mass balance

The group of substances called mercaptans are all that have a functional chemical group made up of a sulphur atom and a hydrogen atom. This is the sulphur analogue of an alcohol group (OH) and such substances are also called thiols.

The second quality recommendations that are considered in this work are those developed by Sintef energy research's project Dynamis [1]. Dynamis used ENCAP's quality recommendations as a starting point, and then made their own assessment of the different components in question. Dynamis, however, only considered transport by pipeline. Their results suggest that the water limits can be raised for the case of EOR without risking formation of hydrates and precipitation of free water. On the other hand, limits for toxic components are lowered for the case corresponding to ENCAP's base case as a result of health and safety considerations. Their new limits are though less strict than for ENCAP's EOR case. Dynamis' quality recommendations are shown in Table 2-8.

Table 2-8: Quality recommendations Dynamis

Component:	Concentration:	Comment:
H_2O	*500 ppm*	*Technical: below solubility limit for H_2O in CO_2. No significant cross effects of H_2O and H_2S, cross effect of H_2O and CH_4 is significant but within limits for water solubility.*
H_2S	*200 ppm*	*Health and safety considerations.*
CO	*2000 ppm*	*Health and safety considerations.*
O_2	*Aquifer: non condensable gases, EOR 100-1000 ppm*	*Technical: range for EOR because of lack of practical experiments on effects of O_2 underground.*
CH_4	*Aquifer: non condensable gases, EOR < 2 %*	*As proposed by ENCAP.*
Non condensable gases[1]	*< 4 %*	*As proposed by ENCAP.*
SO_x	*100 ppm*	*Health and safety considerations.*
NO_x	*100 ppm*	*Health and safety considerations.*
CO_2	*> 95,5 %*	*Balanced with the other components.*

[1]Includes N_2, O_2, Ar, CH_4 and H_2.

2.5. Quality recommendations ship transport

Apart from ENCAP's guidelines for the severe limit case, no recommendations developed especially for ship transport of CO_2 captured from energy production, has been found in the literature. Recommendations for food grade CO_2 is specified by EIGA (European Industrial Gases Association) as in Table 2-9. Yara Praxair transports CO_2 of this quality by ship [9].

Table 2-9: EIGA specification, food grade CO_2

Component:	Specification:
CO_2	*99,9 %*
H_2O	*50 ppm*
O_2	*30 ppm*
CO	*10 ppm*
NH_3	*2,5 ppm*
NO/NO_2	*2,5 ppm each*
Non volatile residue	*10 ppm (weight)*
Non volatile organic residue	*5 ppm (weight)*
PH_3	*0,3 ppm*
Total volatile hydrocarbons	*50 ppm including 20 ppm non methane HC*
Acetaldehyde (CH_3CHO)	*0,2 ppm*
Benzene	*0,02 ppm*
Methanol	*10 ppm*
HCN	*0,5 ppm*
Total sulphur (as S) excluding SO_2	*0,1 ppm*
If total sulphur exceeds 0,1 ppm:	
SO_2	*1 ppm*
H_2S	*0,1 ppm*
COS	*0,1 ppm*

Most likely the main focus when developing these guidelines has been that the probability for negative influence on humans is minimized. Some of the components specified might not even be present in captured CO_2 from power plants, and if they are, it is not easy to say without testing how they would behave in an underground geological storage or used in EOR. Based on these recommendations it is however necessary to comment some of the specified limits in Encap's severe limit case.

Since CO_2 already is being liquefied and transported with the quality given in Table 2-9, the question arises what Encap's reason for the recommended water limit of 5 ppm is. Based on the limits for the EOR case this seems to be done because of liquefaction alone. For CO, it is hard to believe that a concentration as low as 5 ppm is necessary for liquefaction when 10 ppm is safe for human consumption, and CO is included in the inerts lump in Encap's own EOR recommendations.

When it comes to technical considerations regarding liquefaction of CO_2, according to Barrio et al. [10] liquid CO_2 should be stored and transported at around 6.5 bar and -52°C. One of the main concerns regarding water in the CO_2 is the formation of hydrates when the pressure rises and the temperature drops. Hegerland, Jørgensen and Pande [11] have extrapolated data for hydration formation in CO_2 and concluded that the water content should be reduced to 10 ppm. Compared to the EIGA limits this seems high since CO_2 is already being transported by ship containing up to 50 ppm of water. As long as the CO_2 purity is close to 99.9 %, a water content of 50 ppm is further regarded as being low enough not to cause problems when the CO_2 is transported by ship.

As long as substances present in the mixture which is to be liquefied does not cause problems for the liquefaction process, the technical aspect along with EOR recommendations is used as a limitation. No extra measures will be applied to meet Encap's severe limit case. The technical requirement for liquefied CO_2 will be that it is in fact totally liquefied at 6.5 bar and -52°C. Since this is close to the triple point of pure CO_2 (5.18 bar at −56.6 °C) the purity most likely will be very high, probably higher than the Encap severe case lower limit of 95 percent.

2.6. Methods for removal of unwanted substances

When both the compositions entering the CO_2-compression stage and recommended guidelines for CO_2 purity are known, it can be determined what means are necessary in terms of purifying the CO_2. Following is an overview of the abatement means considered for the different components that need to be reduced to meet recommended concentrations.

2.6.1.   Water

The majority of the water in the CO_2-rich gas exiting the capture process is removed by compression and flashing. Flashing involves extracting gas and liquid separately from a vessel were the mixture is, more or less, in phase equilibrium at the given temperature and pressure. Increasing the pressure through compression will shift this equilibrium in such a way that more liquid is precipitated from the gas mixture, the dew point decreases. The phase fraction of liquid and the composition of this liquid is dependent on, other than temperature and pressure, what substances are present in the gas.

An accurate prediction of the vapour liquid equilibrium (VLE) of a multi component mixture is very difficult since it will not only be dependent on the properties of the different components, but also on how the components interact. Simulation software uses numerical methods based on an equation of state to calculate the VLE. These numerical equations are modified versions of for instance the ideal gas law, which uses interaction parameters, usually based on empirical data, to account for the presence of more than one substance.
Even though the actual phase equilibrium is hard to predict, knowledge of the substances involved can give an idea of the resulting liquid phase. The most important properties are volatility and polarity. Of the major components present in the compositions given in sections

2.1, 2.2 and 2.3 (concentration of one percent or more in any of the compositions), at ambient temperature hydrogen is the most volatile, followed by nitrogen, argon, oxygen, carbon dioxide and water. Of these substances only water and carbon dioxide are polar (have a slight electrical charge).

The volatility of the different components suggests that the liquid phase extracted by flashing will be mainly water. However, the fact that both carbon dioxide and water are polar, suggests that removing water from CO_2-rich gas by means of flashing at ambient temperatures might not be sufficient. As seen from Figure 1, measurements show that this is in fact the case for a mixture of CO_2 and water. The solubility of water in gaseous CO_2 never drops below about 800 ppm. At around 55 bar, when the mixture approaches its dew point, the solubility rises rapidly and continues to rise after the mixture is fully condensed. The presence of non-polar substances more volatile than carbon dioxide will decrease the solubility, but it will also increase the dew point. All in all this implicates that for a CO_2-rich mixture, drying by flashing is limited to pressures below around 50 bar, and additional drying will be necessary.
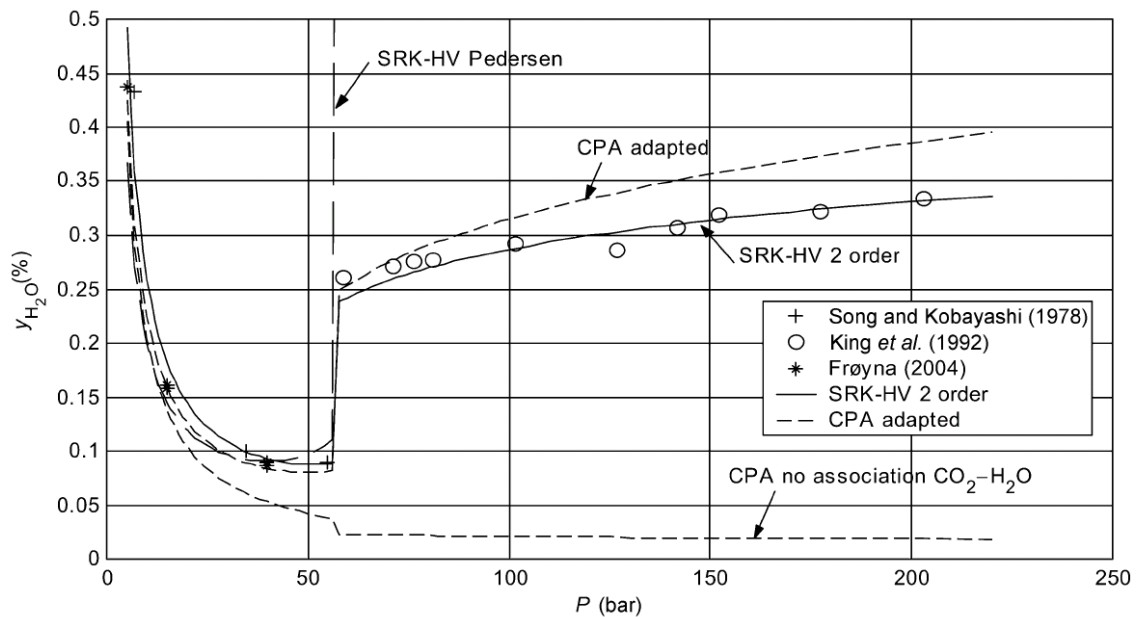
Figure 1: Solubility of water in CO₂ at 20°C [12]

In the gas industry, drying beyond flashing is usually done either by adsorption or absorption. Drying by adsorption is achieved in two different ways. The first is by using a bed containing small pellets with a rough surface. When the gas is lead through the bed, water adheres to the surface of these pellets. The second which is the one considered in this work is to use a so called molecular sieve (MSA). In a molecular sieve, a porous substance with a uniform size distribution of holes adsorbs molecules of a certain size. Substances with a pore size of 3 Angstroms ($3*10^{-10}$ m) will adsorb water and ammonia but not larger molecules [13]. There are no chemical reactions involved with the capture in adsorption processes, and adsorbents are usually regenerated only by using heat. According to NATCO [14], one of the large suppliers of equipment to the gas industry, a molecular sieve can reduce the concentration of water to below 1 ppm. A principal sketch for an adsorption process is shown in Figure 2.
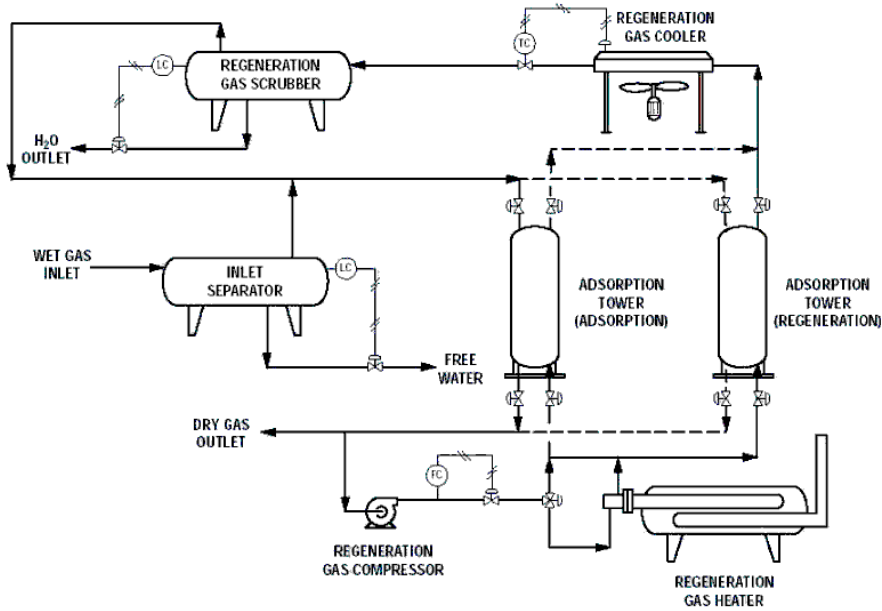
Figure 2: Adsorption process [14]

In an absorption process, the gas containing water will be led up through a column while a dehydrating solvent flows downward. The solvent binds the water by physical absorption; water is more soluble in the solvent than in other components of the gas mixture. The dried gas exits at the top of the column, while the solvent rich in water exits at the bottom. After depressurization to around atmospheric pressure, the solvent is regenerated by heating it and passing it through a regeneration column where the water is boiled off. The solvents used are different types of glycols, and the most common for dehydrating water at the relevant conditions is triethylene glycol or TEG. Depending on configuration a TEG unit can reduce water concentrations to below 10 ppm [15]. A principal sketch for the process is shown in Figure 3.
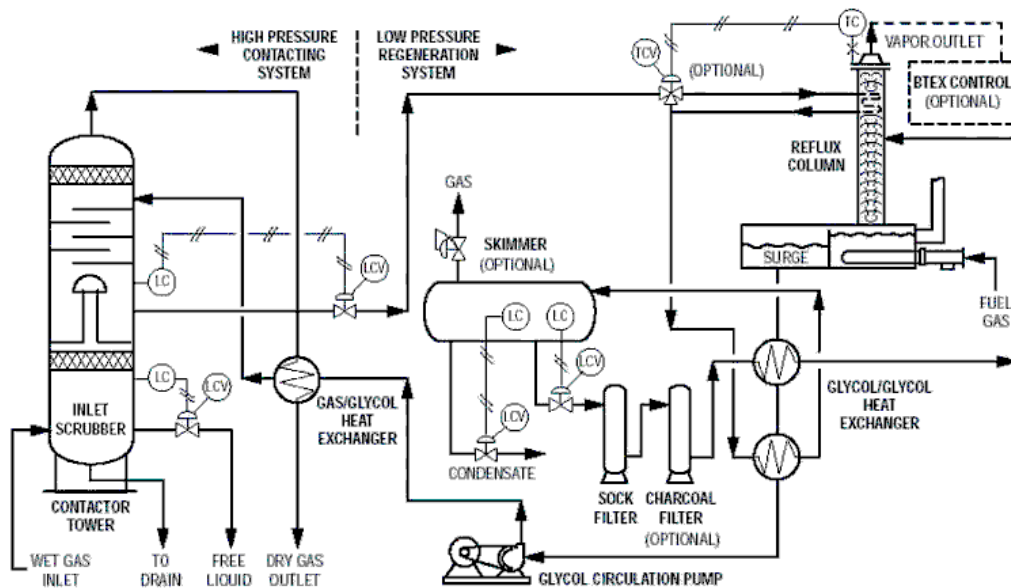
Figure 3: Glycol absorption process [15]

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2.6.2.   Hydrogen, carbon monoxide and hydrogen sulphide

In the case of pre combustion capture the CO_2-rich stream will contain hydrogen and carbon monoxide from the reforming process. If coal is used as fuel there will also be hydrogen sulphide present, and if natural gas is the fuel methane might be present. Reviewing Table 2-1 and Table 2-2 it is apparent that the necessity for removal of these substances is greater in the case of coal as the fuel. The common property for these substances is that they are combustible. It is therefore possible to remove them by including a combustion reactor, either thermal or catalytic.

Catalytic oxidation:
Since there are no oxygen present in the CO_2-rich streams from pre combustion (see Table 2-1 and Table 2-2), both thermal and catalytic oxidation will require using pure oxygen, partly purified oxygen from air or simply air. This may rule out the appliance of the CO_2 in EOR depending on how accurately the oxygen feed can be controlled. According to kohl and Nielsen [13], temperatures are typically over 650°C for thermal oxidation while catalytic oxidation can be carried out at around 320°C. The reaction of the combustibles will develop heat, but to keep the temperature at a level which can sustain the reaction, thermal oxidation will almost certainly need additional fuel since the concentration of the combustibles are rather low. If this is the case for catalytic oxidation will not be determined before the simulations are carried out. Either way, catalytic combustion is the only method considered in this work.

Normally catalytic combustion is not applied to gases with such high levels of CO_2 as for the pre combustion cases. It is therefore necessary to ensure that this will not inhibit the reaction of CO to CO_2. Given the temperature and the equilibrium constant for reaction (2.1), it is possible to calculate the equilibrium ratio between CO and CO_2 in the reaction products of the catalytic oxidizer. Based on an example and equilibrium constant data from a textbook on engineering thermodynamics [16], the equilibrium ratio of CO to CO_2 at 320°C is found to be 1.79 times 10^{-15}. Said in another way, if the concentration of CO_2 was 100 percent, the concentration of CO would be 1.79 times 10^{-15} percent. This means that the catalytic oxidation of CO will be limited by chemical kinetics, not by the concentration of CO_2.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad\qquad (2.1)$$

Catalytic oxidation is achieved by using a reaction vessel containing a metal catalyst which can have various shapes and configurations (see Kohl and Nielsen [13]). According to Kohl and Nielsen [13] the field of catalysis is extremely complex hence no effort has been made to go into the theory, but the effect is that the temperature needed to oxidize a combustible substance is lowered significantly. The metals used are usually from the platinum metal group which consists of platinum, palladium, rhodium, iridium, osmium and ruthenium [17]. For hydrogen, carbon monoxide and methane the reaction products if the combustion is complete will be CO_2 and water, none of which is a problem in this case. When H_2S is oxidized using oxygen or air, reaction (2.2) will occur.

$$H_2S + O_2 \rightarrow H_2O + SO_2 \qquad\qquad (2.2)$$

Again, the formation of water does not cause a problem, but the sulphur dioxide might. Depending on the catalyst, SO_2 may be oxidized to SO_3. For some catalyst applications SO_3

can cause problems [18]. However, no information has been found in the literature that suggests catalytic oxidation of H_2S in a CO_2 rich stream will degrade the catalyst.

The pre combustion cases do not contain any SO_2 initially. Reviewing Table 2-7 and Table 2-8 one can see that the recommended maximum concentrations for SO_2 are equal to or lower than those for H_2S. That means that if H_2S initially is present in concentrations higher than the recommended limits, catalytic oxidation using a PMG catalyst takes care of one problem only to cause another one. As can be seen from Table 2-1 and Table 2-2, this is the case when CO_2 and H_2S are captured together. For this case it is necessary to look at alternative ways to remove the H_2S.

Another method used to remove H_2S from natural gas, is by molecular sieve adsorption. As mentioned in section 2.6.1, molecular sieve adsorption using a pore diameter of 3 Angstroms will remove water and ammonia. If the pore diameter is increased to 4 Angstroms the molecular sieve will also adsorb H_2S, CO_2, SO_2 as well as some light hydrocarbons [13]. The obvious problem is that CO_2 also will be adsorbed. This is not necessarily because CO_2 will be lost (according to Kohl and Nielsen [13] H_2S is adsorbed more strongly than CO_2), but since the mixture is mainly CO_2, the operation time and capacity of the molecular sieve will most likely be reduced in such a manner that its use is not favourable.

Selective catalytic oxidation (H_2S):
A third way is to utilize metal oxide catalysts to selectively remove the H_2S. The general reaction is shown in equation (2.3).

$$MeO + H_2S \rightarrow MeS + H_2O \tag{2.3}$$

There are different metal oxides that may be used. Li, Yen and Shyu [19] have conducted experiments with mixtures of metal oxides of iron and antimony and of iron and tin. Depending on the ratio between the oxides in the catalyst and on the reactor temperature, they obtained 100 percent conversion with 100 percent selectivity for a gas mixture containing one percent H_2S, five percent O_2 and 94 percent N_2. The selectivity was calculated by subtracting the moles of SO_2 produced from the moles of H_2S reacted, divided by the moles of H_2S reacted. If this technology is commercialized it might solve the problem with the H_2S.

2.6.3. Sulphur dioxide

The cases of oxy combustion are the only ones in need of reduction of the SO_2 content (as long as H_2S concentrations above 200 ppm are reduced by selective oxidation). Since the limiting of sulphur emissions from power production became an issue, many methods of removing SO_2 from flue gas have been proposed and developed. To limit the scope of this work only two dedicated SO_2 removal processes are considered, mainly based on reported removal efficiencies. The first is the wet lime/limestone scrubbing process, and the other is an ammonium sulphate process. There are other processes that might prove themselves more feasible for oxy combustion power plants in the future. For an evaluation of flue gas desulfurization methods for oxy combustion plants, see the Encap report on the subject [20], and for an extensive overview of proposed processes both experimental and commercial see Kohl and Nielsen [13].

Wet lime/limestone scrubbing:
Here follows an overview of the process based on the description in Kohl and Nielsen [13]. In the wet lime/limestone process, the flue gas exiting the power plant is lead through a scrubber

where it is contacted with an aqueous slurry of lime (Ca(OH)$_2$) or limestone (CaCO$_3$). The process has three different modes of operation, forced oxidation, natural oxidation and inhibited oxidation. A schematic for the forced oxidation scrubber is shown in Figure 4. The difference between them is the end product. If the lime or limestone oxidizes naturally by consuming some of the oxygen in the flue gas, a mixture of calcium sulphate (CaSO$_4$) and calcium sulphite (CaSO$_3$) is formed. This is what is called natural oxidation. Due to potential operational problems this oxidation is either enhanced (forced oxidation) or inhibited (inhibited oxidation). If the oxidation is enhanced by bubbling air into the slurry, the ratio of calcium sulphate to calcium sulphite will increase. Hydrated calcium sulphate is the same as gypsum which is a saleable by product. The forced oxidation may be carried out in a separate vessel which is desirable for the oxy combustion process to prevent increased concentrations of nitrogen, oxygen and argon from the air used.
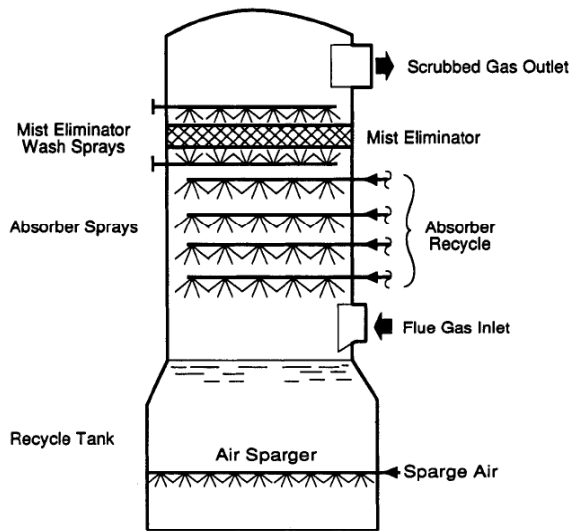
Figure 4: Lime/limestone scrubber, forced oxidation [13]

If the forced oxidation is carried out in a separate vessel, reactions (2.4) through (2.14) describes the basic chemistry of the process.

SO$_2$ dissolution:

$$SO_2(g) = SO_2(aq) \tag{2.4}$$

$$SO_2(aq) + H_2O \rightarrow H^+ + HSO_3^- \tag{2.5}$$

$$HSO_3^- \rightarrow H^+ + SO_3^{2-} \tag{2.6}$$

Lime dissolution:

$$Ca(OH)_2(s) \rightarrow Ca(OH)^+ + OH^- \tag{2.7}$$

$$Ca(OH)^+ \rightarrow Ca^{2+} + OH^- \tag{2.8}$$
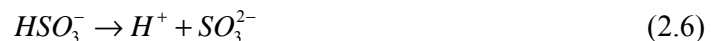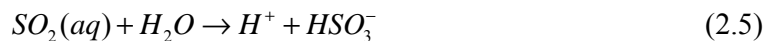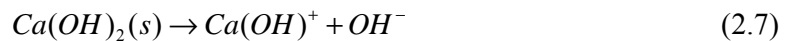
Limestone dissolution:

$$CaCO_3(aq) + H^+ \rightarrow Ca^{2+} + HCO_3^- \tag{2.9}$$

Reaction with dissolved SO$_2$:

$$Ca^{2+} + HSO_3^- \rightarrow CaSO_3(aq) + H^+ \tag{2.10}$$

$$Ca^{2+} + SO_3^{2-} \rightarrow CaSO_3(aq) \tag{2.11}$$
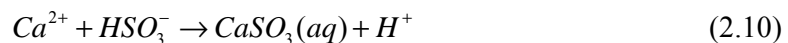
Liberation of CO_2 (limestone):

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$ (2.12)

$$HCO_3^- + H^+ \rightarrow H_2CO_3(aq)$$ (2.13)

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O$$ (2.14)

According to kohl and Nielsen [13] limestone is the process most widely used due to economics (1997). However, since CO_2 is liberated in the process it is important to look at the consequences of scrubbing a CO_2-rich gas. Regarding the dissolution of SO_2 it does not appear to be affected directly by the dissolution of CO_2, since SO_2 and CO_2 form different solutes. Indirectly, an increased partial pressure of CO_2 will drive reaction (2.14) to the left affecting the pH of the solution. This in turn will affect the dissolution of SO_2 and reaction with dissolved limestone. Adjusting the pH with additives may counteract this effect. The issue will not be pursued further in this work. However, experiments should be conducted on the dissolution of SO_2 from CO_2-rich streams, to try to confirm or rule out the application of limestone for oxy combustion processes.

Ammonium sulphate process:
As for the lime/limestone process this overview is based on description of the process in Kohl and Nielsen [13]. The ammonium sulphate process uses ammonia to scrub the inlet gas and produces ammonium sulphate ((NH_4)$_2SO_3$) which is a fertilizer. The process uses commercially available wet lime/limestone equipment, and has the potential of lower scrubbing cost depending on the market for ammonium sulphate and the cost of ammonia. In a report by the Encap project from 2004, it is claimed that there is an excess of ammonium sulphate in industrialized countries from other sources. Anyways, the process have been operated on pilot plants demonstrating high removal efficiencies for high flue gas SO_2 concentrations (>99 % with SO_2 inlet concentrations up to 6100 ppm) [13].

Seemingly there are two main concerns regarding application to an oxy combustion CO_2 capture process. The first is that the process according to Kohl and Nielsen [13] is run with in situ forced oxidation. That means that the oxidation using air takes place in the same vessel as the scrubbing of the flue gas. This might increase the content of nitrogen, oxygen and argon in the CO_2-rich gas, increasing the energy required and/or the size of equipment for purification. On the upside the strong affinity of ammonia for SO_2 can result in more compact equipment with low liquid to gas ratios. The lower liquid to gas ratio might also decrease the needed amount of air for oxidation.

A second concern is that the high volatility of ammonia can lead to ammonia concentrations in the scrubbed gas. This concentration, labelled "ammonia slip" was reported to be less than 3 ppm at the pilot plant described in Kohl and Nielsen [13]. Reviewing section 2.6.1 on water removal one realize that molecular sieves probably could take care of the problem. A pore diameter of 3 Angstroms adsorbs both water and ammonia. Since at least 800 ppm of water would have to be adsorbed, the added need for adsorbing 3 ppm of ammonia most likely would not increase the operation cost connected to regeneration of the molecular sieve.

2.6.4. Nitrogen oxides, NO_x

High temperature combustion with nitrogen present will result in the formation of nitrogen oxides, mainly nitrogen monoxide. Developments in gas turbine technology have reduced NO_x emissions but post combustion removal of NO_x is still considered in this work to meet

CO_2 purity recommendations. In operation today the methods most widely used are selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). SCR uses ammonia and SNCR either ammonia or urea ($(NH_2)_2CO$) reacting with nitrogen oxides downstream the gas turbine to form nitrogen and oxygen. Reaction with urea will also produce CO_2. This is not necessarily a problem (ref. oxidation of CO in section 2.6.2) nevertheless, only the use of SCR is considered in this work. In combination with the ammonium sulphate process for SO_2 removal, the joint use of ammonia might prove beneficial.

The reactions taking place are the same for SCR and SNCR, the difference is at what temperature the reactions are carried out. Typical temperatures are 900-1100°C for SNCR and 300-400°C for SCR [13]. The chemistry of the process is described by reaction (2.15) to (2.18) [13].

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (2.15)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad (2.16)$$

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad (2.17)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \qquad (2.18)$$
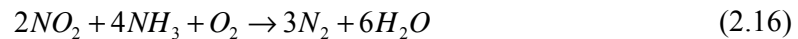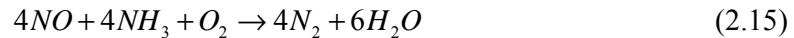
As for the ammonium sulphate process ammonia slip might occur. According to Kohl and Nielsen [13], concentrations higher than 10-15 ppm can lead to the formation of ammonium bisulfate ($(NH_3)HSO_4$) in the low temperature regions of the heat recovery steam generator (HRSG). This salt deposits on the walls and heat transfer surfaces of the HRSG which reduces the heat transfer and increases pressure drop. Proper design of the SCR unit can prevent this from occurring. Figure 5 illustrates the relationship between the feed ammonia to NO_x molar ratio, removal efficiency and unreacted ammonia based on a NO_x inlet concentration of 350 ppm and a reactor temperature of 350°C.

Looking at Table 2-5 and Table 2-8, one can see that a removal efficiency of about 75 percent is sufficient for CO_2 derived from oxy combustion of coal to meet Dynamis' purity recommendations. The concentration of NO_x is initially 410 ppm. Assuming Figure 5 applies, a molar feed ratio of ammonia to NO_x equal to one should give an ammonia slip somewhere in the range of 2-5 ppm. The NO concentration is significantly larger than the NO_2 concentration and NO is a volatile gas that will be partly removed along with other volatile gases later in the process. This might reduce the required SCR removal efficiency even more, suggesting that the problem of salt deposition in the HRSG can be limited and maybe avoided completely. Ammonia exiting the HRSG can be removed by the use of a molecular sieve and possibly also utilization of the ammonium sulphate process.
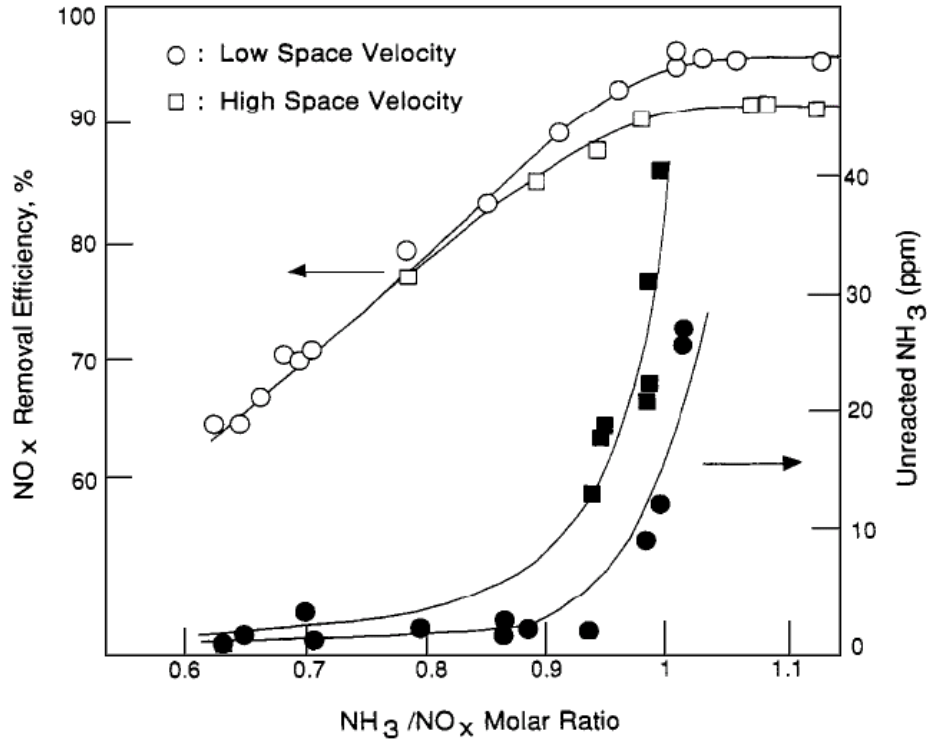
Figure 5: Realtionship between removal efficiency, molar feed rate and unreacted ammonia for SCR [13]

2.6.5. Combined removal of SO_2 and NO_x

Since the content of both SO_2 and NO_x must be reduced from oxy combustion derived CO_2, combined capture is desirable. Several processes have been proposed and the Electric Power Research Institute (EPRI) in the USA has previously performed a technical evaluation of some of the suggested processes. Most of them are in need of either auxiliary power or supplementary firing [21]. A process not included in the mentioned evaluation done by EPRI but suggested by White et al. [22] however, does not. The process they are suggesting used, is based on a process for the production of sulphuric acid called the lead chamber process. They claim this process also will remove any mercury present. This is the only combined SO_2/NO_x-process considered in this work.

The lead chamber process uses NO_x as a catalyst for oxidation of SO_2 to SO_3 which in turn reacts with water to form sulphuric acid (H_2SO_4). Simplified, the process can be described by reaction (2.19) to (2.21) [23].

$$NO + \frac{1}{2}O_2 \rightarrow NO_2 \tag{2.19}$$

$$SO_2 + NO_2 \rightarrow SO_3 + NO \tag{2.20}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{2.21}$$

In the original process the NO is recycled and used again. In the process suggested by White et al. [22], NO_x is further reacted to nitric acid (HNO_3). This step can be described by reaction (2.19) and (2.22).

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \tag{2.22}$$

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In addition to these reactions a gaseous reaction will also occur producing nitric acid (not mentioned in White et al. [22]). This reaction is given in (2.23).

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3 \qquad (2.23)$$
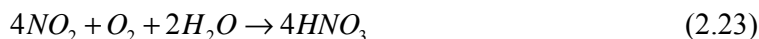
White et al. [22] suggests carrying out the process in two steps with compression between the first and second step. This is based on the fact that the rate of reaction for reaction (2.19) increases with increasing pressure (at a constant temperature), and that little or no nitric acid will be formed before practically all the SO_2 is reacted. The latter is based on that reaction (2.20) is much faster than reaction (2.22). In the chambers where the reactions are carried out, purified gas will exit at the top while acid is drained from the bottom. There has not been found any information that can help predict the chances of sulphuric and nitric acid dissolved in the gas exiting the chambers. This is not considered in the paper by White et al. and no means of removing the acids beyond draining from the chambers are mentioned. Investigations to evaluate the simulation tool Pro/II's ability to accurately predict acid dissolved in vapour has not lead to any conclusions. White et al. [22] have conducted experiments on a test rig, but the results published does not say anything regarding this matter. The subject has to stay unresolved until they publish more results.

In this work the whole process will be carried out at the same pressure, and both sulphuric and nitric acid removed prior to introducing the gas stream to any other equipment. Nitric acid is highly corrosive and it is assumed that a compressor most likely would be damaged from prolonged exposure to it. Confining the process to a single pressure level is justified if there is even the slightest chance that this might happen. Since the reactions governing the sulphuric acid production all have reactants equal to or higher in number than its products, their reaction rates will stay the same or increase with increasing pressure. The chambers will therefore be placed at the highest pressure prior to drying in the deigned process.

2.6.6.   Nitrogen, oxygen, argon and other volatile gases

All the considered compositions for captured CO_2 contain substances more volatile than CO_2 to some extent, from now on called only volatiles. The compositions for oxy combustion derived CO_2 are the only ones in need of volatiles removal to meet the common requirement of less then four percent total "non condensable" gases. The other compositions might need removal of volatiles to achieve liquefaction at the given specification for temperature and pressure of liquefied CO_2 (see section 2.5). In general there are two different ways of removing non combustible volatiles. The first is by cooling and flashing in two stages. Cooling is achieved by expanding purified CO_2 and removed volatiles through valves, decreasing the temperature. The second is by using a distillation column where the cooling is achieved by using an external cooling circuit.

Two stage flashing:
A principal sketch for the configuration of a two stage flashing process is shown in Figure 6. The dried CO_2 stream in need of volatiles removal enters as a gas at the left of the figure. Then it is cooled and partly condensed through the first heat exchanger before gas and liquid is separated at phase equilibrium (not necessarily achieved fully in practise). The extracted liquid phase, leaner in volatiles, is expanded through a valve, decreasing in temperature. After expansion it is lead back through the first heat exchanger cooling the incoming gaseous CO_2-

rich stream. Depending on how much heat is transferred the liquid is partly or fully evaporated.

Gas exiting at the top of the first flash is cooled through the second heat exchanger, partly condensing. Once again the partly condensed mixture is flashed, resulting in a gas phase comprising of volatiles with some CO_2 exiting at the top, and a liquid phase, more pure in CO_2 exiting at the bottom. The gaseous phase is expanded and used to cool the incoming gas in both heat exchangers. The liquid phase is first used to cool the incoming stream in the second heat exchanger once. Then it is expanded through a valve and lead through the second heat exchanger a second time providing additional cooling before it finally is used to cool the incoming gas in the first heat exchanger.
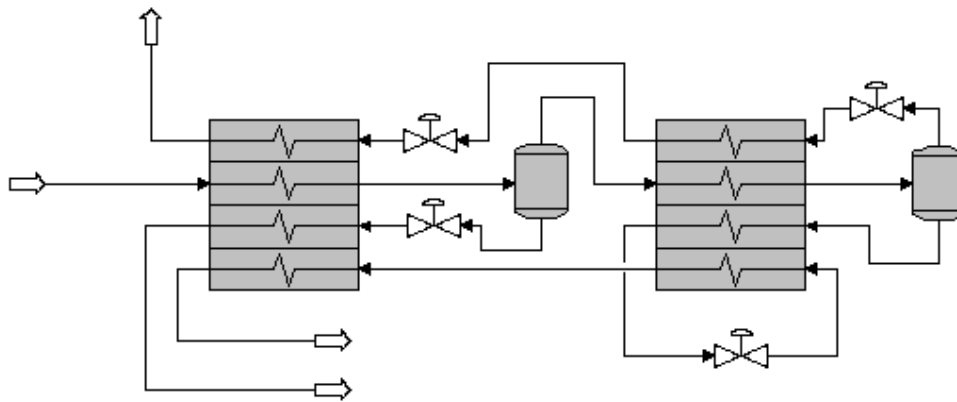
.
Figure 6: Volatiles removal by two stage flashing

At a given inlet pressure the purification performance of this configuration is dependent mainly on the magnitude of the pressure drops through the valves, and the size of the heat transfer surfaces in the heat exchangers. When the gas first starts condensing, the liquid phase will be very pure CO_2, given components less volatile than CO_2 is removed to a certain degree. A further decrease in temperature will decrease the CO_2-concentration, but also the amount of CO_2 exiting with the volatile components. This means that purity decreases when the capture rate increases. Increasing the size of the heat transfer surfaces will allow for a smaller pinch temperature difference. The pinch temperature difference is the smallest temperature difference at which heat transfer can occur between the cold and the hot stream. A low pinch temperature increases the required temperature for the cold stream hence decreasing the needed pressure drop across the valves. This will in turn lower the amount of energy needed for the final compression to the required pipeline pressure.

Distillation:
A principal sketch of a distillation column is shown in Figure 7. The basic principle for the distillation column is that vapour will rise upwards while liquid will drain downwards. Of the liquid exiting at the bottom some is vaporized and led back into the column and some exits as the bottom product. The opposite happens at the top. Some of the vapour exiting at the top is condensed and returned to the column while the rest exits as gaseous top product. In the case of volatiles removal from CO_2 the product CO_2 will exit as the bottom product and volatiles as the top product.

The column consists of several trays apart from the reboiler and the condenser. Each tray is in reality a flash, gas and liquid are in phase equilibrium. Since the temperature obviously is

higher in the reboiler, it will decrease up through the column. The results is that of the vapour exiting the reboiler, more and more condenses up through the column until only the lightest substances remain. For the liquid entering from the condenser the opposite is the case, more and more liquid vaporizes until only the heaviest substances are left as liquid.
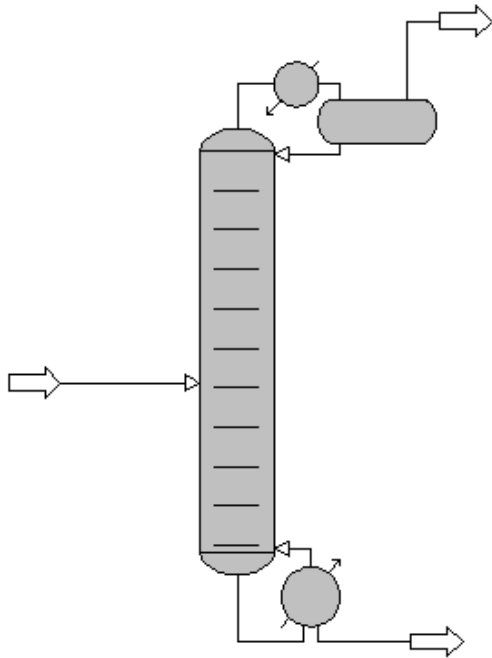
Figure 7: Simple distillation column with reboiler and condenser

An important thing to know when designing distillation columns is how the column parameters affect the column properties like duty, product purity and capture rate. Assuming that a change in the parameters does not change compositions in the column, the mechanisms can be described as given in Table 2-1. This assumption is only valid for infinitesimal changes in the parameters, but the table still gives an indication of how distillation columns work. From the table one can for instance see that an increase in both purity and capture rate will increase the duty for both the reboiler and the condenser. In practise a change in one parameter will affect all properties of the column.

Table 2-10: Influence of column parameters on important column properties

Parameter:	Purity:	Capture rate:	Reboiler duty:	Condenser duty:
$T_{reboiler}$ increases:	Increases	Constant	Increases	Increases
$T_{condenser}$ increases:	Constant	Decreases	Decreases	Decreases
Feed tray number increases:	Constant	Constant	Decreases	Increases
Number of trays increases:	Constant	Constant	Decreases	Decreases

Additional removal of oxygen:
If the processed CO_2 is intended to be used in enhanced oil recovery (EOR) the concentration of oxygen has to be less than 1000 ppm (Dynamis) or even less than 100 ppm (Encap). Since oxygen is the less volatile of the three main volatiles (nitrogen, oxygen and argon), oxygen removal giving a concentration of 100 ppm will probably remove most of the nitrogen and argon as well. This will mean a very high purity and hence high condenser and reboiler duties. The fact that the reboiler needs heat added, suggests that the reboiler duty will not be a

problem since it operates at a temperature below ambient (can be heated by for instance spent cooling water).

The condenser needs heat removed. From Table 2-10 one can see that if the reboiler temperature increases to increase the purity, the temperature of the condenser must be decreased to keep the capture rate constant. The minimum work per duty obtainable is given by the Carnot cycle efficiency in equation (2.24) where W_c is the minimum work for the cooling process, Q is the heat removed, T_h is the temperature where the heat is discharged (fixed by the cooling water temperature) and T_c is the temperature at which the cooling medium absorbs heat. From the equation one can see that a decrease in temperature increases the work required per heat removed.

$$\frac{W_c}{Q} = \frac{T_h - T_c}{T_c} = \frac{T_h}{T_c} - 1 \qquad\qquad (2.24)$$

Since the demand for low concentrations of oxygen for EOR probably will result in a high energy penalty, it is necessary to consider other means of removing oxygen. One alternative may be catalytic deoxygenation [20]. This will imply adding fuel to catalytically react with the oxygen. Since the oxygen levels at the end of the catalytic reactor will be very low (100 ppm), fuels other than hydrogen is expected to form substances typically associated with incomplete combustion. Taking into account that the initial concentration of oxygen to be reduced is several percent, the resulting concentrations of these substances may cause problems. The tolerance for unreacted hydrogen is given by the concentration of other "non condensable" gases, as the maximum total concentration of these is limited to 4 percent.

Looking at the given compositions (see next section) oxygen removal is only relevant for oxy combustion. Since hydrogen is not available from the process, catalytic deoxygenation will involve purchasing hydrogen from some gas supplier. This will increase operational costs. High initial concentrations will also lead to high reactor temperatures if more or less all the oxygen is consumed by burning hydrogen. Without pursuing these concerns any further, the decision is made not to apply catalytic deoxygenation for oxygen removal in this work.

3. Implementing cases

After reviewing the literature, the compositions to be used in the different cases have been established. Guidelines for the target compositions have also been found, though not unambiguous ones. The inlet compositions for the different cases are summarized in tables 10, 11 and 12.

Table 3-1: Conditions pre combustion capture

Condition:	C1a:	C1b:	NG1:
Pressure:	0,8 bar	0,8 bar	1 bar
Temperature:	49°C	49°C	45.3°C
Composition:			
CO_2	92,17 %	97,69%	90,2 %
CO	0,03 %	0,19 %	8,8 ppm
CH_4	0 %	0 %	16 ppm
H_2O	6,56 %	0,28 %	9,6 %
H_2	0,72 %	1,74 %	0,11 %
H_2S	0,49 %	0,01 %	0 %
N_2	0,03 %	0,06 %	532 ppm
Ar	0,00 %	0,03 %	0 %
MDEA	0 %	0 %	9,6 ppm
MEA	0 %	0 %	140 ppm

Table 3-2: Conditions post combustion capture

Condition:	C2:	NG2:
Pressure:	1,5 bar	1,48 bar
Temperature:	37,8°C	37,8°C
Composition:		
CO2	93,2 %	95,5 %
H2O	6,62 %	4,48 %
N2	0,17 %	167,84 ppm
O2	0,01 %	0 %

Table 3-3: Conditions oxy combustion

Condition:	C3:	NG3:
Pressure:	1,02 bar	1.01 bar
Temperature:	35°C	130°C
Composition:		
CO_2	71,46 %	75,07 %
H_2O	5,62 %	15,03 %
N_2	14,34 %	3,16 %
O_2	5,88 %	1,88 %
Ar	2,31 %	4,83 %
NO	0,04 %	0,0125 %
NO_2	0,001 %	0 %
SO_2	0,35 %	0,0163 %
H_2SO_4	0 %	0,00101 %

There are different software that can be used to simulate compression, drying and purification of captured CO_2. Of the ones available for this work, Pro/II from SIMCI was used due to its selection of equations of state (EoS). An equation of state is necessary to be able to efficiently compute the behaviour of multi component mixtures. The starting point for most equations of state is the ideal gas law which then is modified in different ways to better calculate properties of real gas mixtures. Depending on what approach is used, the EoS' accuracy is different for different types of mixtures. To figure out which EoS of the ones available in Pro/II that works

best for the gas compositions from CO_2 capture, comparisons has to be made with experimental data.

3.1. Choice of equation of state

The experimental data of interest when testing EoS' are from measurements of the vapour-liquid equilibrium of mixtures. These measurements will give a certain composition in the vapour and liquid phase of a mixture at a given pressure and temperature. The data available in the literature are limited both in numbers and in extent of the composition of the examined mixture. Two sources were found and used to evaluate the EoS'. The first is experimental data for a mixture of CO_2 and H_2O [24], and the second for a mixture of CO_2 and CH_4 and a mixture of CO_2 and N_2 [25]. Comparison with these measurements will give an indication of the EoS' fit to real conditions in two more or less separate stages in the process.

In the first stage of the process the CO_2 mixture is compressed, cooled and flashed in several stages, were flashing is a term for the process of extracting gas and liquid separately from a vessel where the mixture is in phase equilibrium. After eventual initial cooling the mixture is compressed. Then it is cooled in the compressor intercooler and flashed at the temperature given from the intercooler exit. Vapour is led to the next compression stage and the process is repeated. Drying past the first step is possible due to the fact that an increase in pressure increases the dew point of the mixture. Since virtually all the relevant substances are more volatile than water, water will be the main constituent of the liquid rejected in this part of the process. The most important feature of the EoS will therefore be its ability to accurately calculate the distribution of water in the two phases at the potential flashing conditions.

After the first stage of the process the substances remaining in significant concentrations will be the ones more volatile than water. In conventional combustion processes these will typically be nitrogen, oxygen and argon. This is the case for an oxy combustion process. For pre combustion processes, concentrations of nitrogen, oxygen and argon are usually lower since the CO_2 is removed prior to combustion, which is where these gases are introduced to the process for the first time (an exception is autothermal reforming which uses air or oxygen in the reforming of the hydrocarbon fuel). However, a pre combustion process may give methane and/or hydrogen gas in the captured CO_2. Post combustion processes may also have low concentrations of nitrogen, oxygen and argon depending on the selectivity of the CO_2 absorption process.

In the second part of the process, the water concentration is at a level where cooling by ambient water no longer will result in a water rich liquid phase. This part consists of compression to the final pipeline pressure, and eventually removal of volatile gases. From an EoS point of view, the effect of different EoS' will be the greatest if the stage includes phase equilibrium calculations. Removal of volatile gases is carried out by partly condensation of the mixture. Since CO_2 is the less volatile substance, this will give an increased concentration of CO_2 in the liquid phase and an increased concentration of volatiles in the vapour phase compared to the mixture prior to condensation. The necessary cooling can be achieved either by internal cooling, or external cooling. An external cooling circuit may for instance be a cascade refrigeration cycle where gases are condensed at different pressures and temperatures to extract heat from the CO_2 mixture. The desired EoS will be the one that most accurately calculates the phase equilibrium for a mixture of CO_2 and more volatile gases.

To compare the results from the use of different EoS' in Pro/II to the experimental data, a flow sheet with one flash for each EoS were build. The mixtures involved were then flashed at the temperatures and pressures given from the measurements. Of the 17 available ordinary EoS' in Pro/II, two lacked parameters necessary to carry out calculations for the substances involved. Ten of the EoS' are based on either Peng-Robinson (PR) or Soave-Redlich-Kwong (SRK). These two cubic equations are given from equation (3.1) by setting $u = 2$ and $w = -1$ for PR and $u = 1$ and $w = 0$ for SRK. Of the other variables P is pressure, R is the universal gas constant, T is temperature, v is specific volume and a and b are parameters determined by a mixing rule.

$$P = RT/(v-b) - a(T)/(v^2 + ubv + wb^2) \qquad (3.1)$$

A mixing rule is an equation that accounts for the presence of more than one component in a mixture, and also for the interaction between the different components. Besides whether the EoS' are based on PR or SRK, the mixing rules are what sets them apart. Five of the EoS', uses different equations than equation (3.1) (information is included in the Pro/II help section).

The first data series the EoS' were compared to was the one with CO_2 and H_2O. In this series, the liquid concentration of CO_2 and the vapour concentration of H_2O are given for different pressures at five different temperatures. The average of the deviation for the different pressures (absolute value) is given at each temperature in Table 3-4. From the table one can see that apart from BWRS most of the EoS' have deviations in more or less the same range for the vapour concentration of H_2O. In the liquid phase however, several of the EoS' have large deviations from the measured CO_2 concentration. Based on the data for the liquid phase only SRKK (SRK-Karbadi-Danner), SRKM (SRK-Modified Panagiotopoulos-Reid), SRKS (SRK-SIMCI), HEX (Hexamer) and PRM (PR-Modified Panagiotopoulos-Reid) are suited for use on mixtures comprising of mostly water and CO_2.

Table 3-4: EoS deviations from experimental data CO_2-H_2O

	Deviation from measured data in absolute value (%):									
Conc.:	x_{CO2}					y_{H2O}				
T (K):	278,22	288,26	298,28	308,20	318,23	278,22	288,26	298,28	308,21	318,22
EoS:										
SRK	99,85	99,73	99,55	99,28	98,90	30,31	17,64	8,10	1,88	12,95
SRKK	**36,63**	**24,27**	**14,78**	**3,22**	**7,17**	**29,62**	**16,86**	**8,29**	**1,80**	**13,47**
SRKH	1585,24	NLP[1]	1940,87	2106,41	2169,10	25,40	NLP	8,49	8,28	6,01
SRKP	99,85	99,72	99,54	99,26	98,87	30,25	18,94	8,02	4,29	10,54
SRKM	**6,17**	**4,83**	**3,68**	**4,23**	**5,83**	**30,49**	**19,64**	**8,64**	**5,87**	**9,55**
SRKS	**11,80**	**13,27**	**14,16**	**13,55**	**12,93**	**22,78**	**9,35**	**10,97**	**9,84**	**19,70**
HEX	**11,80**	**13,27**	**14,16**	**13,56**	**12,93**	**22,78**	**9,35**	**10,97**	**9,84**	**19,70**
PR	99,79	99,63	99,40	99,04	98,53	27,65	17,27	8,12	4,13	10,52
PRH	1607,67	NLP	1979,22	2152,76	2225,09	25,89	NLP	8,54	8,37	5,93
PRP	99,79	99,62	98,27	96,11	98,51	31,52	20,25	8,70	5,98	9,47
PRM	**6,03**	**6,13**	**9,80**	**9,21**	**8,92**	**32,94**	**23,37**	**10,96**	**10,56**	**5,97**
BWRS	2873,01	3117,40	3467,62	3906,40	4723,33	73,64	67,86	66,33	55,47	53,55
LKP	98,37	97,40	95,77	94,49	92,29	7,31	9,09	18,22	10,76	21,75
UNIW	1612,69	NLP	NLP	NLP	NLP	25,33	NLP	NLP	NLP	NLP
TBC	96,00	94,05	91,96	89,11	85,84	35,13	25,74	12,62	13,62	5,81

[1]NLP = No liquid phase at one or more of the pressures at the given temperature

The reason some of the EoS' are this inaccurate is probably because their mixing rules aren't capable of handling polar substances well (H_2O is polar). Since several of the other substances are polar, one of the five EoS' mentioned should be used. Among the five, the overall differences between them are minor in the vapour phase while SRKM is unquestionably the

best at calculating the liquid phase. SRKM is hence chosen as the equation of state for the first part of the process.

The second data series give both liquid and vapour concentration of CH_4 in a mixture of CO_2 and CH_4 for different pressures at 3 different temperatures, 219.26 K, 240 K and 270 K. At 240 K and 2.104 MPa the experimental data gives a liquid phase with 3.28 percent CH_4 however, none of the EoS' calculates a liquid phase at all below about 2.91 MPa. At 270 K the EoS' do not calculate any liquid phase at any of the pressures given in the experimental data. One possible reason is that the liquid fraction is smaller than the error tolerance in Pro/II, but it is still important to be observant about the flashing of light gases at temperatures above 240 K and pressures below 3 MPa. For CH_4 this is not a concern since the only composition including CH_4 is the one for natural gas pre combustion with a concentration of 16 ppm, but this still might be an indication for how the EoS' perform when it comes to light, non-polar gases. The deviations at the different temperatures and pressures are given in Table 3-5.

The agreement with the experimental data is quite good except for SRKH (Huron-Vidal), PRH (Huron-Vidal), BWRS (Benedict-Webb-Rubin-Starling), UNIWAALS and TBS (Twu-Bluck-Coon) which have large deviations in the liquid phase. It is easy to see that the deviation in the calculated liquid concentration decreases with decreasing pressure and temperature, emphasising the importance of being observant regarding flashing when light gases are involved. Unlike the first case, the differences between the EoS' are very small; in fact four of them give exactly the same results. These four, SRKP, SRKM, SRKS and HEX, are also the ones with the overall best results. The reason why their results are the same is probably because some of the interaction parameters in the mixing rules become inactive for mixtures without interaction between polar substances, and that the remaining parameters are equal for some of the EoS'. SRK and SRKK also give identical results apart from the calculation at 219.26 K and 3.861 MPa.

Table 3-5: EoS deviations from experimental data CO_2-CH_4

	Deviation from measured data in absolute value (%):											
T (K):	**219,26**						**240**					
Conc.:	x_{CH4}			y_{CH4}			x_{CH4}			y_{CH4}		
P (MPa):	**1,398**	**2,432**	**3,861**	**1,398**	**2,432**	**3,861**	**3,059**	**4,089**	**5,198**	**3,059**	**4,089**	**5,198**
EoS:												
SRK	15,04	11,87	3,48	0,99	0,86	0,51	7,62	5,63	2,51	0,12	0,30	0,43
SRKK	15,04	11,87	2,08	0,99	0,86	0,51	7,62	5,63	2,51	0,12	0,30	0,43
SRKH	233,04	196,39	133,39	5,86	5,86	6,11	143,10	121,22	95,56	8,51	8,60	9,02
SRKP	13,57	10,24	1,61	0,82	0,76	0,42	5,39	2,97	-0,53	0,60	0,56	0,58
SRKM	13,57	10,24	1,61	0,82	0,76	0,42	5,39	2,97	-0,53	0,60	0,56	0,58
SRKS	13,57	10,24	1,61	0,82	0,76	0,42	5,39	2,97	-0,53	0,60	0,56	0,58
HEX	13,57	10,24	1,61	0,82	0,76	0,42	5,39	2,97	-0,53	0,60	0,56	0,58
PR	17,99	13,97	4,99	1,26	0,86	0,38	8,80	6,08	2,36	0,58	0,40	0,29
PRH	240,71	200,58	135,05	6,54	6,08	6,15	144,55	121,75	95,23	8,28	8,25	8,58
PRP	15,04	12,69	6,66	1,37	0,79	0,23	6,04	4,33	1,93	0,19	0,00	-0,14
PRM	16,52	12,46	3,12	1,43	0,90	0,38	6,31	3,57	-0,39	0,25	0,12	0,03
BWRS	120,35	95,58	60,17	5,20	4,15	3,70	59,00	46,16	31,73	5,45	4,94	4,78
LKP	11,80	11,99	11,96	1,70	1,22	0,79	5,52	5,10	4,24	2,03	1,83	1,83
UNIW	232,15	194,41	131,51	6,52	6,11	6,22	139,82	118,10	92,77	8,55	8,55	8,92
TBC	142,77	234,81	NLP[1]	3,21	4,73	NLP	163,86	NLP	NLP	6,57	NLP	NLP

[1]NLP = No liquid phase

The last data series have measurements for the vapour-liquid equilibrium for a mixture of CO_2 and H_2O at 220 and 240 K and a range of pressures. The results are given for both the vapour and liquid concentration of N_2. As for the case with CH_4, the EoS' failed to calculate a liquid

phase for some of the conditions given in the experimental data. At 240 K, the first data point in the measurements is at 2.1 MPa, whereas the EoS' fail to calculate a liquid phase at pressures lower than about 3.2 MPa. Again, this might be because of tolerances in Pro/II, but it still calls for caution regarding calculations. Because of significantly different trends in the deviation for the liquid concentration compared to the vapour concentration, the two is tabulated in separate tables. For reasons that will become apparent, the deviation itself is tabulated instead of the absolute value of the deviation. The results for vapour and liquid are shown in Table 3-6 and Table 3-7 respectively.

Table 3-6: EoS deviations in vapour phase from experimental data CO_2-N_2

	Deviation in y_{N2} from measured data (%):							
T (K):	**220**				**240**			
P (MPa):	**1,509**	**3,075**	**4,595**	**6,313**	**3,208**	**4,089**	**5,674**	**6,262**
EoS:								
SRK	*1,18*	*0,18*	*0,01*	*0,00*	*0,41*	*0,12*	*0,15*	*0,30*
SRKK	*1,18*	*0,18*	*0,01*	*0,00*	*0,41*	*0,12*	*0,15*	*0,30*
SRKH	*1,41*	*0,03*	*-0,35*	*-0,62*	*1,53*	*0,73*	*0,20*	*0,15*
SRKP	*1,07*	*0,20*	*0,14*	*0,27*	*0,95*	*0,61*	*0,76*	*0,97*
SRKM	*1,07*	*0,20*	*0,14*	*0,27*	*0,95*	*0,61*	*0,76*	*0,97*
SRKS	*1,07*	*0,20*	*0,14*	*0,27*	*0,95*	*0,61*	*0,76*	*0,97*
HEX	*1,07*	*0,20*	*0,14*	*0,27*	*0,95*	*0,61*	*0,76*	*0,97*
PR	*1,38*	*0,03*	*-0,25*	*-0,37*	*0,74*	*0,12*	*-0,14*	*-0,07*
PRH	*2,17*	*0,30*	*-0,24*	*-0,68*	*1,75*	*0,83*	*0,11*	*-0,01*
PRP	*1,58*	*0,09*	*-0,24*	*-0,40*	*0,62*	*0,02*	*-0,27*	*-0,24*
PRM	*1,58*	*0,09*	*-0,24*	*-0,40*	*-0,25*	*0,02*	*-0,27*	*-0,24*
BWRS	*3,95*	*2,17*	*1,99*	*2,12*	*3,86*	*3,14*	*2,97*	*3,11*
LKP	*2,70*	*1,35*	*1,10*	*1,05*	*3,61*	*3,04*	*2,86*	*2,97*
UNIW	*2,25*	*0,46*	*0,01*	*-0,30*	*2,10*	*1,24*	*0,65*	*0,60*
TBC	*1,14*	*0,40*	*0,50*	*-91,94*	*1,20*	*1,05*	*NLP[1]*	*NLP*

[1]NLP = No liquid phase

There is not much to say about the results from the vapour phase else than that they are remarkably accurate for about all of the EoS'. Again one can see that SRKP, SRKM, SRKS and HEX calculate the same concentrations as well as SRK and SRKK.

Table 3-7: EoS deviations in liquid phase from experimental data CO_2-N_2

	Deviation in x_{N2} from measured data (%):							
T (K):	**220**				**240**			
P (MPa):	**1,509**	**3,075**	**4,595**	**6,313**	**3,208**	**4,089**	**5,674**	**6,262**
EoS:								
SRK	*9,85*	*10,22*	*8,15*	*6,46*	*7,49*	*6,83*	*5,31*	*5,37*
SRKK	*9,85*	*10,22*	*8,15*	*6,46*	*7,49*	*6,83*	*5,31*	*5,37*
SRKH	*151,52*	*148,90*	*141,43*	*135,22*	*106,51*	*103,96*	*98,50*	*97,73*
SRKP	*-9,85*	*-9,94*	*-12,15*	*-14,04*	*-14,66*	*-15,42*	*-17,30*	*-17,42*
SRKM	*-9,85*	*-9,94*	*-12,15*	*-14,04*	*-14,66*	*-15,42*	*-17,30*	*-17,42*
SRKS	*-9,85*	*-9,94*	*-12,15*	*-14,04*	*-14,66*	*-15,42*	*-17,30*	*-17,42*
HEX	*-9,85*	*-9,94*	*-12,15*	*-14,04*	*-14,66*	*-15,42*	*-17,30*	*-17,42*
PR	*13,64*	*12,98*	*10,48*	*8,27*	*9,45*	*8,37*	*6,27*	*6,09*
PRH	*185,61*	*180,11*	*170,38*	*161,83*	*134,53*	*130,62*	*123,57*	*122,43*
PRP	*21,97*	*21,27*	*18,80*	*16,53*	*17,92*	*17,18*	*15,12*	*15,04*
PRM	*21,97*	*21,27*	*18,80*	*16,53*	*17,92*	*17,18*	*15,12*	*15,04*
BWRS	*87,12*	*73,48*	*59,90*	*48,02*	*35,83*	*30,84*	*22,75*	*20,64*
LKP	*8,33*	*8,56*	*7,32*	*6,80*	*6,84*	*6,17*	*4,77*	*4,89*
UNIW	*164,39*	*160,77*	*152,91*	*146,21*	*118,24*	*115,20*	*109,26*	*108,47*
TBC	*-16,67*	*-8,01*	*4,66*	*835,22*	*-12,05*	*-4,19*	*NLP[1]*	*NLP*

[1]NLP = No liquid phase

The results for the liquid phase are a bit more interesting though. As is the case with CH_4, the Huron-Vidal versions of SRK and PR together with BWRS, UNIW and TBC, do not seem to

be able to calculate the liquid phase accurately. Also, SRK and SRKK give equal results and the same is the case for SRKP, SRKM, SRKS and HEX. As for methane, the accuracy decreases with decreasing pressure and temperature. The interesting part is that while the concentrations calculated by the SRK and SRKK are a bit too big, the concentrations calculated from SRKP, SRKM, SRKS and HEX are a bit small. Positive deviations for one EoS and negative for another has occurred for other measurements, but not as a general trend for an entire series. Also, the difference between these concentrations seems fairly constant with pressure variations at a given temperature.

What is interesting to find out, is what effect a positive or negative deviation in the calculated liquid fraction of nitrogen, yields on important process parameters like CO_2-concentration and capture rate. To do that, it is necessary to look at the phase balance given in equation (3.2) where x is liquid concentration, y is vapour concentration, X is the phase fraction of liquid and Y the phase fraction of vapour.

$$(x_{CO_2} + x_{N_2}) \cdot X + (y_{CO_2} + y_{N_2}) \cdot Y = 1 \qquad (3.2)$$

In case of a negative deviation, the calculated liquid fraction of nitrogen, x_{N2} is too low compared to the one measured, but as seen in Table 3-6, the calculated vapour fraction is more or less correct. This implicates that the phase fraction of the vapour phase, which we know is richer in nitrogen since it is more volatile, in reality is smaller than the calculated one. In turn, this means that the liquid phase in reality will have a larger concentration of nitrogen, but also a larger total amount of CO_2. Ultimately, the real liquid phase, which represents the captured CO_2, will have a lower concentration of CO_2 than the one calculated, but a larger flow rate of CO_2, hence a larger overall capture rate. The opposite is the case if the deviation in the calculated liquid fraction of nitrogen is positive.

If the trends seen for nitrogen also exist for other volatile gases, in majority oxygen and argon, SRK and SRKK will overestimate the total concentration of volatile gases in the captured CO_2, while SRKP, SRKM, SRKS and HEX will underestimate it. The physical solution will then lie somewhere in between. If then the volatiles are flashed off at 220 K (~-53°C) and 3,075 MPa (~31 bar), the exact solution may be estimated with an accuracy of 10 %, with respect to the volatiles removal process. However, nothing certain can be said about how, and how accurate, the EoS' calculate CO_2-O_2 or CO_2-Ar mixtures since no vapour-liquid equilibrium data for such mixtures has been found. It is still advantageous to use both an EoS that underestimates, and one that overestimates the liquid concentration of nitrogen when simulating cases involving volatile substances.

Finally, when it comes down to which EoS' will be used SRK-Modified Panagiotopoulos-Reid (SRKM) will be applied to all cases. Since this EoS underestimates the liquid fraction for nitrogen in CO_2-N_2-mixtures an EoS which overestimates the same liquid fraction will also be applied in cases that involve volatile gases. Based on its performance in the cases for carbon dioxide mixed with methane and water respectively, SRK-Karbadi-Danner (SRKK) is the one selected.

3.2. Assumptions

Before the different cases can be built, assumptions have to be established for the components involved.

Delivery conditions CO$_2$:
According to a Dynamis report (a project of Sintef Energy Research) [3], the required delivery pressure is 110 bar. Depending on the temperature, pure CO$_2$ will be in either supercritical or liquid phase (critical point at 31.1°C and 72.05 bar).

Efficiency compressors and pumps:
Depending on the purity of the processed CO$_2$, the last part of the CO$_2$ compression might be done by pumping. Other parts of the process might also utilize pumps. Compressors are most likely only needed for compression of the captured CO$_2$. Based on data taken from the Dynamis report [3], the polytropic efficiencies for the compressors and pumps are set according to Table 3-8.

Table 3-8: Polytropic efficiencies compressors

Inlet pressure range:	Polytropic efficiency:
1-10 bara	*85 %*
8-35 bara	*80 %*
20-80 bara	*75 %*
40-110 bara	*70 %*
Pumps	*75 %*

Outlet temperature constraint compressors:
To avoid damage to the compressors it is important that the outlet temperature in operation does not get too high. The reason is to protect the oil seal system. If buffer gas is used, the outlet temperature may be as high as 220°C, but usually it is limited to 180°C [26]. For the simulations in Pro/II, 180°C is used as the constraint for compressor outlet temperature.

Intercoolers:
For cooling of the gas exiting the compressors, the assumption is made that sea water at a temperature of 12°C is available. To avoid disturbing the biology of the area where the used cooling water is released back into the sea a maximum release temperature of 22°C is selected. Since relatively large amounts of cooling water are used in the power plant itself (condenser in the steam cycle), it is assumed that the cooling water for the CO$_2$ compression will not need its own pumps. The pressure drop on the water side of the intercoolers is therefore not considered. It is further assumed that cooled gas exiting from the compressor intercoolers has a temperature of 22°C. The limiting temperature difference, the temperature pinch, is defined by the outlet temperatures to be 10°C. The pressure drop on the gas side of the intercoolers is set to 3 percent of the inlet pressure.

When setting the intercooler gas outlet temperature to 22°C, the result is that all the flashing of the captured CO$_2$ to remove water will happen at that temperature. The comparison between the EoS' and experimental data, for a mixture of carbon dioxide and water, showed that the gas phase deviations at 25°C (298 K) vary considerably with pressure. For the chosen EoS, SRKM, the most extreme variation is from a deviation of -11.41 percent at around 15 bar to 18.81 percent at around 25 bar. Considering the average absolute value of the deviation, it is still the second best of the EoS' that calculates the liquid phase fairly accurate as well. The EoS with the smallest deviation in the vapour phase, SRKK, has a deviation four times as high for calculations in the liquid phase. SRKM is therefore kept as the main EoS, but care

must be taken when considering the water content after the initial compression and drying, especially if no other means of drying is utilized.

Heat exchangers:
For heat exchangers that transfers heat between two different streams in the process, a minimal internal temperature approach is set based on the temperature pinch of the compressor intercoolers. This involves assuming a constant ratio between the temperature pinch and the outlet temperature on the hot side in Kelvin. The reason why this is done is to reflect a similar heat transfer coefficient for the heat transfer surfaces of the heat exchangers hence a consistent technology level [27]. With a temperature pinch of 10°C and a hot side outlet temperature of 22°C (295.15 K), this ratio is 0.0339. Where the temperature pinch must be set manually, the pinch is rounded to the nearest half degree. As for the intercooler hot side, the pressure drop on either side of these heat exchangers is set to three percent of the inlet pressure.

If the case includes a volatile removal process, two multiple stream heat exchangers will be used in the case of internal cooling. In these heat exchangers several cold flows will receive heat from one or more hot flows. Each flow runs through its own cell. These cells are designed with a pressure drop of one percent. If the same approach as for the other heat exchangers is used, these heat exchangers will have a temperature pinch somewhere in the range of 6.5-9°C (hot side outlet temperature between -75 and -20°C). Since the temperature pinch is limiting for the performance of this purification method, it is assumed that a temperature pinch of 5°C for both heat exchangers is justifiable in terms of investment cost versus energy penalty.

Pressure drop in various equipment:
The pressure drop in equipment used in gas purification is dependent on gas velocities and the size of the equipment; it will increase with the gas velocity and decrease with increasing size of the equipment. Vendors usually design equipment based on the maximum pressure drop wanted. No vendors have been contacted in this work, but the literature gives some idea of what pressure drops to expect. The assumptions made are based on data from Kohl and Nielsen [13] and Lee et al. [28].

The pressure drop is set to 0.02 bar per tray for all columns, 0.02 bar for catalytic oxidizers, 0.05 bar for the reactors in the modified lead chamber process (regarded as scrubbers) and 0.6 bar for molecular sieves. The latter is a maximum pressure drop to avoid bed crushing if MSA is applied to gases of elevated pressures. Finally it is assumed that the pressure given for the compositions in section 3 is after any scrubbers (ammonium sulphate, lime and limestone), and that the pressure drops in these are compensated for by flue gas fans.

Removal efficiency and additive consumption for purification equipment:
For sulphur dioxide, removal efficiency is set to 99 percent for lime/limestone [29], 99 percent for the ammonium sulphate process (see section 2.6.3) and 98 percent for the modified lead chamber process [22]. For nitrogen oxides, the removal efficiency is set to 90 percent for both SCR [13] and the modified lead chamber process [22]. Consumption of additives for the different removal methods are given in Table 3-9.

Table 3-9: Consumption of additives

Method:	Additive:	Ratio:	Reference:
SCR	*Ammonia (NH₃)*	*1,00 mol/mol$_{rem}$*[1]	*Figure 5*
Ammonium sulphate	*Ammonia (NH₃)*	*0,53 kg/kg$_{rem}$*	[13]
Lime scrubbing	*Lime (CaO)*	*1,02 kg/kg$_{rem}$*	[13]
Limestone scrubbing	*Limestone (CaCO₃)*	*1,83 kg/kg$_{rem}$*	[13]

[1]Affects ammonia slip and may have to be lower in practise

Conversion efficiency catalytic oxidation:

Based on data from Kohl and Nielsen [13] the catalytic conversion efficiency is set to 99 percent for carbon monoxide. Since the equilibrium constant for reaction (3.3) is similar to the one of reaction (2.1) [16] and the catalytic ignition temperature is lower [13, 30], the catalytic conversion efficiency is set to 99 percent for hydrogen as well.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad (3.3)$$

The selective catalytic conversion efficiency for hydrogen sulphide is set to 99 percent at a temperature of 240°C [19]. Calculations performed suggest that the equilibrium constant for equation (2.2) is larger than the one for equation (2.1) at the relevant temperatures. Regarding catalytic ignition temperature Kovalenko et al. [31] have conducted experiments where H_2S was catalytically combusted with oxygen at around 200°C. However, to be on the safe side the conversion efficiency for H_2S in non-selective catalytic oxidizers is set to 90 percent.

TEG reboiler and TEG circulation rate:

The boiling point of TEG at atmospheric pressure is 288°C [32]. Because TEG starts decomposing at lower temperatures, the operating temperature of the reboiler in the TEG regeneration column is typically set to 204°C [14]. According to Carroll [32] it is not recommended to use lower circulation rates of TEG than 17 litres of TEG per kg of water entering the contactor.

External cooling circuits:

For the liquefaction process, external cooling is needed to remove heat in condensers and heat exchangers. To limit the scope of this work no attempt to design these circuits will be made. It is still necessary to estimate the needed energy input for these processes. One way to do this is to assume an efficiency for the cooling process relative to an ideal Carnot cycle. The Carnot cycle efficiency for cooling, gives the theoretical smallest work needed to transfer a given amount of heat from a reservoir with a temperature T_c to a reservoir with a higher temperature T_h. This work is given in equation (2.24) but is repeated in equation (3.4).

$$W_c = Q \cdot \frac{T_h - T_c}{T_c} \qquad (3.4)$$

According to Jacob Stang at Sintef [27] the efficiency relative to the work given in (3.4) can be assumed as 60 percent when the cooling medium absorbs heat by boiling. This will be the case if a pure substance like ammonia, propane or ethane is used as the cooling medium. The work related to external cooling circuits is then given by the expression in equation (3.5). Further, T_h is defined by the cooling water temperature plus the reference temperature pinch,

and T_c as the hot side outlet temperature minus the corresponding temperature pinch (see under "heat exchangers" earlier in this section).

$$W_c = Q \cdot \frac{T_h - T_c}{\eta_{rel} \cdot T_c} = Q \cdot \frac{T_h - T_c}{0,6 \cdot T_c} \qquad (3.5)$$

4. Simulation of the cases

Given the assumptions, the compositions and the recommendations for CO_2-purity, the cases can be simulated to discover what it takes in terms of equipment and energy input to meet the given specifications. The way this is done is to use the basic case of compression and flashing only as a starting point, and then alter the configuration and equipment involved to increase the purity. For some of the cases involving chemical reactions, simplifications are made if some of the involved substances are missing from the Pro/II component library. The overall reactions will be the same.

4.1. Pre combustion capture from coal

4.1.1.   Compression and flashing, case C1a_0

The process consists of four compressors with intercoolers and flashes, and a pump. After the four stages of compression, the mixture is liquefied and pumped to the delivery pressure of 110 bar. The flow diagram is shown in Figure A-1 in Appendix A. The resulting key parameters for the process and the composition of the effluent stream, is given in Table 4-1.

Table 4-1: Results C1a_0

Parameter:	Result:
Total work [kJ/kgCO$_2$]	*370,78*
Total work [kWh/tonCO$_2$]	*102,99*
Cooling water consumption [kgH$_2$O/kgCO$_2$]	*15,92*
CO$_2$out/CO$_2$in [%]	*99,99*
Composition:	
CO2	*98,52 %*
H2O	*1195 ppm*
N2	*321 ppm*
CO	*321 ppm*
H2	*7697 ppm*
H2S	*5236 ppm*

Looking at the results one can see that the amount CO_2 lost in the compression process is minimal. This is good, especially since the capture rate for the pre combustion process itself is 85 percent (see section 2.1). Further it is seen, by comparing the concentrations to Table 2-7, that the H_2O concentration is the only one that is too high to meet the basic underground storage requirements. To remove the water down to an acceptable level, a TEG unit will be applied.

4.1.2.   Adding of a TEG column, case C1a_1

The process consists of four compressors with intercoolers as for case C1a_0. The difference is that after the third intercooler, the gas enters the contact column of the TEG unit. In addition, prior to the third intercooler a heat exchanger is added to partly vaporize the TEG exiting at the bottom of the contact column. The contact column itself, consist of five theoretical trays. The reclamation column is made up of eight theoretical trays in addition to a reboiler and a condenser. The stream exiting at the top of the reclamation column is cooled and flashed to recycle some of the CO_2 lost. For the entire TEG unit a numerical method especially made for glycol was used to ensure the calculations were as accurate as possible. See Figure A-2 in Appendix A for the flow sheet of the process.

The simulation was first done with the minimum recommended circulation ratio of TEG and a reboiler temperature of 150°C. The reboiler temperature was then increased to 204°C and the circulation ratio of TEG increased, if needed, to give a final water concentration of 45 ppm. Results from both cases are shown in Table 4-2. The amount of heat removed from the condenser of the reclamation column is not included in the table since it may be cooled using a small fraction of the spent cooling water.

Table 4-2: Results C1a_1

Parameter:	Max H_2O	Min H_2O
Total work [kJ/kgCO$_2$]	374,32	374,39
Total work [kWh/tonCO$_2$]	103,98	104,00
Duty TEG reboiler [kJ/kgCO$_2$]	1,28	1,65
Circulation ratio TEG [L/kgH$_2$O$_{removed}$]	19,79	20,16
Water removed using TEG [kg/tonCO$_2$]	0,4	0,5
TEG lost	0,0082 %	0,0088%
Cooling water consumption [kgH$_2$O/kgCO$_2$]	16,02	16,03
CO$_2$out/CO$_2$in [%]	99,99	99,99
Composition:		
CO2	98,63 %	98,64 %
H2O	144 ppm	45 ppm
N2	321 ppm	321 ppm
CO	321 ppm	321 ppm
H2	7705 ppm	7706 ppm
H2S	5242 ppm	5242 ppm
TEG	> 1 ppm	> 1 ppm

This composition meets Encap's recommended basic quality for underground storage. To meet any requirements set by Dynamis, or EOR requirements set by Encap the H_2S concentration must be reduced.

4.1.3. Adding of catalytic oxidizers, case C1a_2

To remove H_2S in order to fulfil stricter recommendations, a selective catalytic oxidizer is added. Since the oxidizer will produce heat at elevated temperatures this is combined with the adding of a general catalytic oxidizer to remove CO and H_2 as well, the latter to reduce compression work and increase purity. The process is based on the process with TEG drying. There are no components in Pro/II that can simulate the selective catalytic oxidizer. This is solved by redefining a stream with the same properties as the stream entering the reactor apart from that the flow rate of H_2S is reduced by 99 percent. In the reaction taking place (see equation (2.3)) one molecule of water is produced per molecule of H_2S reacted. The molar flow rate of water is hence redefined with an increase equal in magnitude to the decrease in the molar flow rate of H_2S. The catalytic oxidizer is modelled by a Gibbs reactor which operates by trying to minimize the total Gibbs free energy of the mixture entering the reactor. Reactions are limited by the conversion efficiencies given in section 3.2. The hot stream exiting the catalytic oxidizer is used to preheat the stream entering the selective catalytic oxidizer for H_2S to 240°C.

When the simulation is first run, the recirculation of CO_2 from the TEG unit will lead to a slightly altered inlet composition for the reactor. Running the simulation a couple more times, adjusting the composition slightly every time takes care of this problem. The flow diagram is shown in Figure A-3 in Appendix A. The ordinary catalytic oxidizer needs oxygen to convert

the combustibles. Not knowing how the use of pure oxygen will affect operating cost, the process will be simulated using both pure oxygen and air. The results are shown in Table 4-3.

Table 4-3: Case C1a_2

Parameter:	Oxygen	Air
Total work [kJ/kgCO$_2$]	373,35	385,47
Total work [kWh/tonCO$_2$]	103,71	107,08
Duty TEG reboiler [kJ/kgCO$_2$]	2,00	1,72
Circulation ratio TEG [L/kgH$_2$O$_{removed}$]	30,94	24,46
Water removed using TEG [kg/tonCO$_2$]	0,5	0,5
TEG lost	0,0047 %	0,0068 %
Oxygen consumption [kg/tonCO$_2$]	3,1	3,1 (air)
Cooling water consumption [kgH$_2$O/kgCO$_2$]	17,34	17,50
CO$_2$out/CO$_2$in [%]	99,99	99,99
Composition:		
CO2	99,94 %	98,38 %
H2O	45 ppm	45 ppm
N2	325 ppm	1,58 %
O$_2$	100 ppm	100 ppm
Ar	-	198 ppm
CO	3 ppm	3 ppm
H2	78 ppm	77 ppm
H2S	5 ppm	5 ppm
SO$_3$	7 ppm	6 ppm
TEG	> 1 ppm	> 1 ppm

Both by using pure oxygen and air the resulting composition qualifies for the use in EOR according to both Dynamis and Encap. However, this is given that the oxidant feed can be controlled to give an outlet concentration of 100 ppm. It has not been investigated whether it is possible to control the feed rate that precisely or not. A concentration of 1000 ppm would still satisfy Dynamis' quality recommendations for EOR. If it is not, only applying the selective catalytic reactor would satisfy EOR recommendations but the total work would be higher.

The temperature exiting the catalytic oxidizer is around 280°C in both cases. Recommended outlet temperatures however are usually as high as 540°C [13]. There is a possibility that additional heating is required, but one must remember that the selective catalytic oxidizer for H$_2$S will develop heat. How much is hard to say since neither the reactions involved, nor the enthalpy of formation for all the relevant substances are explicitly known. According to the catalytic ignition temperatures of hydrogen and carbon dioxide (see section 3.2) the temperature should be sufficient to sustain the reaction.

4.1.4.   Liquefaction, case C1a_3

The required purity to liquefy the mixture at 6.5 bar and -52°C is very high hence the energy input required will also be high. As a consequence, using air in the catalytic oxidizer to cut costs makes no sense in this case if the increased cost of removing nitrogen is higher. The case of catalytic oxidation with pure oxygen is therefore the only option considered here.

In the liquefaction process the purified stream exiting from the TEG contactor is first condensed in a heat exchanger using an external cooling circuit. The required outlet temperature for the mixture to be fully condensed is dependent on composition and pressure. After the initial cooling, the stream is depressurized through a valve. This decreases the

temperature and partly vaporizes the mixture. The CO_2 concentration in the liquid phase will at this point be very high. Next, the stream is mixed with liquid exiting at the bottom of a distillation column. The mixture is then cooled and further condensed in the reboiler which actually acts as a condenser. The liquid exiting as bottom product is finally depressurized and cooled to the final state of 6.5 bar and -52°C. The flow diagram for the process is shown in Figure A-4 in Appendix A. Both condensers in the column use external cooling circuits.

Regarding the water content it must be assured that precipitation of water will not lead to formation of ice or hydrates in the process. Since water is less soluble in gaseous CO_2 than in liquid CO_2 (see section 2.6.1) precipitation of water is most likely to occur when gaseous streams are cooled. In the liquefaction case this will be limited to the initial condensing of the mixture coming from the TEG unit. TEG residue in the gas leaving the drying process might inhibit formation of ice and hydrates. Glycol injection is used in gas extraction for this purpose. In regular operation 60 to 80 weight percent of glycol compared to water will inhibit free water formation.

The TEG unit is placed at a pressure around 30 bar dependent on the optimization of pressure ratios for the first three compressors. Tests performed show that with a TEG residue concentration of 0.2 ppm and a pressure of 25 bar, a liquid phase consisting of mainly water and TEG will precipitate from the gaseous stream for water concentrations higher than about 50 ppm. The weight percent of TEG in the resulting liquid phase is more than 60 percent. Thus ice or hydrates will most likely not form in the process but this matter should be investigated further. To be on the safe side a molecular sieve could be used instead of TEG, but in this work the process is kept as it is to limit time consumption and also the number of cases.

For reasons explained in section 3.1 this case will be simulated with two different equations of state. In addition to the one used so far, SRKM, the equation of state called SRKK will also be used. From the evaluation of these equations it is expected that SRKK will result in a higher energy demand. This is because at a given state, it calculates a higher concentration of nitrogen in the liquid phase than SRKM (low temperatures). The results from the simulations are given in Table 4-4. The performance parameters specified for the distillation column is the flow rate of CO_2 in the product and the CO_2 concentration in the product. The magnitude of the flow rate is determined by a tolerance of decrease in overall capture rate of 0.1 percent. The value for the CO_2 concentration is optimized to give the lowest work per kg stored CO_2 with the constraint that the stream is fully condensed at the end state.

Table 4-4: Case C1a_3

Parameter:	SRKM:	SRKK:
Total work [kJ/kgCO$_2$]	502,92	506,09
Total work [kWh/tonCO$_2$]	139,70	140,58
Work liquefaction [kJ/kgCO$_2$]		
Initial condensing [kJ/kgCO$_2$]	81,78	80,28
Column "reboiler" [kJ/kgCO$_2$]	19,80	24,36
Column condenser [kJ/kgCO$_2$]	3,10	2,74
Final liquefier [kJ/kgCO$_2$]	20,22	20,70
Total [kJ/kgCO$_2$]	**124,92**	**128,09**
Increase from C1a_2	34,70 %	35,55 %
Composition:		
CO$_2$	99,97 %	99,97 %
H$_2$O	45 ppm	45 ppm
N$_2$	162 ppm	187 ppm
O$_2$	69 ppm	74 ppm
CO	2 ppm	2 ppm
H$_2$	19 ppm	30 ppm
H$_2$S	5 ppm	5 ppm
SO$_3$	7 ppm	7 ppm
TEG	> 1 ppm	> 1 ppm

Comparing the results for SRKM and SRKK it is seen that the difference in required specific work is less than one percent. Comparing the results to Table 2-7 and Table 2-8 it is clear that the purity needed to liquefy the CO$_2$ is so high for both SRKM and SRKK that all quality recommendations except Encap's severe limit case will be met. It is also apparent that the work for the liquefaction itself and not the increased purification is the main contributor to the increased specific work. On the water issue, though not displayed with the results the TEG concentration entering the initial condenser is 0.24 ppm and free water should accordingly not be formed.

4.1.5.   Compression and flashing, case C1b_0

The second composition considered for pre combustion capture from a coal fired power plant, is the result of separate capture of CO$_2$ and H$_2$S. This will greatly reduce the need for removal of H$_2$S. As for C1a the starting point is compression and water removal by flashing only. The resulting process is identical to the one in section 4.1.1. (flow diagram given in Figure A-1 in Appendix A). Results are given in Table 4-5.

Table 4-5: Results C1b_0

Parameter:	Result:
Total work [kJ/kgCO$_2$]	376,29
Total work [kWh/tonCO$_2$]	104,53
Cooling water consumption [kgH$_2$O/kgCO$_2$]	14,37
CO$_2$out/CO$_2$in [%]	99,99
Composition:	
CO2	97,86 %
H2O	1084 ppm
N2	601 ppm
Ar	301 ppm
CO	1903 ppm
H2	1,74 %
H2S	100 ppm

When comparing the results to the guidelines in Table 2-7 and Table 2-8, one can see that apart from the water content, the composition of the processed CO_2 meets Encap's guidelines for storage in aquifers and Dynamis' guidelines for both aquifers and use in EOR. As for C1a_0 the amount of CO_2 lost in the process is practically nothing. To remove more water a TEG unit is added.

4.1.6. Adding of a TEG column, case C1b_1

Again, the process is identical to the one in section 4.1.2. The flow sheet for the process is shown in Figure A-2 in Appendix A. The results are shown in Table 4-6.

Table 4-6: Results C1b_1

Parameter:	Max H_2O	Min H_2O
Total work [kJ/kgCO$_2$]	379,45	379,48
Total work [kWh/tonCO$_2$]	105,40	105,41
Duty TEG reboiler [kJ/kgCO$_2$]	1,22	1,52
Circulation ratio TEG [L/kgH$_2$O$_{removed}$]	19,66	17,97
Water removed using TEG [kg/tonCO$_2$]	0,4	0,4
TEG lost [%]	0,0101	0,0119
Cooling water consumption [kgH$_2$O/kgCO$_2$]	14,46	14,46
CO$_2$out/CO$_2$in [%]	99,99	99,99
Composition:		
CO2	97,95 %	97,96 %
H2O	131 ppm	43 ppm
N2	602 ppm	602 ppm
Ar	301 ppm	301 ppm
CO	1905 ppm	1905 ppm
H2	1,74 %	1,74 %
H2S	100 ppm	100 ppm
TEG	> 1 ppm	> 1 ppm

As expected, the composition is now suited for aquifer storage according to Encap, and both aquifer storage and use in EOR according to Dynamis. Considering Encap's recommendations for EOR regarding H_2S and the fact that the hydrogen content must be reduced to liquefy the CO_2, a catalytic oxidizer will be added.

4.1.7. Adding a catalytic oxidizer, case C1b_2

As for C1a_2 both pure oxygen and air will be used in the catalytic oxidizer. The case using air will most likely fulfil the most stringent recommendations for EOR. Using pure oxygen the resulting stream should be suited for liquefaction. Both cases have the same configuration shown in Figure A-5 in Appendix A.

The stream entering the catalytic oxidizer is preheated using the hot stream exiting the same unit. If the preheated stream is fed directly to the reactor the simulation will fail to converge. As for case C1a_2 the stream entering the reactor must be redefined. An iterative simulation is performed until the temperature and composition exiting the pre heater is equal to the one redefined in the stream entering the catalytic oxidizer. After the hot gas exits the pre heater it is still hot enough to deliver heat to the reboiler of the TEG reclamation column. A heat exchanger with an exit temperature defined by the reboiler exit temperature and the corresponding temperature pinch is added. The resulting duty of this heat exchanger is subtracted from the required reboiler heat duty. The results are shown in Table 4-7.

Table 4-7: Results C1b_2

Parameter:	Oxygen	Air
Total work [kJ/kgCO$_2$]	373,98	398,98
Total work [kWh/tonCO$_2$]	103,88	110,83
Duty TEG reboiler [kJ/kgCO$_2$]	-22,69	-39,30
Circulation ratio TEG [L/kgH$_2$O$_{removed}$]	22,35	18,02
Water removed using TEG [kg/tonCO$_2$]	0,5	0,4
TEG lost [%]	0,0078	0,0119
Oxygen consumption [kg/tonCO$_2$]	7,8	7,3 (air)
Cooling water consumption [kgH$_2$O/kgCO$_2$]	16,80	16,75
CO$_2$out/CO$_2$in [%]	99,99	99,99
Composition:		
CO2	99,87 %	96,23 %
H2O	45 ppm	43 ppm
N2	612 ppm	3,65 %
O$_2$	100 ppm	100 ppm
Ar	306 ppm	755 ppm
CO	19 ppm	19 ppm
H2	178 ppm	171 ppm
H2S	10 ppm	10 ppm
SO$_2$	2 ppm	2 ppm
SO$_3$	69 ppm	68 ppm
TEG	> 1 ppm	> 1 ppm

The resulting compositions are suitable for EOR both according to Dynamis and Encap. There is however some uncertainty regarding Encap's recommended limit for sulphur dioxides. With no reactions specified for the Gibbs reactor used, the combustion product contains more SO$_3$ than SO$_2$. For the Dynamis recommendations this makes no difference since the specified limit is given for SO$_x$ and not SO$_2$ and SO$_3$ separately. Encap's guidelines however, only specify a limit for SO$_2$. The SO$_2$ concentration is lower than the required limit, but the SO$_3$ concentration is higher than the recommended limit for SO$_2$.

4.1.8.   Liquefaction, case C1b_3

As for C1a_3 using pure oxygen in the catalytic oxidizer is the only option considered for liquefaction and TEG will be kept as the method for drying. The process is identical to the one in Figure A-4 in Appendix A and the results are given in Table 4-8.

Table 4-8: Results C1b_3

Parameter:	SRKM:	SRKK:
Total work [kJ/kgCO$_2$]	493,87	497,78
Total work [kWh/tonCO$_2$]	137,19	138,27
Work liquefaction [kJ/kgCO$_2$]		
Initial condensing [kJ/kgCO$_2$]	65,06	64,75
Column "reboiler" [kJ/kgCO$_2$]	23,19	23,12
Column condenser [kJ/kgCO$_2$]	10,85	10,58
Final liquefier [kJ/kgCO$_2$]	19,67	24,21
Total [kJ/kgCO$_2$]	**118,76**	**122,67**
Increase from C1b_2 [%]	32,06	33,10
Composition:		
CO$_2$	99,96 %	99,95 %
H$_2$O	45 ppm	45 ppm
N$_2$	139 ppm	173 ppm
O$_2$	40 ppm	45 ppm
Ar	114 ppm	133 ppm
CO	5 ppm	5 ppm
H$_2$	16 ppm	28 ppm
H$_2$S	10 ppm	10 ppm
SO$_2$	2 ppm	2 ppm
SO$_3$	70 ppm	70 ppm
TEG	> 1 ppm	> 1 ppm

Again the total work for the two equations of state differs by less than one percent. As for C1a_3 both compositions fulfil all the recommendations except the severe limit case from Encap. The liquefaction itself seems to be the biggest contributor to the increased specific work required as was the case in C1a_3.

4.2. Pre combustion capture from natural gas

For the case of pre combustion capture for power plants using natural gas as fuel, only one starting composition is considered. Natural gas contains considerably less sulphuric components than coal, and in addition these components are often removed to meet sale specifications. There will still probably be some sulphuric components in the gas, but it is assumed that the concentrations are low enough to be unproblematic in terms of meeting the specified recommendations. As a consequence, one should expect that it will be easier to meet the recommended limits.

4.2.1. Compression and flashing, case NG1_0

The compression process is the same as for the cases of pre combustion capture from coal using four compressors with intercoolers. Included in the composition is a small amine residue from the capture process. When the default equation of state is used, this amine residue is not removed with the liquid phase but if a special numerical package for amines is applied, it is. The first flash is therefore run with the default equation of state for a stream without the amine residue and with the amine package for the complete composition. The resulting gaseous amine from flashing with the amine package is then added to the main stream. Apart from the first flashing the process is as shown in Figure A-1 in Appendix A and the results are given in Table 4-9.

Table 4-9: Results NG1_0

Parameter:	Result:
Total work [kJ/kgCO$_2$]	*339,34*
Total work [kWh/tonCO$_2$]	*94,26*
Cooling water consumption [kgH$_2$O/kgCO$_2$]	*15,96*
CO$_2$out/CO$_2$in [%]	*99,98*
Composition:	
CO2	*99,70 %*
H2O	*1134 ppm*
N2	*588 ppm*
CO	*10 ppm*
H2	*1216 ppm*
CH$_4$	*18 ppm*
MEA	*< 1 ppm*

As expected, the resulting exit composition from the process is very pure giving a noticeable decrease in specific work compared to the coal cases. Except from the water concentration, all concentrations are below or at the limit (CO) according to Encap's strictest guidelines (See Table 2-7).

4.2.2.   Adding of a TEG column, case NG1_1

The process is identical to the ones designed for the pre combustion coal cases except from the separate flash for the inlet gas containing amine. The results are shown in Table 4-10 and the flow sheet for the process apart from the added flash mentioned is shown in Figure A-2 in Appendix A.

Table 4-10: Results NG1_1

Parameter:	Max H$_2$O	Min H$_2$O
Total work [kJ/kgCO$_2$]	*342,86*	*342,89*
Total work [kWh/tonCO$_2$]	*95,24*	*95,25*
Duty TEG reboiler [kJ/kgCO$_2$]	*1,29*	*1,59*
Circulation ratio TEG [L/kgH$_2$O$_{removed}$]	*19,71*	*18,00*
Water removed using TEG [kg/tonCO$_2$]	*0,4*	*0,4*
TEG lost	*0,0094 %*	*0,0112 %*
Cooling water consumption [kgH$_2$O/kgCO$_2$]	*16,06*	*16,06*
CO$_2$out/CO$_2$in [%]	*99,98*	*99,98*
Composition:		
CO2	*99,80 %*	*99,81 %*
H2O	*137 ppm*	*45 ppm*
N2	*589 ppm*	*589 ppm*
CO	*10 ppm*	*10 ppm*
H2	*1217 ppm*	*1217 ppm*
CH$_4$	*18 ppm*	*18 ppm*
MEA	*> 1 ppm*	*> 1 ppm*
TEG	*> 1 ppm*	*> 1 ppm*

Looking at the resulting compositions is it clear that CO$_2$ captured from a natural gas pre combustion process may be used in EOR even if only drying by the means of TEG is used. Further one can see that the concentration of combustibles (carbon monoxide, hydrogen and methane), are so small that catalytic oxidation is out of the question. Trials show that the heat developed from combusting these substances is minimal. Liquefaction will be considered for the composition containing the least amount of water.

4.2.3. Liquefaction, case NG1_2

The dried CO_2-rich stream is liquefied using the same configuration as for case C1a_3 and C1b_3 (see Figure A-4 in Appendix A for the flow diagram). As for those cases the equation of state SRKK will be applied as well as the default SRKM. Results are given in Table 4-11.

Table 4-11: Results, NG1_2

Parameter:	SRKM:	SRKK:
Total work [kJ/kgCO$_2$]	468,52	470,30
Total work [kWh/tonCO$_2$]	130,14	130,64
Work liquefaction [kJ/kgCO$_2$]		
Initial condensing [kJ/kgCO$_2$]	60,85	61,05
Column "reboiler" [kJ/kgCO$_2$]	25,68	26,93
Column condenser [kJ/kgCO$_2$]	27,71	25,20
Final liquefier [kJ/kgCO$_2$]	11,23	14,08
Total [kJ/kgCO$_2$]	**125,21**	**126,99**
Increase from NG1_1 [%]	36,64	37,16
Composition:		
CO$_2$	99,98 %	99,98 %
H$_2$O	45 ppm	45 ppm
N$_2$	70 ppm	94 ppm
CO	1 ppm	1 ppm
H$_2$	48 ppm	94 ppm
CH$_4$	5 ppm	6 ppm
MEA	> 1 ppm	> 1 ppm
TEG	> 1 ppm	> 1 ppm

Liquified CO_2 leaving the process is in this case ultra pure, satisfying all recommendations except the severe case, but it is the first case where required work for the condenser is higher than that for the final liquefier. This is because more hydrogen than in the previous simulations must be removed in order to liquefy the CO_2. Finally the difference between the two EoS' is yet again less than one percent.

4.3. Post combustion capture from coal

When the CO_2 is capture post combustion the, levels of impurities are very low. The considered compositions found in the literature contain only water, nitrogen and oxygen in small concentrations apart from the CO_2. As a consequence no means of purification beyond drying is expected to be necessary to meet the given quality recommendations.

4.3.1. Compression and flashing, case C2_0

The process is identical to the basic compression cases for pre combustion (see Figure A-1 in Appendix A for flow diagram). Resulting process parameters and composition is given in Table 4-12.

Table 4-12: Results C2_0

Parameter:	Result:
Total work [kJ/kgCO$_2$]	*304,73*
Total work [kWh/tonCO$_2$]	*84,65*
Cooling water consumption [kgH$_2$O/kgCO$_2$]	*13,70*
CO$_2$out/CO$_2$in [%]	*99,99*
Composition:	
CO2	*99,69 %*
H2O	*1159 ppm*
N2	*1819 ppm*
O$_2$	*107 ppm*

As expected considering the initial composition, the exiting stream is very low in unwanted substances. The oxygen concentration is seven parts per million shy of meeting the strictest EOR requirement. It is assumed that this will not prevent the use of the CO$_2$ for EOR in practise. TEG will further be applied to remove water to an acceptable level.

4.3.2. Adding of a TEG unit, case C2_1

With TEG drying the configuration will be identical to the ones used for the pre combustion cases except from an added compressor. The compressor is needed to compress the CO$_2$ recycled from the TEG unit since the inlet pressure from the process is higher than the reclamation column discharge pressure. Flow diagram for the process is shown in Figure A-2 in Appendix A.

Two different modes of operation will be applied in this case as well as for the others. One where heat required in the reboiler for TEG and TEG circulation rate is minimized, and one where the typical reboiler operation temperature of 204°C is used to achieve a final water concentration of 45 ppm. The latter possibly in combination with an increased circulation rate of TEG. The results are shown in Table 4-13.

Table 4-13: Results C2_1

Parameter:	Max H$_2$O	Min H$_2$O
Total work [kJ/kgCO$_2$]	*303,27*	*303,29*
Total work [kWh/tonCO$_2$]	*84,24*	*84,25*
Duty TEG reboiler [kJ/kgCO$_2$]	*1,34*	*1,62*
Circulation ratio TEG [L/kgH$_2$O$_{removed}$]	*19,66*	*18,01*
Water removed using TEG [kg/tonCO$_2$]	*0,4*	*0,4*
TEG lost [%]	*0,0112*	*0,0132*
Cooling water consumption [kgH$_2$O/kgCO$_2$]	*13,70*	*13,70*
CO$_2$out/CO$_2$in [%]	*99,99*	*99,99*
Composition:		
CO2	*99,79 %*	*99,80 %*
H2O	*126 ppm*	*42 ppm*
N2	*1821 ppm*	*1821 ppm*
O$_2$	*107 ppm*	*107 ppm*
TEG	*> 1 ppm*	*> 1 ppm*

The extra compressor added has little effect on the total specific work (0.027 kJ/kg). Without the CO$_2$ recycling the capture rate would have been 99.91 %. The CO$_2$ exiting with the off gas of the TEG reclamation column would possibly just have been discarded in reality. However, it is recycled in this case to capture as much of the CO$_2$ as possible since the effect on the specific work is negligible.

4.3.3. Liquefaction, case C2_2

The liquefaction process is no different from the processes described earlier (see section 4.1.4) and the flow diagram can be seen in Figure A-4 in Appendix A. The results are given in Table 4-14.

Table 4-14: Results C2_2

Parameter:	SRKM:	SRKK:
Total work [kJ/kgCO_2]	420,53	424,35
Total work [kWh/tonCO_2]	116,81	117,88
Work liquefaction [kJ/kgCO_2]		
Initial condensing [kJ/kgCO_2]	51,93	51,55
Column "reboiler" [kJ/kgCO_2]	22,43	24,35
Column condenser [kJ/kgCO_2]	25,51	25,40
Final liquefier [kJ/kgCO_2]	17,04	19,45
Total [kJ/kgCO_2]	**116,93**	**120,76**
Increase from C2_1 [%]	38,66	39,92
Composition:		
CO_2	99,97 %	99,96 %
H_2O	42 ppm	42 ppm
N_2	259 ppm	315 ppm
O_2	29 ppm	33 ppm
TEG	> 1 ppm	> 1 ppm

The difference between the EoS' in work is less than one percent. All recommended concentration limits, except the water limit for Encap's severe limit case, is now met since the liquefaction brings the oxygen concentration well below 100 ppm. As for case NG1_3 the specific work related to the condenser is higher than for the final liquefier. In this case it is also higher than the work related to the "reboiler" of the distillation column, but it is also the case with the highest initial concentration of nitrogen so far.

4.4. Post combustion capture from natural gas

The composition found resulting from post combustion capture for natural gas power plants contains only CO_2, water and nitrogen. As long as the gas is dried it will be suited for any end use.

4.4.1. Compression and flashing, case NG2_0

The basic process used for compression and flashing, well known by now, is shown in Figure A-1 in Appendix A. Without further ado the results are presented in Table 4-15.

Table 4-15: Results NG2_0

Parameter:	Result:
Total work [kJ/kgCO_2]	304,45
Total work [kWh/tonCO_2]	84,57
Cooling water consumption [kgH_2O/kgCO_2]	13,70
CO_2out/CO_2in [%]	99,99
Composition:	
CO2	99,86 %
H2O	1176 ppm
N2	176 ppm

There is not more needed to be said about these results than that the gas must be dried to comply with any given recommendations.

4.4.2. Adding of a TEG unit, case NG2_1

The configuration for the process is the same as for C2_1; an extra compressor is used to bring the recycled CO_2 to the inlet pressure of the first compressor. The flow diagram can be seen in Figure A-2 in Appendix A and the results are given in Table 4-16.

Table 4-16: Results NG2_1

Parameter:	Max H$_2$O	Min H$_2$O
Total work [kJ/kgCO$_2$]	303,05	303,07
Total work [kWh/tonCO$_2$]	84,74	84,19
Duty TEG reboiler [kJ/kgCO$_2$]	1,34	1,63
Circulation ratio TEG [L/kgH$_2$O$_{removed}$]	19,68	18,02
Water removed using TEG [kg/tonCO$_2$]	0,4	0,4
TEG lost [%]	0,0101	0,0120
Cooling water consumption [kgH$_2$O/kgCO$_2$]	13,69	13,70
CO$_2$out/CO$_2$in [%]	99,99	99,99
Composition:		
CO2	99,97 %	99,98 %
H2O	133 ppm	44 ppm
N2	176 ppm	176 ppm
TEG	> 1 ppm	> 1 ppm

Looking at the resulting composition one can see that the dried CO_2 is of similar purity as liquefied CO_2 for the previous cases. This implies that purification can be left out of the liquefaction process.

4.4.3. Liquefaction, case NG2_2

Because the stream leaving the drying section is so pure, there is no need for further purification. The distillation column is therefore left out of the liquefaction process, and as a result no CO_2 is lost during liquefaction. Without the column the equipment left are three heat exchangers and two valves. Since the heat is removed at a constant temperature, using only two heat exchangers and one valve will lead to an increase in the specific work. The optimal would be using heat exchange at a gliding temperature, but according to Jacob Stang at Sintef [27] the relevant temperatures might be a bit high for this to be a favourable solution. It is assumed that using three cooling circuits is economically justifiable. Flow diagram for the process is shown in Figure A-6 in Appendix A and the results are given in Table 4-17.

Table 4-17: Results NG2_2

Parameter:	SRKM:	SRKK:
Total work [kJ/kgCO$_2$]	409,74	414,25
Total work [kWh/tonCO$_2$]	113,82	115,07
Work liquefaction [kJ/kgCO$_2$]		
Initial condensing [kJ/kgCO$_2$]	53,79	54,12
Column "reboiler" [kJ/kgCO$_2$]	23,57	26,09
Final liquefier [kJ/kgCO$_2$]	29,30	30,95
Total [kJ/kgCO$_2$]	**106,67**	**111,18**
Increase from NG2_1 [%]	35,20	36,68
Increase from C21_1		
CO$_2$	99,98 %	99,98 %
H$_2$O	44 ppm	44 ppm
N$_2$	176 ppm	176 ppm
TEG	> 1 ppm	> 1 ppm

As expected obtaining a liquid phase offers no problems even without volatiles removal. The two EoS's differ in results even if no separation is involved because the properties of the substances are calculated differently. This is the first case where the difference in calculated work by SRKM and SRKK differ by more than one percent. With a difference of 1.1 percent they are still in good agreement.

4.5. Oxy combustion capture from coal

The cases considered so far have been fairly similar in terms of the initial concentration of CO$_2$. For oxy combustion processes the initial concentration is considerably lower. This is mainly because of two things. The first is that the oxygen used to combust the fuel is not totally pure. According to [6] the optimum oxygen quality, somewhat dependent on air ingress, is found to be 95 percent. The second is that the flue gas system from the outlet of the gas turbine to the compression process is not totally air tight. Oxy combustion derived CO$_2$ will also differ from CO$_2$ derived from pre combustion in terms of impurities. Where the impurities in pre combustion is mainly combustible residue originating from the synthesis gas, impurities in oxy combustion will mainly be oxides of nitrogen and sulphur resulting from the combustion.

Water removal:
For the oxy combustion cases molecular sieve drying will be chosen over TEG. There are several reasons for this apart from limiting the scope of this work. The first is that a considerable part of the process will be at temperatures below zero degrees Celsius. To be sure that water will not precipitate causing the formation of ice or hydrates water is reduced to a lower concentration than for previous cases.

If TEG is used, TEG residue might inhibit the formation of a free water phase. However, according to Kohl and Nielsen [13] glycol injection is impractical at temperatures lower than about -40°C because of the high viscosity of glycol solutions at such low temperatures. The concentrations in this case will probably be lower than for glycol injection, but low viscosity fluid in heat exchanger tubes might cause problems regardless. This has a greater impact on the oxy combustion process with two stage flash separation for volatiles, because the heat exchangers used here are more extensive than for the other cases.

Another reason for choosing molecular sieves over TEG is that the pressure at which the drying process is placed has a greater impact for the oxy combustion cases. The increased

content of volatiles adds a substantial amount of work required for the compression. To minimize the total specific work it might be favourable to place the drying at a lower pressure than for the previous cases. This will increase the needed circulation rate of TEG to achieve sufficiently low water concentrations hence also the required reboiler duty.

The diagram in Figure 8 shows how the circulation rate of TEG needed to achieve a water concentration of 45 ppm varies with pressure for cases C1b and C3. The circulation rate is given in litres of TEG circulated per kilograms of water removed. An interesting thing to note is that the circulation rate required for the oxy combustion case seems to increase more with decreasing pressure than for the pre combustion case. The exact reason why will not be explored further, but it seems like the partial pressure of CO_2 has an effect. The rich TEG exiting the contactor has a CO_2 concentration actually higher than the concentration of water. It may seem like the CO_2 dissolved in the TEG enhances the drying effect, lowering the required TEG circulation rate.
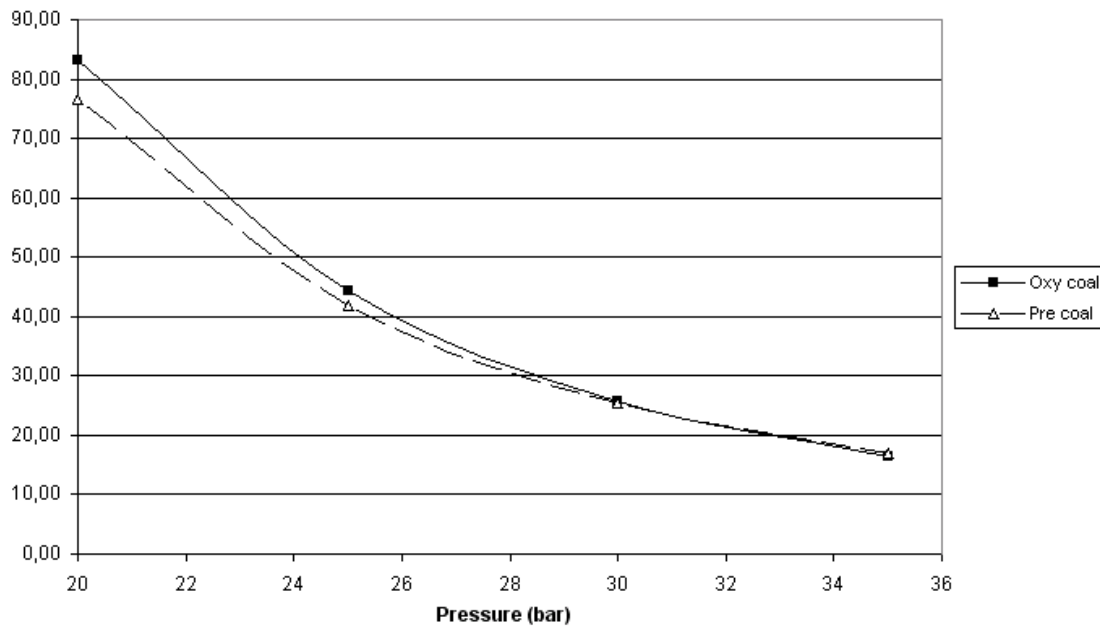

Figure 8: Circulation rate of TEG as a funcion of pressure

As established in section 2.6.1, the solubility of water is higher in liquid CO_2 than in gaseous CO_2. Precipitation of water from the CO_2-rich stream is therefore most likely to occur during cooling of the stream in gaseous form. Pro/II has been used with the SRKM equation of state to generate plots of the point where a water rich phase will precipitate from a gaseous stream. Streams with the same composition as case C3 without water was mixed with water to give concentrations ranging from zero to 500 ppm. These streams were then cooled to the point where a liquid phase started to precipitate. The results are shown in Figure 9.
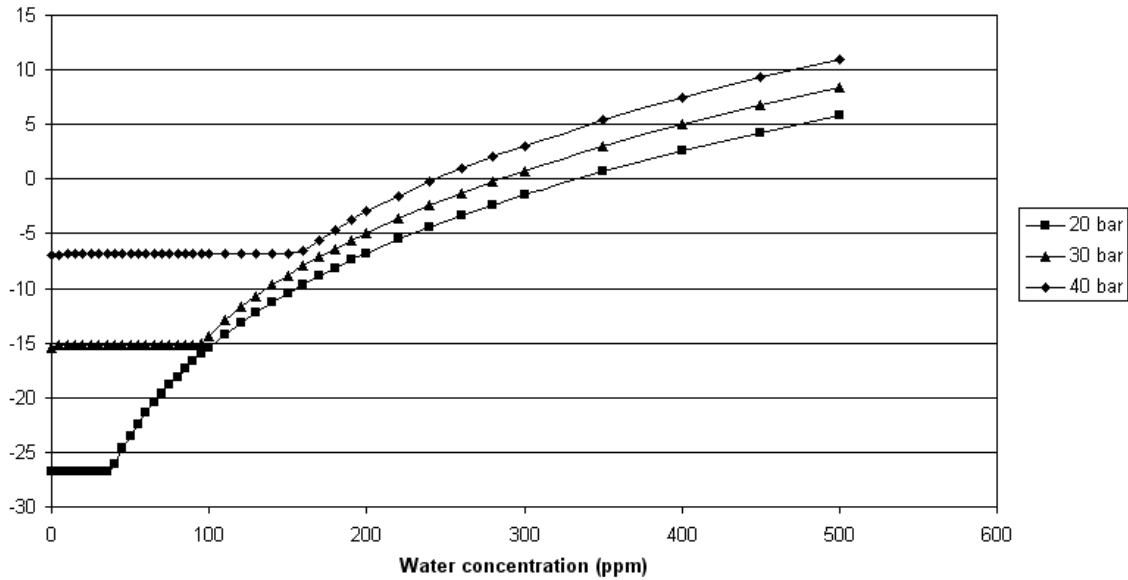
Figure 9: Formation of a H₂O-rich liquid phase as a function of water content

For low water concentrations condensation occurs at a constant temperature giving a CO_2-rich liquid phase. At a certain concentration, depending on the pressure, a water-rich liquid phase will precipitate first. As the concentration is increased further this will take place at higher and higher temperatures. Depending on the temperature this might result in the formation of ice or hydrates. Based on the graph in Figure 9 water will be removed to a water concentration of 25 ppm exiting the purification process.

4.5.1. Compression and flashing, case C3_0

The configuration of the process is equal to the ones used previously apart from the fact that the mixture does not liquefy for pressures equal to or less than the delivery pressure. Flow diagram for the process is shown in Figure A-7 in Appendix A and the results are presented in Table 4-18.

Table 4-18: Results C3_0

Parameter:	Result:
Total work [kJ/kgCO₂]	*527,91*
Total work [kWh/tonCO₂]	*146,64*
Cooling water consumption [kgH₂O/kgCO₂]	*17,08*
CO₂out/CO₂in [%]	*99,98*
Composition:	
CO2	*75,64 %*
H2O	*954 ppm*
N2	*15,18 %*
O₂	*6,22 %*
Ar	*2,45 %*
SO₂	*3704 ppm*
NO	*423 ppm*
NO₂	*10 ppm*

As can be seen from the results this composition is far from being suited for any type of storage. Apart from being to rich in water, the total concentration of volatile substances is

more than 20 percent. In addition the concentrations of both SO_2 and NO_x are too high. The problems considered first are water and volatile substances.

4.5.2. Drying and volatiles removal, case C3_1

The process consists of initial compression with intercooling and flashing, drying using a molecular sieve, a two stage flash separation for volatiles removal, additional compression with intercooling and finally pumping to the delivery pressure. The flow diagram for the process is shown in Figure A-8 in Appendix A. As for the catalytic oxidizers there are no components in Pro/II to simulate molecular sieves. Yet again the solution is to redefine the stream at the same pressure and temperature and with the same flow rates for the different substances apart from water. The water content is set to give a final concentration of 25 ppm. The performance parameter obtained for the molecular sieve is the amount of water removed relative to the amount of CO_2 stored. This parameter may in turn be used to determine the needed dimension for the sieve.

Optimization of this process mainly comes down to a weighing between energy penalty and investment cost. Volatiles removal at a lower pressure will possibly decrease the compression work but it will also lead to larger heat transfer surfaces in the heat exchangers. Since the optimization of this process in Pro/II also have proven to be quite complex, it has been done at three different inlet pressures for the volatiles removal, 20, 25 and 30 bar. The constraints given for the optimization is a minimum overall capture rate of 90.5 % and a maximum total concentration of volatiles of 4 % (where necessary). The results are given in Table 4-19 for SRKM and Table B-1 in Appendix B for SRKK.

Table 4-19: Results C3_1

Parameter:	20 bar:	25 bar:	30 bar
Total work [kJ/kgCO$_2$]	533,02	536,58	541,44
Total work [kWh/tonCO$_2$]	148,06	149,05	150,40
Water removal MSA [kg/tonCO$_2$]	0,91	0,76	0,66
Cooling water consumption [kgH$_2$O/kgCO$_2$]	19,67	19,72	19,75
Total size HX (UA/(kg/s)CO$_2$) [kJ/KkgCO$_2$]	51,15	47,43	45,41
CO$_2$out/CO$_2$in [%]	91,17	91,87	93,20
Composition:			
CO$_2$	97,12 %	96,52 %	95,58 %
H$_2$O	25 ppm	25 ppm	25 ppm
N$_2$	1,03 %	1,33 %	1,81 %
O$_2$	0,97 %	1,19 %	1,53 %
Ar	0,35 %	0,43 %	0,56 %
SO$_2$	0,52 %	0,51 %	0,50 %
NO	74 ppm	87 ppm	107 ppm
NO$_2$	15 ppm	14 ppm	14 ppm

As can be seen from the results a lower inlet pressure gives a lower specific work, but increases the required size of heat transfer surfaces, given a constant overall heat transfer coefficient. For SRKK the work at 25 bar is less than at 20 bar suggesting the real optimum will lie somewhere between these two pressures. The most interesting result is the fact that using SRKK at 30 bar both specified constraints will not be fulfilled. The data given in Table B-1 is the result of minimizing the total concentration of volatiles with a capture rate of 90.5 percent as the only constraint. The real optimum would yield a total volatile concentration higher than the one given. For the other simulations the minimum work did not come in conflict with the constraints. Reviewing Table 3-7 in section 3.1 one can see that at 3.075

MPa which equals 30.75 bar, SRKK overestimates the liquid concentration of nitrogen about as much as SRKM underestimates it. Assuming this applies to oxygen and argon as well the real concentration can be estimated. From the results the mean of the total concentration of volatiles for SRKM at 30 bar and SRKK at 30 bar is calculated to be about 3.99 percent. If the assumptions prove true the inlet pressure for volatiles removal by two-stage flashing will be limited to 30 bar.

Looking at the resulting concentrations of NO_x reveals that if the process is operated at 20 bar additional removal will probably not be necessary unless Encap's severe case recommendations is to be met. Additional removal of NO_x is still included in the next cases to possibly meet the severe limit case and because the performance of the two considered methods (SCR and modified lead chamber process) is more or less independent of the volatiles removal process. Selective catalytic reduction takes place prior to the whole CO_2 conditioning process, and the efficiency of removal as nitric acid increases with pressure. The latter implies that an increasing end concentration of NO_x with increasing pressure in C3_1, might be counteracted somewhat by increased removal efficiency prior to volatiles removal. The SO_2 concentration however has got to be removed regardless of the process pressure. With the volatiles removed this could possibly be done by additional separation since SO_2 is less volatile than CO_2, but the methods considered in this work is SO_2 capture using chemical processes. Apart from the modified lead chamber process, these will not be affected by the two-stage flashing process.

4.5.3.   Removal of SO_2 and NO_x, case C3_2

To limit the number of simulations, the different methods of impurities removal will be applied only to the case of volatiles removal at 20 bar with SRKM. Four different processes will be modelled. Three of them will use SCR for NO_x removal and lime scrubbing, limestone scrubbing and the ammonium sulphate process respectively for removal of SO_2. For these processes, using a molecular sieve offers an advantage in addition to the aforementioned water considerations by also removing possible ammonia slip. The fourth simulation will be done by using the modified led chamber process suggested by White et al. [22].

The processes are modified to be used in Pro/II and the configurations will be different for the actual processes. Using a Pro/II Gibbs reactor in combination with a given reaction set, the reaction of nitrogen dioxide to nitric acid in the modified lead chamber process has to be modelled using two reactors. This is because the number of substances involved limits the number of reactions that can be specified (see pro/II manual for more information). Removal rates of NO_x and SO_2 are based on removal efficiencies given in section 3.2. The reaction rates in the two nitric acid reactors will be set to yield the given removal rate. Where additives are used the consumption of these are computed based on additive to impurity ratios given in Table 3-9. It is assumed that ammonia slip is captured by the molecular sieve (see section 2.6.1). Flow diagrams of the processes are given in Figure A-9 and Figure A-10 in Appendix A and the results are shown in Table 4-20.

Table 4-20: Results C3_2

Parameter:	Amm. sulf.:	Lime:	Limest.:	Lead ch.:
Total work [kJ/kgCO$_2$]	533,75	531,88	532,20	539,86
Total work [kWh/tonCO$_2$]	148,27	147,75	147,83	149,96
Water removal MSA [kg/tonCO$_2$]	0,91	0,90	0,90	0,92
Ammonia consumption [kg/tonCO$_2$]	4,35	0,21	0,21	-
Lime consumption [kg/tonCO$_2$]	-	7,91	14,11	-
Limestone comnsumption [kg/tonCO$_2$]	-	-		
Magnesium oxide consumption [kg/tonCO$_2$]	-	-	-	0,22[1]
Cooling water consumption [kg/kgCO$_2$]	20,83	20,74	20,50	20,40
Total size HX (UA/(kg/s)CO$_2$) [kJ/KkgCO$_2$]	50,48	50,73	51,15	49,99
CO$_2$out/CO$_2$in [%]	90,45	91,06	91,06	90,78
Composition:				
CO$_2$	97,68 %	97,65 %	97,66 %	97,65 %
H$_2$O	25 ppm	25 ppm	25 ppm	25 ppm
N$_2$	1,03 %	1,04 %	1,04 %	1,03 %
O$_2$	0,94 %	0,95 %	0,94 %	0,94 %
Ar	0,35 %	0,35 %	0,35 %	0,35 %
SO$_2$	57 ppm	52 ppm	52 ppm	103 ppm
NO	7 ppm	8 ppm	7 ppm	5 ppm
NO$_2$	15 ppm	15 ppm	15 ppm	26 ppm

[1]Solid product molar MgO concentration of 1.75 %

When simulations are run for the case using the modified lead chamber process, the calculated solubility of nitric acid is almost as high in the vapour phase as in the liquid phase. Whether this is physical or due to limitations in the performance of the equation of state, is not known at this point. There are acid packages available in Pro/II, but for some of the substances in the initial composition, not all the parameters needed to use these packages are present. The problem is solved by adding magnesium oxide in the last of the two nitric acid reactors, removing nitric acid according to equation (4.1).

$$MgO + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2O \qquad (4.1)$$
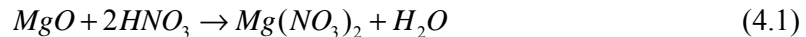
The by product, magnesium nitrate, is a fertilizer which may be sold if this step is carried out in practise.

Due to the default tolerance limits in Pro/II, the capture rate for the ammonium sulphate case has dropped to 90.45 percent. This is a small deviation from the initial constraint of 90.5 percent, but it shows that when additional removal of SO$_2$ and NO$_x$ is applied, minimizing the work seems to yield a lower overall capture rate. If the pressure is lowered below 20 bar, the optimum will most likely come in conflict with the constraint for overall capture.

The results further show that by using two stage flash separation with additional impurities removal, oxy coal derived CO$_2$ meets Dynamis' recommendations for aquifer storage. The oxygen concentration is still too high for the CO$_2$ to be used in EOR by about 10-100 times. Modifying the optimizer in Pro/II to minimize the oxygen concentration proves unsuccessful in terms of approaching the recommended limit. Considering these results volatiles removal using internal cooling is unfitted if the CO$_2$'s end use is to be EOR.

4.5.4. Volatiles removal by distillation, case C3_3

Case C3_1 using SCR for the removal of NO$_x$ and lime scrubbing for SO$_2$ removal will be used as a basis for further simulations. Apart from being the option with the lowest energy

penalty it has other advantages over the other configurations in terms of feasibility. As discussed in section 2.6.3, removal of SO_2 by limestone scrubbing may be limited by the high concentration of CO_2 in the flue gas. Regarding the modified lead chamber process it has not been tested for flue gas concentrations of SO_2 as high as the one given for oxy combustion using coal [22]. As a result the assumed removal efficiency of 98 percent (see section 3.2) might prove hard to obtain.

For the ammonium sulphate process the assumed removal efficiency of 99 percent has been demonstrated for SO_2 concentrations as high as 6100 ppm [13]. The uncertainty connected to this process is economy regarding the saleable by product and the possible increased air ingress by using forced oxidation (see section 2.6.3). Judging by [13] there are uncertainties connected to obtaining maximum removal efficiency for lime scrubbing at high SO_2 concentrations. Confirmation of the assumed removal efficiency of 99 percent for the relevant concentrations has not been found in the literature. However, it is further assumed that 12 years of technology development (the book by Kohl and Nielsen was published in 1997) motivated by emission regulations, has improved the performance of the process.

The simulated process is equal to the lime process in C3_1 as far as to the molecular sieve. The gas exiting the molecular sieve is cooled in the reboiler of the distillations column. It is further cooled by the volatiles exiting the column and using an external cooling circuit before finally entering the distillation column. Exiting the column as liquid, the purified CO_2 is pumped to the delivery pressure and heated by the cooling water from the initial compression. The flow diagram is shown in Figure A-11 in Appendix A. The two streams mixing with gas from the reboiler and liquid from the condenser are streams of 10^{-9} kilo moles of CO_2 per second. Without these streams the calculation will fail to start because of no flow through the column (a Pro/II weakness). At the obtained solution the streams they are mixing with are in the order of magnitude of 0.5 kilo moles per second hence these "starter streams" will not influence the results.

Three different simulations will be run. The first minimizing the work, the second minimizing the work with a constraint for the oxygen concentration of 1000 ppm and the third minimizing the work with the constraint set to 100 ppm. The pressure is varied in the optimization process. Final results are given in Table 4-21 for SRKM and Table B-2 in Appendix B for SRKK.

Table 4-21: Results C3_3

Parameter:	Min work:	1000 ppm O_2:	100 ppm O_2:
Total work [kJ/kgCO$_2$]	580,75	581,28	583,11
Total work [kWh/tonCO$_2$]	161,32	161,47	161,98
Water removal MSA [kg/tonCO$_2$]	0,73	0,86	0,89
Pressure exiting MSA [bar]	25,56	21,48	20,47
Flowing volume exiting MSA [m^3/tonCO$_2$]	27,7	34,7	36,6
Flowing volume entering column [m^3/tonCO$_2$]	11,5	15,7	17,8
Magnesium oxide consumption [kg/tonCO$_2$]	0,21	0,21	0,21
Cooling water consumption [kg/kgCO$_2$]	7,66	7,94	7,95
Total size HX (UA/(kg/s)CO$_2$) [kJ/KkgCO$_2$]	12,06	11,90	11,76
CO$_2$out/CO$_2$in [%]	93,99	90,69	90,58
Composition:			
CO$_2$	99,37 %	99,87 %	99,98 %
H$_2$O	25 ppm	25 ppm	25 ppm
N$_2$	250 ppm	4 ppm	> 1 ppm
O$_2$	4488 ppm	974 ppm	84 ppm
Ar	1432 ppm	202 ppm	15 ppm
SO$_2$	52 ppm	54 ppm	54 ppm
NO	3 ppm	> 1 ppm	> 1 ppm
NO$_2$	14 ppm	15 ppm	15 ppm

The difference in calculated work for SRKM and SRKK are less than one percent. Further, the simulation results show that an oxygen concentration of 100 ppm can be achieved with little increase in energy penalty. However, it requires distillation at a lower pressure. As seen from Table 4-21, this will lead to an increase of more than 50 percent in the total volume relative to the mass flow of captured CO_2 entering the column. Needless to say, this will substantially increase required investment cost for the distillation.

4.5.5. Liquefaction, case C3_4

Judging by the results from C3_3 the composition resulting from distillation down to 100 ppm of oxygen should be pure enough for liquefaction. The process from C3_3 is modified by removing the pump at the end replacing it with a valve and a heat exchanger for final condensing. The resulting flow diagram is given in Figure A-12 in Appendix A and the simulation results are shown in Table 4-22.

Table 4-22: Results C3_4

Parameter:	SRKM:	SRKK:
Total work [kJ/kgCO$_2$]	606,72	611,21
Total work [kWh/tonCO$_2$]	168,53	169,78
Increase from C3_3 [%]	4,05	3,96
Increase from C3_1 (20 bar) [%]	13,83	14,25
Composition:		
CO$_2$	99,98 %	99,98 %
H$_2$O	25 ppm	25 ppm
N$_2$	> 1 ppm	1 ppm
O$_2$	84 ppm	93 ppm
Ar	15 ppm	27 ppm
SO$_2$	54 ppm	54 ppm
NO	> 1 ppm	> 1 ppm
NO$_2$	15 ppm	15 ppm

Difference in calculated work between SRKM and SRKK are also here less than one percent. The results also show that the increased work due to the liquefaction is relatively small compared to case C3_3.

4.6. Oxy combustion capture from natural gas

The flue gas resulting from oxy combustion of natural gas contains lower levels of impurities than from oxy combustion of coal. It is therefore expected that the means required to purify the CO_2 will be less energy demanding.

4.6.1. Compression and flashing, case NG3_0

The process is equal to the other basic compression cases except from C3_0. Flow diagram can be seen in Figure A-1 in Appendix A and the results are given in Table 4-23.

Table 4-23: Results NG3_0

Parameter:	Result:
Total work [kJ/kgCO$_2$]	430,04
Total work [kWh/tonCO$_2$]	119,46
Cooling water consumption [kgH$_2$O/kgCO$_2$]	21,51
CO$_2$out/CO$_2$in [%]	99,98
Composition:	
CO2	88,26 %
H2O	1009 ppm
N2	3,72 %
O$_2$	2,21 %
Ar	5,67 %
SO$_2$	192 ppm
NO	147 ppm

The resulting composition is considerably more pure than for C3_0. Still, the total concentration of volatiles is to high and the concentrations of NO_x and SO_2 needs some reduction.

4.6.2. Drying and volatiles removal, case NG3_1

As for C3_1 the drying method selected is a molecular sieve for the reasons discussed in section 4.5.2. The process used is equal to the one in C3_1 and the flow diagram is shown in Figure A-8 in Appendix A. Results from the simulation are shown in Table 4-24 for SRKM and in Table B-3 in Appendix B for SRKK.

Table 4-24: Results NG3_1

Parameter:	20 bar:	25 bar:	30 bar:
Total work [kJ/kgCO$_2$]	437,29	442,88	439,30
Total work [kWh/tonCO$_2$]	121,47	123,02	122,03
Water removal MSA [kg/tonCO$_2$]	0,74	0,63	0,55
Cooling water consumption [kgH$_2$O/kgCO$_2$]	22,50	22,73	22,66
Total size HX (UA/(kg/s)CO$_2$) [kJ/KkgCO$_2$]	48,91	40,34	43,70
CO$_2$out/CO$_2$in [%]	97,72	96,21	96,77
Composition:			
CO$_2$	97,43 %	96,87 %	96,48 %
H$_2$O	25 ppm	25 ppm	25 ppm
N$_2$	0,49 %	0,65 %	0,76 %
O$_2$	0,61 %	0,72 %	0,80 %
Ar	1,44 %	1,73 %	1,93 %
SO$_2$	216 ppm	218 ppm	219 ppm
NO	44 ppm	47 ppm	51 ppm

Looking at the results it is obvious that the trend in the results regarding change in pressure is not the same as for C3_1. For SRKM the minimum work is still found at the lowest pressure, but operating at 30 bar the energy penalty is less than operating at 25 bar. The reason for these results may be that the Pro/II optimizer did not find the correct optimum at 25 bar. Depending on the starting point optimizers in Pro/II can have a tendency to paint themselves into a corner since they are dependent on numerical derivatives to continue the search for the optimum.

If the correct optimum at 25 bar gives a lower work than at 30 bar the trend is the same as in C3_1. If not the optimum might lie above 30 bar. However, realizing that as for C3_1 the concentration of volatiles is increasing, this optimum would be limited by the total volatiles concentration. In addition results for SRKK shows the same trend as in C3_1 giving the lowest work at 25 bar and a substancial increase up to 30 bar. If the difference in investment cost related to the heat exchangers turns out to be large, this matter should be investigated further. At this point the matter is left and the case operating at 20 bar is selected for further purification.

Considering the resulting compositions reveals that the volatiles removal process has increased the concentration of SO$_2$. This is because SO$_2$ is less volatile than CO$_2$ and hence will not exist in large concentrations in a vapour phase. The nitrogen oxide on the other hand is more volatile than CO$_2$ and the concentration is reduced to a level suitable for the use in EOR both according to Dynamis and Encap. However, both impurities will be handled in the next step.

4.6.3. Removal of SO$_2$ and NO$_x$, case NG3_2

Because of the low concentration of SO$_2$ compared to the oxy combustion case, the modified lead chamber process will be selected as the only additional mean of purification. The process configuration is the same as for C3_2 using the modified lead chamber process. The flow diagram is shown in Figure A-10 in Appendix A and the results are given in Table 4-25.

Table 4-25: Results N3_2

Parameter:	Lead chamber:
Total work [kJ/kgCO$_2$]	*441,00*
Total work [kWh/tonCO$_2$]	*122,50*
Water removal MSA [kg/tonCO$_2$]	*0,77*
Magnesium oxide consumption [kg/tonCO$_2$]	*0,07[1]*
Cooling water consumption [kgH$_2$O/kgCO$_2$]	*22,92*
Total size HX (UA/(kg/s)CO$_2$) [kJ/KkgCO$_2$]	*52,42*
CO$_2$out/CO$_2$in [%]	*94,17*
Composition:	
CO$_2$	*97,91 %*
H$_2$O	*25 ppm*
N$_2$	*0,41 %*
O$_2$	*0,49 %*
Ar	*1,18 %*
SO$_2$	*5 ppm*
NO	*3 ppm*
NO$_2$	*6 ppm*

[1]Solid product contains 1.73 mol % MgO

As the results show the modified lead chamber process gives concentrations below or near the limit for Encap's severe case for NO$_x$ and SO$_2$. Attempts to minimize the oxygen concentration, does not result in levels low enough to meet EOR recommendations. The process is further modified to apply distillation.

4.6.4. Volatiles removal by distillation, case NG3_3

For the volatiles removal process by distillation the CO$_2$ coming from the power plant is first compressed, intercooled and flashed in three stages. Then it is led into the modified led chamber process. First it enters the reactor converting SO$_2$ to sulphuric acid by using NO$_2$ as a catalyst. Then it is cooled before entering a reactor simulating the reaction of NO$_2$ to nitric acid in the liquid phase. Next it goes through the last reactor where the conversion of NO$_2$ to nitric acid takes place in the gaseous phase. As the nitric acid is formed, it reacts with magnesium oxide forming magnesium nitrate. The fertilizer by product is removed in a solids flash separator before the gas is dried in a molecular sieve and finally enters the distillation process. The flow diagram for the process is shown in Figure A-13 in Appendix A and the results are presented in Table 4-26 for SRKM and Table B-4 in Appendix B for SRKK. As for C3_3, the case will first be optimized in terms of minimum work, and then optimized in terms of minimum work applying constraints for the oxygen concentration.

Table 4-26: Results NG3_3

Parameter:	Min work:	100 ppm O$_2$:
Total work [kJ/kgCO$_2$]	483,12	485,90
Total work [kWh/tonCO$_2$]	134,20	134,97
Water removal MSA [kg/tonCO$_2$]	0,68	0,74
Pressure exiting MSA [bar]	23,30	20,82
Flowing volume exiting MSA [m^3/tonCO$_2$]	25,6	29,0
Flowing volume entering column [m^3/tonCO$_2$]	7,9	9,7
Magnesium oxide consumption [kg/tonCO$_2$]	0,07[1]	0,07[2]
Cooling water consumption [kgH$_2$O/kgCO$_2$]	14,91	14,59
CO$_2$out/CO$_2$in [%]	94,50	94,48
Composition:		
CO$_2$	99,79 %	99,98 %
H$_2$O	25 ppm	25 ppm
N$_2$	5 ppm	> 1 ppm
O$_2$	824 ppm	89 ppm
Ar	1280 ppm	104 ppm
SO$_2$	5 ppm	5 ppm
NO	> 1 ppm	> 1 ppm
NO$_2$	6 ppm	6 ppm

[1]Solid product molar MgO concentration of 2.23 %
[2]Solid product molar MgO concentration of 1.85 %

The simulation results show that for SRKM the minimum work coincides with an oxygen concentration less than 1000 ppm. As a result, moving from the point of minimum work to the point where all EOR recommendations is met will give a smaller increase in energy penalty and needed size for the distillation column. The flowing volume entering the column per mass flow of CO$_2$ exiting the process is around 20 percent larger when an oxygen concentration of 100 ppm is obtained. The same trends seen for the SRKM results are seen for the SRKK results but the optimum gives an oxygen concentration of 1263 ppm. The increased work to obtain 100 pmm of oxygen with SRKK is still less than one percent. Finally, as for C3_3, the composition containing 100 ppm of oxygen is pure enough for liquefaction.

4.6.5.   Liquefaction, case NG3_4

The liquefaction process is identical to the one used in C3_4; the pump after the distillation is replaced by a valve reducing the pressure to 6.5 bar and a heat exchanger cooling the mixture to -52°C totally condensing it. The corresponding flow diagram can be seen in Figure A-14 in Appendix A and the results for both SRKM and SRKK are given in Table 4-27.

Table 4-27: Results NG3_4

Parameter:	SRKM:	SRKK:
Total work [kJ/kgCO$_2$]	510,17	513,87
Total work [kWh/tonCO$_2$]	141,71	142,74
Increase from NG3_3 [%]	5,00	5,26
Increase from NG3_1 (20 bar) [%]	16,67	17,59
Composition:		
CO$_2$	99,98 %	99,98 %
H$_2$O	25 ppm	25 ppm
N$_2$	> 1 ppm	> 1 ppm
O$_2$	89 ppm	92 ppm
Ar	104 ppm	178 ppm
SO$_2$	5 ppm	5 ppm
NO	> 1 ppm	> 1 ppm
NO$_2$	6 ppm	6 ppm

The difference between SRKM and SRKK is also for the final case less than one percent. As expected the CO_2 exiting from the bottom of the distillation column using both EoS' condenses fully at the required conditions.

5. Results and discussion

When all the simulation results are obtained, it is time to examine what implications the work related to the CO_2 conditioning will have on the overall efficiency of the power plant. Starting out with the efficiency for the power plant with CO_2 capture, a correlation for produced CO_2 from the given process is used to calculate the efficiency reduction. This correlation can be found by defining a CO_2 emission index as the ratio between the mass of CO_2 produced from a process, relative to the energy in the fuel consumed given as the lower heating value. The expression for such an index is given in Equation (5.1).

$$\chi = \frac{m_{CO_2}}{Q_{LHV}} = \frac{m_{CO_2} \cdot \eta}{W} \tag{5.1}$$

Further, knowing the specific work requirement for the conditioning process, the efficiency reduction due to CO_2 conditioning is given in equation (5.2).

$$\Delta\eta = \eta_{cap} \cdot w_{cond} \cdot \chi \tag{5.2}$$

Another parameter that will be used to evaluate the different processes is the capture efficiency which can be defined as given in equation (5.3).

$$\eta_{cap,e} = 1 - \frac{\eta_{ref}}{\eta_{CO_2}}(1 - \eta_{cap}) \tag{5.3}$$

For an oxy combustion process the capture rate of the conditioning process and the overall capture rate are one and the same. For pre and post combustion processes the overall capture rate will be a product between the capture rate for the actual capture process, and the capture rate for the conditioning process as defined in equation (5.4).

$$\eta_{cap,tot} = \eta_{cap,CO_2} \cdot \eta_{cap,cond} \tag{5.4}$$

Having established the basis for evaluation, the CO_2 emission index together with reference efficiencies must be established for the different capture methods. For the pre combustion cases using coal, the needed data is included in the source the compositions where taken from [2]. In the source where the natural gas pre combustion composition was found [3], the necessary data is not included. The data is instead taken from a paper performing a quantitative comparison of different capture methods [33]. Doing this will possibly affect the results, because the capture rate given with the composition is higher than the one given where the data needed in this section were found. A higher capture rate might give lower purity for the captured CO_2. Applying the data involves the assumption that the effect of a change in capture rate on the required work for conditioning is small.

The composition used in the case of post combustion from coal, is taken from a source without information that can be used to calculate the parameters needed. Data for post combustion capture from both natural gas and coal is found in the source used for the natural gas case.

The source used for natural gas oxy combustion does not include the necessary data. They are instead gotten from the same source used for natural gas pre combustion [33]. Data for coal oxy combustion is given were the used composition was found. The calculated emission indexes are presented in Table 5-1 along with efficiencies without CO_2 capture (η_{ref}), efficiencies with capture but without CO_2 compression/conditioning (η_{CO2}) and capture rates used for the evaluation.

Table 5-1: Parameters for efficiency calculations

Case:	χ (kgCO$_2$/MJ$_{LHV}$):	η_{ref} (%):	η_{CO2} (%):	η_{cap} (%):
C1a	0,09138	43,1	36,9	85
C1b	0,09138	43,1	36,1	85
NG1	0,05778	56,7	49,1	90
C2	0,09081	44,0	38,0	85
NG2	0,05849	55,6	49,6	85
C3	0,09039	44,3	39,7	Varies
NG3	0,05788	56,7	50	Varies

For the natural gas case NG2, the reference efficiency used will be 56.7 percent. This is done because the other two natural gas cases both are using it, and because the efficiencies with capture are fairly similar.

5.1. Encap recommendations for basic underground storage

The limits applying in this case are given in Table 2-7 section 2.4. All cases where some kind of drying is applied, will meet these recommended guidelines. Implications for overall efficiency for the capture methods are given in Table 5-2 for coal and Table 5-3 for natural gas.

Table 5-2: Encap aquifer coal cases

Property:	C1a_1	C1b_1	C2_1	C3_1
Efficiency with capture [%]	36,9	36,1	38,0	39,7
Efficiency reduction [%-points]	2,91	2,95	2,34	4,39
Efficiency reduction [%]	7,88	8,16	6,16	11,06
Overall efficiency [%]	**34,0**	**33,2**	**35,7**	**35,3**
Capture efficiency [%]	**81,0**	**80,5**	**81,5**	**88,9**

As seen from the table the highest overall efficiency is achieved with the use of post combustion capture (C2_1). Given the fact that the capture rate for the oxy combustion process is more than 5 percent higher than for the others, it is a bit surprising that it performs almost as well as the post combustion case. However, while the pre and post combustion processes are more or less identical, the oxy combustion process differs quite a bit. In terms of drying, the oxy combustion case uses a molecular sieve. According to [3], cost and energy requirement is similar. The major difference is that the oxy combustion case uses two multi stream heat exchangers to lower the content of volatile substances. This will increase the investment cost considerably compared to the other cases.

Regarding capture efficiency the pre and post combustion processes perform abut the same. The oxy combustion process outperforms them despite the fact that the relative overall efficiency reduction is the largest. This is due to the higher capture rate. Lowering the capture rate for the oxy combustion process would lower the capture efficiency but also decrease the efficiency reduction.

Considering the results for the two pre combustion cases, it is clear that separate removal of H_2S and CO_2 offers no advantage in terms of energy penalty if sour gas transport is utilized. This is both due to the fact that the efficiency is reduced as a result of separate capture, and that the concentration of carbon monoxide and hydrogen in the captured stream will increase. Especially hydrogen has a noticeable effect on the compression work.

Table 5-3: Encap aquifer natural gas cases

Property:	NG1_1	NG2_1	NG3_1
Efficiency with capture [%]	*49,1*	*49,6*	*50,0*
Efficiency reduction [%-points]	*1,78*	*1,51*	*2,47*
Efficiency reduction [%]	*3,63*	*3,57*	*5,06*
Overall efficiency [%]	*47,3*	*48,1*	*47,5*
Capture efficiency [%]	*88,0*	*82,3*	*97,3*

As for the coal cases natural gas post combustion capture shows the best performance in terms of overall efficiency. For pre combustion capture the concentrations of combustible volatiles are much lower than for coal. This narrows the gap between pre and post combustion even though the capture rate for pre combustion in this case is 90 %. CO_2 capture from natural gas in general gives more similar results.

In terms of investment cost the oxy combustion case will stand out using natural gas as well. The same configuration with two multi stream heat exchangers as used for the coal oxy combustion case is applied to remove volatiles. The total required size of heat transfer surfaces is smaller at a given pressure due to lower concentrations of volatiles, but it will still represent an increase in required investment cost compared to pre and post combustion.

Since all three cases have different capture rates the capture efficiencies differ considerably. The optimums in terms of energy efficiency in simulations on natural gas oxy combustion cases, give high capture rates, in this case as high as 97.72 percent. From the discussion in section 3.1 the real optimum is expected to give lower capture rates. Considering the same discussion and looking at the results obtained with the other equation of state used (SRKK), the actual capture rates may well be around 96.5 percent which is still high.

5.2.   Dynamis aquifer recommendations

Compared to Encap's recommendations for aquifer storage, the Dynamis guidelines lower the tolerance for impurities significantly. In the development of these guidelines focus has been on minimizing health risks if the transport pipelines crack. Several of the impurities which are present in a captured CO_2 stream are hazardous to humans at relatively small concentration levels. This has implications on the conditioning process when H_2S is captured along with CO_2 for coal pre combustion, and when CO_2 is captured from both coal and natural gas when oxy combustion is applied.

For case C1a_2, H_2S is removed by applying a selective catalytic oxidizer. There has not been found any examples of this type of reactor being commercialized, but promising experiments has been carried out as mentioned in section 2.6.2. For the oxy combustion cases conventional technology used for control of nitrogen oxides and flue gas desulphurization is applied. An experimental method for combined capture removing NO_x and SO_2 as nitric and sulphuric acid respectively is also considered. The combination of selective catalytic reduction of NO_x

and wet lime scrubbing for SO_2 showed the best performance and may also be the configuration most feasible applied to CO_2-rich flue gas.

The performance results for the coal cases that fulfil the requirements are given in Table 5-4. For C1a_2 a conventional catalytic oxidizer is applied in addition to the selective catalytic oxidizer, reducing the concentrations of combustible components but also consuming oxygen. Using air will remove the need for buying oxygen reducing the cost involved but increasing the compression work. Purification of the oxy combustion case to meet the requirements means consuming both ammonia and lime at rates given in the table.

Table 5-4: Dynamis aquifer coal cases

Property:	C1a_2 (O_2)	C1a_2 (air)	C1b_1	C2_1	C3_2
Efficiency with capture [%]	36,9	36,9	36,1	38,0	39,7
Efficiency reduction [%-points]	2,90	2,99	2,95	2,34	4,38
Efficiency reduction [%]	7,86	8,11	8,16	6,16	11,03
Overall efficiency [%]	**34,0**	**33,9**	**33,2**	**35,7**	**35,3**
Capture efficiency [%]	**81,0**	**80,9**	**80,5**	**81,5**	**88,8**
Oxygen consumption [kg/tonCO$_2$]	3,1	-	-	-	-
Ammonia consumption [kg/tonCO$_2$]	-	-	-	-	0,21
Lime consumption [kg/tonCO$_2$]	-	-	-	-	7,91

The CO_2 captured by post combustion has no need for removal of impurities and still performs the best. Yet again the oxy combustion case outperforms pre combustion and demonstrates the highest capture efficiency. The simulation results actually show a decrease in specific energy consumption, though with a slightly lower capture rate. The down side is that even more equipment is needed, and the assumed performance of the lime stone scrubbing applied to high flue gas concentrations is not verified. Regarding combined versus separate capture of H_2S and CO_2, C1a is still the more efficient, but it will need higher investment costs. Further technology development will also be necessary regarding the removal of H_2S by selective catalytic oxidation.

The pre and post combustion conditioning methods for natural gas are the same as for Encap's aquifer guidelines. The oxy combustion case now includes reactors using the modified lead chamber process suggested by White et al. [22] to remove most of the NO_x and SO_2. This purification method involves less extensive equipment then the other considered methods to remove NO_x and SO_2. In the paper by White et al. [22] there is no mention of needed additives. However, simulations of the reactions involved results in high nitric acid concentrations in the gaseous phase (in the order of 100 ppm). These concentrations are reduced to acceptable levels by adding magnesium oxide at a rate given in Table 5-5. It is not determined whether or not this is necessary in practise, nor if these concentrations reflect chemical mechanisms or inadequate performance by the applied equation of state.

The overall performance of the oxy combustion case is up from the previously considered case due to a lower capture rate at the point of minimum specific energy consumption. The capture efficiency is lower for the same reason.

Table 5-5: Dynamis aquifer natural gas cases

Property:	NG1_1	NG2_1	NG3_2
Efficiency with capture [%]	49,1	49,6	50,0
Efficiency reduction [%-points]	1,78	1,51	2,40
Efficiency reduction [%]	3,63	3,04	4,81
Overall efficiency [%]	**47,3**	**48,1**	**47,6**
Capture efficiency [%]	**88,0**	**82,31**	**93,1**
Magnesium oxide consumption [kg/tonCO$_2$]	-	**-**	0,07

5.3. Dynamis EOR recommendations

At this level of quality requirements limitations regarding tolerance for oxygen is included. Exothermic reactions between oil and oxygen in the reservoir can raise the temperature above tolerated levels at the injection point. Because of lack of experience and knowledge regarding this problem, Dynamis does not specify an absolute limit rather a range that is 100-1000 ppm. This has no implications for other than the oxy combustion processes, as long as oxygen fed to the catalytic oxidizer for case C1a_2 can be controlled accurately enough. The two stage flash separation process applied so far for the oxy combustion cases, does not show the ability to produce oxygen concentrations low enough to meet the requirements. As a result, distillation is necessary.

The low temperatures involved with distillation create the need for external cooling circuits. Specific work increases by about 10 percent and the capture decreases with about 0.4 percent at the process energy efficiency optimum. Together this reduces the overall efficiency by 0.4 percent. Oxy combustion still performs better than pre combustion due to higher base plant efficiency. The low pressure needed to achieve an oxygen concentration of 1000 ppm will increase the size of the distillation column compared to the optimum point for specific energy consumption. Pro/II reports the flowing volume entering the column relative to the amount of CO$_2$ captured to be around 35 percent higher. The pressures in question are around 25 bar at the optimum point and 21 bar when the oxygen concentration is reduced to 1000 ppm. No inquiry has been performed to reveal the consequences in terms of practical feasibility of such a column.

Table 5-6: Dynamis EOR coal cases

Property:	C1a_2 (O$_2$)	C1a_2 (air)	C1b_1	C2_1	C3_3[1]
Efficiency with capture [%]	36,9	36,9	36,1	38,0	39,7
Efficiency reduction [%-points]	2,90	3,00	2,95	2,34	4,77
Efficiency reduction [%]	7,86	8,11	8,16	6,16	12,00
Overall efficiency [%]	**34,0**	**33,9**	**33,2**	**35,7**	**34,9**
Capture efficiency [%]	**81,0**	**81,0**	**80,5**	**81,5**	**88,2**
Oxygen consumption [kg/tonCO$_2$]	3,1	-	-	-	**-**
Ammonia consumption [kg/tonCO$_2$]	-	-	-	-	0,21
Lime consumption [kg/tonCO$_2$]	-	-	-	-	7,94

[1]The version with an oxygen concentration of 1000 ppm

When distillation is applied to the oxy combustion natural gas case the point of minimized specific energy requirement, results in an oxygen concentration of 824 ppm. This is when using the default equation of state (SRKM). For the alternative equation of state the oxygen requirement is met at a lower pressure than for the optimum point. However, the volumetric flow entering the column relative to the mass flow of captured CO$_2$ seems to be about the same (see Table B-2 in Appendix B). This flow rate is about half the one for the coal case. As

seen from the results in Table 5-7 the performance is better than for the pre combustion here as well.

Table 5-7: Dynamis EOR natural gas cases

Property:	NG1_1	NG2_1	NG3_3
Efficiency with capture [%]	49,1	49,6	50,0
Efficiency reduction [%-points]	1,78	1,51	2,64
Efficiency reduction [%]	3,63	3,04	5,29
Overall efficiency [%]	**47,3**	**48,1**	**47,4**
Capture efficiency [%]	**88,0**	**82,3**	**93,4**
Magnesium oxide consumption [kg/tonCO$_2$]	-	-	0,07

5.4. Encap EOR recommendations

In addition to an absolute limit for the oxygen concentration of 100 ppm, the second EOR recommendation also limits the concentration of water, SO$_2$ and H$_2$S to 50 ppm. The same limit is also applied for carbonyl sulphide (COS) and mercaptans but none of these are present in the considered compositions. For coal pre combustion with separate capture of H$_2$S and CO$_2$ this means that adding a catalytic combustor to the conditioning process is necessary. For the oxy combustion cases the distillation column pressure must be lowered even more giving larger volumetric flow rates (up about 15 percent for coal and 25 percent for natural gas).

Results given in Table 5-7, shows the same trend as seen for all the quality recommendations so far. The post combustion case performs the best followed by the oxy combustion case which also demonstrates the highest capture efficiency. Reduction in the combustible volatiles concentrations by catalytic oxidation for C1b, does not improve the performance. It remains the less efficient of the pre combustion cases, now also with a similar need for conditioning equipment as C1a.

Table 5-8: Encap EOR coal cases

Property:	C1a_2_O$_2$	C1a_2_air	C1b_2_O$_2$[1]	C1b_2_air[1]	C2_1	C3_3[2]
Efficiency with capture [%]	36,9	36,9	36,1	36,1	38,0	39,7
Efficiency reduction [%-points]	2,90	3,00	2,90	3,10	2,34	4,77
Efficiency reduction [%]	7,86	8,11	8,05	8,58	6,16	12,03
Overall efficiency [%]	**34,0**	**33,9**	**33,2**	**33,0**	**35,7**	**34,9**
Capture efficiency [%]	**81,0**	**81,0**	**80,5**	**80,4**	**81,5**	**88,1**
Oxygen consumpt. [kg/tonCO$_2$]	3,1	-	7,8	-	-	-
Ammonia consumpt. [kg/tonCO$_2$]	-	-	-	-	-	0,21
Lime consumpt. [kg/tonCO$_2$]	-	-	-	-	-	7,95

[1]Given that a SO$_3$ concentration above 50 ppm is acceptable
[2]The version with an oxygen concentration of 100 ppm

The performance results for the natural gas cases are given in Table 5-9. As one can see, the steady increasing work requirement needed for the oxy combustion case to keep up with quality requirements, has finally given an overall efficiency as low as for the pre combustion case. It however still gives the highest capture efficiency.

Table 5-9: Encap EOR natural gas cases

Property:	NG1_1	NG2_1	NG3_3[1]
Efficiency with capture [%]	49,1	49,6	50,0
Efficiency reduction [%-points]	1,78	1,51	2,66
Efficiency reduction [%]	3,63	3,04	5,31
Overall efficiency [%]	**47,3**	**48,1**	**47,3**
Capture efficiency [%]	**88,0**	**82,3**	**93,4**
Magnesium oxide consumption [kg/tonCO$_2$]	-	-	0,07

[1]The version with an oxygen concentration of 100 ppm

5.5. Liquefaction

Finally the last stage in any of the conditioning processes, liquefaction, is considered. Encap has given a quality recommendation which they call the severe limit case. This is meant for strict health, safety and environmental regulations (HSE) and liquefaction for the use in EOR. However, the real limitation for the liquefaction process will be the needed purity to obtain a fully condensed liquid phase at the given conditions for storage and ship transport. None of the considered compositions liquefy at CO_2 concentrations lower than 99.96 percent. It may seem like cases with slightly higher concentrations of substances less volatile than CO_2 increases the boiling point for the mixture. This effect has not been studied in particular, but most likely it has little or no implications for the overall efficiency.

Apart from the post combustion natural gas case, all the processes need a distillation column in order to obtain purity required for liquefaction. Except from the oxy combustion cases the configuration for this column is the same, and a detailed description is given in section 4.1.4. The post combustion natural gas case can obtain purity suited for liquefaction simply by drying. For the oxy combustion cases the process giving an oxygen concentration of 100 ppm is modified for liquefaction simply by replacing the final pump by a valve and a heat exchanger.

The results for the coal cases are given in Table 5-10. The best performance is obtained by the post combustion case but the oxy combustion case gives an overall efficiency only 0.1 percentage points lower. As for the previously considered quality recommendations, it shows higher capture efficiency. The column used in the oxy combustion case will though be substantially larger. The results for the pre combustion cases establishes that given the selective catalytic oxidizer for H_2S will be commercialized, combined capture of H_2S and CO_2 from pre combustion will probably be the method of choice.

Table 5-10: Liquefaction coal cases

Property:	C1a_3	C1b_3	C2_2	C3_4
Efficiency with capture [%]	36,9	36,1	38,0	39,7
Efficiency reduction [%-points]	3,90	3,83	3,24	4,97
Efficiency reduction [%]	10,57	10,61	8,53	12,51
Overall efficiency [%]	**33,0**	**32,3**	**34,8**	**34,7**
Capture efficiency [%]	**80,3**	**79,8**	**80,9**	**88,0**
Oxygen consumption [kg/tonCO$_2$]	3,1	7,8	-	-
Ammonia consumption [(kg/tonCO$_2$]	-	-	-	0,21
Lime consumption [kg/tonCO$_2$]	-	-	-	7,95

As seen from the natural gas results in Table 5-11, the performance for the oxy combustion case is the same as when the Encap EOR recommendations is applied while the other cases decrease in performance. As for the coal cases, the difference between post combustion and

oxy combustion in terms of overall efficiency is small. The post combustion case offers a great advantage by the fact that it does not require a column at all.

Table 5-11: Liquefaction natural gas cases

Property:	NG1_2	NG2_2	NG3_4
Efficiency with capture [%]	49,1	49,6	50,0
Efficiency reduction [%-points]	2,43	2,03	2,78
Efficiency reduction [%]	4,96	4,10	5,58
Overall efficiency [%]	**46,7**	**47,6**	**47,3**
Capture efficiency [%]	**87,7**	**82,0**	**93,4**
Magnesium oxide consumption [kg/tonCO$_2$]	-	-	0,07

Finally, reductions in overall efficiency and capture efficiency for the case of liquefaction relative to the Encap recommendations for aquifer storage, is given in Table 5-12. As one can see the oxy combustion cases has the lowest relative decrease in overall efficiency but the highest relative decrease in capture efficiency. All in all the relative changes are fairly small.

Table 5-12: Relative change Encap aquifer to liquefaction

Efficiency:	C1a	C1b	C2	C3	NG1	NG2	NG3
Overall [%]	2,94	2,71	2,52	1,70	1,27	1,04	0,42
Capture [%]	0,86	0,87	0,74	1,01	0,34	0,36	4,01

6. Conclusions

Terminating this work there are some end conclusions to be made. Along the way several more or less surprising things have been discovered but the first worth mentioning is though not so surprising. When working with numerical simulations, having tools that perform well in terms of reflecting reality is important. The evaluation of the equations of state in the simulation program Pro/II showed that these equations should be selected carefully. This is especially the case when oxy combustion processes are considered. Selecting an unfit equation may give large deviations in calculations. This is particularly the case when separation processes including components with different properties are considered. In this work the equation of state found to perform the best was a modified version of Soave-Redlich-Kwong Panagiotopoulos-Reid.

When dealing with two stage flash separation of oxy combustion derived CO_2, simulations show that this process is limited in terms of inlet pressure. The reason is that the higher pressure, the more nitrogen, oxygen and argon will condense. This will give total concentrations of volatile substances higher than the widely accepted maximum limit of 4 percent. In this work the upper pressure limit was found to be around 30 bar. Decreasing the pressure will increase the potential for energy efficiency along with the needed size of heat exchanger surfaces. At 20 bar the specific energy consumption was 1.6 percent lower and the total needed heat exchanger surface 12.6 percent higher than at 30 bar. Depending on what other means of purification is applied, at these pressures the energy optimum will struggle to meet requirements of a capture rate of 90 percent.

To make CO_2 capture more economically feasible EOR is the preferred end use for the processed CO_2. For oxy combustion the greatest challenge is reducing the content of oxygen to acceptable levels. Simulations show that meeting given recommendations for the oxygen concentration is possible. The downside is that it will require distillation at low pressures. Two stage flash separation will not achieve concentrations of 1000 ppm much less 100 ppm. Simulations performed obtained concentrations below 100 ppm for pressures around 20 bar. For oxy combustion of coal this will result in distillation equipment about 50 percent larger than at around 25 bar where the energy efficiency seem to be the highest.

The potentially low pressures involved with separation of volatiles from oxy combustion derived CO_2 has implications for the drying process. If TEG drying is applied, a drop in pressure from 30 to 20 bar will more than triple the required circulation ratio of TEG at a specified water concentration. The reboiler duty will hence increase and so will the size of TEG equipment and pressure drop through the system. Another effect discovered for oxy combustion is that the lower partial pressure of CO_2 decreases the efficiency of the drying compared to other capture processes. At high CO_2 concentrations the needed circulation ratio for TEG goes down because water will be dissolved in CO_2 exiting with the rich TEG. It is concluded that TEG drying is less suited for oxy combustion derived CO_2 than for CO_2 derived from pre or post combustion.

Regarding pre combustion capture one of the initial questions was how systems with separate capture of H_2S and CO_2 will perform compared to systems with combined capture. The capture process itself is more energy demanding for separate capture. The simulation results show that if selective catalytic oxidizers for H_2S removal become available, combined capture will perform better for all considered scenarios.

Regarding liquefaction, simulations showed that the relative increase compared to meeting the less strict quality recommendations ranges from 13.8 percent for natural gas oxy combustion, to 38.7 percent for coal post combustion in terms of specific work. In terms of overall power plant efficiency natural gas oxy combustion again gives the lowest relative increase of 0.4 percent. The highest is for pre combustion of coal with combined capture of H_2S and CO_2 with 2.9 percent. The efficiency penalty due to applying more strict recommendations regarding CO_2 purity is less than expected. For oxy combustion processes it seems like the needed investment and availability of adapted purification methods will be the limiting factor rather than energy penalty.

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Appendix A. Flow diagrams
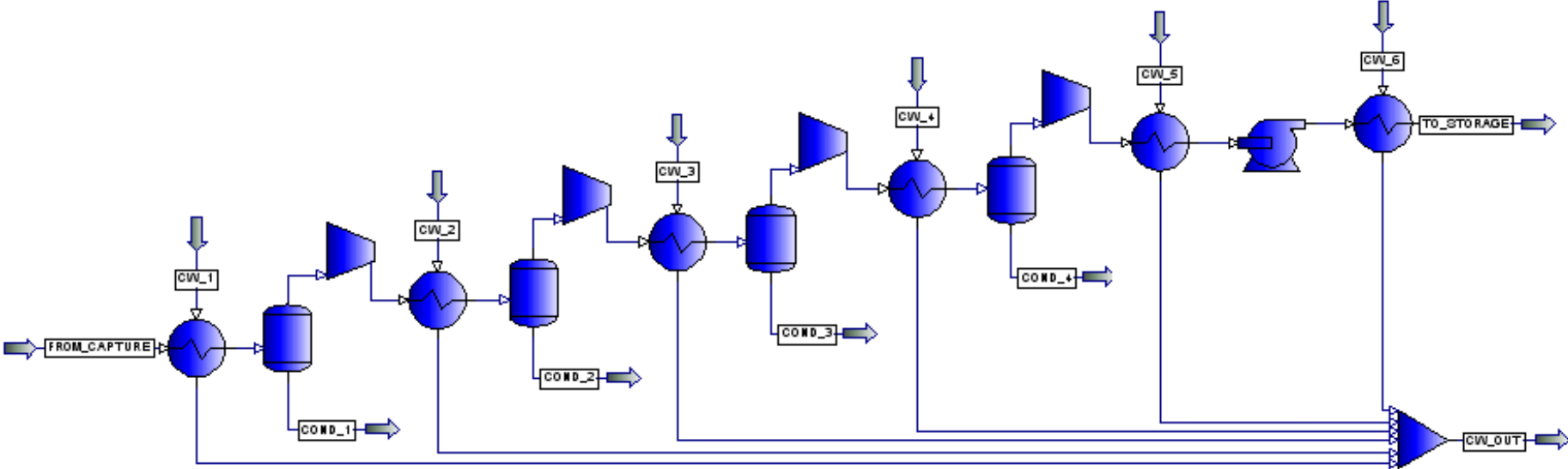
Figure A-1: Compression and flashing
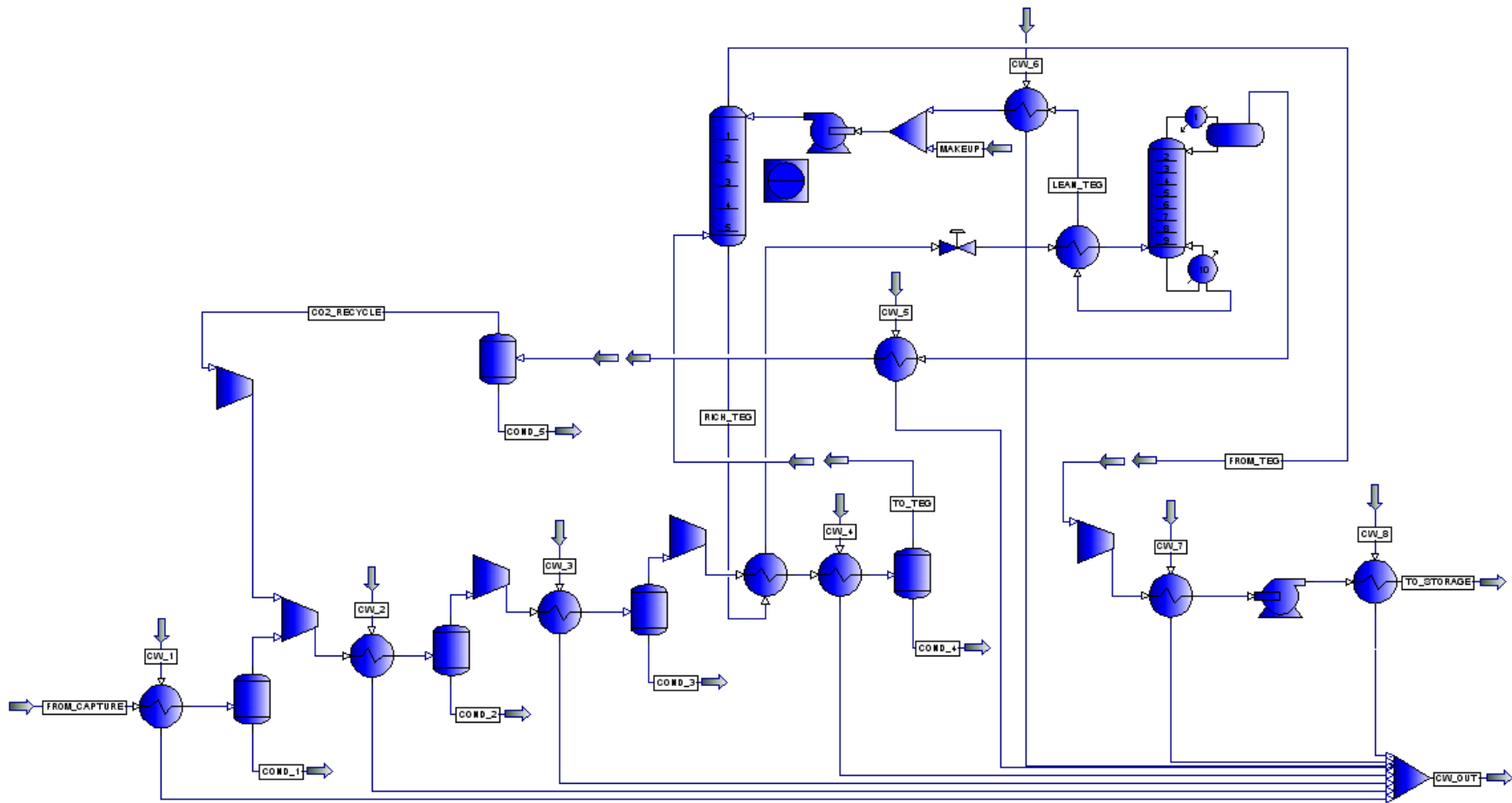
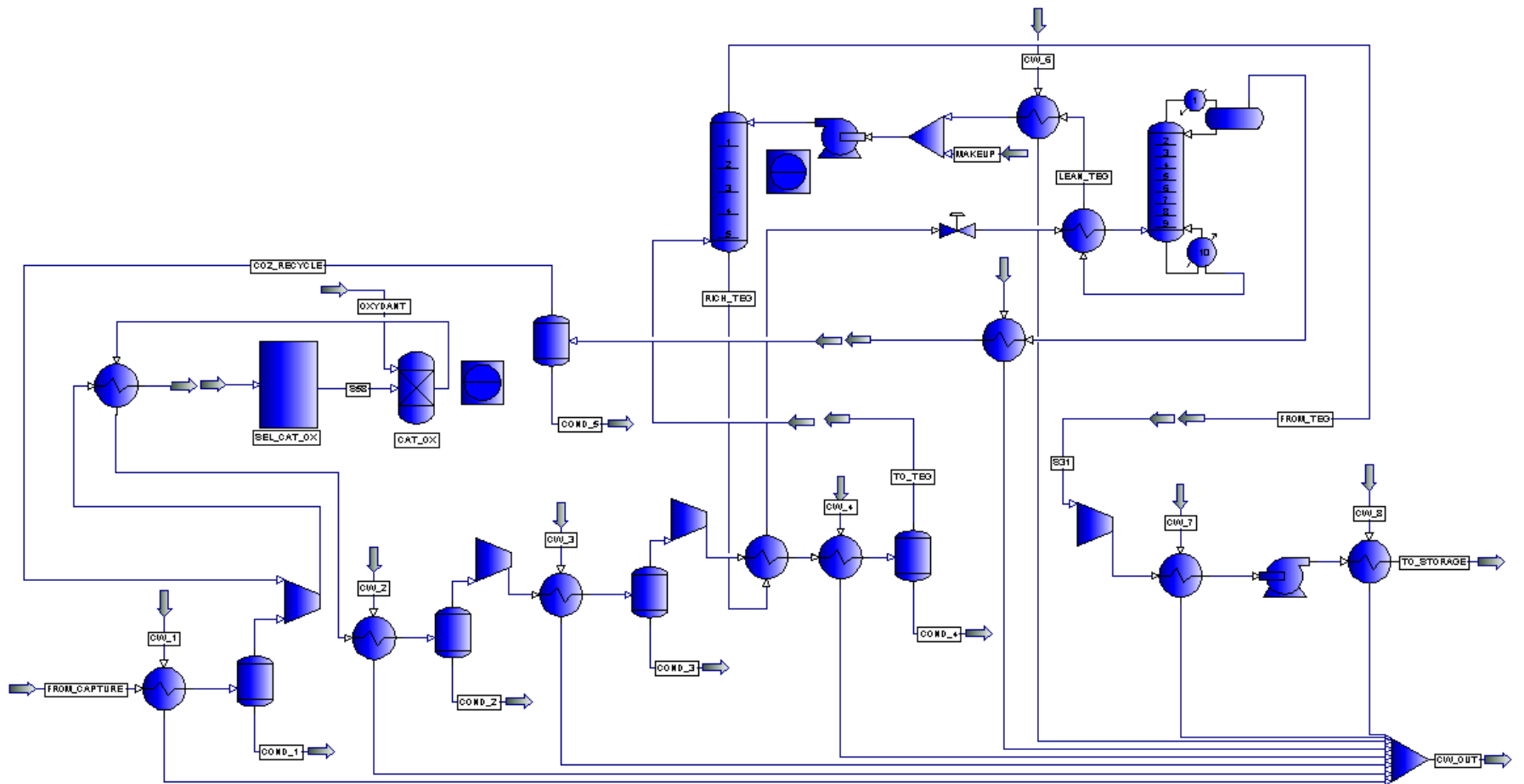**Figure A-2: Drying using TEG**

Figure A-3: TEG drying, selective catalytic oxidizer for H₂S and catalytic oxidizer for other combustibles
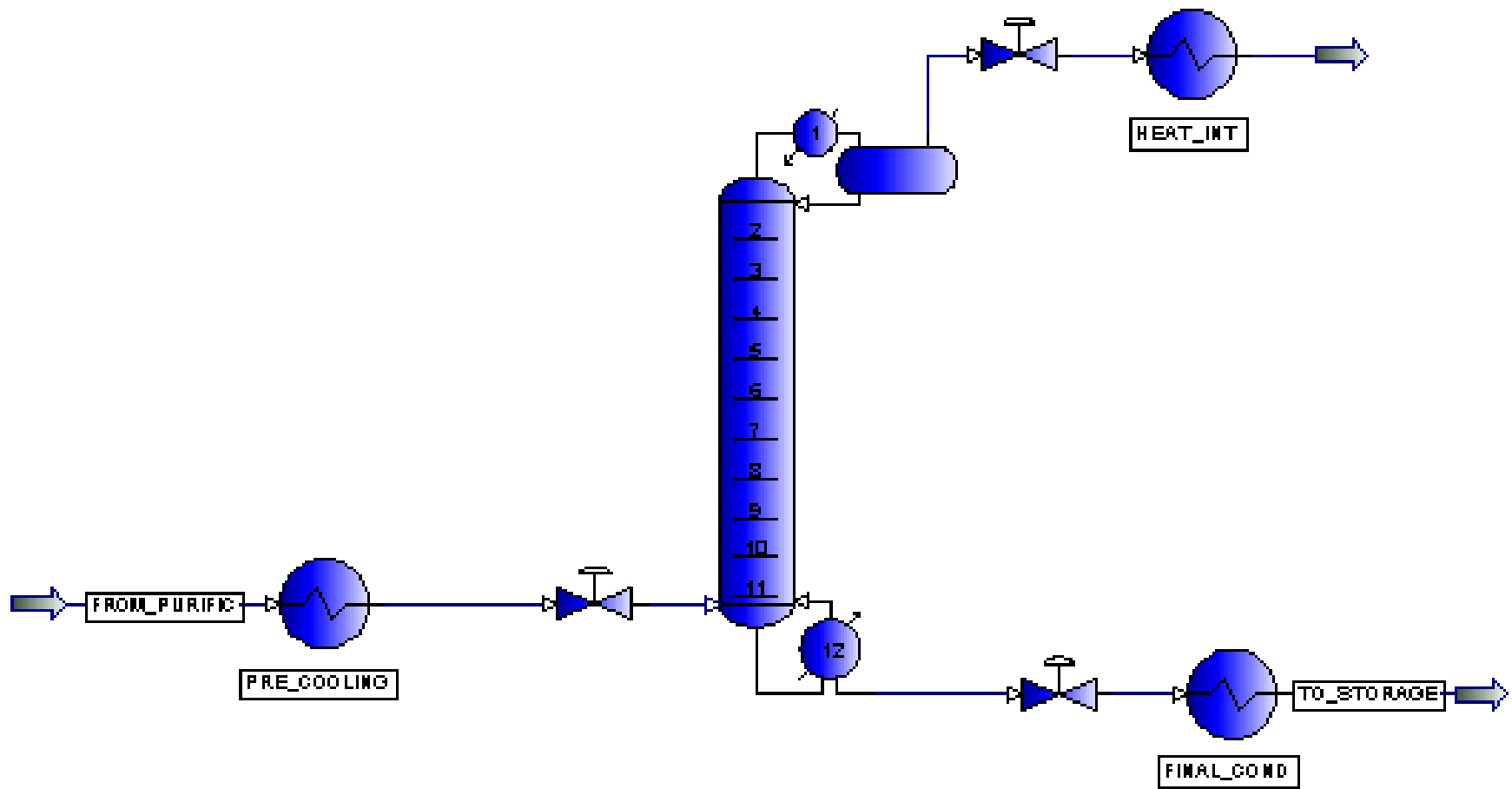
III

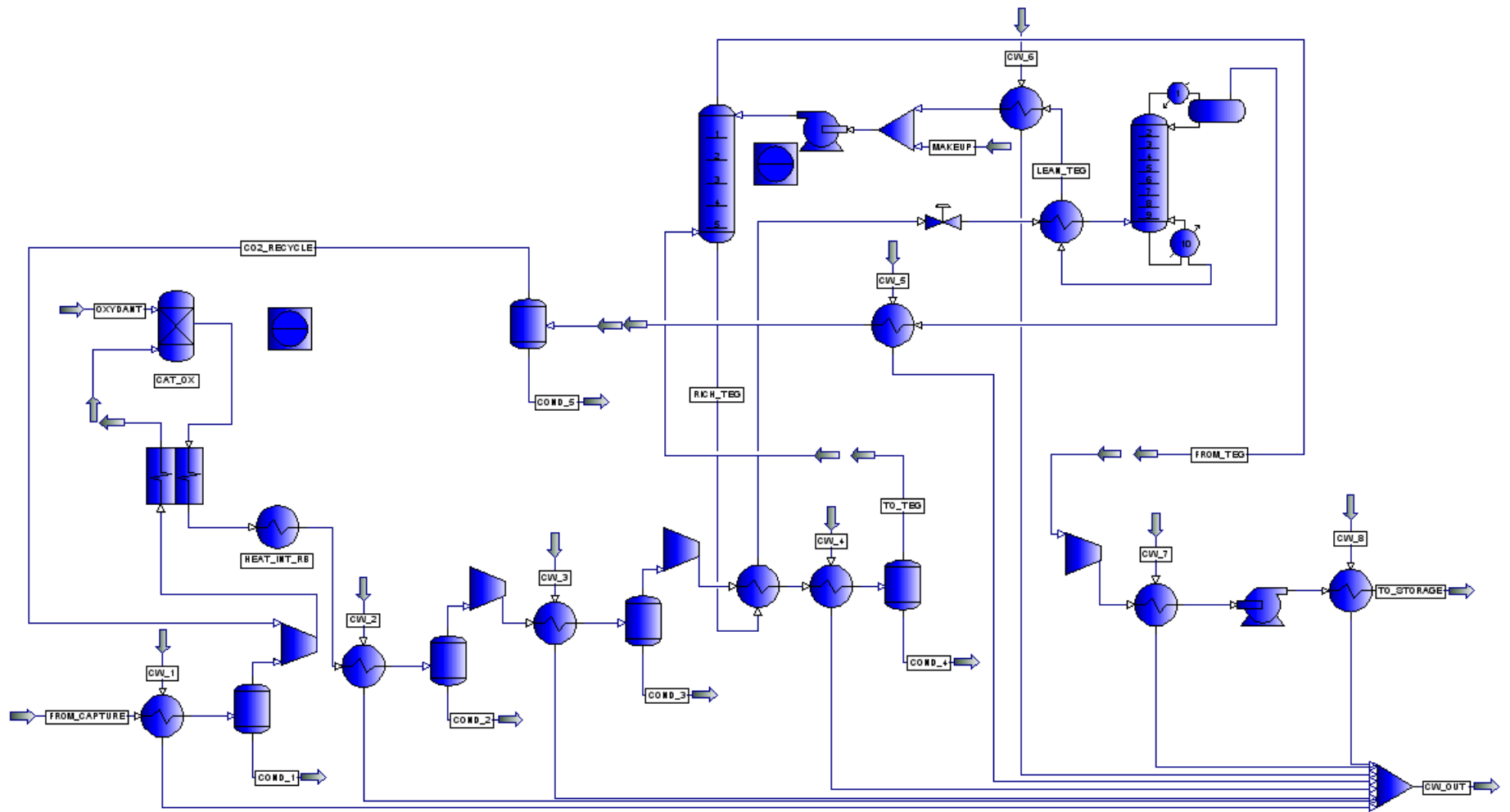**Figure A-4: Liquefaction process with volatiles removal**

IV

Figure A-5: Drying with TEG and catalytic oxidation with heat integration

V

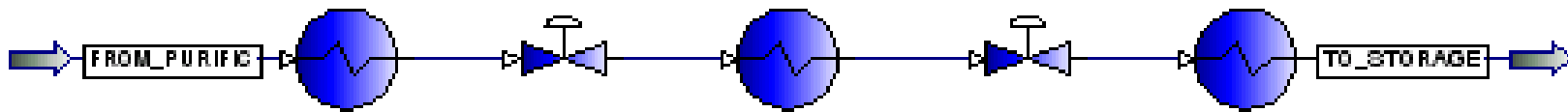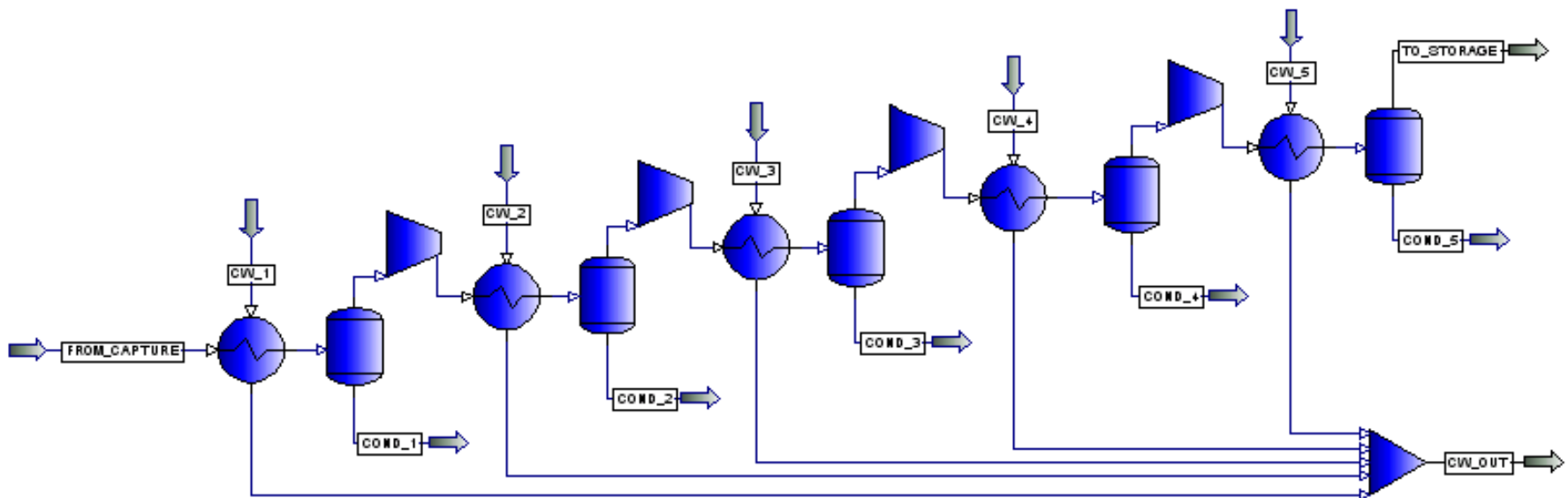**Figure A-6: Liquefaction without volatiles removal**

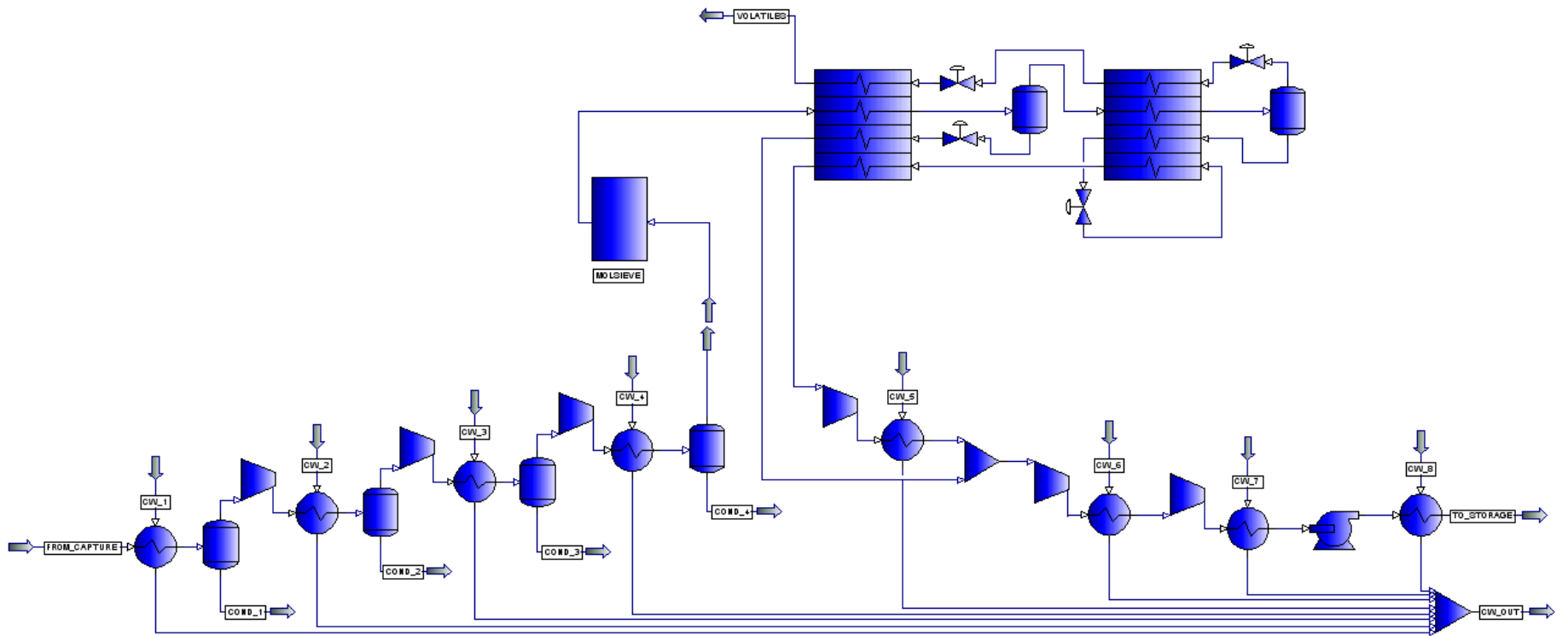
Figure A-7: Compressions and flashing for coal oxy combustion

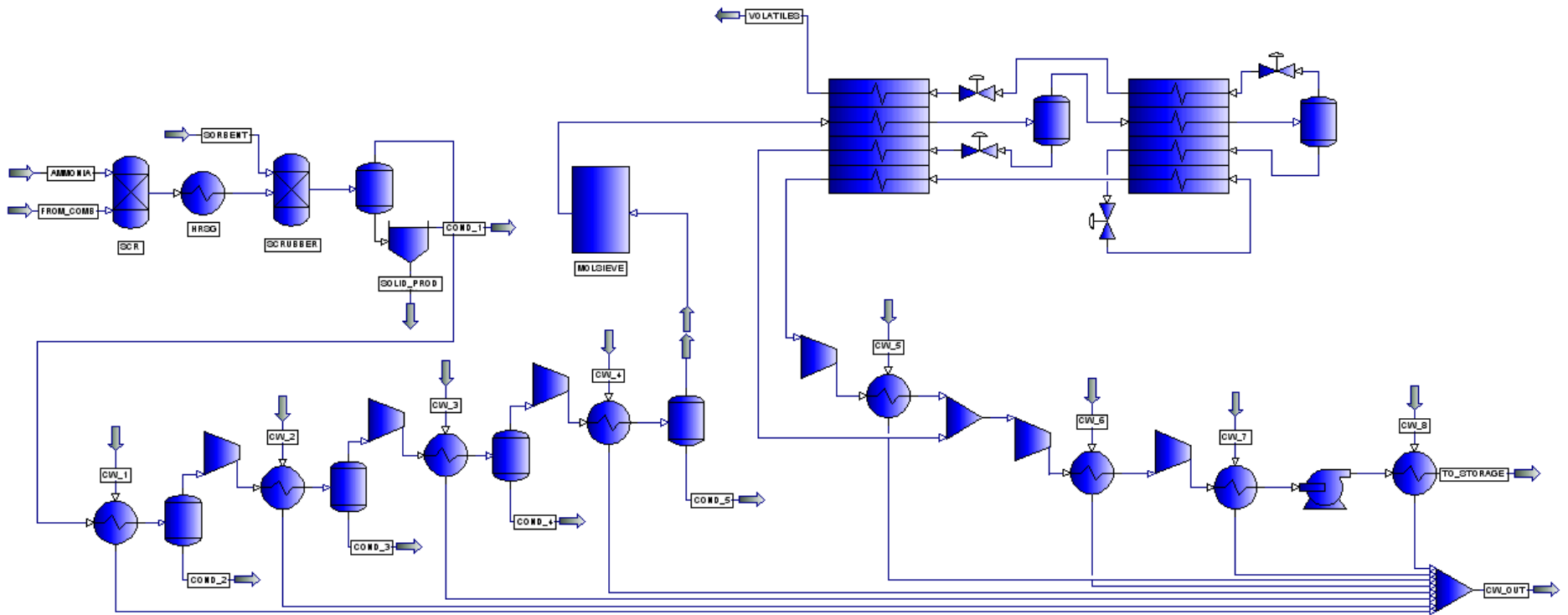**Figure A-8: Volatiles removal by two stage flashing**

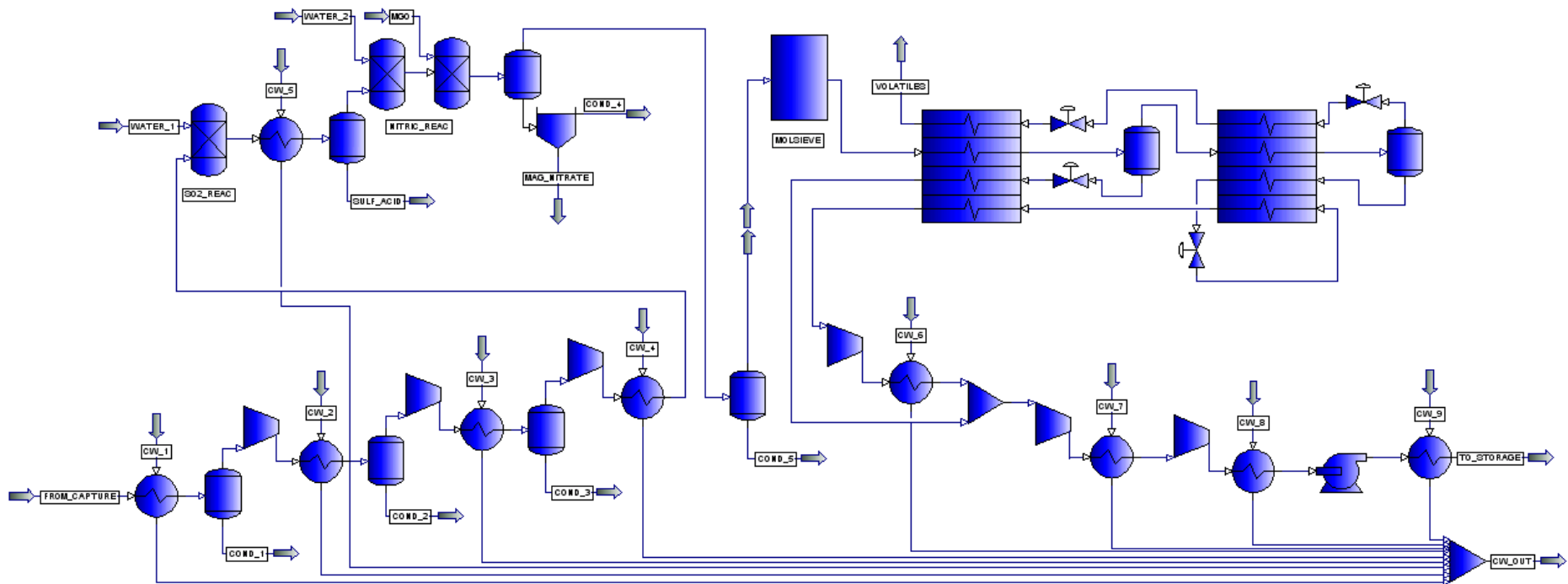**Figure A-9: Removal of NO$_x$ with SCR and SO$_2$ by wet scrubbing**

Figure A-10: The modified lead chamber process for combined removal of NO$_x$ and SO$_2$
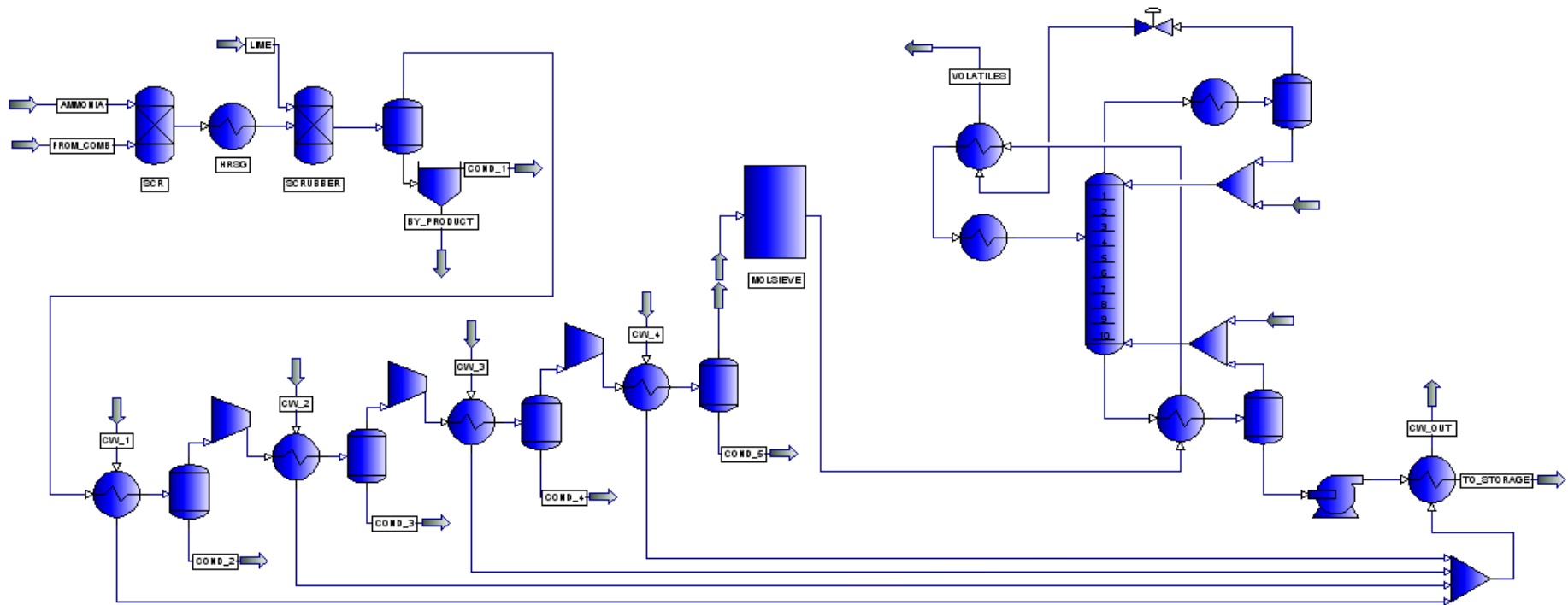
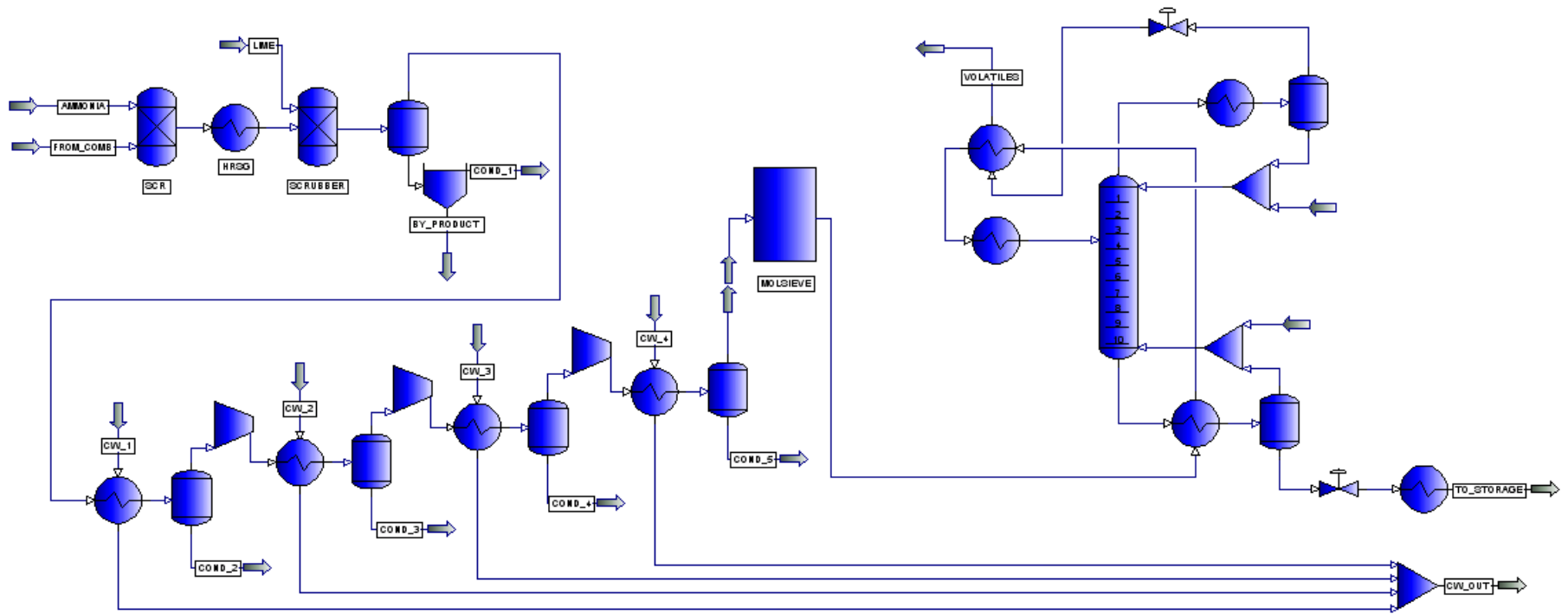**Figure A-11: Volatiles removal by distillation, coal oxy combustion**

X

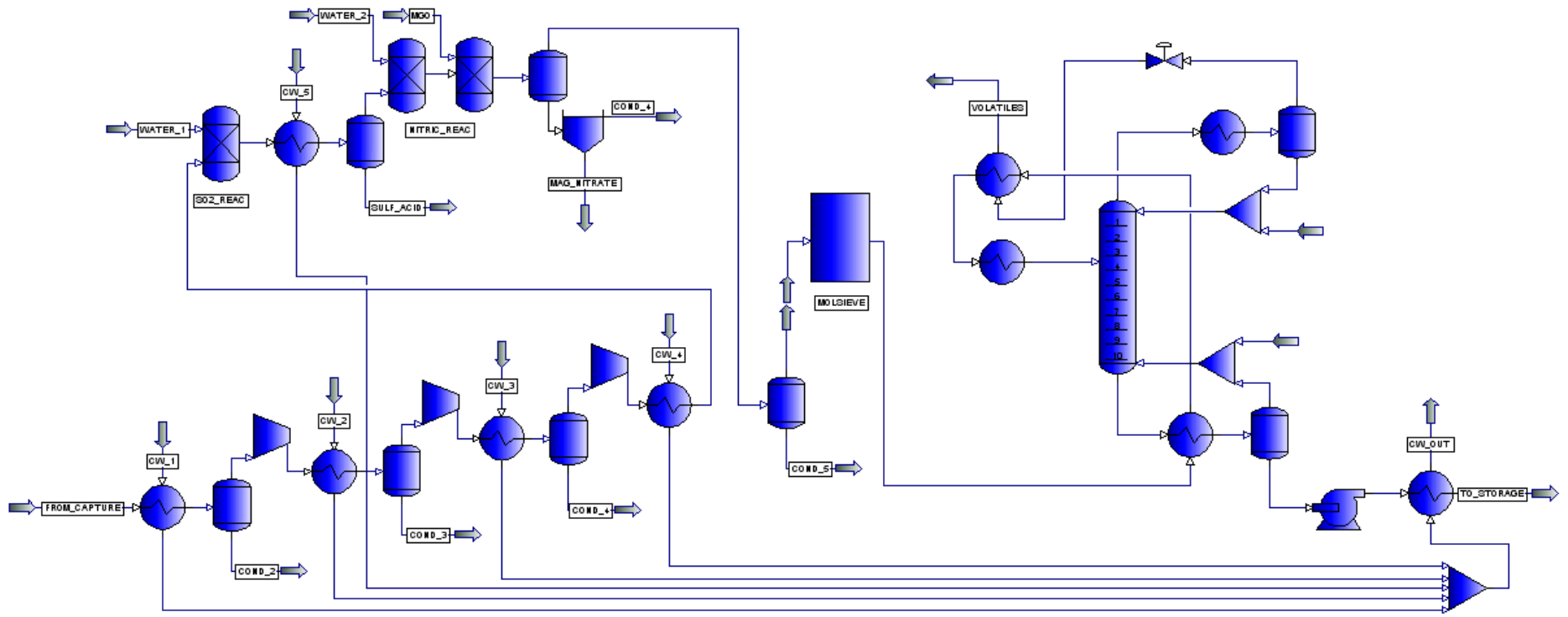**Figure A-12: Liquefaction for coal oxy combustion**

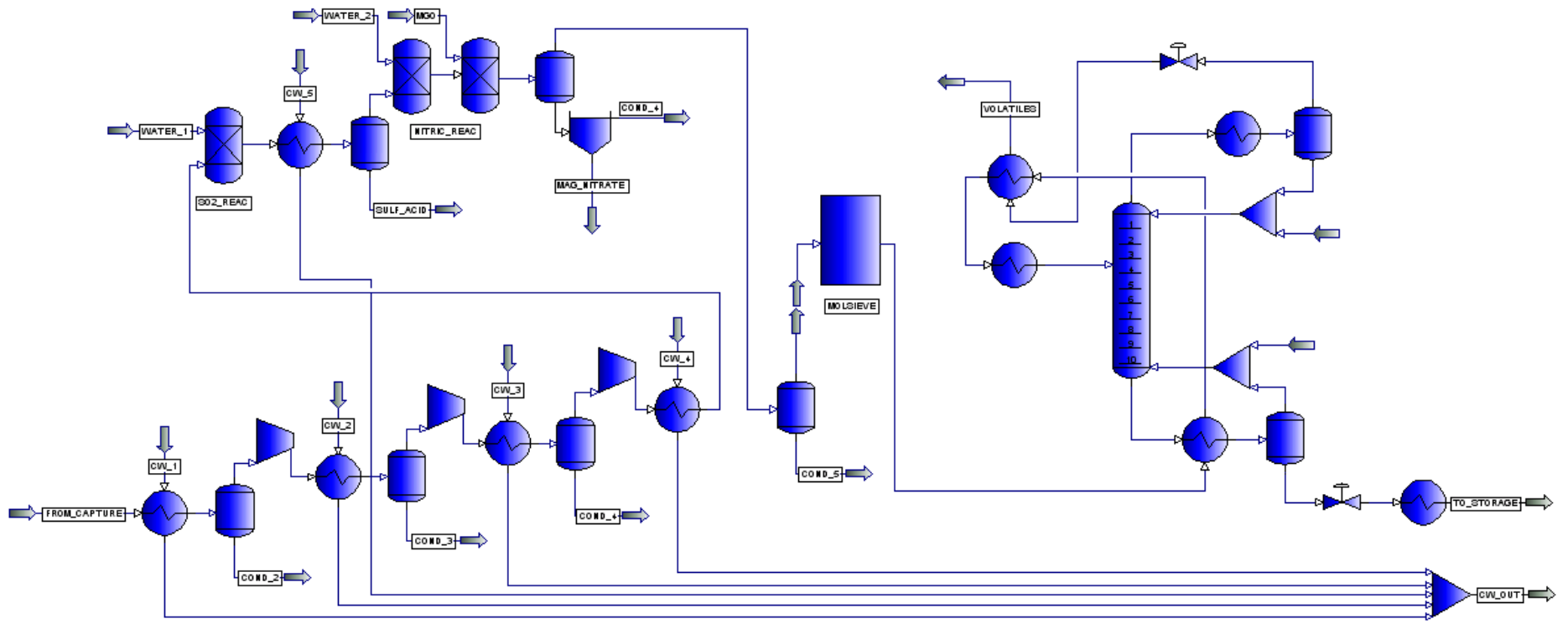**Figure A-13: Volatiles removal by distillation, natural gas oxy combustion**

Figure A-14: Liquefaction for natural gas oxy combustion

Appendix B.   Simulation results SRKK

Table B-1: Results C3_1 SRKK

Parameter:	20 bar:	25 bar:	30 bar[1]
Total work [kJ/kgCO$_2$]	534,97	532,96	565,56
Total work [kWh/tonCO$_2$]	148,60	148,04	157,10
Water removal MSA [kg/tonCO$_2$]	0,91	0,74	0,68
Cooling water consumption [kgH$_2$O/kgCO$_2$]	19,64	19,48	20,32
Total size HX (UA/(kg/s)CO$_2$) [kJ/KkgCO$_2$]	51,03	47,72	27,59
CO$_2$out/CO$_2$in	90,86 %	94,09 %	90,50 %
Composition:			
CO$_2$	96,73 %	95,77 %	95,39 %
H$_2$O	25 ppm	25 ppm	25 ppm
N$_2$	1,25 %	1,74 %	1,98 %
O$_2$	1,08 %	1,43 %	1,53 %
Ar	0,40 %	0,54 %	0,58 %
SO$_2$	0,52 %	0,50 %	0,52 %
NO	84 ppm	110 ppm	109 ppm
NO$_2$	15 ppm	14 ppm	14 ppm

[1]Did not converge with the given constraints, final volatiles concentration of 4.08 %

Table B-2: Results C3_3 SRKK

Parameter:	Min work:	1000 ppm O$_2$:	100 ppm O$_2$:
Total work (kJ/kgCO$_2$)	581,03	583,39	587,92
Total work (kWh/tonCO$_2$)	161,40	162,05	163,31
Water removal MSA (kg/tonCO$_2$)	0,79	0,89	0,92
Pressure exiting MSA (bar)	23,53	20,66	19,53
Flowing volume exiting MSA (m^3/tonCO$_2$)	30,7	36,2	38,0
Flowing volume entering column (m^3/kgCO$_2$)	13,3	12,7	19,6
Ammonia consumption (kg/tonCO$_2$)	0,21	0,22	0,21
Lime consumption (kg/tonCO$_2$)	7,79	7,96	7,86
Cooling water consumption (kg/kgCO$_2$)	11,99	11,81	11,48
CO$_2$out/CO$_2$in	92,41 %	90,40 %	91,57 %
Composition:			
CO$_2$	99,49 %	99,87 %	99,98 %
H$_2$O	25 ppm	25 ppm	25 ppm
N$_2$	264 ppm	7 ppm	1 ppm
O$_2$	3512 ppm	922 ppm	91 ppm
Ar	1249 ppm	284 ppm	27 ppm
SO$_2$	53 ppm	54 ppm	53 ppm
NO	2 ppm	1 ppm	> 1 ppm
NO$_2$	15 ppm	15 ppm	15 ppm

Table B-3: Results NG3_1 SRKK

Parameter:	20 bar:	25 bar:	30 bar:
Total work [kJ/kgCO$_2$]	437,00	436,23	446,73
Total work [kWh/tonCO$_2$]	121,39	121,17	124,09
Water removal MSA [kg/tonCO$_2$]	0,75	0,64	0,67
Cooling water consumption [kgH$_2$O/kgCO$_2$]	22,61	22,63	22,78
Total size HX (UA/(kg/s)CO$_2$) [kJ/KkgCO$_2$]	49,07	49,11	43,26
CO$_2$out/CO$_2$in	95,54 %	94,99 %	95,27 %
Composition:			
CO$_2$	97,31 %	96,93 %	96,27 %
H$_2$O	25 ppm	25 ppm	25 ppm
N$_2$	0,55 %	0,65 %	0,83 %
O$_2$	0,61 %	0,69 %	0,82 %

Ar	*1,50 %*	*1,70 %*	*2,04 %*
SO₂	*221 ppm*	*224 ppm*	*222 ppm*
NO	*42 ppm*	*46 ppm*	*53 ppm*

Table B-4: Results NG3_3 SRKK

Parameter:	Min work:	1000 ppm O_2:	100 ppm O_2:
Total work [kJ/kgCO_2]	*483,69*	*485,25*	*488,21*
Total work [kWh/tonCO_2]	*134,36*	*134,79*	*135,61*
Water removal MSA [kg/tonCO_2]	*0,67*	*0,72*	*0,78*
Pressure exiting MSA [bar]	*23,54*	*21,78*	*19,93*
Flowing volume exiting MSA [m³/tonCO_2]	*25,2*	*27,7*	*30,8*
Flowing volume entering column [m³/tonCO_2]	*7,5*	*8,5*	*10,8*
Magnesium oxide consumption [kg/tonCO_2]	*0,07[1]*	*0,07[3]*	*0,07[2]*
Cooling water consumption [kgH₂O/kgCO_2]	*14,91*	*14,80*	*14,68*
CO_2out/CO_2in	*94,69 %*	*93,92 %*	*93,13 %*
Composition:			
CO_2	*99,59 %*	*99,79 %*	*99,97 %*
H_2O	*25 ppm*	*25 ppm*	*25 ppm*
N_2	*26 ppm*	*7 ppm*	*> 1 ppm*
O_2	*1263 ppm*	*670 ppm*	*92 ppm*
Ar	*2799 ppm*	*1401 ppm*	*178 ppm*
SO_2	*5 ppm*	*5 ppm*	*5 ppm*
NO	*> 1 ppm*	*> 1 ppm*	*> 1 ppm*
NO_2	*6 ppm*	*6 ppm*	*6 ppm*

[1]Solid product molar MgO concentration of 2.26 %
[2]Solid product molar MgO concentration of 1.73 %
[3]Solid product molar MgO concentration of 2.00 %