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**Recovery of un-combusted fuel
in a gas turbine power cycle with
Chemical Looping Combustion.**

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1 ABSTRACT

Chemical Loping Combustion (CLC) is a novel combustion technology in which the exhaust gas is inherently divided into oxygen depleted air in one stream and CO₂ and water vapour in another. This is however under the ideal condition that the fuel conversion is complete, i.e. all the hydrocarbons in the fuel is transformed to heat, water vapour and CO₂. The CO₂ capture rate can under such ideal conditions be almost 100%. But both thermodynamic calculations as well as practical experiments show that complete fuel conversion might not always be expected. The present work examines different ways of recovering unconverted fuel from the gas conditioning process to a CLC reactor and simulates a number of power cycles with CO₂ conditioning and compression to see how incomplete fuel conversion (and recycling) can affect cycle efficiency. Three main ways of recovering the unconverted fuel has been investigated when varying the fuel conversion between 100-90%. From the CLC reduction reactor three different compositions of the unconverted fuel has been investigated 1) only methane, 2) a mix of hydrocarbons as in the NG, 3) H₂ and CO. The different cases were tested in two different cycles, one, 'A-', without CO₂ turbine and one, 'B-' with CO₂ turbine. The efficiency for cycle 'A-' at 100% fuel conversion and CO₂ compression to 200 bar was 50,37% while it for 'B-' was 51,84%.

The unconverted fuel can be separated in a distillation column and recirculated to the CLC reactor. Two main drawbacks were noticed when simulating those cases, accumulation of incombustible volatiles in the recirculation loop and a large fraction of CO₂ recycled to the reactor, i.e. large additional CO₂ compression work. The accumulation of incombustible volatiles, in the simulations N₂ from the fuel, was handled by a bleed stream which introduced CO₂ emissions to the atmosphere and had a negative impact on cycle efficiency. With a fuel conversion rate at 95% the CO₂ capture rate was 95%, and the cycle electrical efficiency was 48,85% (compared to 47,75 without any recovery) in cycle 'A-'. Simulations were also performed without any N₂ in the fuel and hence without bleed stream. At 95% fuel conversion rate the CO₂ capture was 100% and the electrical efficiency was 49,45% which shows the influence small fractions of inerts can have as they accumulate.

The unconverted fuel can instead be separated in a distillation column and brought to a burner prior the air turbine. This way no accumulation of inerts occurs and the design and control of the CLC reactor becomes simpler. There will however be CO₂ emissions to the atmosphere. At 95% fuel conversion the CO₂ capture rate was around 90% and the electrical efficiency was 49,57% in cycle 'A-'.

One alternative mentioned in the literature is the possibility to inject oxygen from an ASU directly after the CLC reduction reactor and thus oxidize the unconverted fuel. Simulations show that this alternative has around double "extra work/recovered energy" ratio (which is the work for the ASU plus the extra CO₂ compression work divided by the recovered fuel energy), meaning that it is less efficient than the other alternatives. It is also questionable if it is possible to oxidize such small amount of hydrocarbons in a CO₂ stream, and if it is possible, how much excess air would be necessary? The excess air has to be taken care of, most probably in a distillation column which will lead to further efficiency penalties and CO₂ emissions which will probably make this alternative less attractive. This case was tested in cycle 'B-' but due to bad utilization of the heat the efficiency at 95% conversion rate was no higher than 49,26% but with 100% capture rate.

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2 NOMENCLATURE AND ABBREVIATIONS

Abbreviation

GHG	GreenHouse Gas
IPCC	Intergovernmental Panel on Climate Change
CLC	Chemical Looping Combustion
FBC	Fluidized Bed Combustion
PFBC	Pressurized Fluidized Bed Combustion
ppm	Parts Per Million
LHV	Lower Heating Value
ASU	Air Supply Unit

Symbol	Explanation	Dimension
P	Pressure	[kN/m ²]
T	Temperature	[K]
m	mass	[kg]
\dot{m}	mass flow	[kg/s]
R	Perfect Gas Constant	[J/kg*K]
V	Specific volume	[m ³ /kg]
η	Efficiency	[-]
γ	C_p/C_v	[-]
W	Work	[kJ]
w	Specific work	[kJ/kg]
n	Polytropic exponent	[-]
H	Enthalpy	[kJ]
Q	heat	[kJ]
ϕ	Work/recovered work	[-]

3 INTRODUCTION

The climate on earth is getting warmer and a clear global warming trend can be seen over the last decade [15]. The reason to the warming is still unknown, whether it is natural variations, if it is connected to the activity of the sun, if it is man made greenhouse gases (GHG) emissions, or if it is a combination of many causes. However, lately there has been a growing (but not complete) consensus that the global warming trend is due to man made GHG emissions. IPCC claims that “*It is likely that there has been significant anthropogenic warming over the past 50 years averaged over each continent (except Antarctica)*” [15]. Still if consensus is not the same as fact or truth, it seems reasonable to try to minimize the emissions of GHG based on the facts we have today.

The most important of the GHG and the one that appears to be easiest to do something about is carbon dioxide (CO₂) [15]. One big contributor to the CO₂ emissions is the power industry with around 26% of the CO₂ emissions measured in CO₂ equivalents in 2004 [15]. The large use of fossil fuel in the power industry, which can not easily be replaced, calls for new solutions to cut down the emissions. One solution and possibly the only solution in the short term is to capture the CO₂ from the power production process and store it in an appropriate way, in the ground onshore or offshore. To be able to capture and store the CO₂ it has to be divided from the other products and/or components of combustion somewhere in the power process. Depending on the technology applied these products/components are often mainly water and nitrogen but also oxygen. The water can easily be separated but it is more difficult to separate the nitrogen and oxygen. There is however a number of different technologies which can be applied to separate CO₂ from the flue gas. They can be divided in three main categories, which will just very briefly be described here;

- Post-combustion capture
- Pre-combustion capture
- Oxy-fuel combustion capture

Post-combustion is the most straightforward alternative, the combustion goes on as usual and the capture takes place after the combustion as the name suggests. The CO₂ is “washed” from the flue gas by chemical absorption, most often by the use of some sort of amine. This is probably the most promising alternative in the short term since the technology is well known. There is however challenges with e.g. scale-up of the process, toxicity and/or degradation of the chemicals employed, equipment cost and efficiency penalty inflicted on the power process.

In pre-combustion capture the carbon is removed from the fuel before the combustion, giving a fuel consisting of mainly H_2 . This can be achieved in a number of ways, gasification of solid fuels or partial oxidation of natural gas will give a synthetic gas consisting of H_2 , CO and CO_2 . This gas can then be shifted to increase the content of H_2 and CO_2 , from which the CO_2 can be removed through an absorption process, similar to that of post combustion capture, but at higher pressure, giving more favourable separation process conditions. Solutions have also been envisaged with H_2 separation through a membrane.

Oxy-fuel combustion is based on combustion with mainly oxygen which ideally would give only CO_2 and H_2O as flue gas. This can be done in different ways; the air stream can be handled so that the oxygen is divided from the nitrogen with a cryogenic Air Separation Unit (ASU), giving a stream of (almost) pure oxygen. Since the energy penalty for air separation with cryogenic ASU is quite high (around 10%

[29]) other methods are also investigated, where air separation by membranes is proposed as a future alternative. Another technology that can be categorised as oxy-fuel is Chemical Looping Combustion (CLC) where the oxygen for combustion is brought to the fuel bound with oxidized species. This oxidized specie gives away its oxygen to the fuel and is then looped back to another chamber where it gets into contact with air and gets oxidized again. The fuel never gets in contact with air and hence there is no nitrogen in the CO_2 . More of the basics of CLC can be found in chapter 4.

3.1 Definition of study

As described above there are a number of ways to separate and capture CO_2 where the application of CLC could be one way. This study focuses on a gap in the research about CLC, namely what will happen if the conversion of fuel turns out to be incomplete, and how this unconverted fuel should be handled in the gas compression and conditioning process. In almost all papers on power processes with CLC the assumption of 100% fuel conversion is made even if there is both theoretical and practical work done on reactors and oxygen carrier materials that shows that 100% fuel conversion might not to be expected.

It was suggested in a work by Aspelund and Jordal [4] that the streams from so called innovative reactors, to which CLC belongs, could consist of unconverted fuel and that this fuel could be separated and brought back to the reactor. In the same study it was concluded that a distillation column would be preferred before a flash separator to avoid too much CO_2 in the volatile stream.

In the present study complete power cycles with gas compression and conditioning with separation of volatiles in a distillation column will be simulated in order to see how incomplete fuel conversion will affect the cycle efficiency and how the recycle could/should be designed.

3.2 Limitations and constraints

The thesis is limited in the literature studies; this is no benchmarking work regarding the latest advantages regarding the development of CLC. A short background is needed to understand the choices made in the work but for further and more detailed information the reader is kindly asked to look for other sources.

The work has focus on process simulations to see how unconverted fuel could be handled. The reactor is modelled in the simplest way possible as a “black box” with mass and heat balances. The fuel conversion rate in percentage of the fuel LHV is an input, i.e. it is determined by the reactor model. This model is however insufficient to simulate the CLC reactor in detail, including e.g. how it would respond to the introduction of a recirculation stream. The reactor is further considered to be perfect without any leakage from the oxidation reactor to the reduction reactor and hence will there be no presence of air in the exhaust stream.

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4 CHEMICAL LOOPING COMBUSTION (CLC)

4.1 An introduction

CLC stands for Chemical Looping Combustion. It is different to ordinary combustion as the combustion is divided into two different reactions. First an oxygen carrier is oxidized by air in one reactor. This oxidized oxygen carrier is then looped to another reactor where the oxygen carrier is reduced and the oxygen reacts (combust) with fuel instead. The reduced oxygen carrier is looped back to the first reactor where it is re-oxidized and looped again. The combustion is flameless, chemical, and the oxygen carrier is looped, hence the name. The fuel and the air will never come in direct contact as in ordinary combustion and the flue gas will ideally be free from air-derived nitrogen. Most articles (and most research [25]) about CLC are about gaseous fuels and most often the gas thought of is natural gas. Solid fuels like coal or coke have also been proposed and tested for CLC but the coal or coke will then first be gasified in the reduction reactor (or in a stand alone gasifier) to syngas (CO and H₂) which in turn will react with the metal oxide [20]. CLC with solid fuels will not be further studied in this thesis. The two chemical reactions which define the CLC process when using methane as fuel are seen in Eq. 1 and Eq. 2. The principle is the same when using other higher hydrocarbons or a mixture of different (as in natural gas), but with different stoichiometry and a more complex reaction pattern.



The reactions take place in two reactors, one which is commonly called the oxidation reactor and one that is called the reduction reactor, according to the oxidation and reduction of the metal. In reaction one (1) air oxidizes some metal (Me) to form metal oxide (MeO). This metal oxide is looped to the reduction reactor where reaction two (2) takes place, where fuel (CH₄) is converted to H₂O and CO₂ and the metal oxide is reduced back to metal (Me). In Fig. 1 the basic layout of an ideal CLC reactor with methane as fuel can be seen.

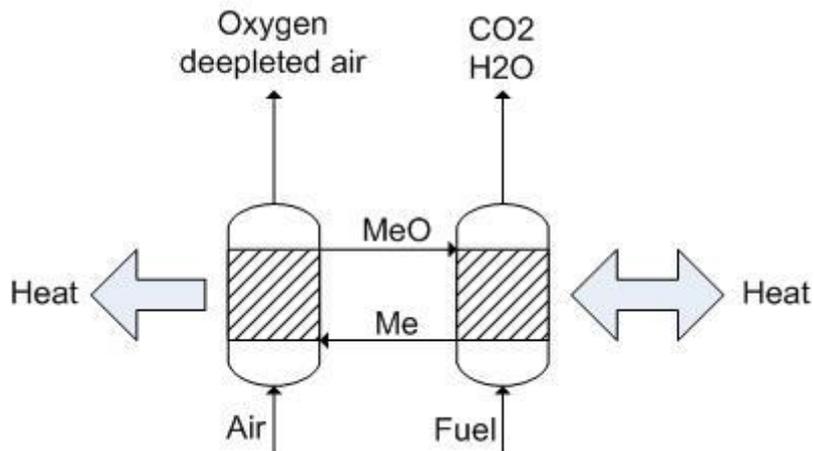
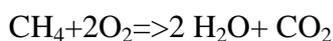


Fig. 1. Ideal CLC reactor.

In most cases the oxidation reaction is exothermic and the reduction is endothermic. This is however dependent of the metal and fuel used. With e.g. Cu as the oxygen carrier and CH₄ as fuel both reactions are exothermic (therefore the double arrow in Fig. 1) [25]. It should be emphasized that with a control volume around the reactors the sum of the reaction components and the released heat is the same as with ordinary combustion but with the difference of having the stream of CO₂ undiluted. This can be seen in Eq. 1 and Eq. 2 and in comparing them with Eq. 3 which is the reaction when combusting methane in air. It can be seen that the net sum of Eq. 1 and Eq. 2 is the same as Eq. 3.



Eq. 3

The concept has been shown to have less exergy destruction than an ordinary combustion process [3] and was originally proposed by Richer and Knoche in 1983 [32] as a way to lower the entropy production of combustion. Though less exergy destruction compared to ordinary combustion, the CLC implemented in a state of the art power plant process without CO₂ capture shows only minor efficiency benefits or in some cases a reduced efficiency compared to the efficiencies reach by today's state of the art power plants with ordinary combustion of natural gas [3], [36]. The biggest reason to the modest efficiency improvements are the relative low temperature accepted in the oxidation reactor (see chapter 5.2). Instead, the major advantage of CLC and the reason to the big attention it has received lately is the separation of the fuel and air streams which ideally would give an undiluted stream of combustion gases, CO₂ and H₂O. This stream could in turn be divided by simple condensing of the water and the CO₂ can be compressed and handled in the most appropriate way, e.g. stored in the ground or under the sea. Because of the inherent separation, the processing and compression of CO₂ reduces the efficiency with only a few percent [18]. Compared to other CO₂ capture technologies that reduce the efficiency of the plant with between

5-10 percentage points [7] this appears to make CLC an attractive technology to reduce CO₂ discharge.

The CLC technology is still a novel technology and the need for more research is big in many of the key areas. Nevertheless there has been a number of prototypes built and the concept is been showed to work on a lab scale, see chapter 4.4.

4.2 Reactor design

The very basic idea of CLC is to divide the combustion process into two different reactors/compartments. Three ways to achieve this division has been proposed; a circulating fluidized bed or a rotating reactor or a membrane assisted reactor. The rotating reactor and the membrane assisted reactor will not be further explained as they are a very novel technology and the literature about them is very limited. The circulating fluidized bed is the alternative that is mostly mentioned in the literature and the alternative that has been mostly explored so far. This could be because this alternative seems to be the most logical and straightforward option. The knowledge and experience from Fluidized Bed Combustion (FBC) and Pressurized Fluidized Bed Combustion (PFBC) is significant and a lot of this knowledge and technology could be adapted to the construction of a CLC reactor. Lyngfeldt et al 2001 [24] proposed an interconnected dual fluidized bed system as seen Fig. 2.

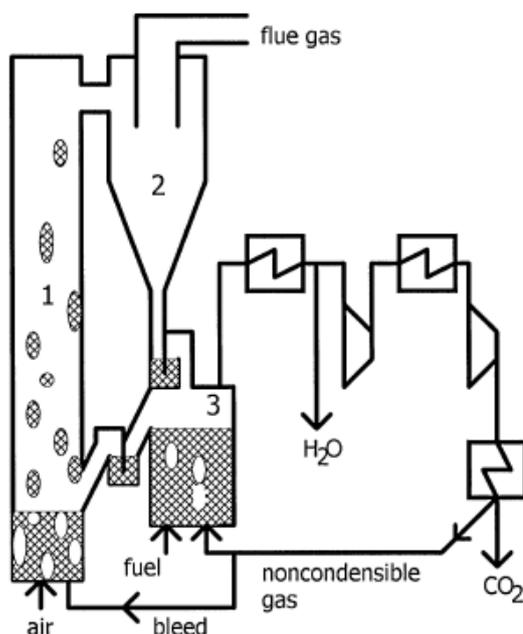


Fig. 2 CLC reactor as proposed by Lyngfeldt et al 2001 [30]

The oxygen carrier is oxidized in the oxidation reactor (1), it is separated from the oxygen depleted air in a cyclone (2) before going through a loop seal (to avoid gas mixing) into the reduction reactor (2). Here the fuel is oxidized and the reduced oxygen carrier goes through one more loop seal before re-entering the oxidation reactor (1). In the oxidation reactor (1) the air flow is approximately ten times larger than in the reduction reactor (3) so to keep the size down the gas speed in the oxidation reactor is high while the speed in the reduction reactor is slower. The high speed in the oxidation reactor gives the driving force for the oxygen carrier. As seen in the figure the oxygen carrier is caught in a cyclone (2) and brought back by gravity to the reduction reactor (3). To avoid gas mixing the oxygen carrier goes through two loop seals, one before and one after the reduction reactor. This should be fluidized by steam to work. Even if this suggested design is for a non pressurised reactor the basic principle is the same for a pressurized CLC reactor. (The reactor has to be pressurized to work in a GT cycle but CLC has also been proposed for non pressurized steam plants [15].) It can be seen that in the proposed design it has been foreseen that the fuel conversion might be incomplete, and a recirculation of non condensable gases has been included with a bleed stream to the oxidation reactor to avoid accumulation of non combustible gases such as N_2 . How this recirculation would work was however not further explained in the paper. The proposed design was later realised and built at Chalmers 2002/2003 within the EU project GRACE [23]. See chapter 4.4 for further details.

According to the literature about CLC experiments and lab scale prototypes it seems like almost all use this principal design in one form or another. While the principle is easy the specific design is complicated. As pointed out by M.M Hossain [14] the design of a CLC reactor is very critical and are interdependent of a number of parameters whereof the characteristics of the selected oxygen carrier is of most importance. For a given thermal power in a CLC reactor the air and fuel flow, air fuel ratio, is fixed. The amount of bed material is then decided through mass and heat balances, where the heat balance is the limiting factor for most oxygen carriers [24]. Different oxygen carriers have different reactivity and the combination of the amount of bed mass in the different reactors and the solid circulation rate decides the residence time for the oxygen carrier in the different reactors [14]. The bed mass and solid circulation rate has an impact on the required size of the reactor(s) which in turn influences the flow regimes in the reactors which in turn influences the solids circulation. The interdependency of the different variables can be seen in Fig. 3 which is a design process for CLC suggested by Lyngfeldt et al 2001 [24].

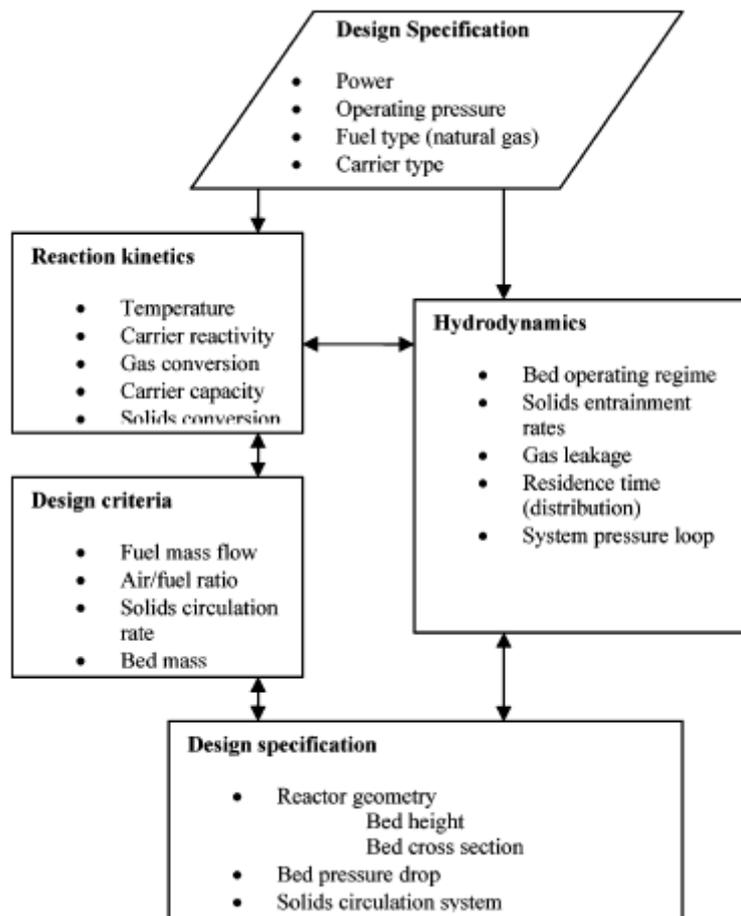


Fig. 3 CLC design scheme as proposed by Lyngfeldt et al 2001 [24].

As seen in the figure the design of a CLC reactor is a complex matter. As mentioned before, almost all literature and/or experiments on CLC presuppose or aims for 100% fuel conversion. But with the possibility to construct the reactor with less than 100% fuel conversion it is possible to have different aims, for example to minimize reactor size or to use a different kind of oxygen carrier. For example, in a study by A.Abad et al (2001) [1] where Fe_2O_3 was tested for use in a CLC reactor the authors proposed that it could be advantageous to work with lower solid inventories than that needed for complete conversion of the fuel. In that study the non converted fuel was proposed to be oxidized by adding oxygen at the outlet of the reduction reactor.

A recirculation of unconverted fuel and other gases (mostly CO_2) will however have a most dramatic influence on the design of the reactor. In a study by A.Abad et al (2006) [2] test are made were small portions of nitrogen (<3%) are mixed with the fuel in the reactor showing a vast increase in methane in the exhaust stream. A reactor which employs recirculation could therefore have a much lower conversion rate which in turn must be handled by a bigger recirculation. As seen in chapter 9.4 the recirculation of CO_2 and nitrogen can be rather large. If it is

possible/beneficial or not to construct a reactor to work under such conditions will however not be investigated in this thesis as it will only investigate the possibility of recirculation at a theoretical level. To avoid the problem with recirculated CO_2 to the reactor it would be possible to combust/oxidize the recirculated fuel after the CLC reactor and before the air turbine instead. This would lead to increased CO_2 emissions but could be a way to handle both the problem with incomplete fuel conversion and the relatively low TIT in CLC. Another proposed solution is to combust the unconverted fuel right after the CLC reduction reactor with oxygen from an ASU as suggested e.g. by Abad et al [1]. Both solutions will be further studied in this thesis.

4.3 Oxygen carriers

The most essential part of a CLC reactor system is the oxygen carrier. The oxygen carrier transports the oxygen from the air to combust (convert) the fuel in the reduction reactor. This process is most often endothermic and the oxygen carrier therefore also works as a heat exchanger, bringing heat to the reduction reactor. As pointed out earlier the construction of a CLC reactor is not a straight forward path, but rather a compromise between different desired characteristics whereof also the oxygen carrier has to be compromise. A good oxygen carrier should however possess the following list of characteristics which has been revealed through a literature study of oxygen carriers thought to be used in a Fluidized Bed [28], [14], [23].

The oxygen carrier should:

- Have a high oxygen carrying ability (mole O_2 /mole metal)
- Have a high reactivity with both fuel and air.
- Achieve a high conversion of the fuel in a reasonable time
- Be economically sound.
- Have a low impact on the environment
- Be stable under repeated oxidation/reduction cycles at high temperatures
- Be fluidizable

Major efforts have been made to examine different kind of oxygen carriers to try to find a suitable oxygen carrier for CLC. Over 600 materials have been tested [25] and there is a vast literature covering tests and comparisons between different carriers. The oxygen carriers of most interest today would according the literature be NiO/Ni , $\text{Cu}_2\text{O/Cu}$, and $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ [25], [28], [14], [23],[30]. Most oxygen carriers need some support material, which is an inert that helps to

increase the wanted characteristic of the carrier. Examples of inerts are SiO₂, TiO₂, ZrO₂, Al₂O₃, YSZ and bentonite [14]. The inert also works as a heat exchanger, carrying heat from the exothermic oxidation to the endothermic reduction (not the case when using Cu). The issue of finding appropriate oxygen carriers is complex due to the many different demands on the oxygen carrier. Ni has the highest capability to transport oxygen and a high reactivity rate which would give less reactor bed material and therefore a smaller sized reactor. But Ni has a thermodynamic constraint that makes only 99,5% fuel conversion possible and Ni is toxic and expensive [25]. Cu reacts exothermically in both reactors which would decrease the amount of oxygen carrier needed to achieve the needed temperature for the reaction in the reduction reactor but has a low melting point (1085°C) [30]. Fe is cheap and easy to handle but has a poor ability to transport oxygen compared to the other two metals, which leads to the need for more bed material [23].

The pros and cons of different oxygen carriers together with the many different materials that in turn can be combined in different proportions with different inert material and which can be made by different production methods makes it hard to decide which is the best alternative. It has to be seen in the totality of the reactor and plant. Economic, thermodynamic, environmental, health and construction considerations have to be combined. The simulations in this thesis are based on the work by Naqvi [28], and in the calculations for the reactor NiO is assumed to be the oxygen carrier. This assumption will therefore indirectly affect this study as it affects the stream data around the reactor. This will be further explained in 7.1.

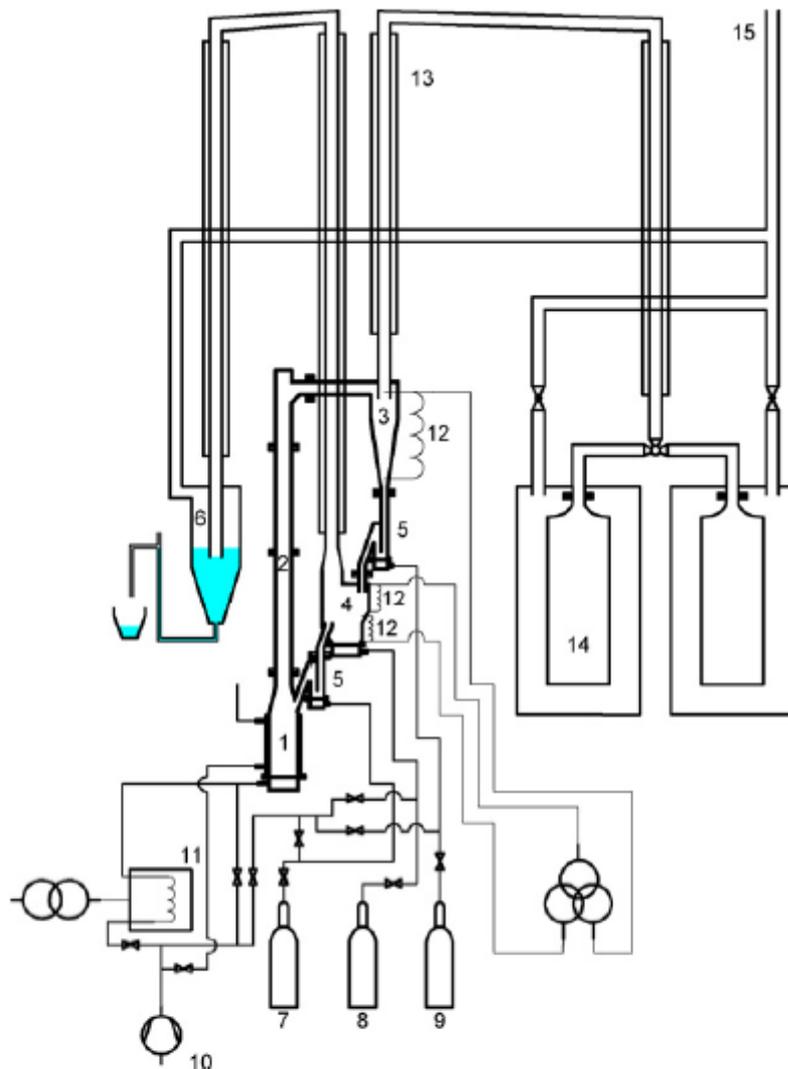
4.4 Reactor prototypes

The first working CLC reactor was built at Chalmers University in Sweden (Lyngfeldt et al 2004 [23]; Lyngfeldt and Thunman 2005 [26]). The working principle was as described in chapter 4.2 and a drawing of the prototype can be seen in

Fig. 4. It was first operated in 2003 with Ni as oxygen carrier and the results show that the concept worked. The conversion rate was high, between 0,05 and 1% methane (higher methane rate at higher temperatures) and equilibrium portions of CO at 0,55% and H₂ at around 1% [26] was seen in the exhaust stream. As the prototype showed no bigger obstacle for CLC, a smaller 300 W experimental reactor has also been built to test different oxygen carriers at a lower cost [16].

Even if Chalmers University was first to present a working reactor, a number of prototypes have been constructed lately. At Vienna University of Technology a 120 kW CLC prototype was built

in 2007 and first operated in 2008 [19]. At Korea Institute of Energy Research a 50 kW prototype was built which showed good result with Ni/bentonite as oxygen carrier [33]. In Spain a 10 kW prototype has been built and tested with CuO–Al₂O₃ oxygen carrier [11]. The results from the different prototypes will not be further discussed here but in short the results are promising. The conversion rate is high but small fractions of methane and/or CO and hydrogen is found in the exhaust stream.



Drawing of prototype reactor system, also indicating the cooling and particle separation systems. (1) Air reactor, (2) riser, (3) cyclone, (4) fuel reactor, (5) upper and lower particle locks, (6) water seal, (7) nitrogen, (8) natural gas, (9) nitrogen, (10) air, (11) preheater, (12) heating coils, (13) finned tubes for cooling of gas streams, (14) filters and (15) connection to chimney.

Fig. 4. CLC reactor prototype. From [22]

5 THERMODYNAMIC CYCLE ANALYSIS

As mentioned earlier, CLC was first proposed by Richter and Knoche in 1983 with the expectation to improve combustion processes and therefore increase the potential for mechanical work. This is done by preventing direct contact between fuel and air and instead supporting intermediate chemical reactions which gives lower entropy production [32]. However it is not clear whether or not the theoretical exergy gain the lower entropy production gives can be utilized, it depends on many factors such as the implementation of the CLC reactor in a power

cycle and the configuration of the system as a whole. In a study by Anheden et al [3] it is shown that the exergy content in the exhaust stream is considerably lower for a CLC-GT cycle than for a GT cycle with ordinary combustion (22,69 compared to 27,49% fuel chemical energy). It is also concluded that some of the exergy in the exhaust stream could be used in a bottoming cycle and that a bottoming cycle connected to the ordinary GT cycle would be more efficient than a similar arrangement for the CLC cycle due to the lower temperature out from the CLC reactor. It should also be remembered that the exergy gain can disappear if the CLC reactor shows to have for example bigger pressure drops than a regular combustion or if the fuel conversion turns out to be incomplete [3]. Simulations by for example Naqvi, Wolf, Brandvoll & Bolland [28], [36], [8] shows that CLC implemented in a power cycle can give an efficiency in level with modern CC power plants but in the lower end of the efficiency scale. But when adding CO₂ separation to the reference CC power plants the CLC with its inherent CO₂ separation shows a greater efficiency [36], [28], [8], provided that the exhaust consists only of CO₂ and H₂O, i.e. 100% fuel conversion.

The subject of this thesis is not to construct or optimize a power cycle but to see the connection between the power cycle and the CO₂ compression and conditioning process. The next paragraph is therefore just a short review about some of the basic components used in the art of transforming fuel to electricity and of the cycles they are implemented in, studied in this work.

5.1 Transforming fuel to electric power

In order to harness the chemical energy in a fuel and transform it into electric power one usually employs some sort of heat engine that transforms the chemical energy in the fuel to a rotational work which in turn is transformed to electric power by a generator. The heat engine could be e.g. an Otto motor (gasoline engine), a Stirling engine, a diesel motor, or a gas or steam turbine cycle. Electrical power plants most often use either a gas turbine or a steam turbine cycle or a combination of the two. All heat engines have in common that they work between two temperatures, one high temperature where heat is admitted and one low where heat is rejected. No heat engine can reach a higher efficiency than the ideal Carnot cycle [37]. The Carnot's theorem postulates that the maximum efficiency of a heat engine can never be higher than

$$\eta = 1 - \frac{T_C}{T_H} \tag{Eq. 4}$$

where T_C is the cold reservoir and T_H is the hot reservoir.

5.2 The gas turbine cycle

The gas turbine works in cyclic matter which is commonly referred to as the Brayton cycle. The cycle is seen in Fig. 5.

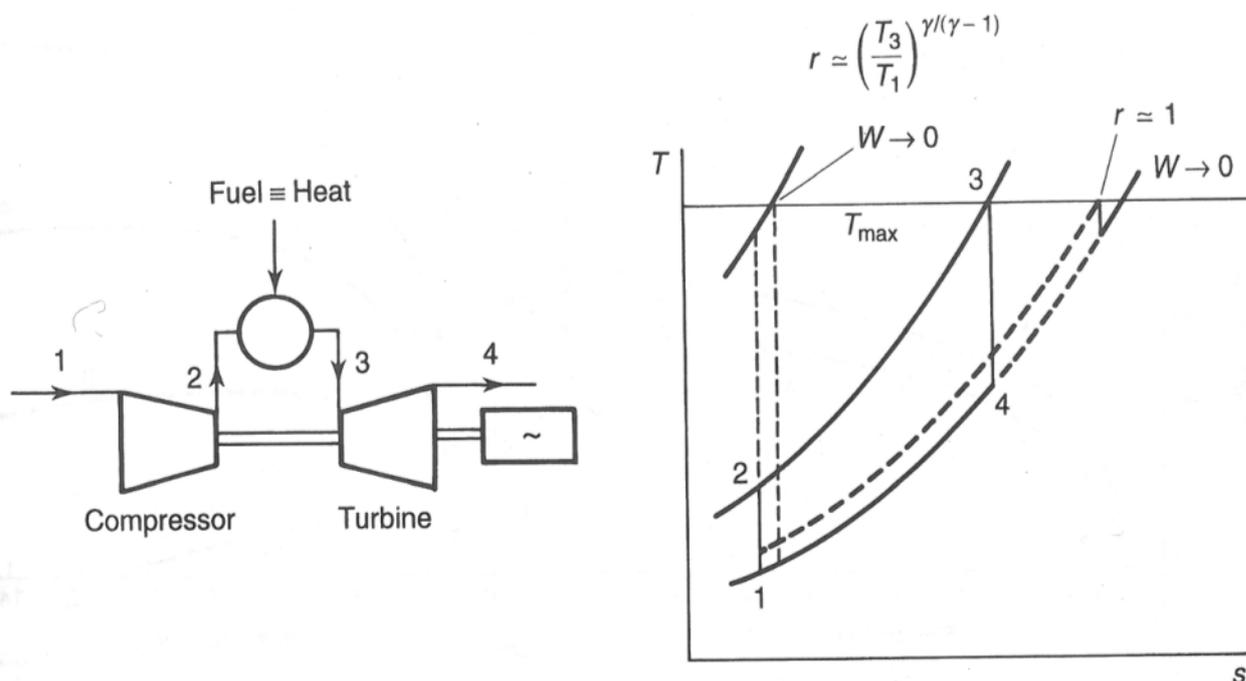


Fig. 5. The gas turbine cycle from [37].

In the figure above the cycle seems closed but in reality the cycle is most often open, e.g. the compressor uses new air instead of recycling the flue gases from the turbine. The basic principle is;

- Isentropic compression of air in a compressor between 1-2
- Isobar heat addition in the combustion chamber between 2-3
- Isentropic expansion in a gas turbine between 3-4
- Isobar heat rejection to the ambient between 4-1

In a real cycle the compression and expansion will not be isentropic due to friction and heat losses in the turbine and compressor. The heat addition will not isobar due to pressure losses in the combustor chamber. The efficiency of the ideal cycle is expressed as;

$$\eta = 1 - \left(\frac{1}{r}\right)^{\frac{\gamma-1}{\gamma}} \tag{Eq. 5}$$

where r is the pressure ratio P3/P1 and $\gamma = \frac{c_p}{c_v}$ for the specific working gas. The specific work of

the cycle is:

$$\frac{W}{c_p T_1} = t \left(1 - \frac{1}{r^{\frac{\gamma-1}{\gamma}}} \right) - (r^{\frac{\gamma-1}{\gamma}} - 1) \quad \text{Eq. 6}$$

where t is T_3/T_1 . The term $\frac{W}{c_p T_1}$ is a convenient way to show the work in dimensionless form though T_1 and c_p are not design parameters. In Fig. 6 the efficiency as a function of pressure ratio is shown as well as the specific work as a function of t .

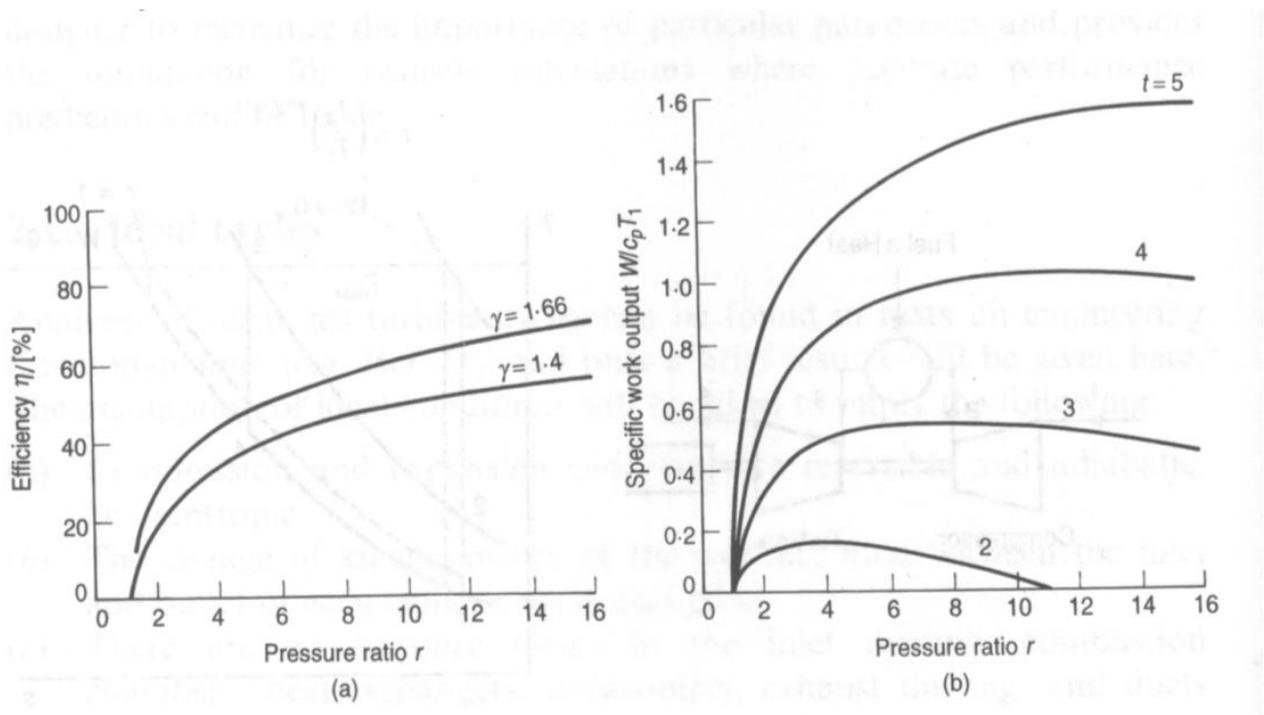


Fig. 6. Efficiency and specific work vs. pressure ratio.[34]

As seen in Fig. 6 the construction of a gas turbine is a compromise between efficiency and work output. At a given maximum temperature the work first increases with a higher pressure ratio before it decreases to zero at the maximum pressure ratio. See Fig. 6. A typical modern gas turbine with a combustor outlet temperature at 1100°C can reach efficiencies at around 35% [13]. Compared to the Carnot cycle working between the same temperatures which gives a theoretical efficiency of 79%, this is very low and that is due to the unused heat in the leaving flue gases.

The efficiency of the cycle is only depending on the pressure ratio and the specific heat of the gas. The pressure ratio however depends on the maximum temperature allowed in the cycle, see Fig. 5. A higher temperature can give a higher pressure ratio and thus efficiency for a certain work output which is required to make the machine economical and practical. The highest temperature is

found after the combustor chamber at the inlet to the turbine and is referred to as Turbine Inlet Temperature, TIT. A higher TIT allows for higher pressure and thus higher efficiencies. If replacing the conventional burner with a CLC reactor the TIT will have to be lowered due to the metallurgical limitations of the reactors and the oxygen carriers. Most literature mentions 1200°C as a temperature which could be reached in a not too distant the future. The problem is both to construct a reactor which can withstand such high temperatures and to find oxygen carriers that can do the same. For the reactor there have been proposals to garb the reactor with tile to make it withstand the high temperatures.

5.3 The combined cycle

The most efficient way today to transform the chemical energy tied in gaseous fuels to electric power is to use a gas turbine combined with a bottoming steam cycle, a so called Combined Cycle (CC). The basic principle is shown in Fig. 7 below.

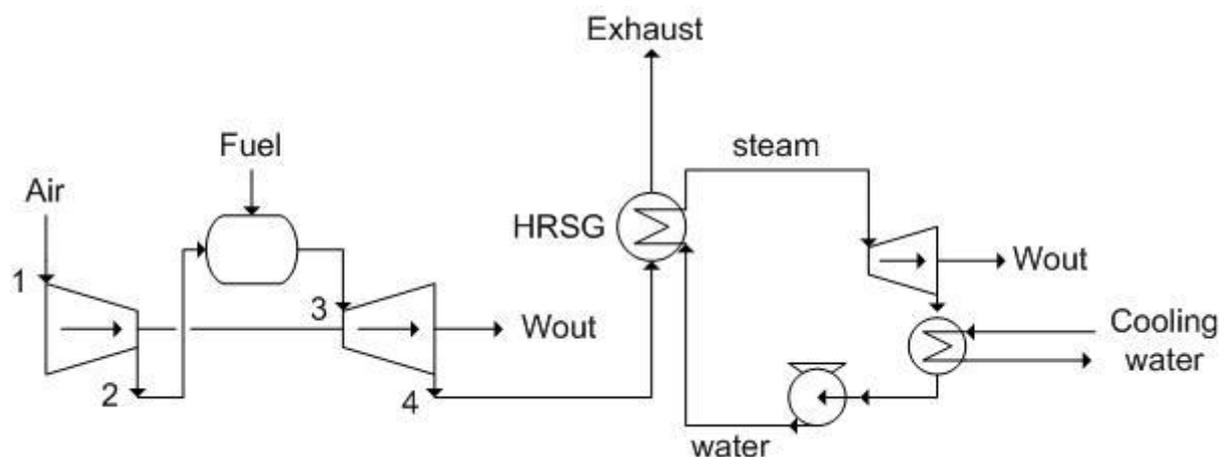


Fig. 7. Gas turbine with steam bottoming cycle, i.e. a combined cycle.

The heat remaining in the flue gas leaving the gas turbine is recovered in the Heat Recovery Steam Generator (HRSG) to produce steam that is utilized in the steam turbine. A CC always reaches higher efficiencies than the gas turbine or steam cycle alone. This is because a CC works between higher temperature differences. In a CC the highest temperature is found after the combustor chamber (TIT) and the lowest temperature is where the steam condenses after the last turbine. According to the Carnot postulate this opens for the possibility of a high efficiency when constructed in a smart way. The efficiency of a CC can be expressed as:

$$\eta_{CC} = \eta_{GT} - \eta_{ST} (1 - \eta_{GT}) \frac{(T_{04} - T_{STACK})}{(T_{04} - T_a)} \quad \text{Eq. 7}$$

In the above equation T_{04} is the temperature of the exhaust gases from the gas turbine and T_a is the ambient temperature and T_{STACK} is the stack temperature. In CLC the stack temperature can be lower than in ordinary CC due to the lack of water in the exhaust gas (there is only some water from the humid air). This can have a significant impact on cycle efficiency; a change from 120°C to 70°C can increase cycle efficiency with 2% points. The interconnection between the two cycles makes cycle optimization more difficult. For example, by changing the pressure ratio in a certain gas turbine its efficiency could rise at the same time that the flue gas temperature would decrease. If the flue gases are to be utilized in a HRSG in a CC this would lead to a decrease in the steam cycle efficiency and whether or not the overall efficiency would increase or decrease depends on which one of the two that has the biggest impact. Due to the lower temperature in a CLC compared to a regular combustion the temperature out of the turbine and hence into the bottoming cycle will be lower for CLC.

The bottoming cycle and HRSG design is a very complicated matter and to utilize the most of the energy a number of techniques are used. The higher the pressure and temperature of steam, the more efficient the cycle gets, remembering Carnot's postulate. The cycle can be further equipped with different pressure levels, a number of reheat and preheat utilities etc. That is its own field of science and it is not the scope of this work to neither construct nor explain all features of the bottoming cycle. In the modelling chapter a short explanation of the steam cycle used will be made.

With state of the art technology and smart construction of the CC in order to minimize exergy losses, efficiencies close to 60% can be achieved in Natural Gas Combined Cycles (NGCC) [13]. This is without carbon capture, conditioning and compression which with post combustion or by oxy-fuel combustion would have an efficiency penalty at around 8-10 percentage points [36]. A CLC power cycle must therefore achieve an efficiency of at least 50% to be competitive.

5.4 Turbine cooling

With modern combustion chambers high TIT can be achieved which calls for blade cooling due to metallurgical limits of the materials. A modern gas turbine can allow TIT at around 1400°C [33] Ryu Ho-Jung, Jin Gyoung-Tae & Yi Chang-Keun. "DEMONSTRATION OF INHERENT CO₂ SEPARATION AND NO NO_x EMISSION IN A 50kW CHEMICAL-LOOPING

COMBUSTOR: CONTINUOUS REDUCTION AND OXIDATION EXPERIMENT”. Korea Institute of Energy Research, Daejeon 305-343, Korea

[34] and in CLC applications the maximum temperatures that could be reached is thought to be 1200°C. Even at 1200°C blade cooling is necessary. To cool the turbine blades air is bled from the compressor to the turbine. This air is certainly warm, in the order of a few hundred degrees, but much cooler than the air from the combustion chamber. The bleed air is taken from different pressure levels in the compressor to meet the pressure level in the turbine where the cooling is applied. The turbine blades are casted with small channels where the cooling air circulated to chill the blades from inside. The air is then most often let out in the trailing edge or at the top of the blade and the cooling air and the working air are mixed, referred to as open-loop air cooling. The first blades closest to the combustion chamber are often equipped with film cooling, i.e. cooling air are bled from the blades through small holes creating a film of cooling air round them. In practice cooling of turbine blades is a very complex matter; however it can be modeled for the purpose of studying gas turbine cycles in flowsheet simulators in a very simple way. In this thesis the turbine cooling model used is the same as in a report by Hanne M. Kvamsdal et al. [18] where the details can be seen. The practical implementation in Hysys will be described in chapter 7.3.

5.5 CO₂ turbine and cooling

In one of the cycles simulated in this thesis a CO₂/H₂O turbine is used at a TIT of 980°C which would require some sort of blade cooling [28]. But the CO₂ stream should not be diluted with air which prevents the use of air from the compressor to be used for open-loop air cooling. The alternatives left are therefore to either use a closed-loop air or steam cooling where the cooling agent is kept separated from the working medium or possibly to use “cold” steam from the steam cycle in open-loop cooling. Both alternatives are complex and novel and it will not be further investigated in this thesis how the cooling could be done.

5.6 Turbine polytropic efficiency

When modeling the power process in Hysys, the model for the turbine is already complete, based on heat and mass balances. But it has one important variable that has to be determined; the polytropic efficiency. The expansion in a turbine is not isentropic due to irreversibilities like

friction and heat losses. To account for this the polytropic efficiency is used. It is also possible to specify the isentropic efficiency instead but it is more common to use the polytrophic efficiency since it is easier to compare different turbines working on different pressure ratios with the polytrophic efficiency

[33] Ryu Ho-Jung, Jin Gyoung-Tae & Yi Chang-Keun. “DEMONSTRATION OF INHERENT CO₂ SEPARATION AND NO NO_x EMISSION IN A 50kW CHEMICAL-LOOPING COMBUSTOR: CONTINUOUS REDUCTION AND OXIDATION EXPERIMENT”. Korea Institute of Energy Research, Daejeon 305-343, Korea

[34]. The cooling model used in this thesis will call for the use of two turbines when modeling, one cooled and one un-cooled. The un-cooled will have a polytropic efficiency of 90.7%¹ while the cooled will have a polytropic efficiency according to the cooling model and therefore different in the different cases This will be further explained in chapter 7.3 and the data for the different cycles are found in Table 3.

¹ In Case A the polytropic efficiency is 90,7% and in case B 90% due to a mistake. The difference in cycle efficiency is however very small.

6 CO₂ COMPRESSION AND CONDITIONING - AN OVERVIEW

Upstream the conditioning process the stream consists of CO₂, H₂O and small amounts of natural gas and nitrogen. The water in the stream can easily be condensed and the hydrocarbons from the natural gas can be removed in a more complex way in a distillation column. The next paragraph will give the theoretical background needed to design the compression and conditioning process.

6.1 CO₂ gas quality

The design of the conditioning and compression process depends on how the CO₂ stream will be handled after the compression. Depending on if the gas will be transported by boat or by pipeline different pressures and rates of impurities can be allowed. There are still no regulations addressing the quality of CO₂ for transport and long time storage, though in a work by De Visser et al [35] recommendations for the amount of different impurities for pipeline transport are proposed. These recommendations are shown in Table 1 .

Component	Concentration	Limitation	Reason
H ₂ O	500 ppm	Design and operational considerations	Corrosion, Hydrates
H ₂ S	200 ppm	Health and safety considerations	STEL
CO	2000 ppm	Health and safety considerations	STEL
CH ₄	Aquifer<4 vol%, EOR<2 vol.%	As proposed in ENCAP project	Costs, energy
N ₂	<4 vol.% (all non-condensable gasses)	As proposed in ENCAP project	Costs
O ₂	Unknown	Literature not consistent	Challenges in the reservoir
Ar	<4 vol.% (all non-condensable gasses)	As proposed in ENCAP project	Costs
H ₂	<4 vol.% (all non-condensable gasses)	Reduction of H ₂ is recommended due to its energy content	Costs, energy
CO ₂	> 95.5%	Balanced with other compounds	

Table 1. Recommendations for pipeline transport. [35]

In this thesis it is assumed that the CO₂ will be delivered to a pipeline for transportation with an inlet pressure of 200 bars. The conditioning process has therefore to achieve less than 500 ppm water in the CO₂ stream and keep the volume fraction non condensable gases below 4%. The reason to keep the fraction of water down is to avoid free water formation which could lead to hydrate formation and/or corrosion [35] as well as to avoid higher work input for compression and transport and the need for bigger pumps and pipes. The solubility of water in the CO₂ is dependent on the temperature, pressure and content of the CO₂ stream. With higher pressure, lower temperature and increasing content of CH₄ the solubility decreases [35], [6] (when in gas phase). Fig. 8 from [6] shows calculations of solubility of water in CO₂ gas and liquid. This is calculated with SRK-HV (Soave Redlich Kwong – Huron Vidal) and does not seem to correspond exactly to Hysys where it is possible to reach 500 ppm with simple condensation of the water at 13°C. This

is probably due to the presence of methane in the stream. It is known that a small fraction of methane in CO₂ will decrease the water solubility quite significantly.

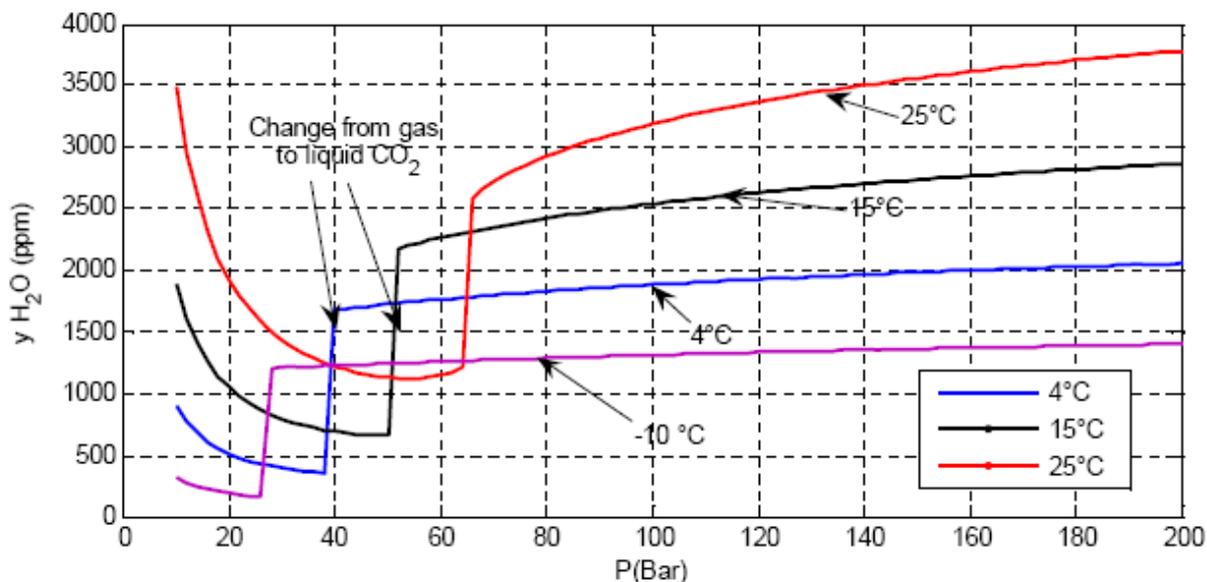


Fig. 8 Solubility of water in CO₂ from [6].

To keep the simulations simple 500 ppm is accepted, but to decrease investment costs in compressors, pumps and pipelines it would probably be better to dry the CO₂ to single digit ppm by regenerative adsorption columns [5]. As will be seen in the results in chapter 9 there is no risk to exceed the recommendations on dilutants in the CO₂ stream for any case except one case where oxygen is present in the CO₂ stream (“Aa-O-No N₂-95” and “Aa-O- N₂-95”). As seen in Table 1 there is no consistency in literature about how high the content of O₂ can be, but there is a strong belief that the content of O₂ has to be kept on a very low level and preferably it should be avoided in the CO₂ stream [17].

6.2 Exhaust gas content

What the stream from the CLC reduction reactor will actually consist of is not clear and depends on such parameters as the type of oxygen carrier, the amount of bed mass, the residence time in the respective reactors etc. At 100% conversion rate it would consist of only CO₂ and water. With a conversion rate lower than 100% fuel will be present in the reduction stream and side reactions might also occur in the reduction reactor, giving H₂ and CO due to incomplete oxidation of the fuel [27], [16], [21], [10], [27]. When using Ni as oxygen carrier there will always be CO and H₂ in the exhaust stream due to a thermodynamic constraint on Ni [27], [10], [6]. The rates of CO and H₂ differ but will always be higher or the same as the equilibrium rate. As can be seen in Mattisson et al [27] the equilibrium portions of H₂ and CO in the exhaust stream could be rather

large (around 2% at 1200°C after water condensation) and interestingly showing an increasing trend with increasing temperature. The presence of H₂ in the exhaust stream is problematic due to a number of reasons. First it has a high LHV that should be used in the power generating process instead of getting stored in the ground. Secondly its high specific volume makes it very energy intensive to compress. A short example from Hysys simulations shows that to compress a certain amount of CO₂ diluted with 2 mol% methane from 1 to 200 bar (in a certain cycle) requires 3,4% more energy to compress compared to undiluted CO₂. If the CO₂ in the same simulation is instead diluted with 2 mol% hydrogen the extra energy requirement is 9,7%, i.e. almost three times as much. Another problem is that H₂ in CO₂ changes the phase equilibrium, more than any other dilutants [6]. One effect of this is that a CO₂ stream diluted with H₂ requires much higher pressure to condense which in turn requires more compressors and more cooling before it is liquefied. It should not be introduced to a pump or a distillation column before it is liquefied which make the presence of H₂ effect not only the energy requirements but also the investment costs as more pumps are needed.

With other oxygen carriers complete oxidation of the fuel may be obtained if all of the gas molecules get into contact with the oxygen carriers for a long enough time. To fulfill this it is possible that the amount of bed material and the required residence time in the reactor makes the required reactor size very large. A.Abad et al 2006 [1] suggest that it might be advantageous to work with lower solid inventories than those needed for complete fuel conversion. Instead a reasonably sized reactor with a reasonable amount of bed mass could have some bubbles of unconverted fuel out from the reduction stream as proposed by Wolf [36]. These bubbles could then be thought of as homogenous, i.e. the content of the bubbles is the same as the content of the incoming stream, i.e. all the different hydrocarbons will have the same degree of conversion in the reactor. This is one of the cases studied in the simulations. In the other case imaginable (and simulated) the bubbles are inhomogeneous; it is thought that the heavier hydrocarbons react to a higher degree, leaving only unconverted methane in the exhaust stream. The third case simulated is a case where it will be only CO and H₂ in the exhaust stream. How the cases are simulated will be further explained in chapter 8.

6.3 Compression of CO₂

Compression of a gas from pressure 1 (P1) to pressure 2 (P2) requires minimum work if the process is reversible. The specific work is then expressed as:

$$w_{rev} = \int_1^2 v dP$$

Eq. 8

To keep the required work down the specific volume of the gas should be kept as low as possible. The specific volume of the gas is directly depending on the temperature of the gas, if the gas considered can be treated as an ideal gas. When the pressure of the gas increases the temperature and specific volume also increases which leads to a higher work input to compress the gas further. The optimum compression is therefore isothermal and should take place at the lowest temperature possible. But an isotherm compression is not practically possible and in reality a system of multistage compression with intercooling in between the compression stages is employed. The number of intercoolers depends on the compressor(s) used and the gas to be compressed. The large volume of CO₂ in a power plant suggest the use of centrifugal compressors. The pressure level wanted and the possibility of intercooling urge for a chain of compressors. There are two different ways to create a chain of centrifugal compressors; inline and integral gear type (multishaft) centrifugals. In the inline arrangement the different impellers are connected to one single axis. Every impeller raises the pressure according to the pressure ratio and intercooling is possible after each impeller. In the gear type centrifugal the impellers are mounted on a pinion on a spur gear. Intercooling is possible after each impeller and the main advantage compared to the inline compressor is that every impeller can have its own optimum velocity [31]. Which of the two types that should be used is outside the topic of this thesis. In Hysys the train of compressors is modeled as a train of individual compressors with intercooling in between, while in reality it is as described above one compressor withholding many stages (impellers) and possibly even internal heat exchangers for intercooling. The number of intercoolers used will directly affect the power requirement so it is reasonable to believe that in an application like a power plant, the extra investment cost for intercooling between every pressure level would pay off. Eight stages CO₂ compressors used in Urea plant have five intercoolers and reach a polytropic efficiency of 83% [31]. The efficiency in a CCS application could be higher if using intercoolers after every stage, but in this thesis 83% will be used.

By imposing intercooling the relationship in pressure ratio between the different compressors must be determined. It could be argued that for practical reasons the same pressure level should be used for the different stages but it is also the most energy effective. Assuming a polytropic process going from pressure level P1 to P2 with intercooling at Px:

$$w_{IN} = w_1 + w_2 = \frac{nRT_1}{n-1} \left[\left(\frac{P_x}{P_1} \right)^{(n-1)/n} - 1 \right] + \frac{nRT_1}{n-1} \left[\left(\frac{P_2}{P_x} \right)^{(n-1)/n} - 1 \right] \quad \text{Eq. 9}$$

The only variable in the equation is P_x and by deriving it with respect to P_x and setting it to zero the result is:

$$P_x = \sqrt{(P_1 P_2)} \Leftrightarrow \frac{P_x}{P_1} = \frac{P_2}{P_x} \quad \text{Eq. 10}$$

This shows that in a process with many compressors (stages) with intercooling the optimum design is to keep the pressure ratio over the different compressors at the same level. Due to the high molecular weight of CO_2 , which affects the Mach number, the speed of the impellers has to be kept low to avoid a Mach number higher than unity [31]. The consequence is that it is hard to achieve a higher pressure ratio than 1.7:1-2.0:1 [31].

At a certain pressure, depending on the cooling water available (and where the column is introduced, more about this in chapter 7.5.1.), the CO_2 can be condensed and then pumped to its final pressure. This is the most efficient way to compress the CO_2 due to the lower specific volume of CO_2 in dense phase compared to saturated or superheated CO_2 steam, remembering that the compression work is equal to specific volume times the pressure rise. Condensation at the lowest possible pressure is therefore beneficial.

One aspect that can be easily overlooked is the inlet pressures impact on the energy requirement, see Fig. 9;

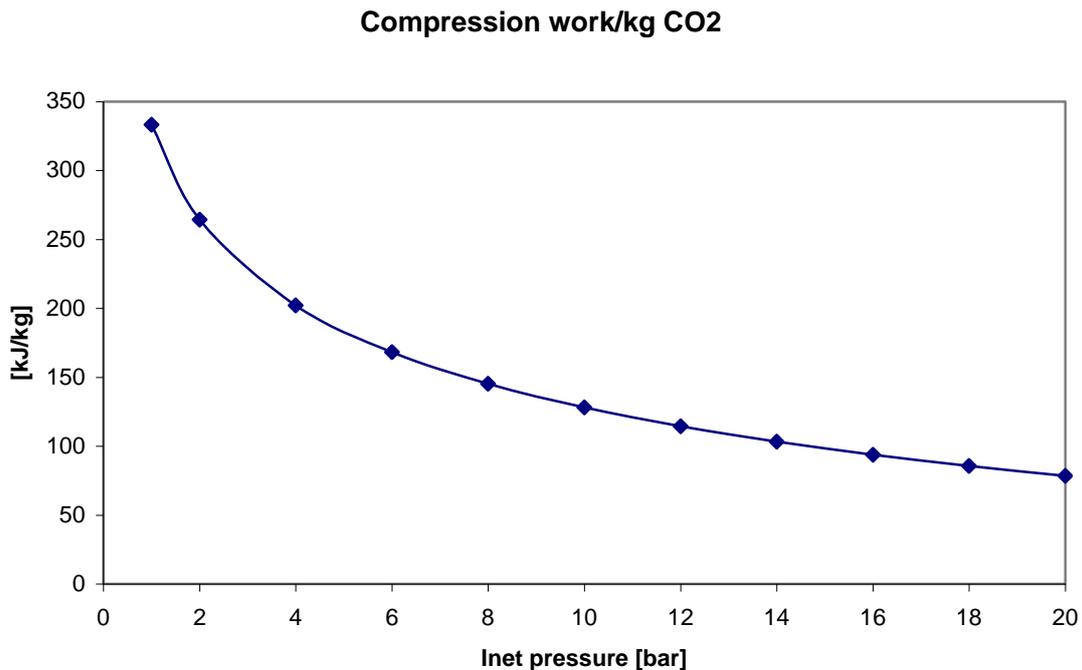


Fig. 9. Compression work/kg CO₂.

The figure shows the work requirements per kg of CO₂ when compressing from different inlet pressures to 200 bar (to 55 bar with compressors, the rest with a pump). In this example three compressors with intercooling in-between was used, which made the pressure ratio over each compressor vary from 3,8 to 1,4. This will of course have a small effect on the work requirement by reason of the higher compressor temperatures. But the real reason to the shape of the graph is found in the expression of work requirement for compression with the specific volume replaced by the ideal gas law as in Eq. 11

$$w_{rev} = \int_1^2 v dP = \int_1^2 \frac{RT}{P} dP = RT * \int_1^2 \frac{1}{P} dP = RT [\ln(2) - \ln(1)] = RT \ln\left(\frac{2}{1}\right) \quad \text{Eq. 11}$$

If R and T are thought to be constant the work to compress a gas is only dependent on the pressure ratio and not the absolute pressure- to compress from one bar to two bar costs the same energy as to compress from ten to twenty if the temperature is thought to be constant. Therefore it requires much more work to compress a gas from a low starting pressure as the pressure ratio gets bigger. This will be of interest when comparing two of the cycles used in this work.

6.4 Distillation column

Distillation is the separation of a liquid or vapor mixture which can be either binary or multi-component by the addition and removal of heat. The basic principle is that in a mixture of substances the ones with the highest vapor pressure will evaporate first. The vapor pressure is dependent on the temperature and the concentration of the substance in subject. A substance with a high vapor pressure is called volatile and will boil at a low temperature. In Fig. 10 a boiling point diagram is shown. It shows a state where a binary substance (two components) gas and liquid phase are in equilibrium with each other. The boiling point for a substance A is found where the concentration of A is one and the boiling point for B is found where the concentration of A is zero. In between the equilibrium concentrations of A in the liquid phase and the gas phase can be read. The bigger the differences between the liquid and gas phase concentrations are, the easier it is to separate the substances by distillation. A measurement of this is the relative volatility.

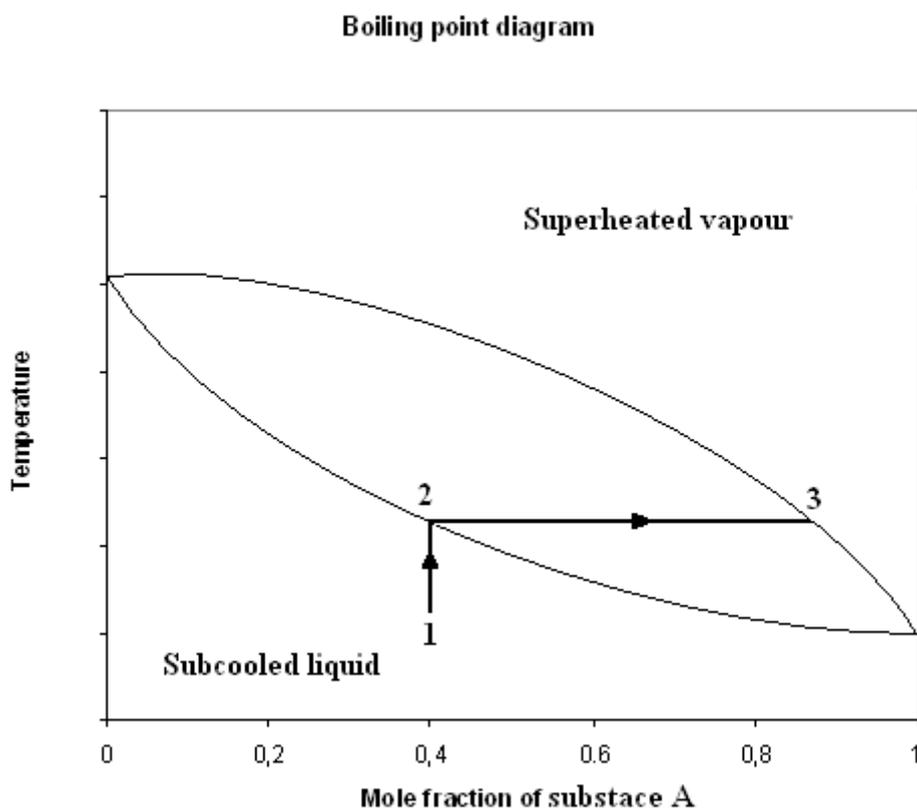


Fig. 10. Boiling point diagram.

An example: imagine that you have a liquid with a composition of 40% of substance A and 60% of substance B, shown in the figure by point 1. By applying heat and raising the temperature to

point 2 the liquid starts to evaporate. The vapors composition can now be read at point 3, the concentration of A is now 90% and B is of course 10%. This is more than twice the concentration of substance A in point 1 (or 2). By condensation of the vapor a new mixture with a higher concentration of A is produced. To reach an even higher concentration the procedure has to be done again and this is the idea of distillation columns, a repetition of partial evaporation and condensation.

The distillation column is a tube (column) containing a number of stages. In the bottom of the column there is a reboiler and in the top there is a condenser and between them the feed stream is introduced. See Fig. 11.

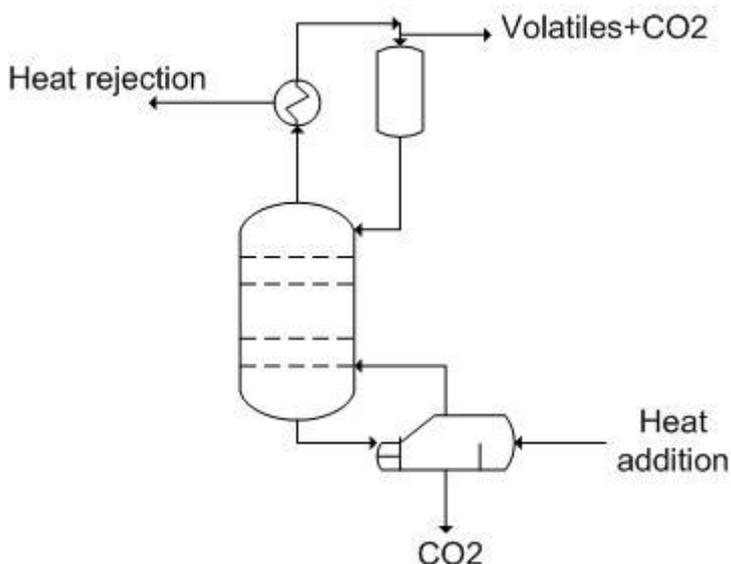


Fig. 11. The distillation column

The reboiler in the bottom takes some of the outgoing liquid and vaporizes it. The vapor enters the column in the bottom and rises to the first stage. The stages are designed so that the vapor gets in good contact with downward flowing liquid whereupon heat is transferred from the vapor to the liquid. For every stage upwards the temperature increases. When heat leaves the vapor some of it is condensed, primary the less volatile component(s). The heat transferred makes the liquid boil, primary the most volatile(s) component(s). The liquid continuing downwards to the below stage will therefore have a higher concentration of less volatile component(s). Opposite to this the vapor entering the next upper stage will have a higher concentration of more volatile component(s). By each step upwards the vapor will be more concentrated with the volatile component(s) while the downward flowing liquid will be richer in the less volatile component(s) on its way down. At the top some of the vapor is condensed to feed the column with downward flowing liquid which is called reflux. The reflux can be partial or total. If it is total all the condensed liquid is returned to

the column while in the partial case some is drawn out as liquid at the top. The non-condensed vapor at the top is the distillate stream which is richest in volatiles.

As one can imagine there are a number of variables in a distillation column, some of them are the reboiler duty, condenser duty, recovery rate, reflux rate, pressure in column, number of stages, stage efficiency etc. The temperature of the reboiler is that of the saturation temperature of the mixed fluid. In general a high condenser duty would reduce the content of less volatile components in the top stream (in this case CO₂) while a high reboiler duty would reduce the amount of volatiles in the bottom stream (CO₂ transport stream) [5]. The duty of the reboiler and condenser is of course connected to the temperature but also to the flow rate inside the column. In the simulations performed in this thesis the rate of recovery is set together with the column pressure and condenser temperature. This makes the column easy to control and fits the purpose of maximizing cycle efficiency. The rate of recovery of a certain specie is called the Recovery Rate (RR) and is simply a measurement of how much of the specie that enters the column that leaves with the volatiles at the top. Due to the use of recirculation of cooling CO₂ in the simulations the Recovery Rate is instead a measurement of how much of a certain specie that leaves the reactor that is brought back to the reactor (except in the case of bleed). This will be further explained in chapter 7.4.1.

7 MODELING AND SIMULATIONS

The previous chapters have presented the basic knowledge and tools to design the power process and the compression and conditioning process in an effective way. The present chapter will show how it is designed in Hysys for the simulations.

7.1 The CLC reactor implementation

To simulate a CC with CLC the reactor needs to be simulated in some way. How the reactor will be designed, how much bed material that will be used, how long residence time the bed material will have, which pressure drop that could be expected are just some of the questions that to this day do not have any straight answers. As in all process modeling, simplifications have to be made, but in this case the simplification has to be very big. This can be defended by remembering that the purpose of the thesis is not to study the CLC reactor but to see if recirculation of unconverted fuel is possible. The simplified reactor model is based on a control volume applied over the oxidation and reduction reactors as shown in Fig. 12

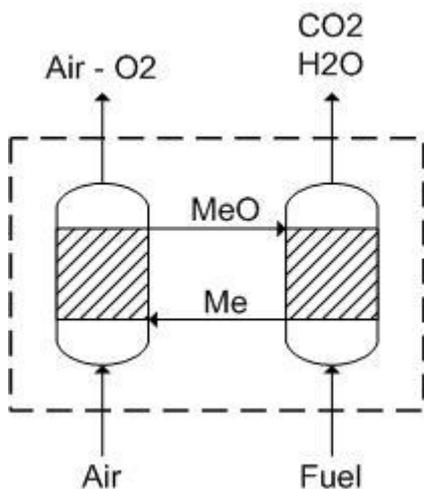


Fig. 12. CLC reactor with applied control volume.

By applying one control volume over the two CLC reactors the conditions for the streams in and out can be determined by heat and mass balances as shown in Eq. 12 and Eq. 13 when considering an adiabatic reactor.

$$\dot{H}_{air,in} + \dot{H}_{fuel} = \dot{H}_{air,out} + \dot{H}_{CO_2/H_2O} - \dot{Q}_{LHV} \quad \text{Eq. 12}$$

$$\dot{m}_{air,in} + \dot{m}_{fuel,in} = \dot{m}_{air,out} + \dot{m}_{exhaust} \quad \text{Eq. 13}$$

where

$$\dot{Q}_{LHV} = \dot{Q}_{OX} - \dot{Q}_{RED} \quad \text{Eq. 14}$$

With a certain expected thermal power and knowledge about how the reactor works, the streams can be defined in conjunction with the design of the rest of the cycle in order to achieve maximum cycle efficiency. In this thesis, data from Naqvi [28] are employed to define all the streams but the fuel stream. The fuel stream is controlled to keep the outgoing CO₂ stream temperature at its defined level. This way the reactor is fully defined. The calculations and assumptions that has been made regarding solid conversion rate, oxygen carrier residence time in the reduction reactor, oxygen carrier used, thermal power of the plant etc to define the out and ingoing streams can be found in [28]. The computational assumptions regarding the inlet streams and the rest of the cycle can be found in Table 3.

The Hysys implementation of the reactor model can be seen in Fig. 13 with a control volume added as in Fig. 12.

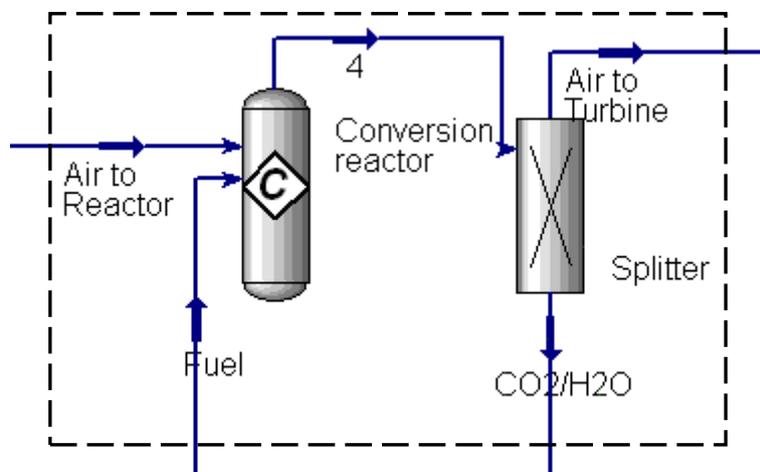


Fig. 13. CLC reactor model implementation in Hysys.

The implementation uses a conversion reactor which is a predefined reactor type in Hysys. In this reactor type the stoichiometry of the conversion of the different hydrocarbons present in the assumed natural gas fuel is defined:



For every reaction it is in Hysys possible to define the conversion rate, which decides to which degree the different reactions are completed. This makes it very easy to change the fuel conversion rate for different hydrocarbons. The conversion rate is, if all the reactions are set to the same conversion rate, a measurement of energy conversion based on the Lower Heating Value (LHV) of the fuel. After the conversion reactor a splitter is introduced which splits the streams so that the CO_2 , H_2O and hydrocarbons go one way and the excess air goes another. The splitter has to be controlled so that the same amount of H_2O and CO_2 that enters with the air also leaves with the air and not with the CO_2 stream and so that the small amount of nitrogen in the fuel leaves with the CO_2 rich stream (this small amount will have a significant impact on the results, see chapter 9). Since the calculations around the reactor are heat and mass balances there are still degrees of freedom around the reactor. For example, the temperature of the ingoing air is adjusted to keep a minimum temperature approach in the heat exchanger prior to the oxidation reactor. The mass flow of fuel is increased in the same way to keep the temperature out from the reactor constant when the conversion rate is lowered. In that sense, the input data from Naqvi is just a starting data. How a real reactor would react to these kind of changes and recirculation streams is outside this topic but it has to be emphasized that the reactor model should be seen as just a model to be used to study fuel recirculation. A real reactor would of course have to be designed for a certain fuel conversion and recirculation which in turn, depending on the oxygen carrier, bed mass, residence time etc, would give the optimum temperatures in and out from the reactor. As mentioned in chapter 4.2 it is uncertain if a reactor would work with a recirculation stream. Therefore one more case is studied were the recirculated fuel is combusted prior to the air turbine which increases the TIT at the same time as the problem with unconverted fuel is addressed.

7.2 Different CLC CC cycle layouts

The implementation of a CLC reactor in a Combined Cycle (CC) requires some major changes to the cycle design. A CLC reactor has first of all two outgoing streams instead of one. In addition, the temperatures of the streams are considerably lower than the combustion gas from an ordinary GT burner, in this work 1200 respective 980°C. The two streams can be utilized in a number of different ways and a number of different cycle layouts have been proposed by among others Wolf, Consonni et al. and Naqvi [36],

[9], [28]. The present chapter describes two cycles proposed by Naqvi that have been used as “base case cycles” in this thesis. The cycle configurations and data are more or less directly copied from Naqvi and modeled in Hysys. The big difference is that another turbine cooling model is implemented, and of course, that less than 100% fuel conversion has been tested together

with new features such as fuel recirculation, burner after reactor and ASU/combustor. When changing the fuel conversion rate the fuel flow into the CLC reactor model is increased in order to keep the temperature out from the reduction reactor constant. The flow into the reactor is also affected by the recirculation of unconverted fuel which also brings a great portion of CO_2 (and N_2 in some cases) to the reactor. The fuel and air streams are preheated (se

Fig. 16 and

Fig. 15) and to keep the minimum temperature approach constant in those heat exchangers, the temperatures of the fuel and air streams are adjusted. Those adjustments are very small, in the order of maximum 10°C and should not effect how the theoretical reactor would work. The efficiency of the cycles with 100% fuel conversion is almost identical to the one Naqvi presented (as seen in chapter 7.3.2 and 7.3.1), indicating that the cycles are more or less the same. The data for the cycles are/can be found in Table 3.

7.3 Turbine cooling

The turbine cooling model is implemented in Hysys as shown in the principal schematic in Fig. 14

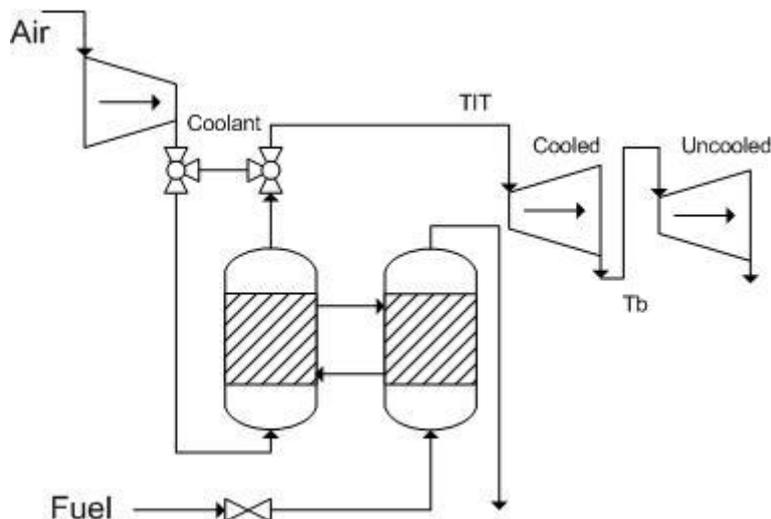


Fig. 14. Cooling model.

The amount of cooling air is found from the cooling model and depends upon the pressure ratio, the TIT and the assumed maximum blade temperature, T_b . In the cooling model, the cooling air is bypassed the reactor and mixed with the hot stream from the reactor before the expansion in the cooled turbine down to the assumed T_b . The cooled turbine is given a lower polytropic efficiency, as determined by the cooling model. After leaving the cooled turbine the stream enters the second (un-cooled) turbine unit which has a polytropic efficiency according to a state of the art gas turbine. It should be emphasized that the feature with two turbines is just a model characteristic to model the cooling in a simple way, and should be thought of as one turbine with

one cooled part followed by an un-cooled part. The equations for determining the coolant mass flow and the reduced polytropic efficiency have not been implemented in Hysys, but were obtained from an existing process flowsheet in the Pro/II process simulator available at SINTEF Energy Research.

7.3.1 Cycle A: Air turbine and preheater

Instead of including a CO₂ turbine to utilize the heat in the CO₂/ H₂O vapor, this heat could be used to preheat both the air and the fuel streams. One obvious advantage of this design is that the CO₂ is already pressurized when entering the compression chain compared to cycle B where the CO₂/ H₂O stream enters the compression chain at almost atmospheric pressure. The cycle has a pressure ratio of 10 and reactor outlet temperatures of 1200 and 980°C respectively. It employs the same turbine cooling model but in this case there is no CO₂ turbine that needs cooling. The cycle has a efficiency at 51,2% (50,9% Naqvi) excluding CO₂ compression and 50,37% (50% Naqvi) including CO₂ compression, in both cases with 100% fuel conversion. In two cases (“Aa-C/B-No N₂-95%” and “Aa-C/B-No N₂-95%”) a burner has been implemented between the oxidation reactor and the air turbine in order to combust the recovered fuel. Further details are to be found in Fig. 24 and chapter 8.2.2.

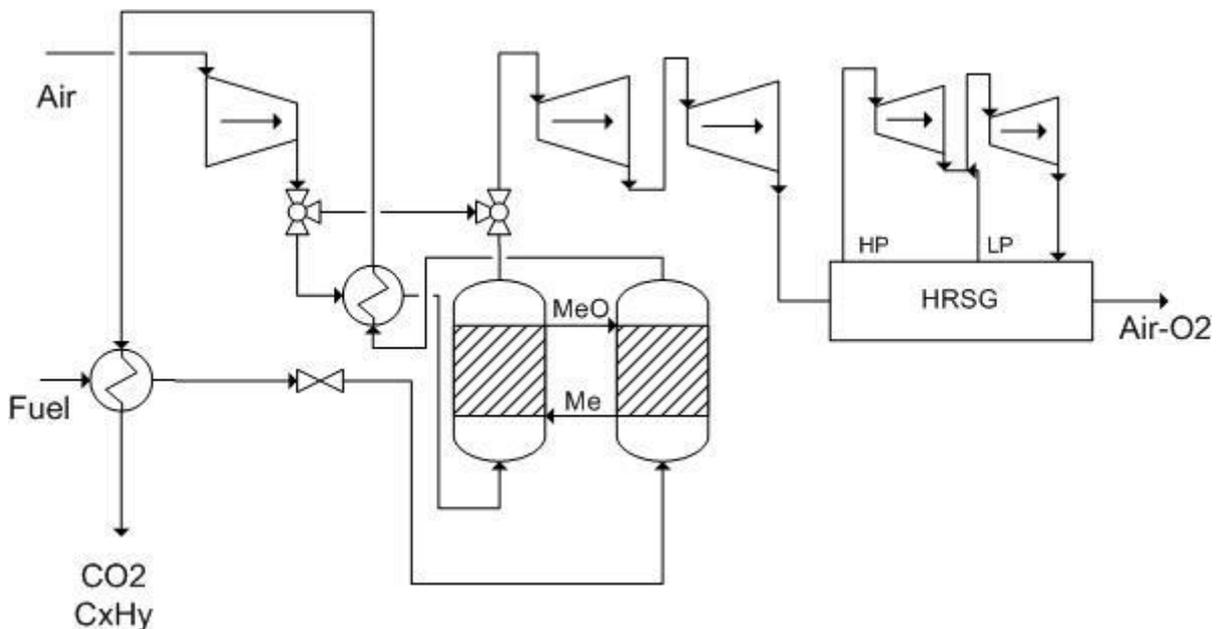


Fig. 15. Cycle A.

7.4 The compressor train and the distillation column

The pressure ratio of the compressors should be between 1.7:1 and 2:1 [31]. In the simulations it is assumed that the pressure ratio can be maximum 2:1 according to the previous chapter. Depending on which of the two cycles A or B that is simulated, the compressor trains with distillation column looks like in Fig. 17 or Fig. 18.

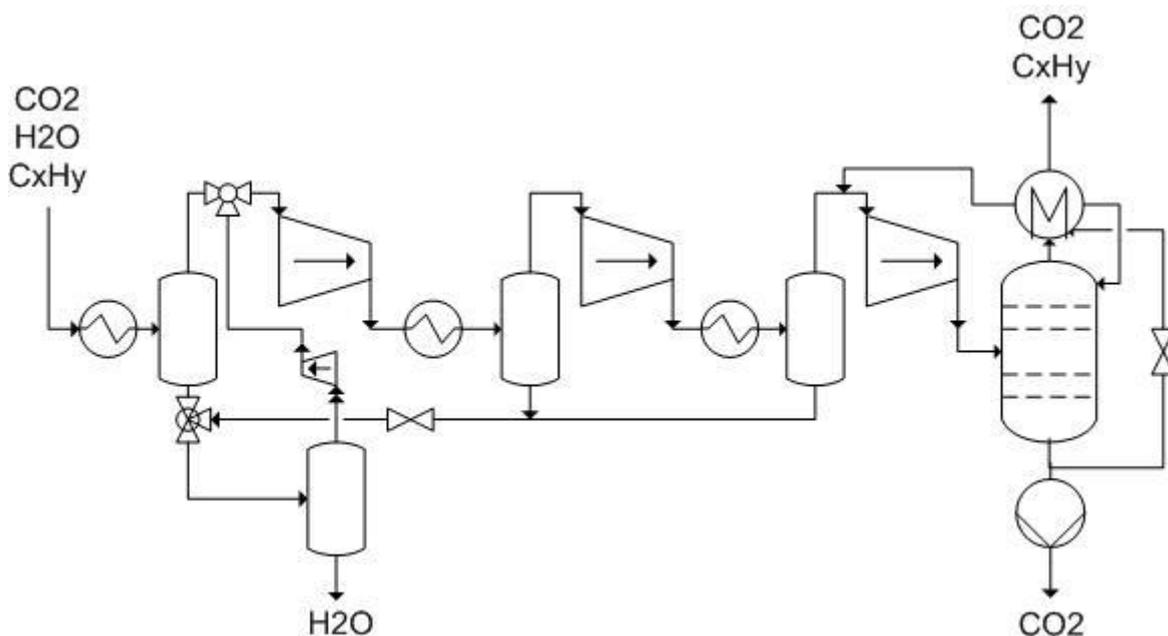


Fig. 17. Compressor train for cycle A.

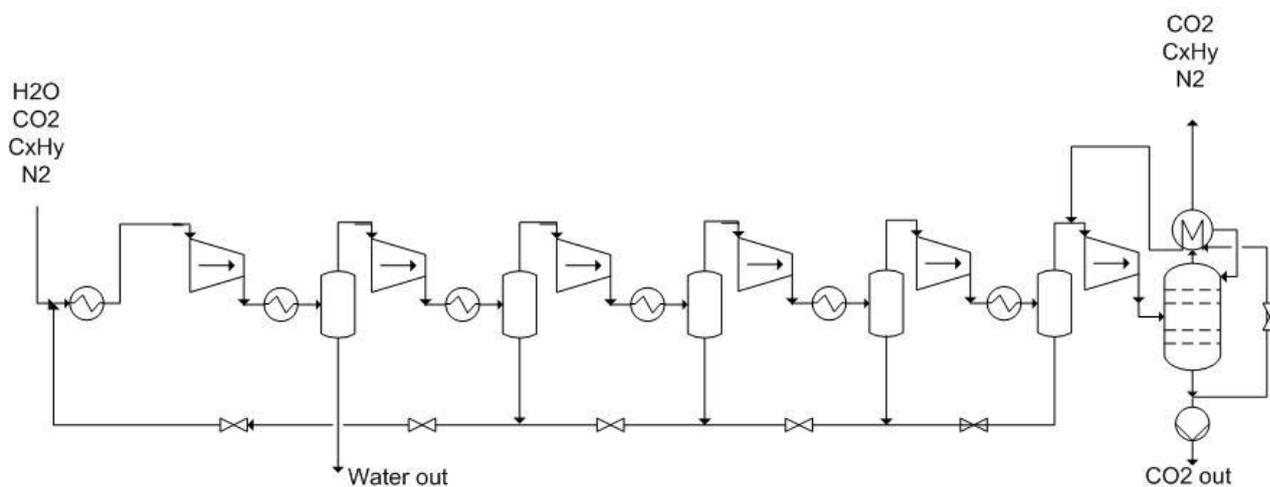


Fig. 18. Compressor train for cycle B.

The specific compressor pressure ratio depends on the pressure at which the CO₂ is entering the compressor train and at which pressure the column is introduced, but is around 2 for both cases and same for every compressor (stage). After each compressor the stream is cooled in chillers

where the water is condensed and then separated in gravity separators. The separated water contains small amounts of CO₂ and to minimize the amount of CO₂ leaving the process with the water, all the separated water streams are reintroduced to the first separator. This way less CO₂ will leave with the water stream because less CO₂ can be solved in water at low pressure [4]. In cycle B where the first separation drum is at a pressure higher than atmospheric pressure one more separation drum is introduced at atmospheric pressure where all water streams are introduced. The CO₂ leaving at the top of this separator has to be compressed by an extra compressor but due to the small amounts of gas the extra power required is relatively small and does not affect the efficiency of the cycle in a significant way. This recirculation is in cycle 'A-' unnecessary because there is only a very small amount of CO₂ in the streams out from the separation columns, in the order of single-digit kilograms per hour. But in cycle 'B-' in which the first column is at such high pressure it makes sense, the water stream from the first separation contains in the order of thousand kg CO₂ /h which is then reduced too in the order of a hundred kg CO₂/h.

It would be possible to continue to use compressors to compress the CO₂ all the way to two hundred bars, but the most efficient way to reach 200 bars is to condensate the CO₂ at a certain pressure (determined by the cooling water temperature) and then pump it to 200 bars as mentioned in chapter 6.3. With cooling water at 8°C and an approach temperature in the condenser at 8 K the lowest pressure for condensation is around 53 bars when the CO₂ stream is diluted with methane or higher hydrocarbons. In the cases where the stream is diluted with hydrogen ("Ac-") the situation is different; the condensation pressure is dramatically increased [6]. This case is therefore treated a bit differently and the pump will be introduced at the pressure necessary which in some cases calls for more compressors. See chapter 8.1 for further details.

The separation of volatiles in the distillation column requires energy, both to chill the condenser and to heat the reboiler. The distillation column is placed after the compressor train, at which pressure will be discussed in the next paragraph. The cooling duty for the condenser is taken from the stream of CO₂ leaving the column at the bottom. By throttling (expanding) this stream in a throttling valve its temperature decreases. In reality this cold stream of expanded CO₂ would chill the top stream from the column in a heat exchanger in a condenser as shown in Fig. 17 and Fig. 18 but in Hysys it has to be modeled as shown in Fig. 19.

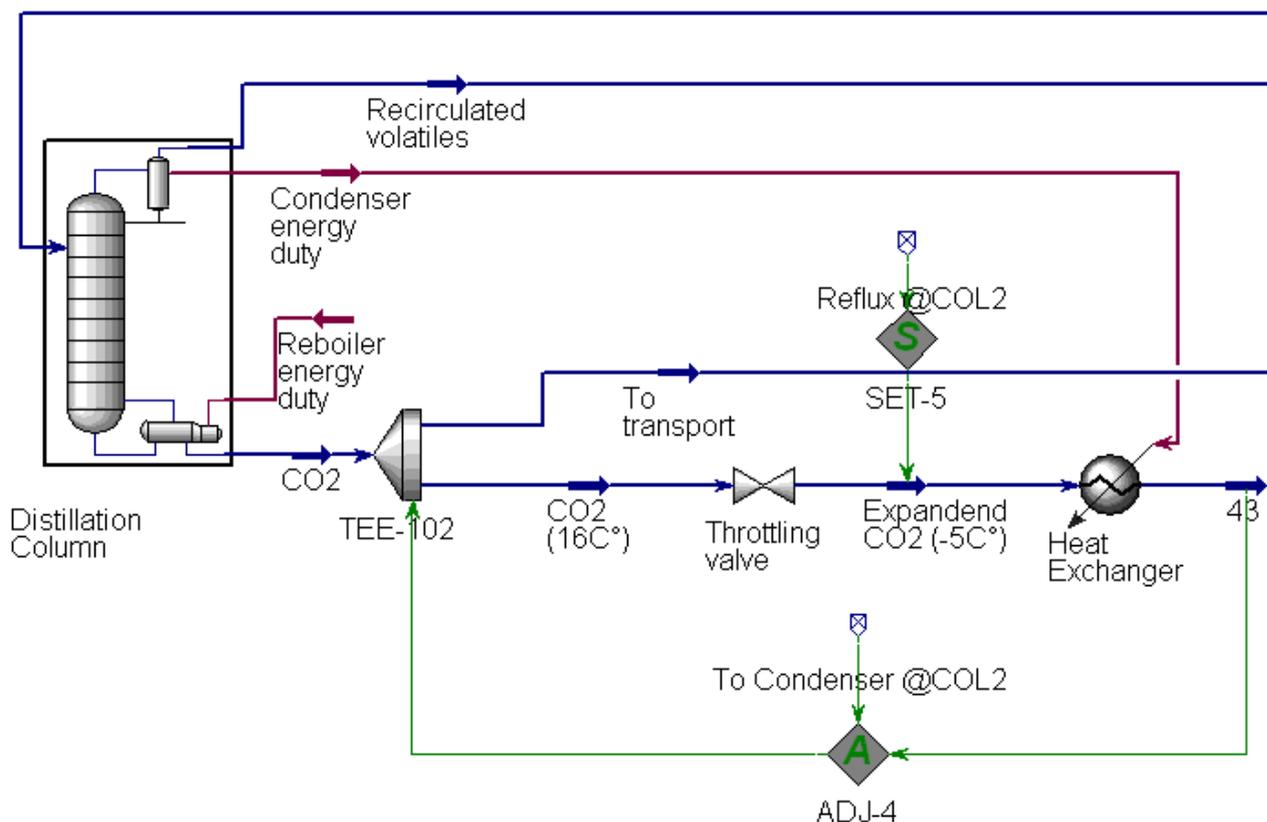


Fig. 19. Distillation cooling modelling.

It is modeled this way because it is not possible to connect a heat exchanger at the top of the column, instead there is an energy stream going out from the top of the column which is the energy that is removed in the top condenser. This energy stream is heating the expanded CO₂ stream. By fixing the temperatures before and after the heater “Heat exchanger” the simulations will be as if the cold CO₂ chilled the condenser stream in a heat exchanger. The amount of CO₂ that has to be expanded is controlled by the temperature of the stream entering the column condenser (leaving the heater) and the pressure the CO₂ stream is expanded too is sat by the temperature of the liquid leaving the column condenser. The approach temperatures in the imagined heat exchanger is set to 5 K which means that the expanded CO₂ has to reach a temperature 5 K below the condenser temperature in the column and that the stream after the heater has to be 5 K colder than the stream entering the condenser in the column. This way it is modeled as if the streams meet in a counter current heat exchanger, see Fig. 22.

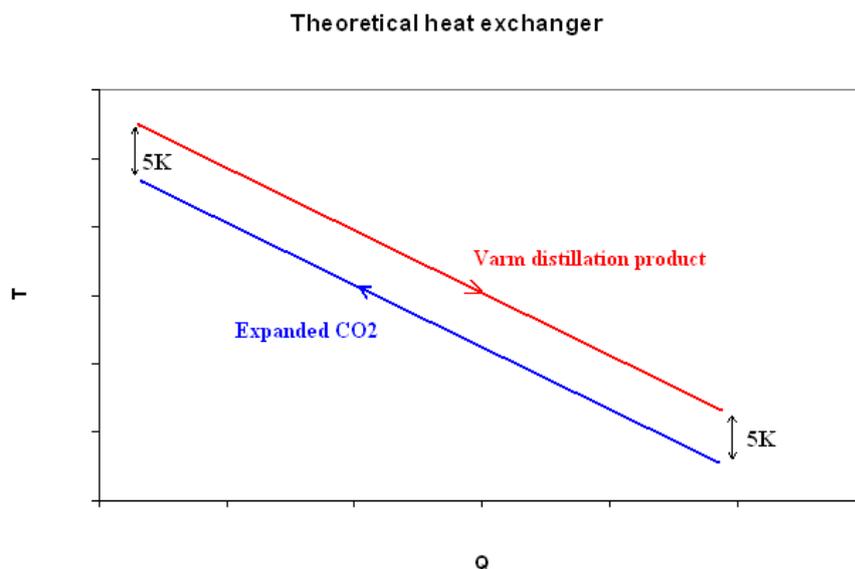


Fig. 20. Principle of the theoretical counter current heat exchanger.

The expanded and heated CO₂ is then reintroduced to the compressor train just before the last compressor at a pressure that in all cases is slightly higher than the stream it is reintroduced to.

The energy stream to the reboiler is not handled in any way in the simulations. This is because there is always low value heat available that could be used, either from the steam cycle or by using heat from the intercoolers between the CO₂ compressors. The temperature in the reboiler is in all cases around 15°C but the heat flow needed is big, between 4 and 24 MW depending on the case. Using heat from the intercoolers would be possible, the temperatures and the amount of heat is more than enough. The question is if it would be practically possible/desirable when taking the size and costs for heat exchangers into account. The other possibility, heating with steam, is practically possible and probably the easiest way of doing it [5]. The penalty to cycle efficiency would be depending on how the heat exchanger could be constructed, if different pressure levels on different sides could be accepted which in turn would decide whether valuable steam has to be extracted from the turbine or if waste heat from the steam cycle condenser could be used. If a distillation column is going to be used in the conditioning process connected to a power cycle this is something that needs further attention.

7.4.1 Recovery Rate in the column

As already mentioned the Recovery Rate (RR) is a measurement of the recovery of a certain specie in the column. This is a parameter that is possible to define in the column model in Hysys. But due to the recirculation of CO₂ leaving at column bottom there is an enrichment of for

example methane in that recirculation loop, see Fig. 21. So if a certain RR of methane is defined in the column this might be more than the amount of methane leaving the reactor, taking the simulation into a loop that does not converge. Instead the RR is defined as a percentage of the amount of mole of a certain specie leaving the reactor. This way the RR in the column is smaller than the actual RR in the cycle. The specie that is defined in the RR is in one case hydrogen where in all the other cases it is methane.

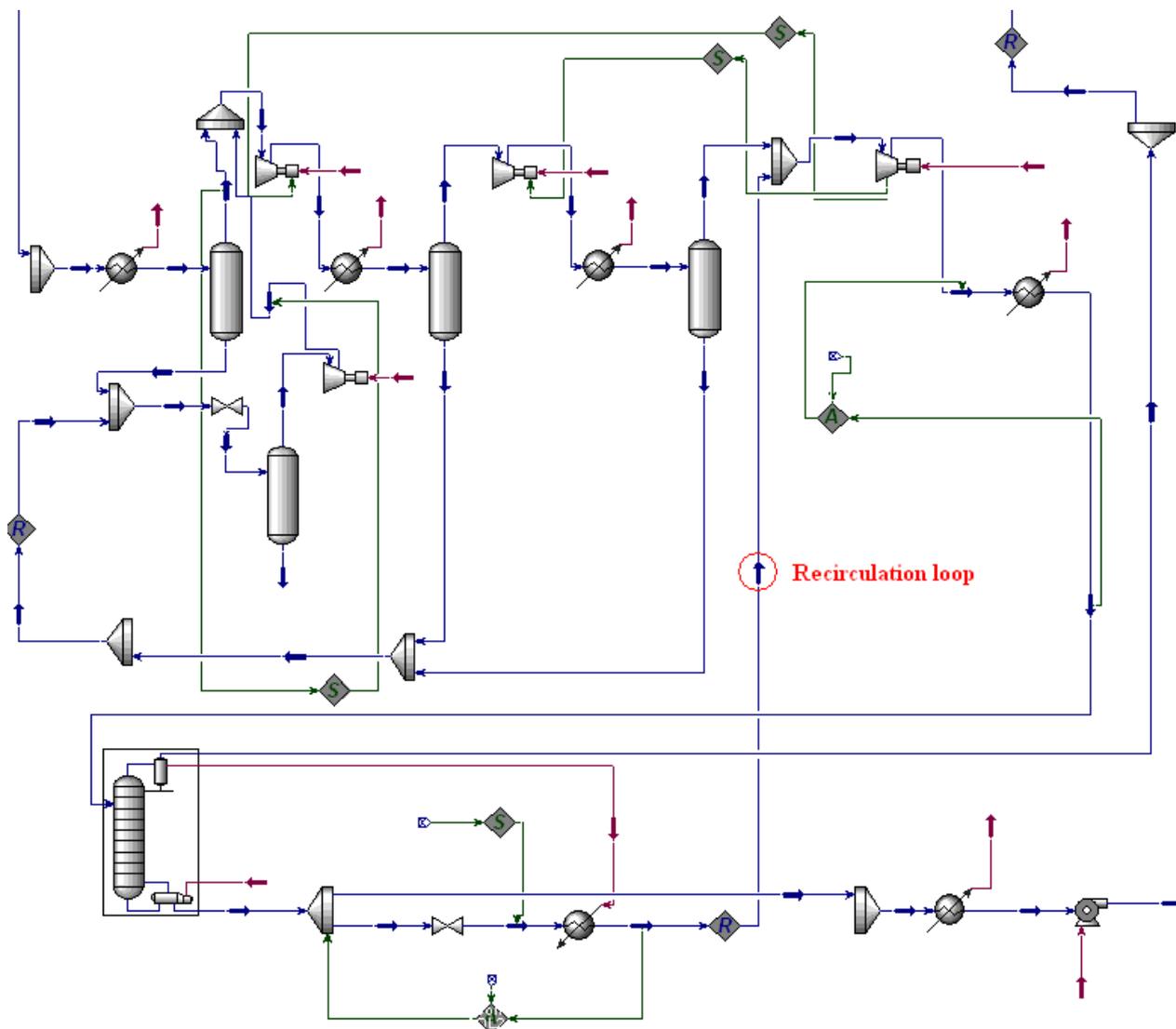


Fig. 21. Recirculation of cooling CO₂.

7.5 Power cycles with compression, conditioning and recycle

To be able to optimize the distillation column it has to be connected to the rest of the cycle. In Fig. 22, Fig. 23, Fig. 24 and Fig. 25 cycle 'A-' and 'B-' with their respective gas conditioning and compression chains are shown with simplified illustrations of HRSG and steam turbine(s). Fig. 24 and Fig. 25 show the cycles with burner and ASU respectively. It can be seen in

Fig. 22 and Fig. 23 that one more feature has been added, a bleed stream on the recirculated stream. This is necessary to handle the accumulation of nitrogen in the recirculation loop. The simulations will be done both with and without considering the presence of nitrogen and hence both with and without a bleed stream. There will be more to read about this in chapter 8.

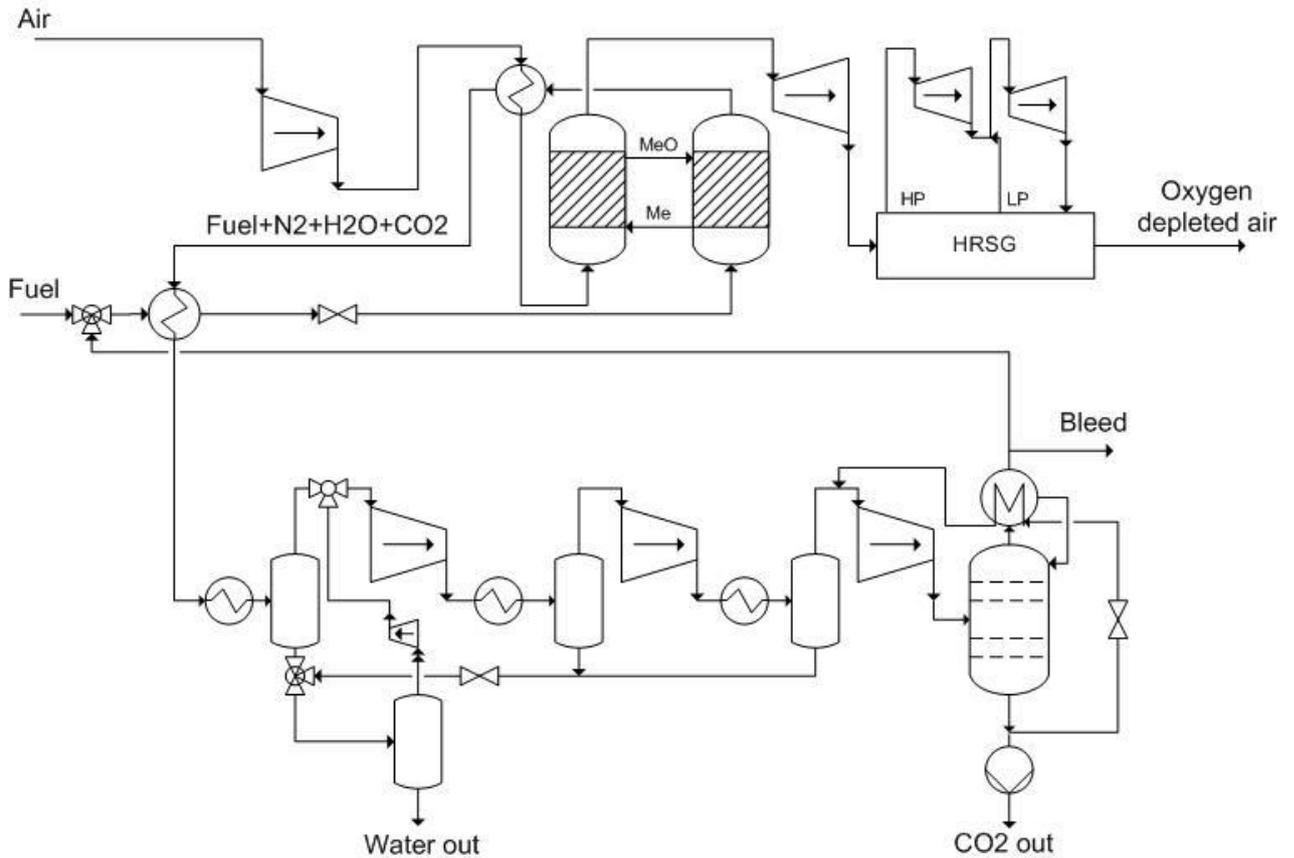


Fig. 22. Cycle A with compression, conditioning and recirculation.

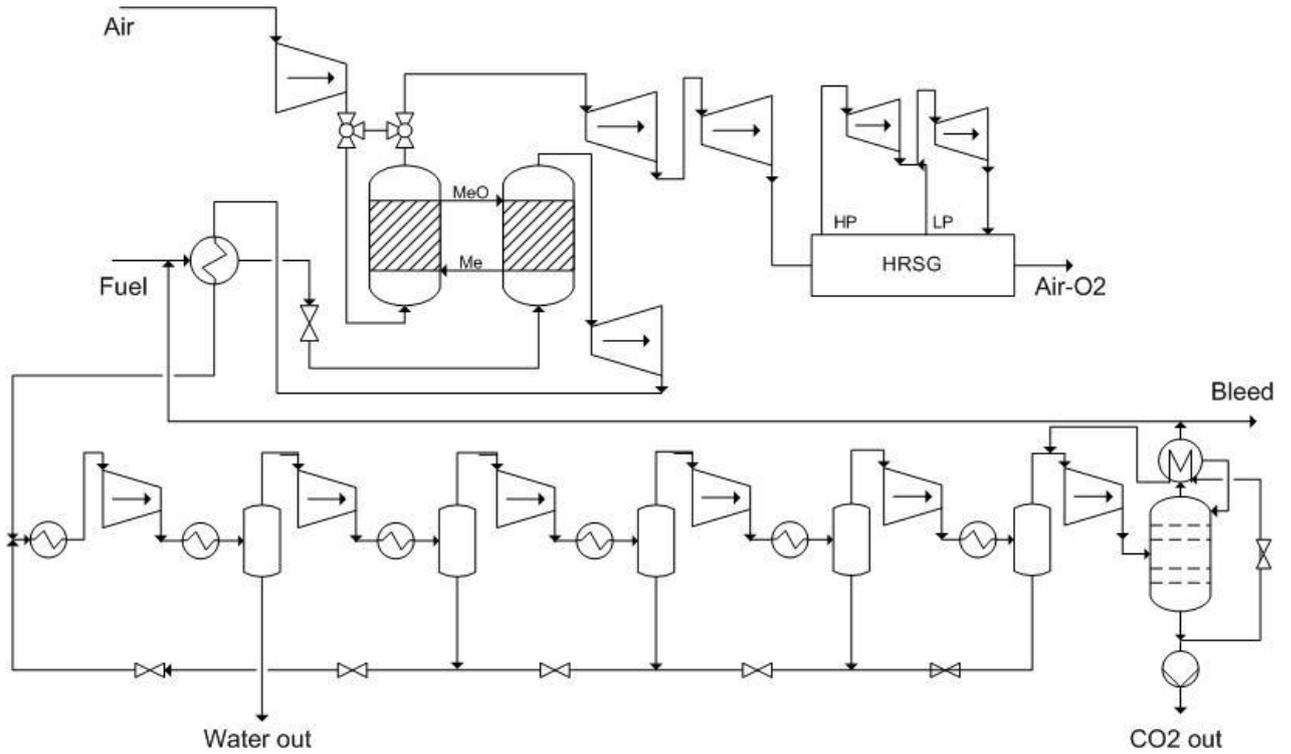


Fig. 23. Cycle B with compression, conditioning and recirculation.

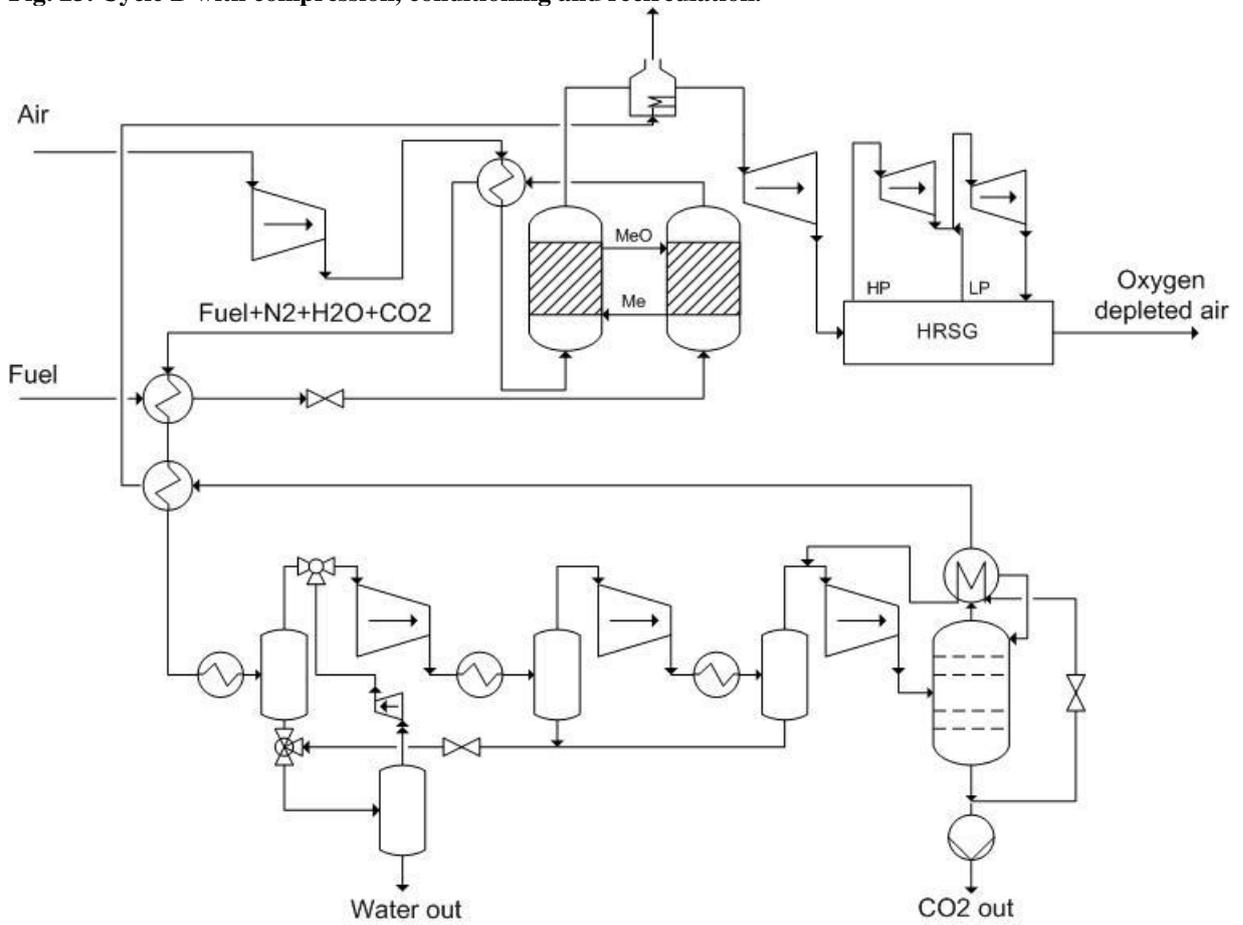


Fig. 24. Cycle A with compression, conditioning and recirculation to a burner.

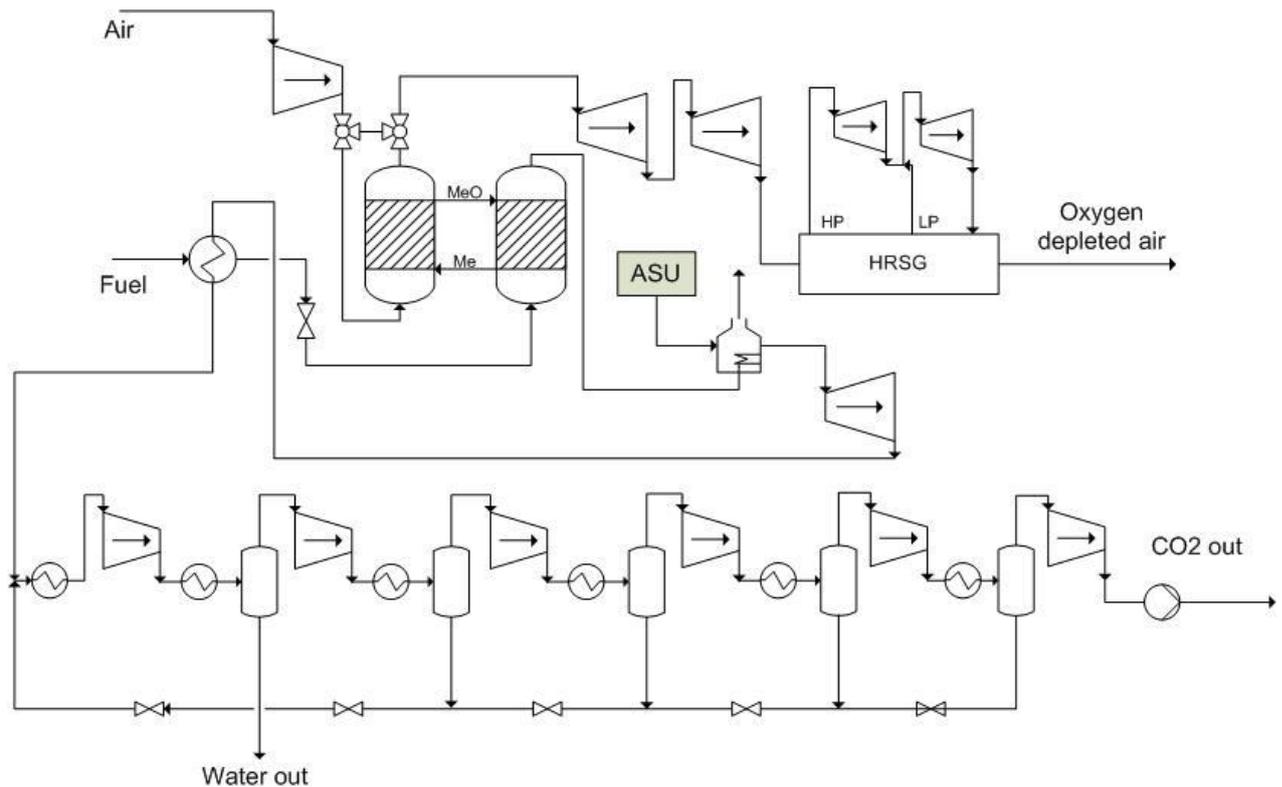


Fig. 25. Cycle B with ASU.

7.5.1 Introduction and optimization of the distillation column

The place for the introduction of the distillation column in the compression train has to be found and the other important parameters for the column have to be decided, such as the condenser temperature and the Recovery Rate (RR). In the study of Aspelund and Jordal [4] the column is introduced at 60 bars. It is concluded that a higher pressure decreases the separability but that a higher temperature difference between the reboiler and the condenser can be achieved. It is further concluded that the optimum pressure of the distillation column should be found on a case to case basis. Beneath a discussion follows about where the column should be introduced and at which condenser temperature and RR it should be operated.

The required reboiler temperature increases with increasing pressure, which could lower the cycle efficiency if steam is used for heat addition to the reboiler. The raised reboiler temperature would also cause the cooling duty to increase which calls for more CO₂ to be expanded and hence recompressed which would lower the overall efficiency.

The volatiles and CO₂ leaving at the top of the column will be expanded down to reactor pressure. At a higher column pressure more of previous compression work will be lost in the expansion of the top stream.

At a higher column pressure less CO₂ will follow the top stream back to the reactor to get expanded and recompressed and hence less compression work will be required.

The part of the CO₂ leaving at the bottom of the column that is not expanded will be bypassed the expansion-heat exchanger and pumped to 200 bars. As mentioned earlier the pump should be introduced at the lowest pressure possible to lower the compression work. However this has only a small impact compared to the other factors mentioned.

Simulations have to be done to find out were to put the column. In Fig. 26 the efficiency of cycle 'A-' with a conversion rate (CR) of 99% and recovery rate (RR) of 95% is plotted against the column pressure (further explanation of the of the cycle name are to be found in chapter 8).

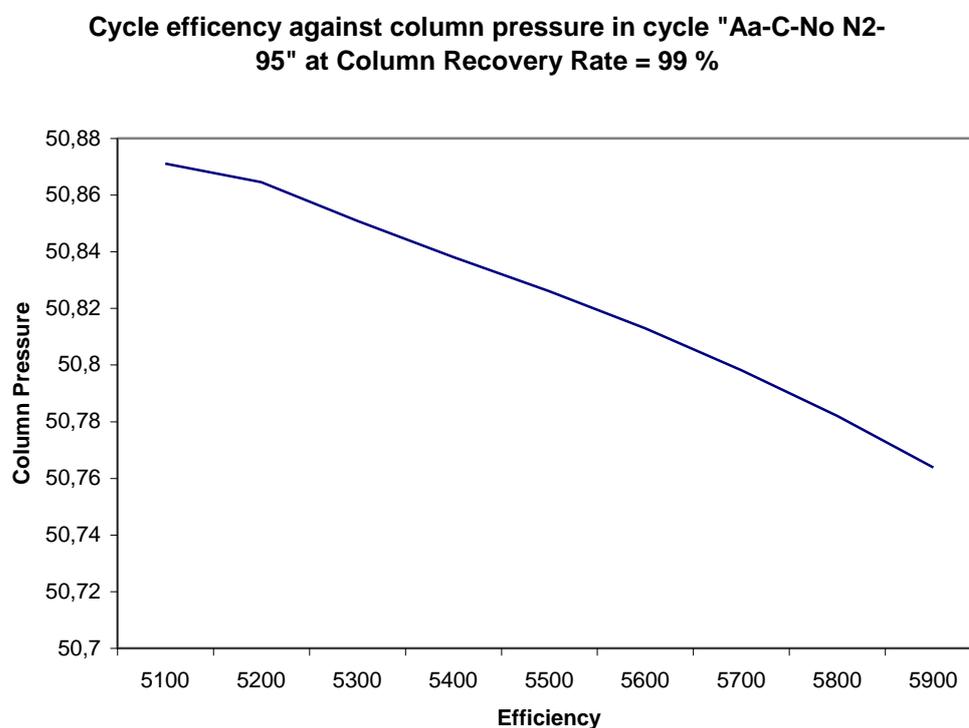


Fig. 26. Column pressure vs. efficiency.

The condenser temperature is kept constant; by varying it to optimize it for the specific pressure the slope of the line would be a little bit less steep but with the same declining trend. The result is valid for this particular case, in another cycle with different RR and CR the picture would be different and case studies show that the optimum pressure for all cases is to be found between 53 and 57 bar. As seen in Fig. 26 the difference is very small and it is not worth the effort to try to

find the optimum pressure for every cycle. Most cases benefits from introducing the column at the lowest pressure possible. Therefore, in order to be consequent in the simulations, the column is introduced at the lowest pressure possible taking into account the limitation of cooling water and approach temperature, i.e. condensation at around 53 bars at 15°C.

The second variable that has to be optimized for the column is the condenser temperature. With a lower condenser temperature less CO₂ will follow the volatiles in the top stream and be recirculated and hence expanded and compressed once again. But with a lower condenser temperature more of the CO₂ leaving at the bottom has to be expanded to cool the condenser and this expanded CO₂ has to be recompressed as well. The overall result is that there is an optimum condenser temperature which gives the best cycle efficiency as seen in Fig. 27.

Recirculated CO₂ and efficiency against condenser temperature in cycle "Aa-C-No N2-95" at Column Recovery Rate = 95 %

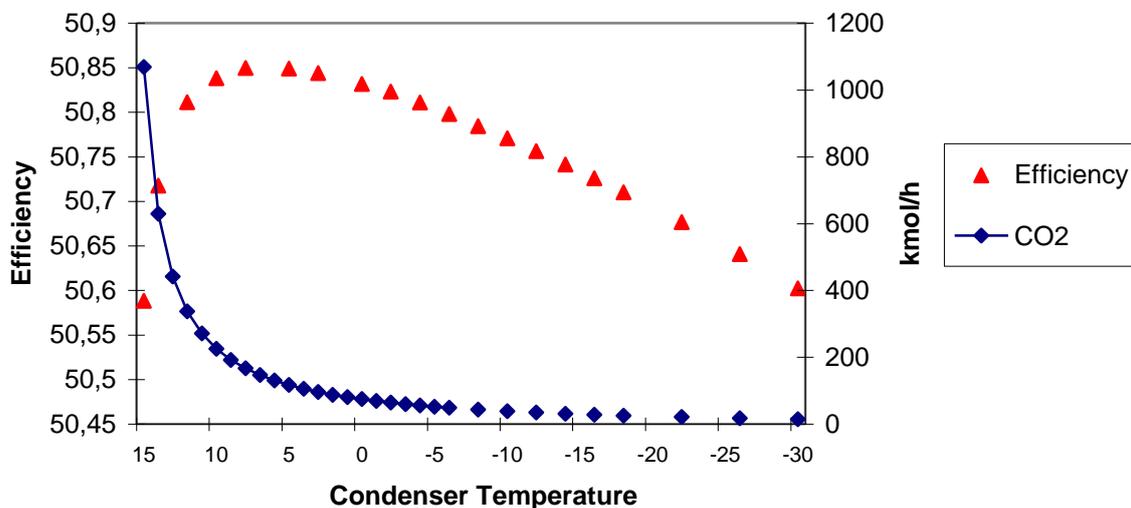


Fig. 27. Optimum condenser temperature.

Once again the figure just shows this especially RR and Conversion Rate (CR) but the trend is the same for the other cases. Please note that the scale on the x-axis goes from plus to minus. Before the optimum efficiency is reached there is a lot of CO₂ leaving with the top stream that has to be heated and recompressed. After the point where optimum efficiency is reached there is less CO₂ in the top stream but instead more CO₂ in the bottom stream that has to be expanded and then recompressed. At the optimum point the amount of CO₂ in the top stream and the amount of CO₂ that has to be expanded are on a level that gives the highest efficiency of the cycle. It is seen in the figure that the cycle is not that sensitive to the temperature between certain frames, for example

the efficiency difference is only hundredths of a percent when going from eight to zero degrees condenser temperature. Therefore other requirements can be prioritized, for example the rate of volatiles in the outgoing stream or the rate of CO₂ in the volatile stream which are both depending on the condenser temperature. In some cases the condenser temperature is lowered to keep the CO₂ emissions down, see Table 3. As mentioned, at different CR and RR the optimum temperature varies a bit but it does not affect the cycle efficiency in a great way as long as it sat to a reasonable level. The condenser temperature will therefore be constant for every specific case in the simulations as a way to make the simulations easier and the results more comparable. There are however differences between the different cases, see Table 3.

The third and last parameter that has to be set in the column is the RR. The RR controls how much of an ingoing specie that leaves at the top. In most cases it is the RR of methane that is controlled but in one cases (“Ac-“) the amount of hydrogen is controlled. With a higher RR more unconverted fuel is recycled back to the CLC reactor and hence has a positive impact on cycle efficiency. But with a higher RR the duty for both the condenser and the reboiler increases and as a consequence more cooling is needed which has a negative impact on cycle efficiency. Also, with a higher RR more CO₂ will follow the volatiles out in the top which has a negative impact on cycle efficiency.

This short discussion about column pressure, condenser temperature and the Recovery Rate shows that optimizing the column operating parameters in the cycle is a complicated issue. All three parameters are interconnected and affect each other; treating them one by one is a minor simplification. However it is a good simplification to do to be able to find a compromise for the column parameters.

The column can also be optimized for other things than just the cycle efficiency, such as the CO₂ stream quality or the top stream CO₂ content. As can be seen in the test results the CO₂ stream quality does not contradict with the gas quality proposed in the Dynamics report [49] for CO₂ streams and does not need further conditioning. The top stream CO₂ content is however something that could be adjusted by lowering the condenser temperature. As has been discussed in chapter 4.2 and 7.1 the uncertainties about the reactor are still very large and to set a maximum CO₂ recirculation mass flow to the reactor would only be a wild guess. (The recirculated CO₂ mass flow can be seen in chapter 9.) Instead the column is designed for optimum cycle efficiency in the present work except for cases with burner where the condenser temperature is lowered to

keep the CO₂ emissions down. Fig. 27 shows how a lower condenser temperature gives a smaller amount of CO₂ in the top stream.

The content of nitrogen in the top stream (in the cases with nitrogen present) is however something that can not easily be adjusted. A bigger bleed stream will lower the amount but will have a negative impact on the cycle efficiency. The amount of nitrogen in the reactor can be seen in chapter 9 for the different cases. In Fig. 28 a summary of the different parameters effect has been made to further emphasize the difficulties to optimize the cycle with the column.

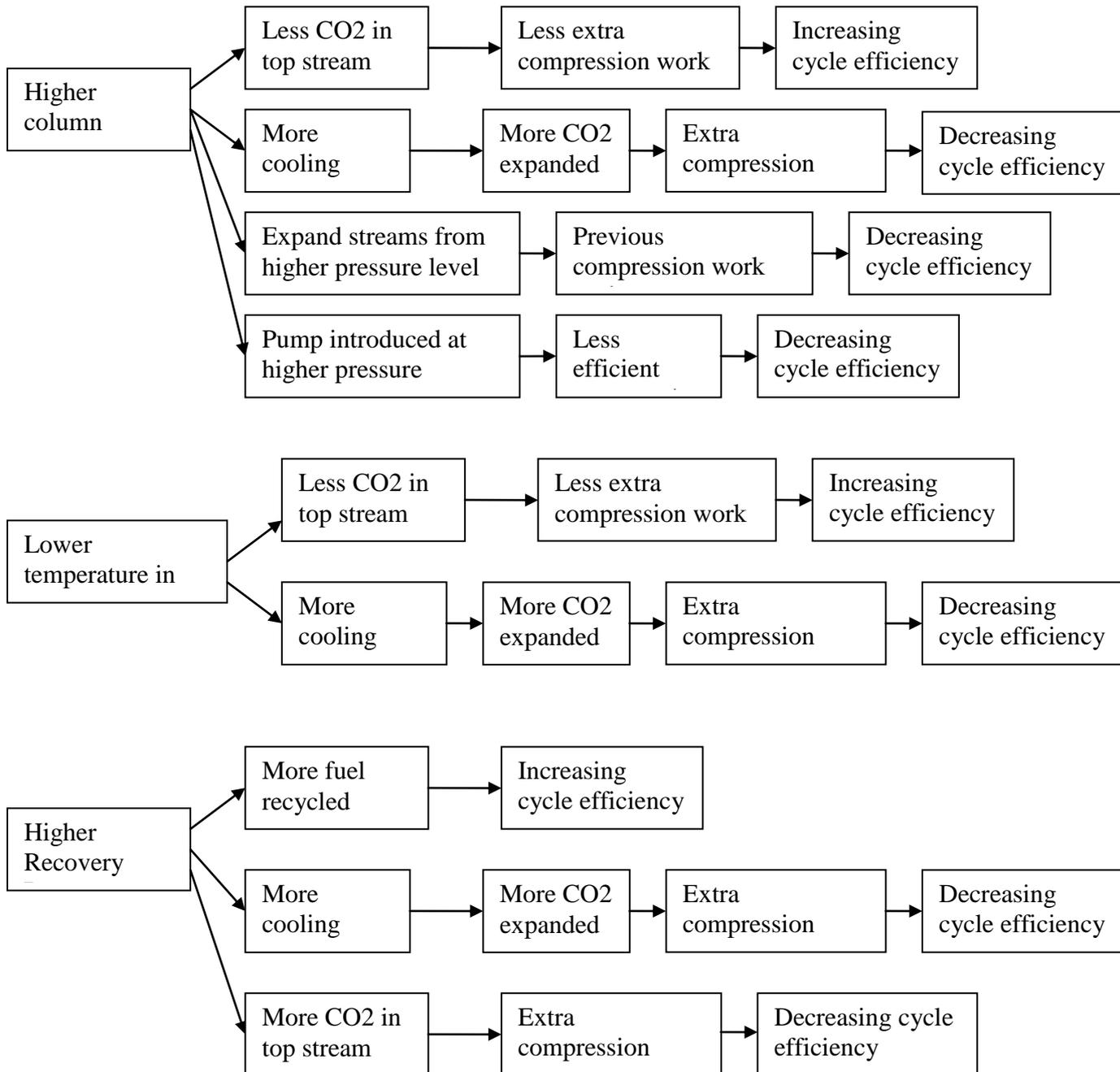


Fig. 28. Distillation column optimisation parameters.

7.6 Steam cycle modeling

The steam cycle was just briefly mentioned in chapter 5 as it is of no greater interest to study any further in the present work. The input data for the steam cycle is taken from Naqvi, i.e. the pressure levels, steam temperatures and approach temperatures in the heat exchangers. In order to meet these defined values the mass flow of steam and the mass flow ratio between the High Pressure (HP) steam turbine and the Low Pressure (LP) steam turbine was adjusted in Hysys. A schematic picture of the steam cycle is showed in Fig. 29.

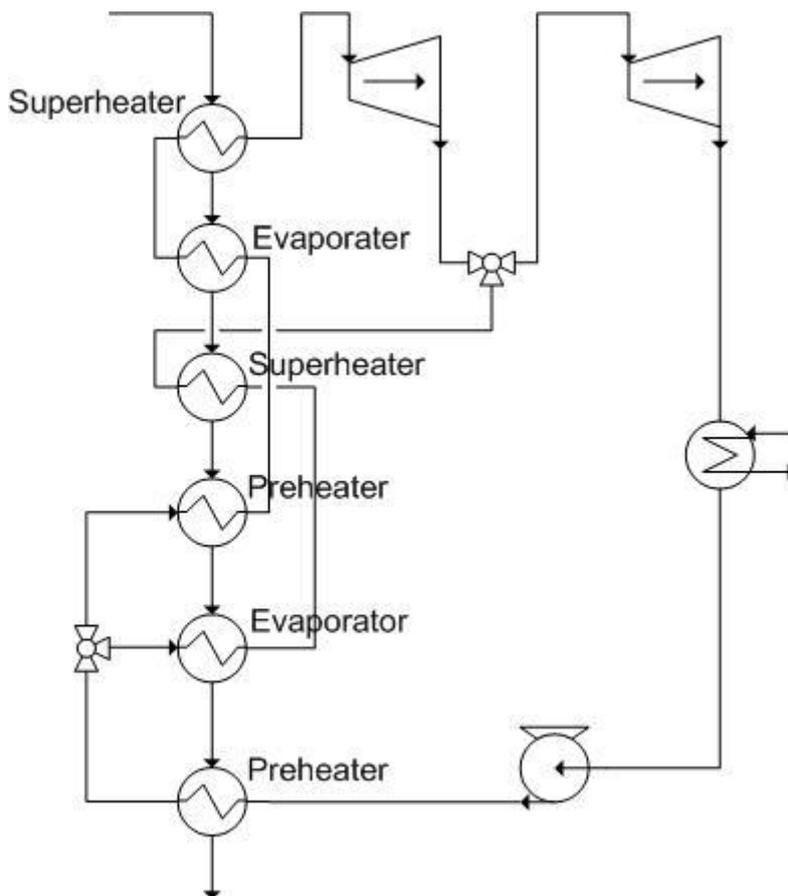


Fig. 29. Steam cycle.

The steam cycle efficiency is calculated according to Eq.20;

$$\eta_{ST} = \frac{W_{netout}}{\Delta h_{steam}} \quad \text{Eq. 20}$$

where W_{netout} is steam turbine power output minus the recirculation pump work and Δh_{steam} is the enthalpy increase of the steam over the HRSG (the heat exchangers). In the base case steam cycle efficiency is around 35,77% which can be considered normal [].

8 INVESTIGATED CASES

The main goal of the work covered in this thesis has been to perform and analyze process simulations of a complete CLC CC including CO₂ conditioning and compression to 200 bar, with special focus on the compression and conditioning process. In the simulations the main parameters have been

- Conversion rate of natural gas in the CLC reactor
- Recovery rate of fuel components from the distillation column

The volatiles are separated in a distillation column and returned to the reactor or combusted prior to the air turbine except in one case where they instead are combusted with oxygen right after the CLC reactor. The results of the study (chapter 9) show how incomplete fuel conversion affects the overall efficiency of the plant and how the conditioning process could be designed. The present chapter will explain the different cases simulated in the thesis.

With the theoretic knowledge from preceding chapters it is possible to connect cycle ‘A-‘ and ‘B-‘ with the gas conditioning and compression processes and model them in Hysys. The two cycles are further divided into subcategories as shown in Table 2.

Table 2. Different cycles and cases.

Cycles	Fuel components in CO ₂ stream	Fuel recovery method	Assumed inert in fuel	Recovery Rate
A	a: Same fractions of hydrocarbons as in NG fuel	C: Column	N ₂	95%
			None	90%
				95%
		99%		
		C/B: Column/Burner	N ₂	95%
			None	95%
	b: Only methane	C: Column	None	90%
				95%
				99%
	c: H ₂ & CO ₂	C: Column	N ₂	99%
None			99%	
C/B: Column/Burner		N ₂	99%	
B	a: Same fractions of hydrocarbons as in NG fuel	O: Oxidation (ASU)	None	100% ²
		C: Column	None	90%
				95%
	C:Column	None	99%	
			95%	

The cycle ‘A’ and ‘B’ has already been introduced in chapter 7.3.2 and 7.3.1 and an explanation to the subcategories will follow beneath. The name of the different cases when found in chapter 9 will be the sum of there notation in Table 2. Example:

Cycle A with all hydrocarbons present in the exhaust stream with 95% of the unconverted fuel separated in a column and brought back to the reactor, where no consideration has been taken to the nitrogen in the fuel, is called; Aa-C-No N₂-95%.

² No distillation column is used but all the hydrocarbons are oxidized.
 Prosjektnummer Rappnr

8.1 Exhaust stream content

Cycle A and B are divided into different subcategories ‘a’, ‘b’, ‘c’ depending on the assumed composition of the fuel components in the CO₂ stream as seen in the table. As previously discussed in chapter 6.2 it is not clear what the exhaust stream will consist of which motivates the examination of different cases. Subcategory ‘a’ and ‘b’ are simple to simulate; the rate of fuel conversion is set in the reactor so that the conversion rate is a measurement of the amount of the fuel LHV that is converted to thermal energy. In ‘a’ all hydrocarbons are present in the exhaust stream while in ‘b’ only methane is present. Therefore in ‘a’ the conversion rate of every hydrocarbon is the same and in accordance with the specific conversion rate. In ‘b’ on the other hand, where only methane is converted its conversion rate in the reactor has to be slightly lower than the actual conversion rate based on the LHV due to the complete conversion of the heavier hydrocarbons.

Case ‘c’'s fuel composition has been set up in order to investigate what happens if there is CO and H₂ in the exhaust stream. As has been discussed earlier there are still uncertainties of what the exhaust stream from a CLC will consist of. Mattisson et al 2004 [27] studied the equilibrium portions of CO and H₂ in the exhaust stream when using Ni as oxygen carrier. The Ni acts as a catalyst so that the methane is reformed and shifted inside the reactor. Therefore there will be CO and H₂ but no methane in the exhaust stream from such a reactor at ideal conditions. The equilibrium portions were rather large, around 2,5% CO and 2% H₂ after condensation of water. With the simple reactor model used in the present work (Fig. 13) it is however not possible to get H₂ and CO out from the reactor. Instead an extra conversion reactor is added to the CO₂ rich exhaust stream in case ‘b’. The unconverted methane is then reformed according to Eq. 21 (methane-steam reforming);



This requires heat which lowers the temperature of the stream. The stream will not have the equilibrium proportions as were expected in a CLC reactor with Ni as oxygen carrier in [27], instead the fraction of H₂ will be three times higher than CO due to the stoichiometry of the reforming reaction. In the study of Mattison et al [27], which is based on a more complex thermodynamical calculation than just methane steam reforming, the molar fractions were approximately the same for CO and H₂ (2,5 respective 2 mol%). The incomplete conversion of fuel in percentage of LHV will in the simulations in the present work not be taken any lower than

to 98% due to the problems of having too high proportions of H_2 in the stream, but this is also the lowest fuel conversion calculated in [27] as the temperature do not exceed $1200^\circ C$ in the study. With increasing temperature the conversion rate decreases. As the condensation point increases with increasing H_2 content the pump is introduced at a higher pressure in the base case simulations without separation of H_2 . For 98% conversion rate the pressure is as high as 117 bar which of course has a negative impact on cycle efficiency. The compressor train has not been changed so the pressure ratio for those cases are higher than 2.

8.2 Recovery method

The recovery of unconverted fuel can be done in a number of ways, this section gives an explanation to the different recovery methods simulated and a short mention on there respective pros and cons.

8.2.1 C: Column

In these cases the unconverted fuel is separated in a distillation column and brought back to the CLC reduction reactor to be oxidized. A problem can be the rather high amount of CO_2 that follows the recovered fuel to the reactor as well as the accumulation of incombustibles, such as nitrogen. The case is referred to as “C: Column” in Table 2.

8.2.2 C/B: Column/burner

As showed in Fig. 24 the fuel that has been recovered in a distillation column can be brought to a burner after the CLC oxidation reactor and prior to the air turbine. This way the reactor has not to be built to accept large amounts of recycled CO_2 and no problem with accumulation of incombustibles can occur as there is no loop. But instead there will be emissions of CO_2 to the atmosphere, which can exceed 10%.

8.2.3 O: Oxidation ASU

Instead of applying a distillation column, the unconverted fuel could be directly oxidized after the CLC reactor (which has been proposed earlier by others A.Abad et al 2007 [1]). This solution makes most sense in cycle B with CO₂ turbine in order to utilize the heat for power generation, and the oxidation chamber should then be put prior to the CO₂ turbine. Due to the low content of hydrocarbons in the stream the oxidation will be a flameless combustion

[11] de Diego Luis F., García-Labiano Francisco, Gaya'n Pilar, Celaya Javier, Palacios Jose' M., Adanez Juan. "Operation of a 10 kWth chemical-looping combustor during 200 h with a CuO–Al₂O₃ oxygen carrier". Fuel 86 (2007) 1036–1045

[12]. Further assumptions are that the oxidation is complete and the excess oxygen rate is of that size that the exhaust gas has a content of 3% oxygen. The oxygen for the flameless combustion reactor comes from a cryogenic ASU, which has not been modeled in Hysys, but a power penalty of 812 kJ/kg O₂ is used [18]. Data for the stream can be found in Table 3. The temperature of the stream entering the CO₂ turbine will then be between 1000 and 1475°C (depending on the conversion rate) which calls for turbine blade cooling. As mentioned earlier this is problematic for a CO₂ turbine, it has to be cooled with steam and/or by closed loop cooling. Either way, it has not been done and any estimation regarding it will be only a guess. In this case the polytropic efficiency of the CO₂ turbine is lowered to 80% as a way of compensating for the unknown cooling penalty [17]. The biggest problem with this case is the oxygen content in the CO₂ stream. It will also show that there are problems with utilizing the extra heat, see chapter 9.

8.3 Inerts

The next sub category is whether or not the nitrogen in the fuel will be taken into account. As foreseen by Aspelund and Jordal [4] there will be an accumulation of inert volatile components such as nitrogen and argon in the reactor if and when applying recirculation of volatiles. In this thesis, assuming that there is no leakage between the oxidation and reduction reactors, there will be no argon in the stream, but there will be nitrogen, due to its presence in the assumed natural gas composition (Table 3). This small portion of nitrogen gets accumulated in the recirculation loop and evolves to a serious problem. A bleed stream is therefore necessary to keep equilibrium between ingoing and outgoing nitrogen. This bleed stream would probably be hard to utilize in any economical way and here it is believed that the hydrocarbons are combusted (as methane is a very strong GHG) and then the stream is vented to the atmosphere together with the CO₂ following the bleed stream, leading to CO₂ emissions to the atmosphere. The size of this bleed stream is a matter of optimization. With a smaller bleed stream the concentration of nitrogen in

the recirculation loop will increase, causing more work when compressed. But at the same time a smaller bleed stream will let a smaller portion of the hydrocarbons escape, which has a positive impact on the efficiency. Due to the many recirculation streams and adjustments in the Hysys flowsheet, the calculations with bleed stream are very time consuming. In the present work the bleed stream is 15% of the column top stream, but there is no claim that this is optimum. However it is in the right order of magnitude, Aspelund and Jordal [4] mention 10% bleed stream to avoid accumulation of inerts but that is not optimum for these cycles.

The cases without nitrogen can be thought of as a “best case” scenario if it would be possible to easily divert nitrogen without energy penalty, maybe in some sort of PSA or in an ideal case with nitrogen-free fuel. The best case scenarios offer the opportunity to see what the biggest problem with fuel recirculation is; the accumulation of non-condensable inerts. Please notice that it is only the cycles with recirculation to the reactor that will have problems with the nitrogen content in the fuel, in the “column/burner” and “oxidation” case no loop is present and therefore no accumulation of incombustibles.

8.4 Recovery Rate

All the simulated cases are tested at three different Recovery Rates, i.e. the rate to which the fuel is recovered, see chapter 6.4 and 7.4.1. A higher RR has a higher energy requirement but recovers more energy back to the reactor. Depending on the different cycles and conversion rates it can be more or less beneficial to recover more or less, see chapter 9.

9 RESULTS FROM THE SIMULATIONS

Due to the many question marks and unknowns in this thesis, in particular concerning the behavior of the CLC reactor, a great number of simulations have been performed in a more or less trial and error sort of way. Therefore the number of results is much higher than the number of interesting results. In this chapter the most interesting results are gathered and analyzed. The cycles and cases will not be shown one and one but in comparison with one another under the relevant heading. Explanations to the different cycle abbreviations can be found in chapter 8.

9.1 Efficiency

The main parameter is of course the cycle thermal efficiency. If it is not beneficial to recirculate the unconverted fuel from an efficiency point of view, the other parameters as the exhaust gas quality or the CO₂ stream quality are of no interest. In Fig. 30, Fig. 31, and Fig. 32 case ‘Aa-’, ‘Ab-’ and ‘Ba-’ are shown. It should be emphasized that applying a certain recovery method at a certain conversion rate does not automatically mean that one moves straight up in the efficiency diagram. Depending on how the reactor and the cycle react to the recirculation one might move either to the right or to the left.

9.1.1 Fig. 30 and Fig. 31

Fig. 30 and

Fig. 31 shows cycle ‘Aa-’ and ‘Ab-’. The four cases at the top of the legends (Aa-C-No N₂-99%, Aa-C-No N₂-95%, Aa-C-No N₂-90%, No recirculation, Ab-C-No N₂-99%, Ab-C-No N₂-95%, Ab-C-No N₂-90%, No recirculation) all show a very similar behavior between the two figures (the fourth, “No recirculation” is when no fuel is recirculated). The only differences in the cases are the fuel content in the CO₂ stream. Cases ‘-b’ show a slightly higher efficiency as a higher degree of the fuel LHV is recovered. As seen in the figures there is no big difference between the different Recovery Rates (RR). However it is clear that the lower the conversion rate the more beneficial it is to recover a greater portion of the unconverted fuel, i.e. the slope of the 99% RR line is lower than the slope of the 95% RR line and the 95% RR line has a lower slope than the 90% RR line.

The next case in Fig. 30 is “Aa-C-N₂-95%” which has a bleed stream to let the nitrogen be vented out. The bleed stream is 15% of the column top stream and the recovery rate in the distillation

column is 95% (some of the recovered stream is bleed away so the actual RR is lower). The bleed stream has a negative impact on cycle efficiency since some hydrocarbons are vented with the nitrogen. The vented hydrocarbons are thought to be combusted which give a low CO₂ emission, see chapter 9.6.

The two following cases are “Aa-C/B-No N₂-95%” and “Aa-C/B- N₂-95%” which recovers the fuel in a distillation column and combusts it in a burner prior to the air turbine. There is no problem with the nitrogen content in the fuel, it makes no noticeable difference between the two cases as the amount is very low. The efficiency is high but there is an emission of CO₂ to the atmosphere, see chapter 9.6.

9.1.2 Fig. 32

Fig. 32 shows cycle ‘Ba-’. The top four cases in the legend looks a lot like the first four in cycle ‘Aa’ or ‘Ab’ except all of them have a higher efficiency as cycle ‘B-’ has a higher efficiency than cycle ‘A-’. But it does not seem as there are any bigger differences to recover to cycle ‘B-’ than to cycle ‘A-’. The last case “Ba-O-No N₂-95%” is a case where the unconverted fuel is directly oxidized after the CLC reactor. The poor efficiency is due to the inability to use the extra heat produced in an efficient way. The stream out from the CO₂ turbine is over 500°C and all this heat is just chilled away prior to the CO₂ compression chain. This result does not show that oxidation with oxygen does not work; it rather shows that this cycle configuration is ineffective. See chapter 9.2. One extra simulation was made were a HRSG was connected to the exhaust stream from the CO₂ turbine at 95% conversion rate. The result showed a higher efficiency than in the base case were all fuel was converted, showing this cycle’s poor ability to harness the heat at the present design.

Electrical efficiency against Conversion Rate at different Recovery Rates in cycle Aa-

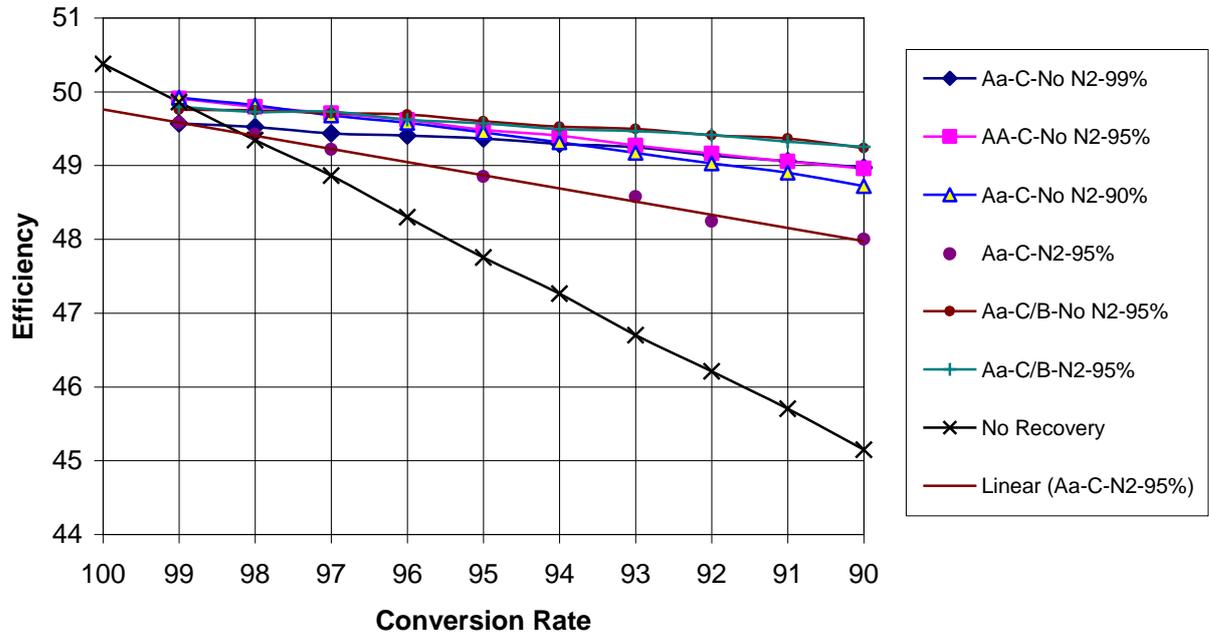


Fig. 30. Cycle 'Aa-'.

Electrical efficiency against Conversion Rate at different Recovery Rates in cycle Ab-

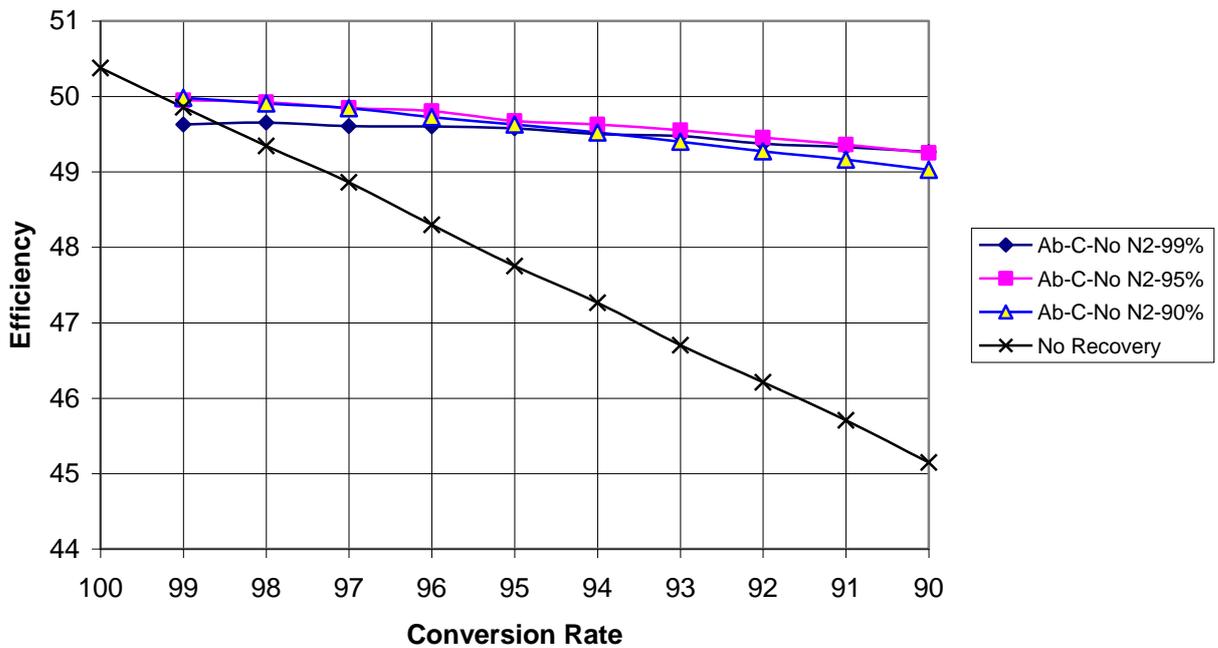


Fig. 31. Cycle 'Ab-'.

Overall efficiency against Conversion Rate at different Recovery Rates in cycle Ba

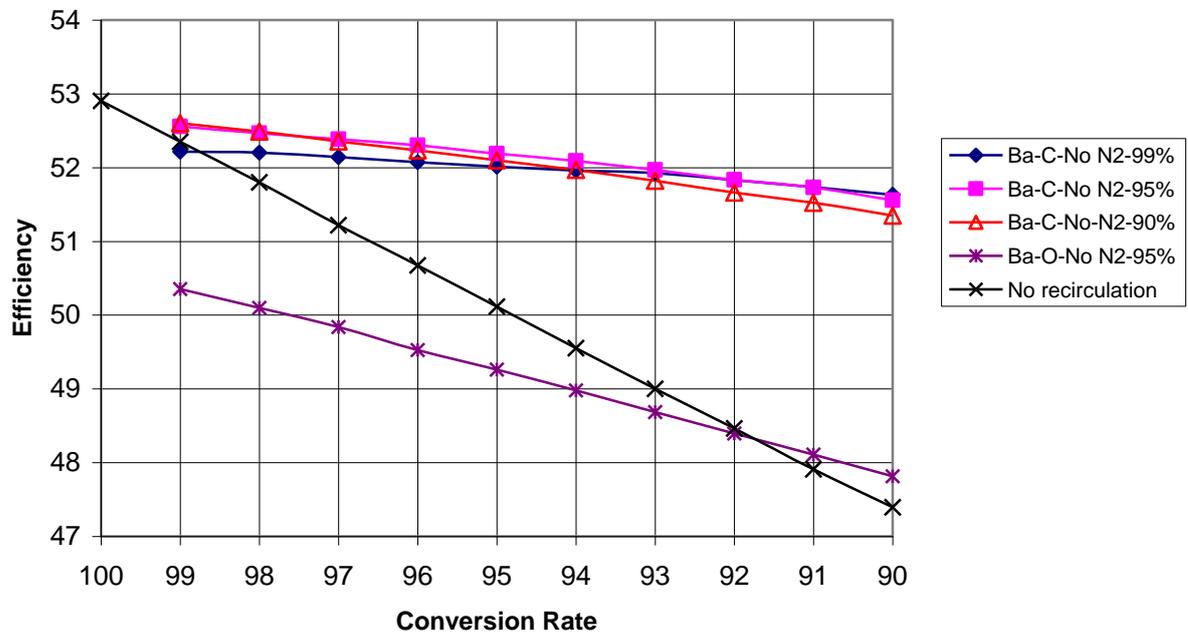


Fig. 32. Cycle Ba-.

9.2 Work/Recovered energy, ϕ

A parameter called “work/recovered energy”, denoted by ϕ , is introduced. This parameter is used to get an understanding of when it is beneficial to recover the energy in the exhaust stream. It is calculated in different ways in different cycles. In cycles with a distillation column and recirculation to the reactor ϕ is calculated as in Eq. 22 which is to be read together with Fig. 33 and is valid for cycle ‘A-’. ϕ is calculated in a similar way in cycle ‘B-’ with distillation and recirculation to the CLC reactor but in that case(s) there are more compressor stages.

$$\phi = \frac{\text{work}}{\text{recovered energy}} = \frac{(\dot{m}_{CO_2@1} + \dot{m}_{N_2@1}) * (w1 + w2) + (\dot{m}_{CO_2@1} + \dot{m}_{N_2@1} + \dot{m}_{CO_2@4} + \dot{m}_{N_2@4}) * w3}{LHV_1 * \dot{m}_1 * \eta_{cycle}} \quad \text{Eq. 22}$$

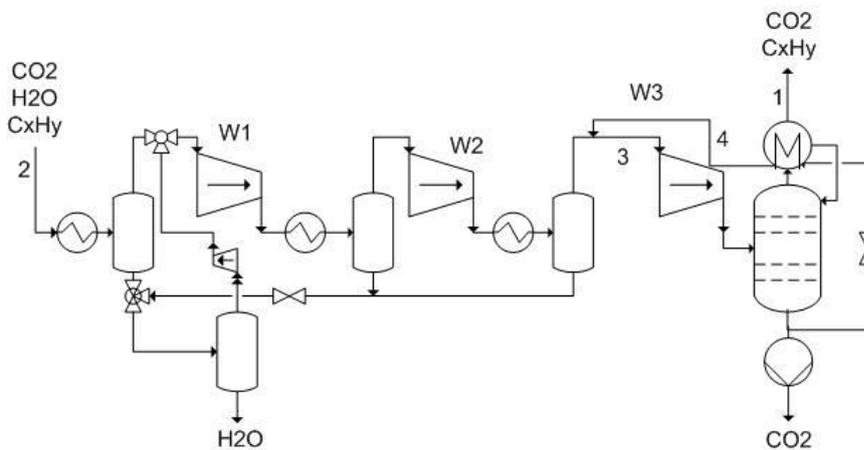


Fig. 33. Calculation of ϕ .

The work is calculated by taking the mass flow of the recirculated CO₂ and N₂ times the specific work in every compressor. This way the extra work that is required due to the recirculation of CO₂ and N₂ is calculated (the recirculated fuel is oxidized and the amount of fuel leaving at the bottom of the column and hence recirculated in the third compressor in Fig. 33 is negligible). The recovered energy is simply the recirculated stream’s LHV times the mass times the efficiency of the cycle. The reason to multiply it with the efficiency is to account for the different energy qualities, chemically tied up energy vs. electric power.

In the case with column and a burner (C/B) ϕ is calculated as shown in Eq. 23 which should also be read with Fig. 33. As seen the extra work needed is to compress the CO₂ (and N₂ but it’s a really small amount) that has been used to cool the column condenser.

$\varphi = \frac{\text{work}}{\text{recovered energy}} = \frac{(\dot{m}_{CO_2@4} + \dot{m}_{N_2@4}) * w_3}{LHV_1 * \dot{m}_1 * \eta_{cycle}}$	Eq. 23
---	---------------

In the case with oxidation of the unconverted fuel just after the reactor (Ba-O-No N₂-95%, Ba-O N₂-95%) φ is calculated as in Eq. 24. All of the unconverted fuel is assumed to be oxidized and an excess air mass flow of 3% of the exhaust stream is applied. The energy for the extra compressor needed to compress the oxygen before combustion is included in the equation as well as the extra work required in the compressor train to compress the oxygen in the CO₂ stream.

$$\varphi = \frac{\text{work}}{\text{recovered energy}} = \frac{\dot{m}_{Oxygen} * (w_{ASU} + w_{compressortrain}) + W_{extracompressor}}{\dot{m}_{unconvertedfuel} * LHV_{fuel} * \eta_{cycle}} \quad \text{Eq. 24}$$

When φ reaches unity it is no longer beneficial to recover any unconverted fuel. It can be seen in Fig. 34, Fig. 35 and Fig. 36 that φ reaches unity for the cases with 99% recovery rate at high conversion rates as well as for the case “Aa-C- N₂-95%” (which is the bleed case) at 99% conversion rates and “Ba-O-No N₂” at 99% recovery rate. For all other cases and all conversion rates it is beneficial to recover the unconverted fuel. Compare with Fig. 30, Fig. 31 and Fig. 32 showing the efficiency, for every case except case “Aa-C- N₂-95%” and “Ba-O-No N₂-95%” the efficiency goes below the base case efficiency at the same conversion rate point where φ reaches unity, i.e. where it stops to be beneficial to recover the unconverted fuel. For case “Aa-C-N₂-95%” this point is not at the same place on the conversion rate scale. This is because some of the recovered fuel is bled off which lowers cycle efficiency (the recovery rate to the reactor is actually lower than 95%). The curve for cycle “Aa-C- N₂-95%” still shows a great potential for fuel recovery with bleed stream and shows that there is potential for further optimization both regarding size (of bleed) and recovery rate (they are interconnected). Curve “Ba-O-No N₂-95%” in Fig. 36 shows such low efficiency as the recovered energy is not utilized in an effective way, see chapter 9.1.2.

Between cycle ‘Aa-’ and ‘Ba-’ in Fig. 34 and Fig. 36 the difference is quite surprisingly really small. More work for compression are to be expected since the compression in cycle ‘B-’ is done from almost atmospheric pressure (compare Fig. 9). Though, it is clear from the figure that the extra compression work is small in comparison with the energy recovered. The case “Ba-O-No N₂-95%” shows higher energy requirement but it should still be beneficial to cycle efficiency to

recover in such a way for all recovery rates except 99%. But as seen in Fig. 32 the efficiency is really low for this case which tells that the recovered energy is not used in an effective way.

Case “Aa-C/B-No N₂-95%” as seen in Fig. 34 with an distillation column and a burner prior the air turbine has a lower condenser temperature to avoid too much CO₂ emissions (which requires more CO₂ to be recirculated to cool the condenser). There is no recirculation to the reactor and hence no recirculation through the compressor chain (except for cooling), see Eq. 23. The result is a curve in the middle. It is interesting to notice that even though ϕ is higher for “Aa-C/B-No N₂-95%” the efficiency is also higher, see Fig. 30. The only explanation is that the cycle makes better use of the recovered fuel; the extra heat is well utilized in the air turbine and the following HRSG.

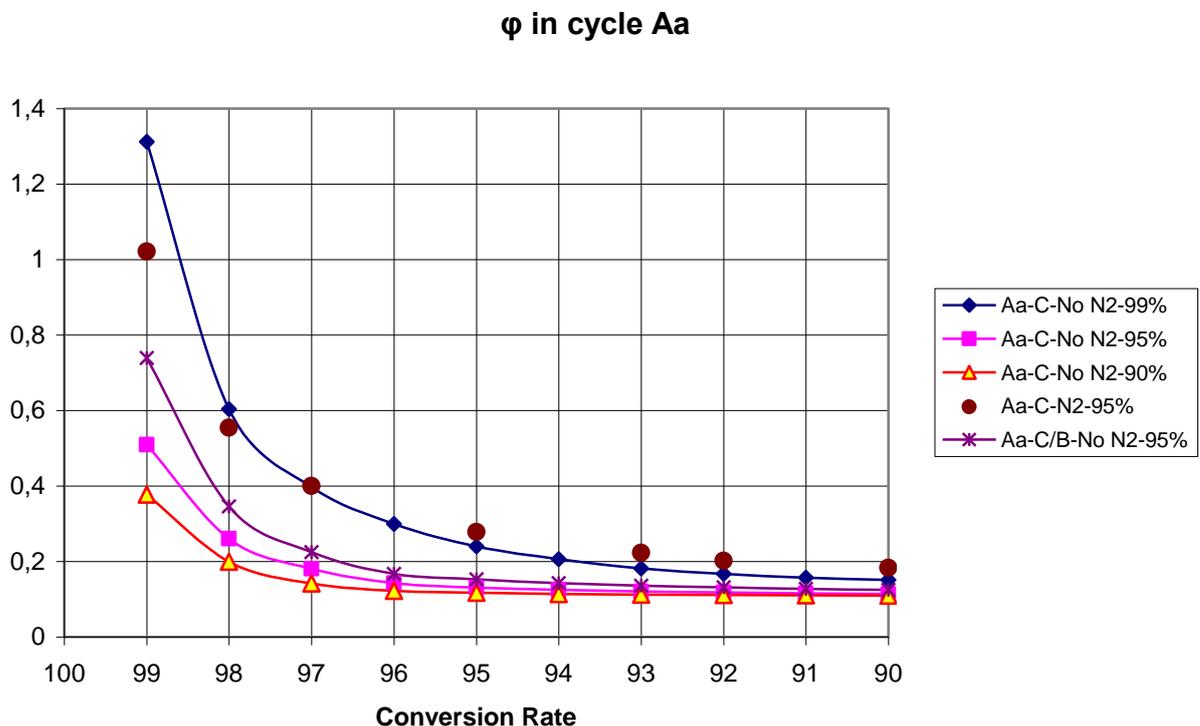


Fig. 34. ϕ in cycle Aa.

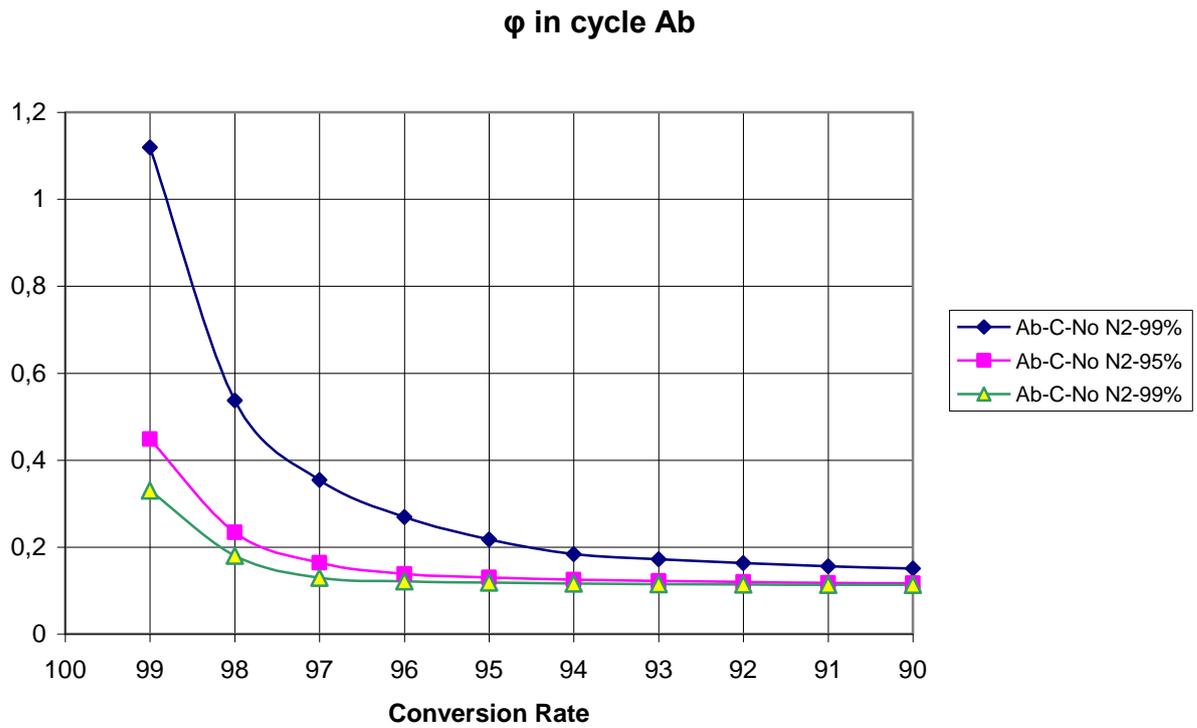


Fig. 35. ϕ in cycle Ab.

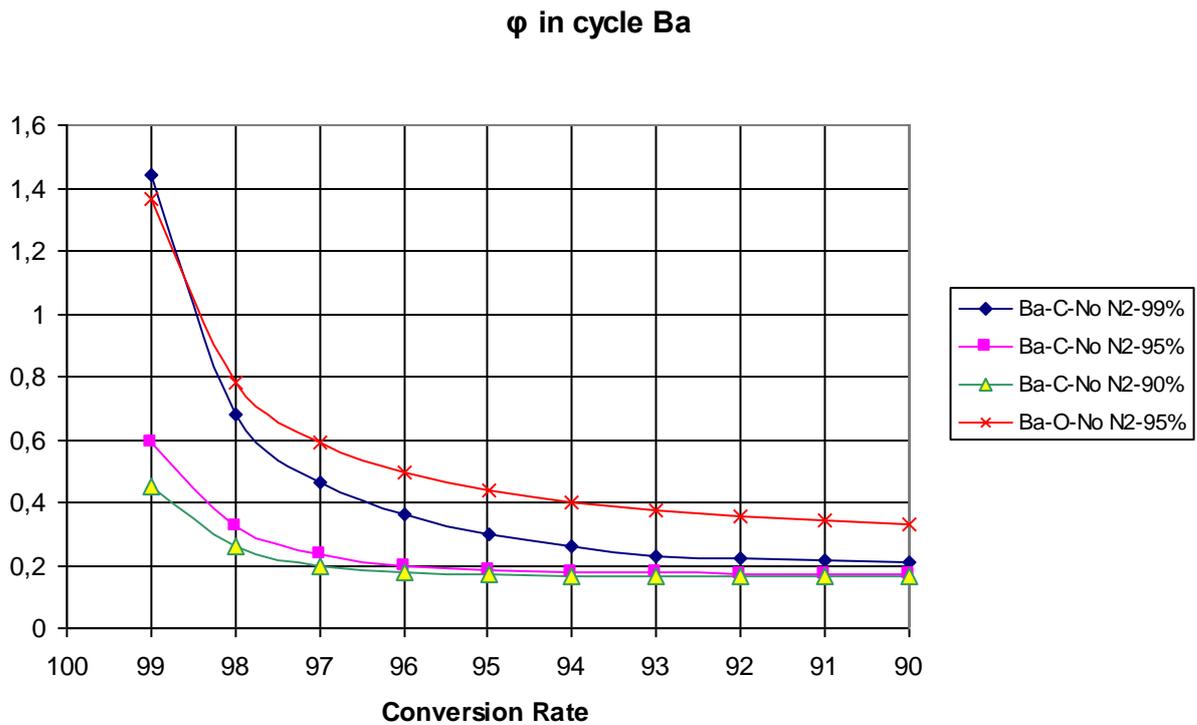


Fig. 36. ϕ in cycle Ba

9.3 Work/kg CO₂

It is interesting to compare how much energy that is needed to compress and condition the exhaust stream from the different cycles. The work is simply the power duty for the compressors and the CO₂ pump.

By first comparing the cases that are the same in the two cycles (distillation column, recirculation to reactor, no N₂) in Fig. 37 and Fig. 38 it can be seen that the cases built on cycle B requires much more energy to compress (and condition) the CO₂. This is understood by reading chapter 6.3 and it is due to the lower inlet pressure to the compressor chain in cycle B. The shape of the lines with an increasing trend as the conversion rate raises can not be explained by the increased recirculation of CO₂ as more fuel is recirculated back to the reactor. This is clear by looking at Case “Ac-C/B-No N₂-95%” in Fig. 37 which has no recirculation but shows the same trend as the curves with recirculation (except “Aa-C- N₂-95%”). Instead the shape of the curves can be understood by looking at Fig. 39 which shows the column condenser duty. The higher condenser duty the more CO₂ has to be expanded and recirculated for cooling, see chapter 7.4. As “Aa-C-No N₂-95%” and “Aa-C/B-No N₂-95%” show almost the same behavior, even though “Aa-C/B-No N₂-95%” does not have recirculation to the reactor, it must be the character of the reactor that gives the increase in condenser duty and hence increased work per kg as the conversion rate goes down. Case “Aa-C- N₂-95%” (distillation column, bleed) has an almost straight line as seen in Fig. 37. This can also be seen in column condenser duty in Fig. 39 and the author can give no clear explanation other than it is the content of nitrogen that effects the properties of CO₂ and hence affects the column. It can further be seen that the recirculation of N₂ requires a lot of energy in the compressors; the condenser duty is lower than for example “Aa-C-No N₂-99%” but the work per kg CO₂ is higher (for most conversion rates). This can be further understood by reading chapter 6.2.

In Fig. 38 a protruding curve can be seen. Case “Ba-O-No N₂-95%” (oxidation after CLC reactor) have an almost straight line, the work per kg CO₂ is the same for all conversion rates as could be expected. This curve would look almost identical even if N₂ was present as there is no loop.

Work/CO₂ in cycle Aa

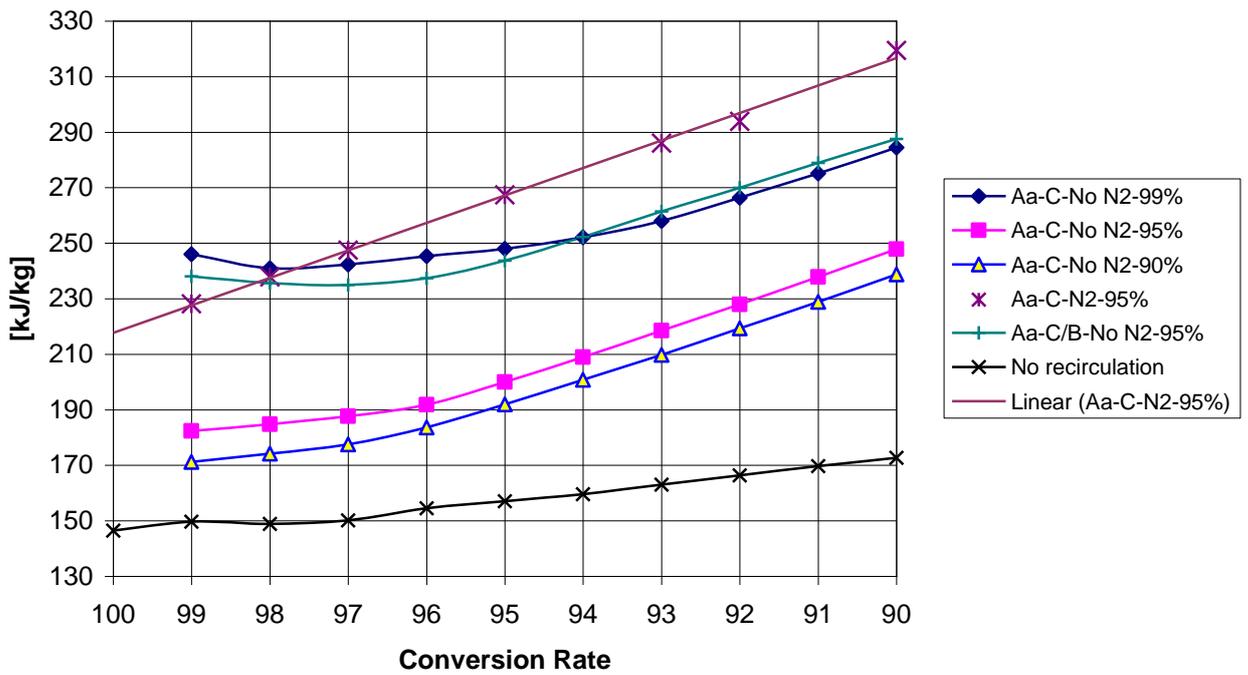


Fig. 37. Work/ CO₂ in cycle Aa.

Work/kg CO₂ in cycle Ba

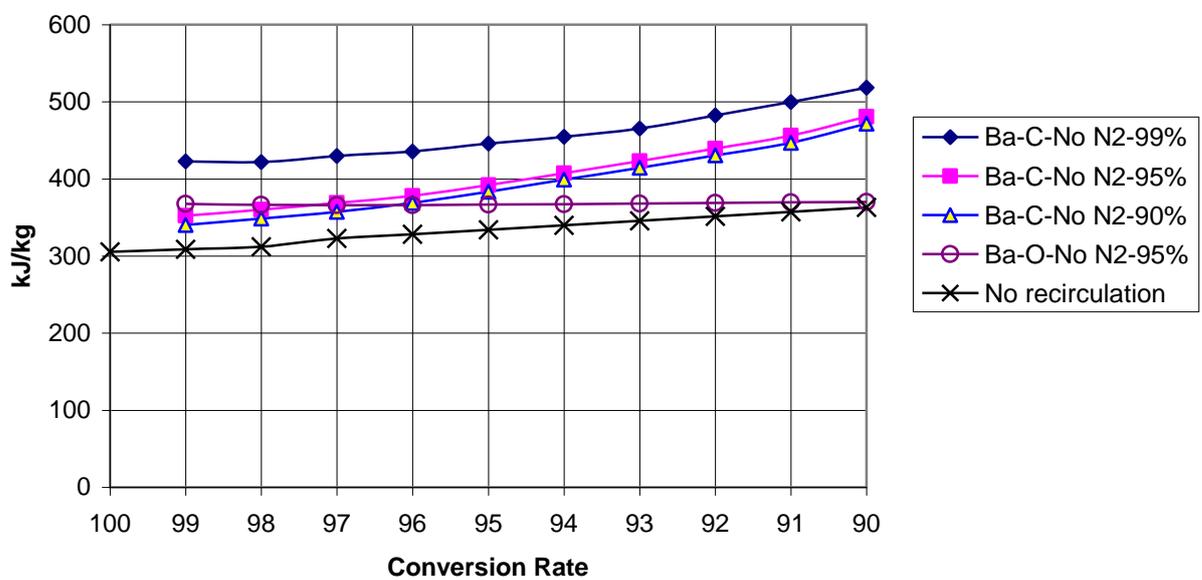


Fig. 38. Work/kg CO₂ in cycle Ba.

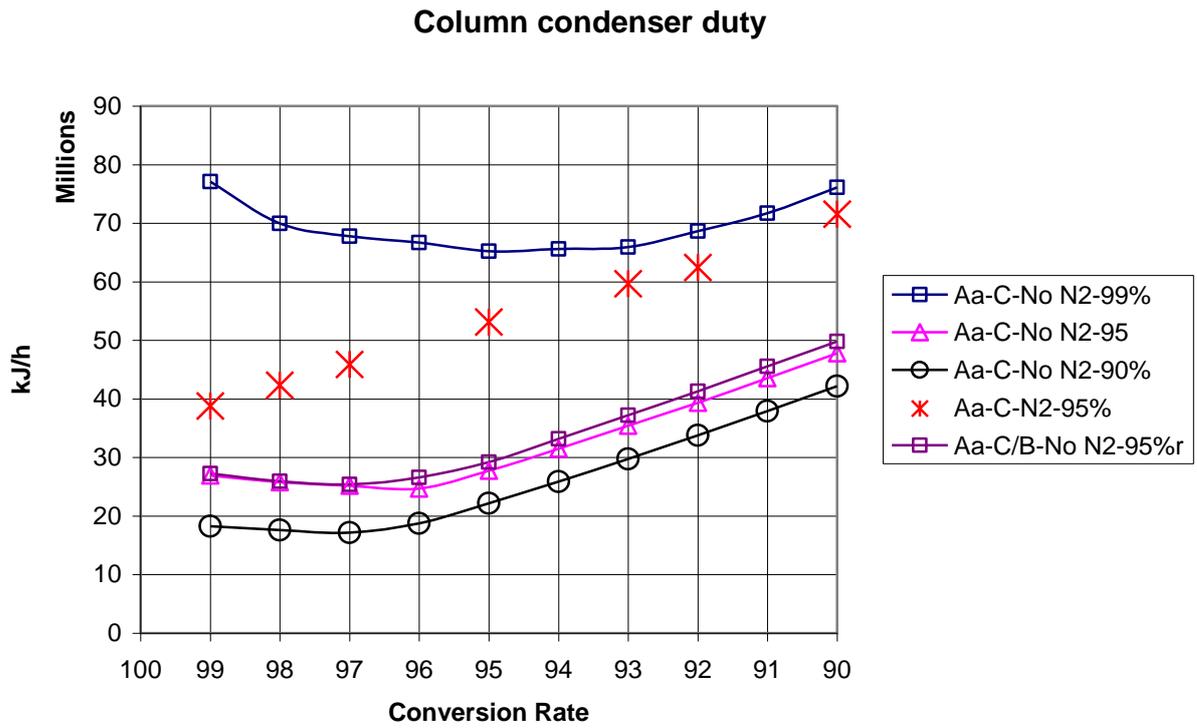


Fig. 39. Column condenser duty.

9.4 Recirculated CO₂/fuel

As already mentioned in chapter 4.2 and 7.1 some CO₂ will follow the recirculated fuel back to the reactor. The amount can be adjusted by the temperature in the column condenser but in the present work the focus has been to achieve high cycle efficiency and then see how big the different streams are. In Fig. 40 the recirculated CO₂/Fuel into the reactor is shown.

As there is no bigger differences between cycle A and B in this regard only results from cycle A are shown. As can be seen the portion goes from around 0,5 kg/kg to 0,70 kg/kg when no N₂ is present and between 0,40 kg/kg and 1,1 kg/kg with N₂. The difference should be due to the effect the presence of N₂ has on the CO₂ and the function of the column. It might be more interesting to look at Fig. 41 where the molar relationship is showed. As both the fuel and the CO₂ are to be treated as ideal gases this shows the volume relationship between the recirculated CO₂ and the fuel. Therefore it gives a clue about the size of the up-scaling needed if recirculation to the reactor is to be used.

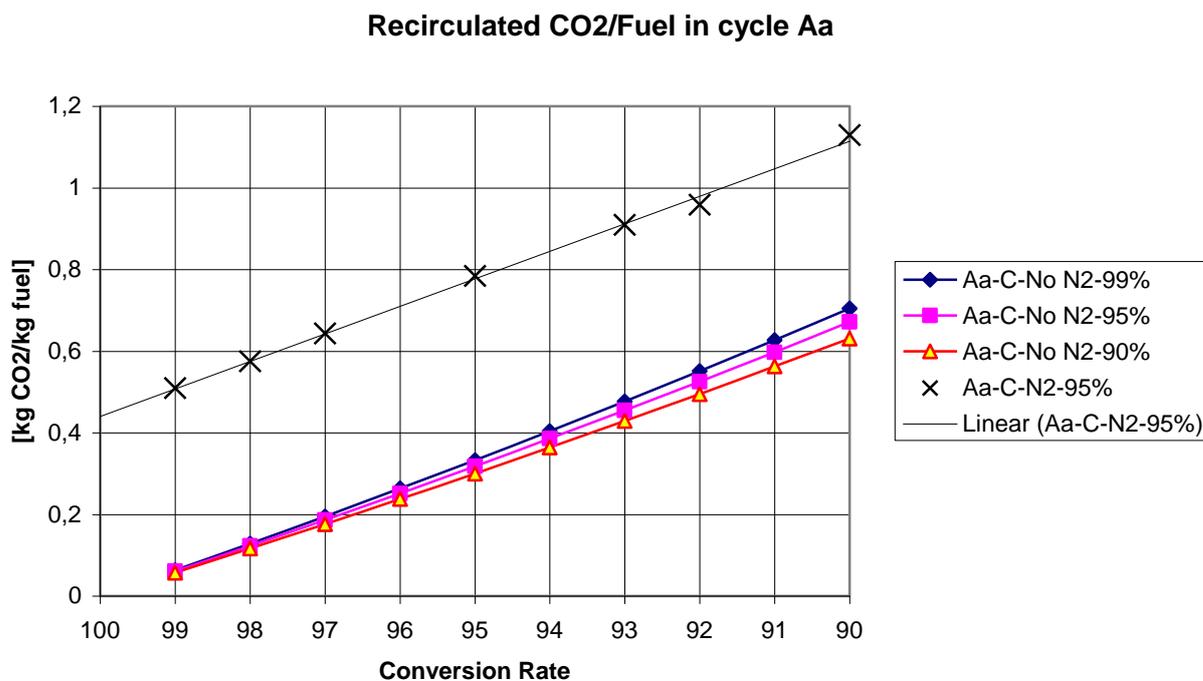


Fig. 40. Recirculated CO₂/Fuel in cycle Aa mass based.

Recirculated CO₂/Fuel in cycle Aa

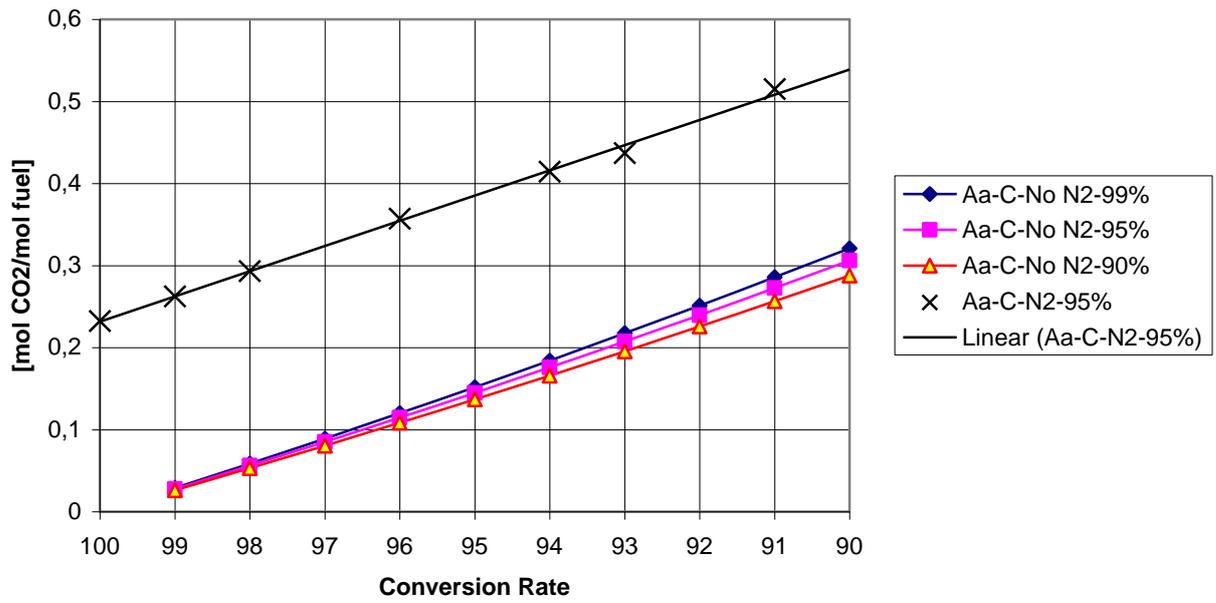


Fig. 41. Recirculated CO₂/Fuel in cycle Aa molar based.

9.5 Recirculated CO₂/ CO₂ out from the reactor

It could also be of interest to see how much of the CO₂ that leaves the reactor that is recirculated CO₂, compared to how much that has just been generated. This can also give an indication of the required up-scaling for a reactor with recirculation.

Fig. 42 shows the results for the cases in cycle A. There are no bigger differences when looking on cycle B. It can be seen that cases without N₂ have much less recirculated CO₂ and this has to do with the N₂ effect on CO₂ and the function of the column.

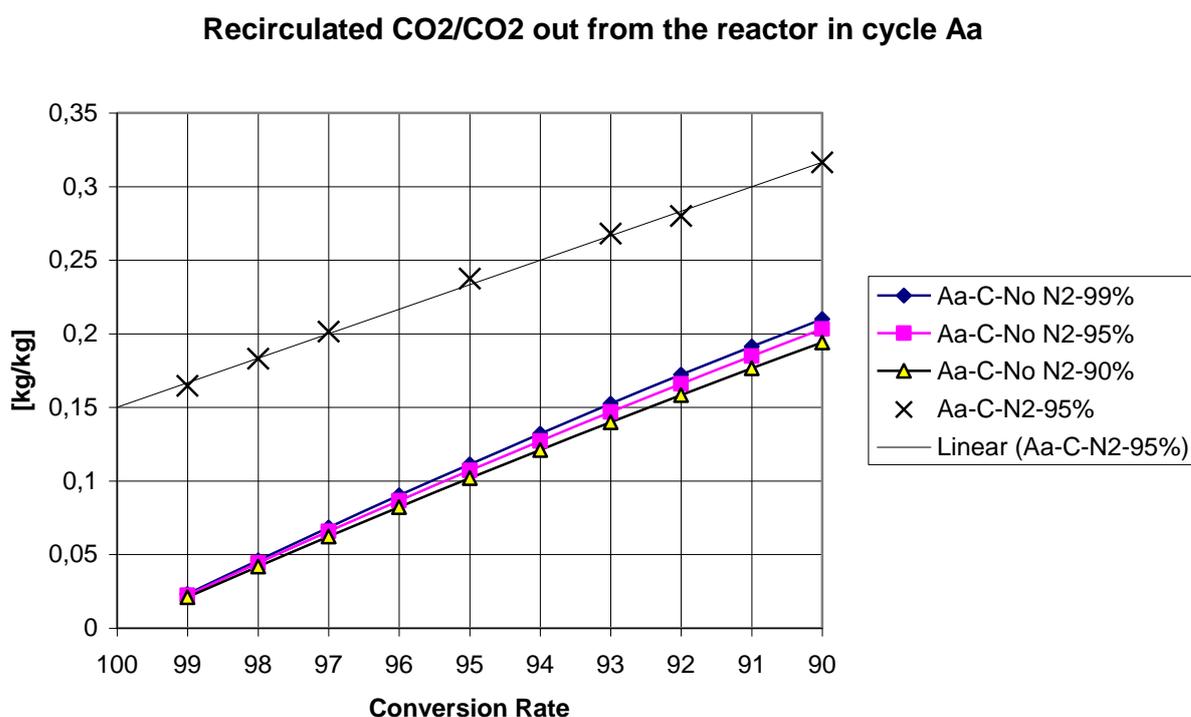


Fig. 42. Recirculated CO₂/ CO₂ out from the reactor in cycle Aa.

9.6 CO₂ emissions to the atmosphere

It has been discussed in chapter 5 that CLC is most competitive when used in a cycle which captures the CO₂ created. Among the cycles studied in the present work there are two that have CO₂ emissions to the atmosphere; cycle “Aa-C/B-No N₂-95%” and “Aa-C- N₂-95%”. All other cycles have minimal emissions of CO₂ that leave with the condensed water (but this is negligible), but are also based on the assumption that there is no nitrogen present in the fuel.

As can be seen in Fig. 43 cycle “Aa-C- N₂-95%” (bleed stream) has a capture rate above 90% but “Aa-C/B-No N₂-95%” and “Aa-C/B- N₂-95% go below 90% as the conversion rate goes below 95%. It would be possible to increase this capture rate by either have a lower condenser temperature in the column or by applying a two column system. The first alternative decreases cycle efficiency to a large extent. How a two column system would work has not been tested and could be a topic for further research. The presence of N₂ makes more CO₂ follow the volatiles at the top and hence increases the CO₂ emissions, even if the effect is not very dramatic.

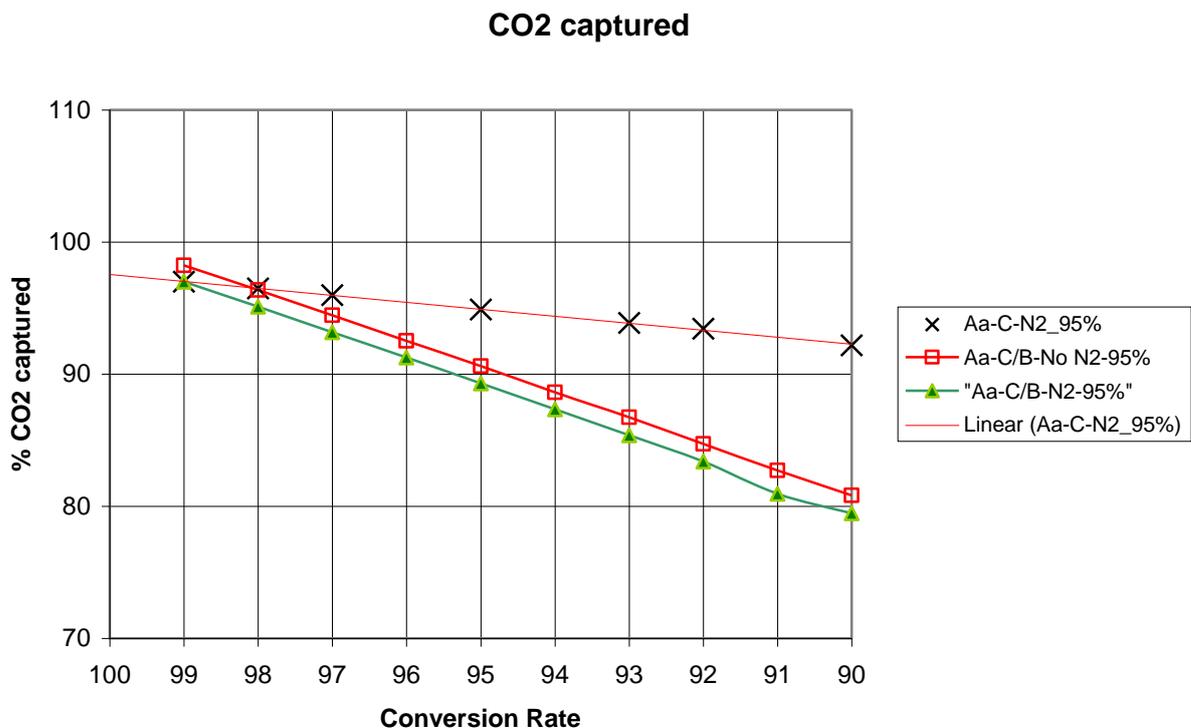


Fig. 43. CO₂ captured.

9.7 Contents in stream(s) before conditioning

The content in the stream before the conditioning and compression is dependent on the CLC reactor as discussed in chapter 6.1. Fig. 44 and Fig. 45 show the content in cycle ‘Aa-’ with and without N_2 . The content is shown before water condensation and the water- CO_2 relationship is about 60-40 mol%. This means that after water condensation the rate of methane and N_2 is little more than the double. The figure of ‘Aa-’ is not that surprising, the content of methane is much higher than the other hydrocarbons as the natural gas consists mostly of methane and it increases linearly with lower fuel conversion as expected. Cycle ‘B-’ shows the same pattern and in case ‘-b’ only methane is present (and maybe N_2). At higher recovery rate the content of hydrocarbon decreases and vice versa. Fig. 45 shows that the content of N_2 is kept on an almost constant level. This is because of the bleed stream that bleeds of as much N_2 that enters with the fuel. This way the N_2 level will be constant at a level decided by the size of the bleed stream.

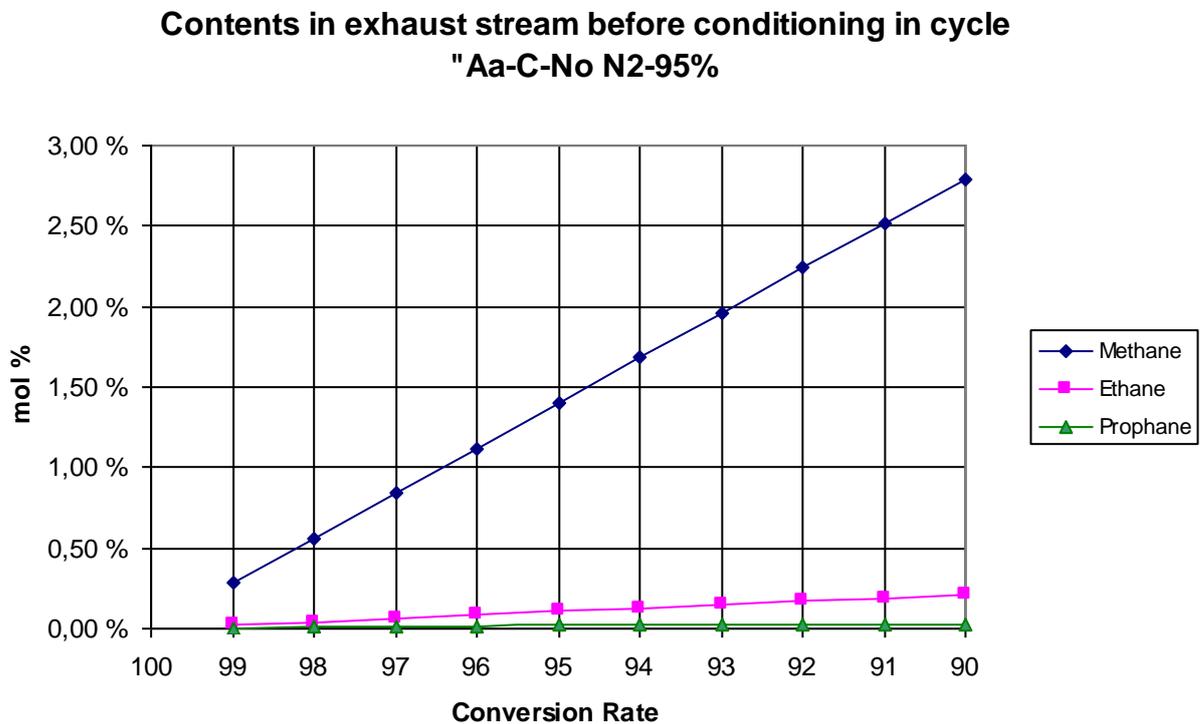


Fig. 44. Contents in exhaust stream before conditioning in cycle “Aa-C-No N_2 -95”.

**Contents in exhaust stream before conditioning in cycle
“Aa-C-N2-95%”**

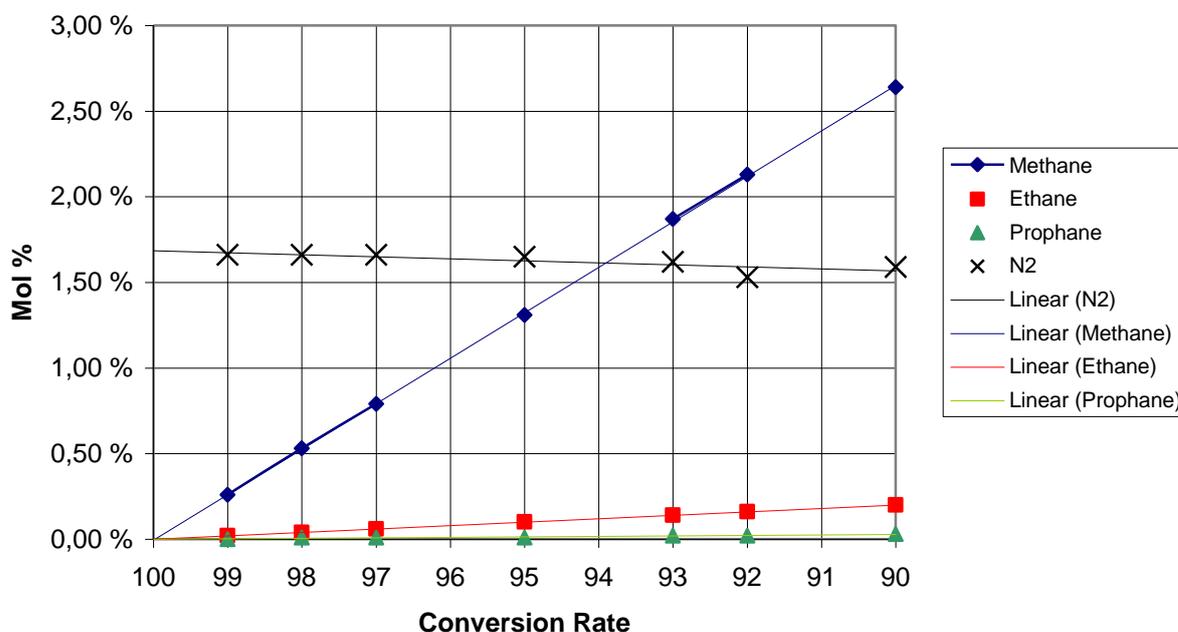


Fig. 45. Contents in exhaust stream before conditioning at 95% RR in cycle “Aa-C- N₂-95%”.

9.7.1 Content in recirculation stream(s)

Fig. 46 and Fig. 47 show the contents in the recirculation stream for cycle “Aa-C-No N₂-95”. The first shows the result in mol% and the other in mol. As methane is the controlled variable it is clear that it should have a linearly increasing trend as the conversion rate decreases as seen in Fig. 47. It is clear from Fig. 46 that the relationship between methane and CO₂ is constant. Case “Aa-C/B-No N₂-95” and “Aa-C/B-No N₂-95” (the cases with burner prior to the air turbine) has a ratio between CO₂ and methane around 60-40 mol% due to the lower condenser temperature. Case “Aa-C- N₂-95” can be seen in Fig. 48 and Fig. 49 and shows a very different appearance. Fig. 49 shows that the N₂ content is constant; the bleed stream keeps the ingoing and outgoing N₂ on an even level. The concentration of CO₂ is constant around 75 mol% while methane and N₂ together makes up most of the missing 25 mol% as seen in Fig. 48. The result is, as the amount of methane is controlled by the recovery rate, that the recirculation stream is much bigger in cycle “Aa-C- N₂-95” than in the other cycles as seen in Fig. 50.

Contents in recirculated stream in cycle "Aa-C-No N2-95%"

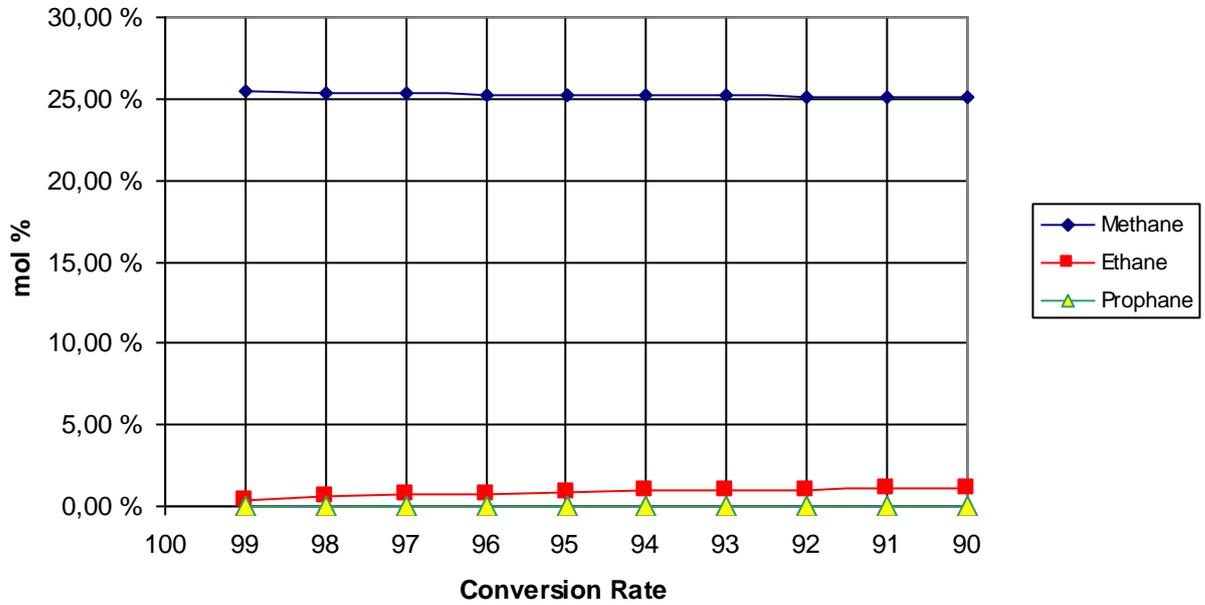


Fig. 46. Contents in recirculated stream in cycle "Aa-C-No N₂-95%".

Contents in recirculated stream in cycle "Aa-C-No N2-95%"

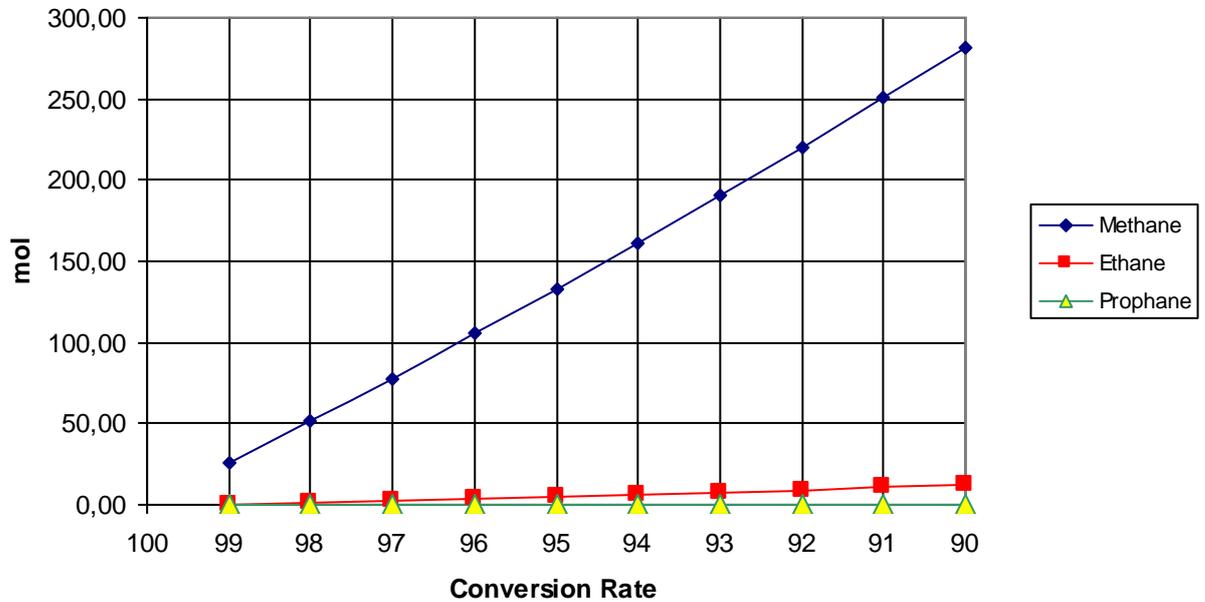


Fig. 47. Contents in recirculated stream in cycle "Aa-C-No N₂-95%".

**Contents in recirculation stream in cycle
"Aa-C-N2-95%"**

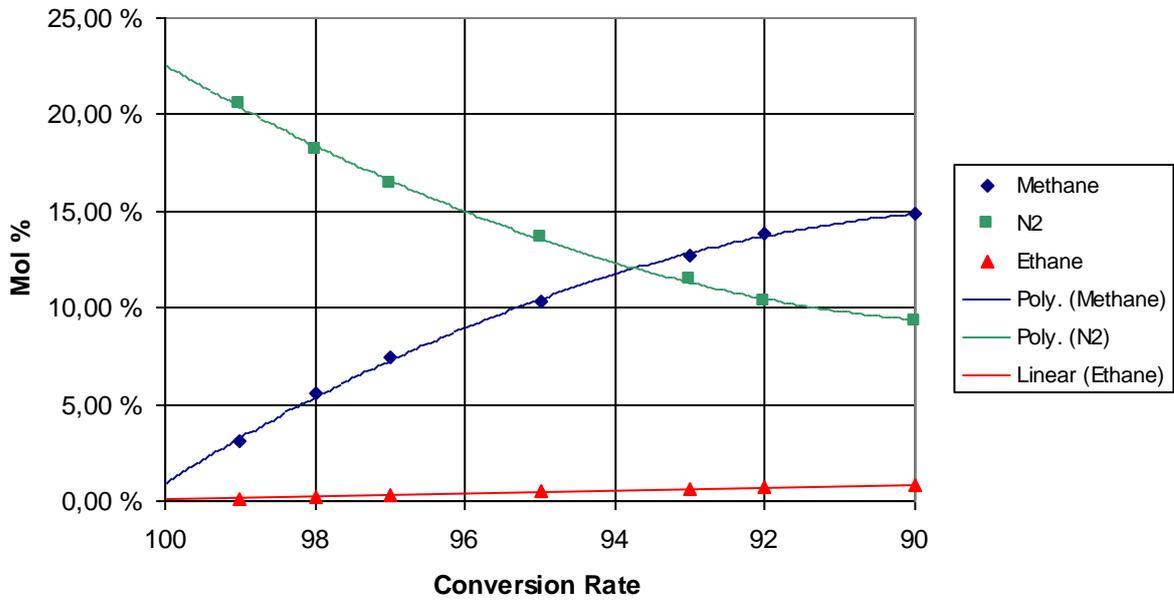


Fig. 48. Contents in recirculation stream in cycle "Aa-C- N₂-95%".

**Contents in recirculation stream in cycle
"Aa-C-N2-95%"**

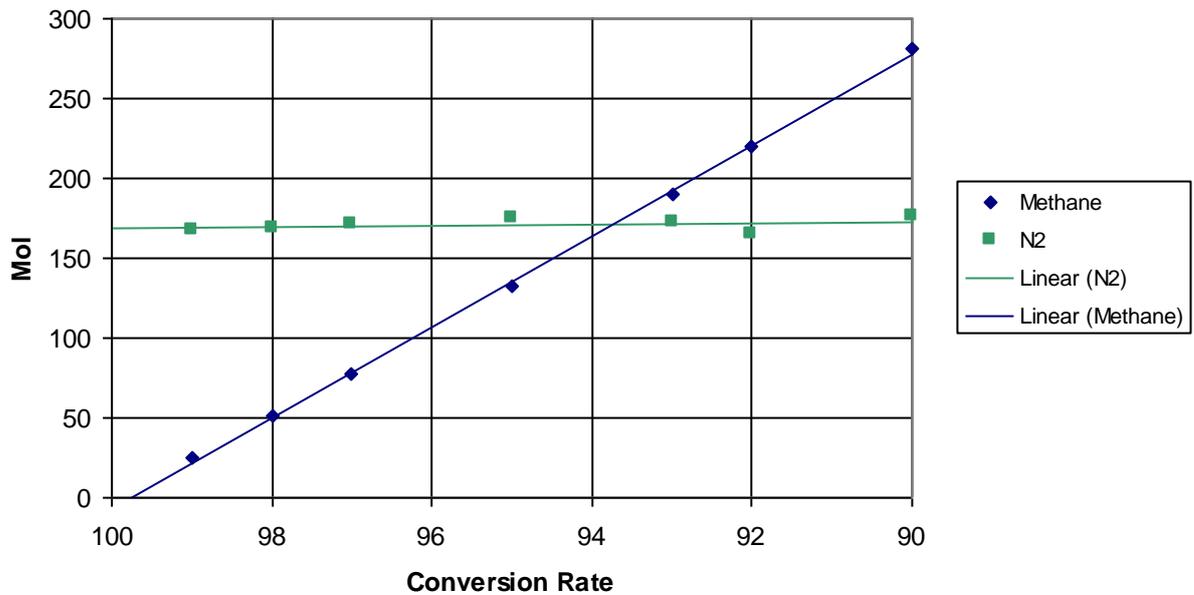


Fig. 49. Contents in recirculation stream in cycle "Aa-C- N₂-95%".

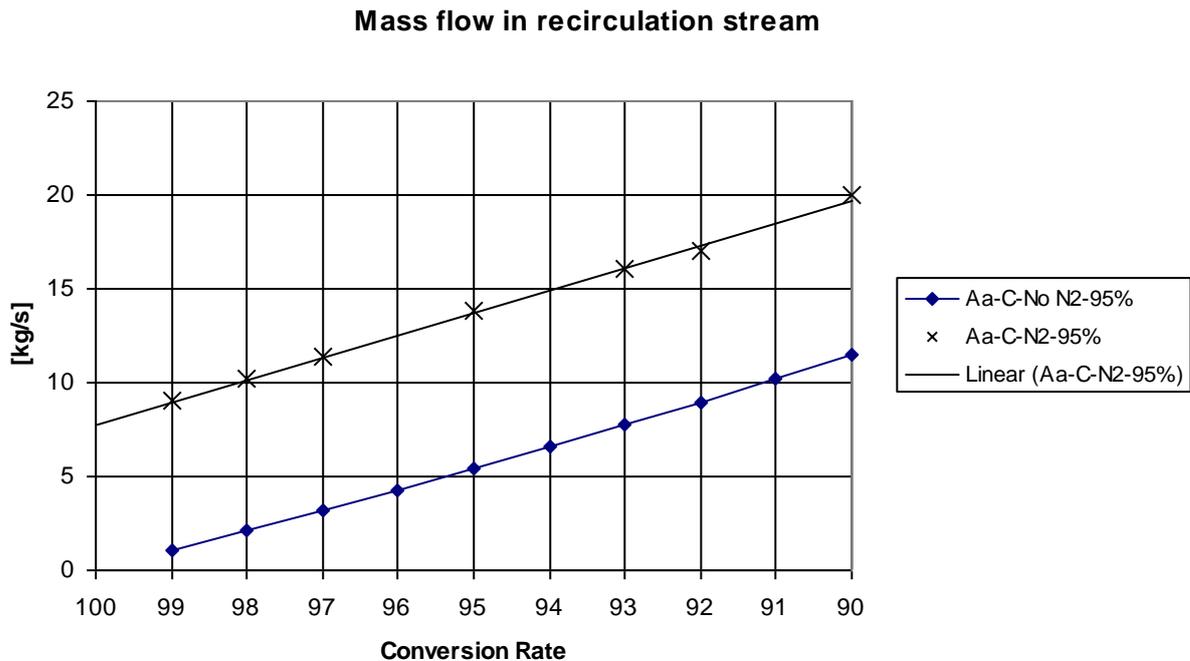


Fig. 50. Mass flow in recirculation stream.

9.7.2 Content in stream(s) for transport and storage

In cycles with distillation column some hydrocarbons will follow the CO_2 out in the bottom to be stored together with the CO_2 (to an amount controlled by the recovery rate). The rates should not be higher than those shown in chapter 6.1. There is no bigger difference between the cycles employing a distillation column. The difference occurs between the different recovery rates as seen in Fig. 51 and Fig. 52. The rates of hydrocarbons are much lower than the recommendations in [35]. The rate of water is almost 500 ppm and as concluded in chapter 6.1 it should probably be better to dry the CO_2 to single ppm digit by regenerative adsorption columns [5]. The only difference in cycles with N_2 present is that there will also be a small amount of N_2 in the transport stream, around 0,03%-0,04% which is equal to around 300 ppm and a much smaller amount than the recommendation of less than 4%.

In cycles “Ba-O-No N_2 -95” and “Ba-O- N_2 -95” (oxidation of the hydrocarbons after the CLC reactor) the transport stream consist of a significant portion of O_2 , see Fig. 53. As this would not be approved as transport or storage quality an extra distillation column would be needed to separate the O_2 . This would lead to CO_2 emissions to the atmosphere as well as further energy penalties to the cycle. How big the oxygen content in the exhaust stream has to be to achieve 100% oxidation can however be a topic for further investigation, here it is assumed to be 3%

[11] de Diego Luis F., García-Labiano Francisco, Gaya'n Pilar, Celaya Javier, Palacios Jose' M., Adanez Juan. "Operation of a 10 kWth chemical-looping combustor during 200 h with a CuO–Al2O3 oxygen carrier". *Fuel* 86 (2007) 1036–1045

[12].

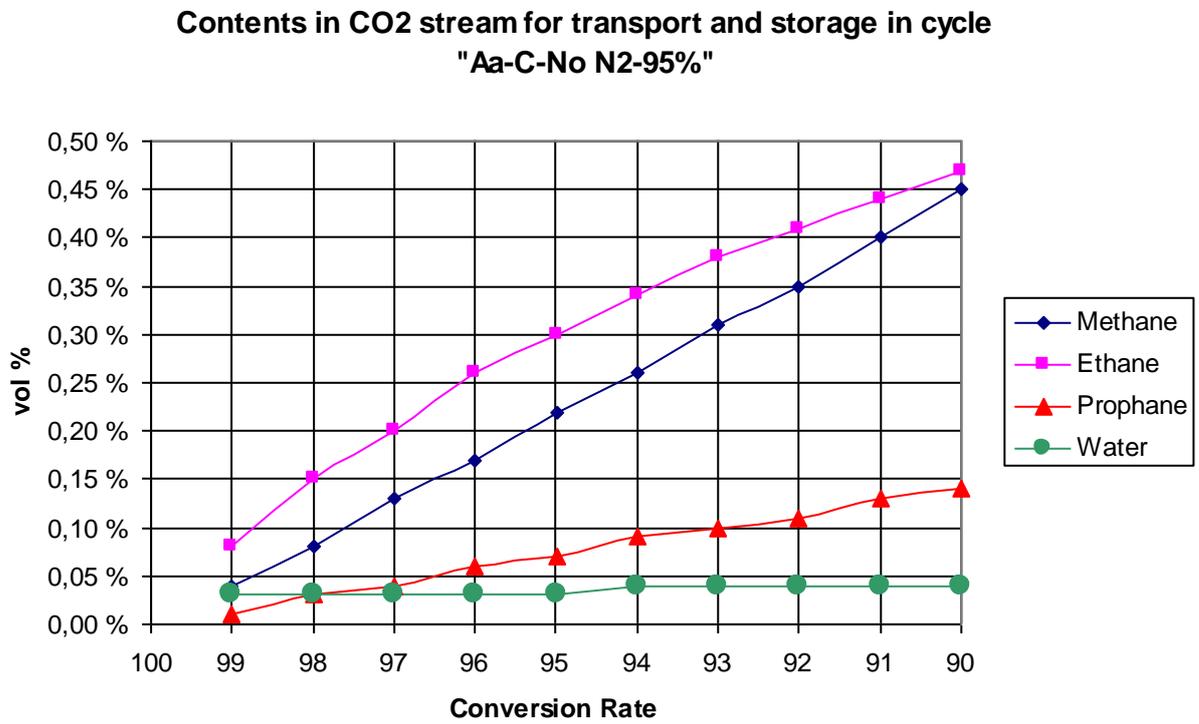


Fig. 51. Contents in CO₂ stream for transport and storage in cycle "Aa-C-No N₂-95%".

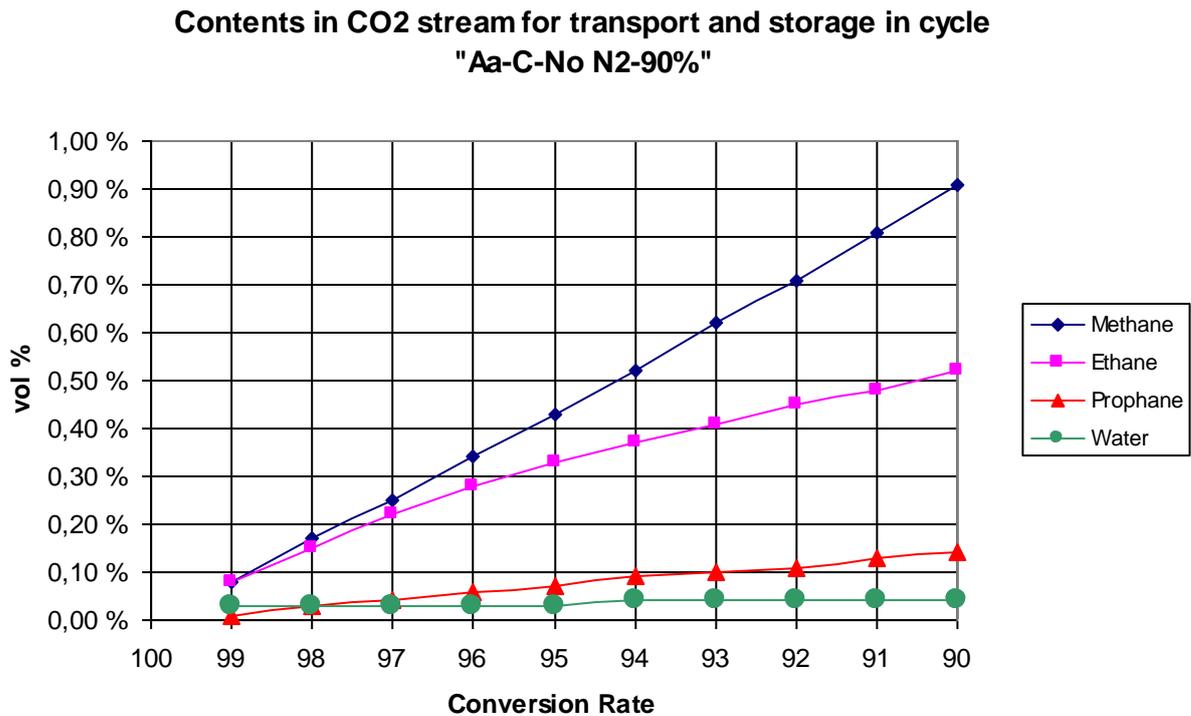


Fig. 52. Contents in CO₂ stream for transport and storage in cycle “Aa-C-No N₂-90%”.

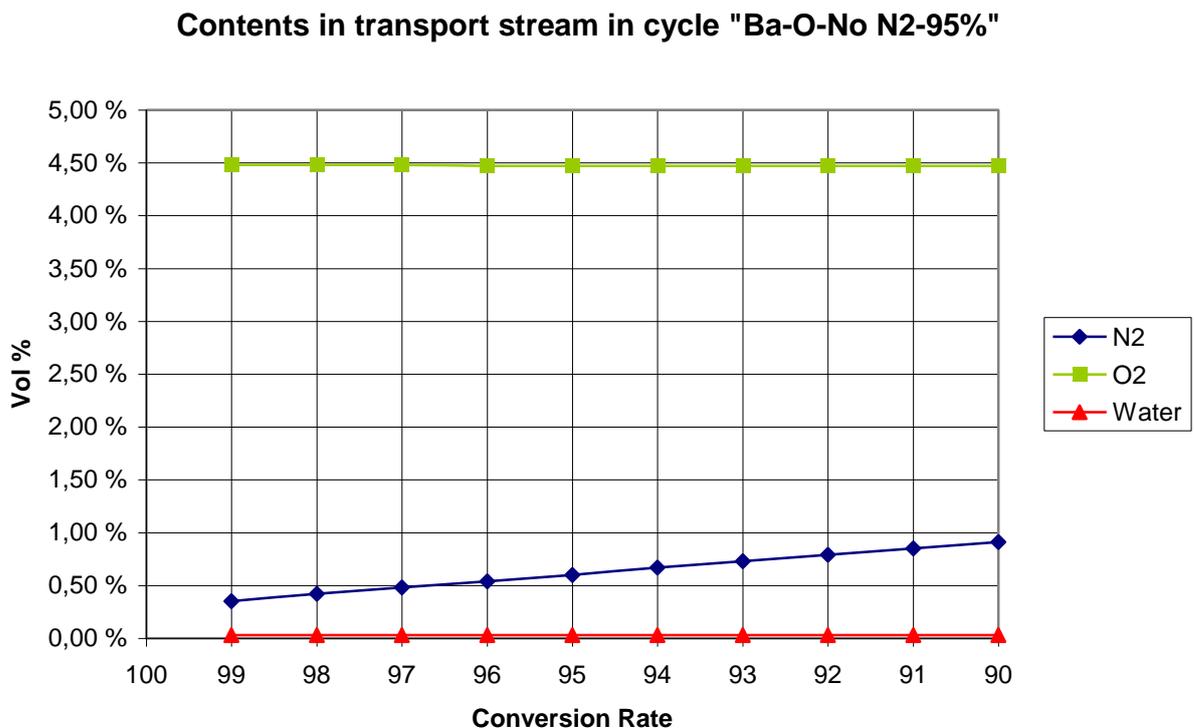


Fig. 53. Contents in transport stream in cycle “Ba-O-No N₂-95%”.

It can be concluded that the transport streams from all cycles have a very high purity of CO₂ ranging from 98,37% (“Aa-C-No N₂-90%” at a conversion rate at 90%) to 99,84% (“Aa-C-No N₂-99%” at a conversion rate at 99%) except cycle “Ba-O-No N₂-95%” and “Ba-O- N₂-95%”. The

other cycles has purities well above the recommended and can therefore be transported and stored. Cycle “Ba-O-No N₂-95%” and “Ba-O- N₂-95%” on the other hand would need extra conditioning, most probably in the form of an extra distillation column. This would lead to further energy penalties as well as CO₂ emissions to the atmosphere.

10 SIMULATION WITH CO AND H₂ IN THE EXHAUST STREAM

Case “c” in terms of fuel composition out of the reduction reactor is as already mentioned different from the other cases as the exhaust stream contains of H₂ and CO. It seems as if the exhaust stream would most probably be diluted with CO and H₂ to certain extend when using Ni as oxygen carrier [27],

[9] which makes it interesting to examine further a compression and conditioning process with those as dilutants.

It turns out that the presence of H₂ in the CO₂ rapidly increases the mixture condensation point which gives problems with the compression chain, which would have to be redesigned if going below 98% conversion rate. There are also problems in the distillation column when applying less than 99% recovery (as both CO and H₂ are very volatile) but as it is better to recover more this is not really a problem. But when recycling H₂ and CO the cycle becomes very unstable and it is problematic to make it converge. As realizing those problems the question arises whether it is so problematic with some percentage of CO and H₂ in a CO₂ stream or if it is the Hysys thermodynamic model that is inadequate. It is also clear that the presence of H₂ in the stream increases the compression work, see chapter 6.2 as well as [6] which has a negative impact on cycle efficiency

Fig. 54 shows the efficiency for cycle “Ac-C- N₂-99%”, “Ac-C-No N₂-99%” and “Ac-C/B- N₂-99%”. Cycle “Ac-C- N₂-99%” has a 10% bleed stream to vent the N₂ as this turns out to be a good size of the bleed stream for this cycle. As the cases cover so short range of fuel conversion rates they are hard to compare with the previous cycles but the slope of the lines is around three times as steep as those for the other comparable cases due to increased compression work when H₂ is present. It can be seen that it gets beneficial to recover the unconverted CO and H₂ almost immediately, .i.e. at very high conversion rates. This is because of the high energy content in H₂ and CO which also makes the “no recirculation” line become so steep. From an efficiency point of view, cycle “Ac-C/B- N₂-99%” seems like a very interesting alternative for such a cycle. When studying Fig. 56, which shows the CO₂ emissions, however, it can be seen that these rather quickly go below 90%. The contents in the stream to the combustor are mostly CO₂ and the other contents can be seen in Fig. 55. If it turns out that the H₂ content has to be higher and the CO₂ content lower to combust in an effective way this would be possible by controlling the column different, but with efficiency penalties. The CO₂ following the combustion stream will lead to

CO₂ emissions as well as the CO₂ that is generated in the combustion of CO. The rates of CO₂ capture can be seen in Fig. 56.

Electrical efficiency at different Recovery Rates in cycle "Aa-"

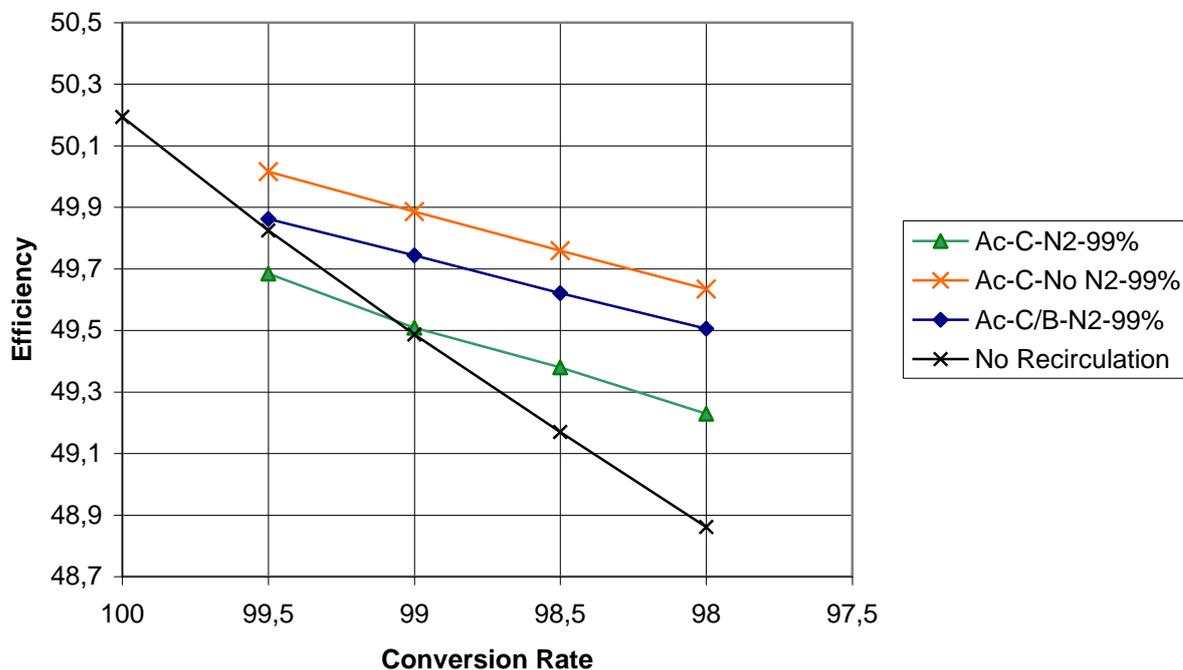


Fig. 54. Electrical efficiency at different Recovery Rates in cycle "Aa-".

Contents in stream to combustor

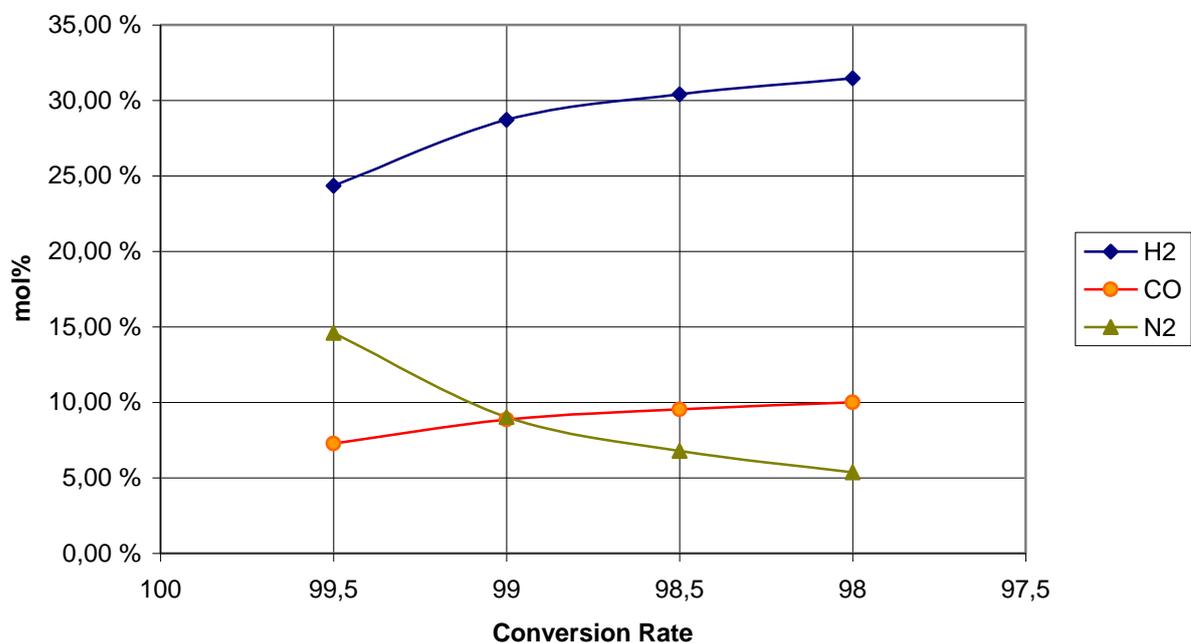


Fig. 55. Contents in stream to combustor.

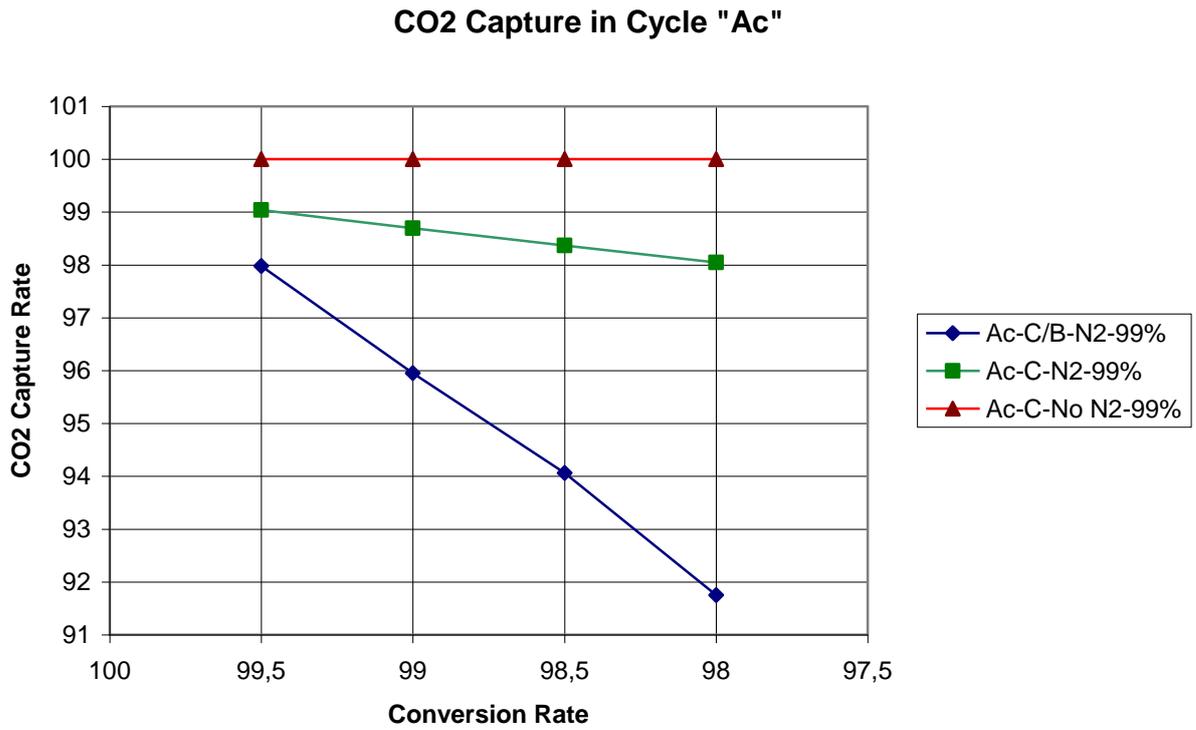


Fig. 56. CO₂ Capture in Cycle "Ac".

11 DISCUSSION AND CONCLUSIONS

CLC is a novel combustion method with inherent separation of CO₂ and air. It has on lab scale level showed high fuel conversion rates but it is not clear if such high fuel conversion rates can be expected if and when the technology is scaled up. This thesis has investigated possible power process configurations that may enable to aim for less than 100% fuel conversion when constructing a CLC reactor. Such different aims could be to use cheaper and more environmentally friendly oxygen carriers and/or to keep reactor size down. The simulations have been performed in Hysys flowsheet simulator.

Three different ways of handling the unconverted fuel has been examined; separation and recirculation to the CLC reduction reactor, separation and combustion prior to the air turbine and direct oxidization after the CLC reactor with (almost) pure oxygen. Since the composition of the assumed unconverted fuel was unknown, and not possible to determine with the very simple reactor model applied, three different cases were examined: 1) a mix of hydrocarbons as present in the natural gas, 2) only methane and 3) hydrogen and carbon monoxide.

When recirculating the unconverted fuel to the reduction reactor the content of N₂ in the fuel turns out to be a problem as it gets accumulated in the recirculation loop. Other volatile inerts could also be accumulated if present in fuel or due to leakage in the reactor, for example argon. To handle this problem a bleed stream is introduced. By simulating both with and without the presence of N₂ the negative efficiency impact of the bleed stream is shown. The introduction of bleed also introduces CO₂ emissions to the atmosphere. If it would be possible to by any means separate N₂ (and other inerts) from methane without big energy penalties, maybe by some sort of PSA, this would be desirable. Ideally, it would be desirable to have a fuel stream completely free of volatile inerts, since this could enable a zero-emission power plant regardless of whether the fuel conversion in the CLC reactor is complete or not.

To avoid a recirculation loop and hence recirculation of volatile inerts such as N₂, the separated unconverted fuel can be combusted in a combustor prior to the air turbine. The unconverted fuel gets combusted and the TIT gets raised which has a positive impact on GT cycle efficiency. It has the advantage that the CLC reactor does not have to be constructed to allow large quantities of recirculated CO₂ and the controlling of the reactor would be easier without feedbacks. It seems to the author that this alternative is the most promising, not at least in case C with only methane and carbon monoxide in the exhaust stream. Such cycle would however lead to CO₂ emissions to the

atmosphere. The size of the emissions can be controlled by column condenser temperature or by introducing a second column. Lowering condenser temperature has a very negative impact on cycle efficiency. How the cycle efficiency would react to an introduction of a second column has not been tested and could be a topic for further research.

The next alternative simulated is what is often suggested in the literature [9,??]; oxidation of combustibles right after the CLC reactor by the addition of oxygen from an ASU. In the simulations performed this alternative shows very bad efficiency but it can be concluded that it is because of the design of the cycle rather than the principle itself. The recovered energy is not utilized in an effective way. It can be seen that the cost/recovered energy (ϕ) is around the double compared to the other cases but still far from unity which tells that it should be possible to construct a cycle with good efficiency with this alternative. There is however uncertainties regarding the possibility to oxidize such small amounts of combustibles (a few percent) in a CO₂ stream and how much excess air that would be needed. The excess air would have to be taken care of in some way, most probably in a distillation column, which will further lower cycle efficiency and introduce CO₂ emissions to the atmosphere. The question regarding the combustion and the excess air could be worth further investigations.

The difference between having only methane and having a mix of hydrocarbons in the exhaust stream showed negligible in almost every way, the only difference is that there is only methane in the CO₂ stream in cases with only methane in the exhaust stream while in the cases with a mix there is also a mix in the CO₂ stream. But case ‘-c’ with hydrogen and carbon monoxide as combustible components in the CO₂ showed a great difference from the other cases. The presence of hydrogen in the CO₂ stream has a major impact on the physical properties of the CO₂ stream, such as the condensation point. It became hard to make the cycle converge and the question arose if the Hysys thermodynamic model (SRK) was to be trusted in this case. As this case is most probably closest to reality when using e.g. Ni as oxygen carrier it should be further investigated, not at least to see how a CO₂ and H₂ mixture would behave in the compression chain. The simulations performed in this thesis shows good potential for recovery from such a cycle, not the least to a combustor, but with a significant CO₂ emission penalty. However, possibilities for optimization of the distillation column or the the introduction of a two column system might exist and should be further investigated.

12 FURTHER RESEARCH

It is clear that this work has just been a small glint on the possibility to recover volatiles in the exhaust stream from a CLC process. Far too much is unknown to make any certain conclusions. The very basic issue, what the exhaust stream will consist of, is unknown. This is of course something that has to be determined, especially if the up scaling of CLC reveals a problem with achieving 100% fuel conversion and recirculation becomes an option.

Another question is if it is even possible to recirculate unconverted fuel to the reactor as it will bring CO₂ to the reactor to a larger or lesser extent. How would a CLC reactor respond to the presence of extra CO₂? What are the limits for other compounds than fuel in the reactor? How would this effect the conversion rate? How could such application be controlled, especially in the start-up phase? As research continues a better model of the reactor would be desirable were more parameters could be investigated in comparison to the “black box” used in this thesis.

The most significant “practical” problem discovered in this thesis is the accumulation of inert volatiles, such as nitrogen in the recirculation loop. As seen in the results, recirculation of unconverted fuel could be an attractive way to handle incomplete fuel conversion and may also be a way to minimize reactor size and bed mass. But the small amount of nitrogen accumulated in the recirculation loop poses a serious threat to the efficiency gain as seen in the results. Separation of nitrogen from methane is not possible in a separation column; instead a bleed stream has been used. This bleed stream should be optimized which has not been made to full extend in this work. However this should not have a crucial influence on the efficiency. Instead other possibilities to separate the methane could be investigated; the use of a PSA has been proposed and could be a topic for further research.

If the unconverted fuel is to be oxidized after the CLC reactor by a separate oxygen stream the practical possibilities have to be investigated. If it turns out to be a possible alternative, the cycle has to be designed in such way that the heat is utilized with good efficiency. Furthermore the excess oxygen must be separated from the CO₂, probably in a distillation column, and the CO₂ emissions and energy penalties for this has to be investigated.

If a distillation column is used and the recovered fuel is burned prior the air turbine, further work could address the problem with high CO₂ emissions. It could perhaps be possible to separate more

CO₂ in a second column with a moderate energy penalty, making this alternative even more interesting.

In the cycle 'B-' (cases with CO₂ turbine) there is a big question mark on the turbines polytropic efficiency and how cooling could be implemented. To realize a CLC cycle with a CO₂ turbine would require further research on CO₂ turbines and CO₂ turbine cooling.

As studies have shown CO and H₂ in the exhaust from a CLC reactor, especially when using Ni as oxygen carrier, this should be further investigated. In the present work it turned out to be problematic to have H₂ in the compression stream as it had high effect on the physical properties. There were also uncertainties if the results were reliable or if it was the Hysys thermodynamic model that was inadequate. More research on how CO₂ diluted with for example H₂ could give better models.

This work has only focused on CLC with natural gas as fuel; it could maybe be as interesting to see how gas recirculation could be used together with CLC using solid fuels as they often show high rates of unconverted fuel (gas) in the exhaust stream.

Table 3. Computational assumptions.
Fuel feed stream
Composition

N ₂	mol%	0,89
CO ₂	mol%	2
C1	mol%	89
C2	mol%	7
C3	mol%	1
C4	mol%	0,05

Properties

pressure	bar	70
temperature	°C	10
density	kg/m ³	64,27
molecular weight	g/mol	18,02
LHV	kJ/kmole	8,379e5

Air feed stream
Composition

N ₂	mol%	77,32
CO ₂	mol%	0,03
H ₂ O	mol%	1,01
Ar	mol%	0,92
O ₂	mol%	20,72

Properties

pressure	bar	1,013
temperature	°C	15

Oxygen feed stream
Composition

O ₂		95
N ₂		2
Ar		3

Properties

pressure	bar	2,38
temperature	°C	15
Energy production requirement	kJ/kg O ₂	812

CO₂ outlet
Composition

CO ₂ concentration		91*-99,9
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Properties

pressure	bar	200
temperature	°C	36

Cooling water

Inlet temperature	°C	8
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Heat exchanger

pressure drop	%	3
ΔT _{min} gas/gas	°C	25
ΔT _{min} gas/liquid	°C	10

CO ₂ compression intercooler out temperature	°C	13
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HRS

pressure drop gas side	mbar	40
steam out/exhaust in	°C	30
pinch point	°C	10
LP steam pipe Δp	%	9
HP steam pipe Δp	%	7
HP pressure	bar	60
LP pressure	bar	5
Condenser pressure	Bar	0,04
Max steam temperature	°C	580
Reactors		
pressure drop	%	5
Oxygen depleted air out temperature	°C	1200
CO ₂ stream temperature	°C	980
Turbomachinery efficiencies		
GT compressor polytropic efficiency	%	91,5
GT polytropic efficiency	%	90,7**, 90****
GT CO ₂ turbine polytropic efficiency	%	87 (81****)
CO ₂ compressor(s) polytropic efficiency(s)	%	83
HP steam turbine adiabatic efficiency	%	90
LP steam turbine adiabatic efficiency	%	88
Steam cycle pump adiabatic efficiency	%	75
CO ₂ pump adiabatic efficiencies	%	75
Auxiliaries		
Generator mechanical efficiency	%	98
Case specific variables		
<i>Condenser temperature</i>		
All cases with recirculation to reactor (“-C-“) except cases “Ac-“	°C	0
Case “Ac-C- N ₂ -99%”	°C	-8
Case “Ac-C-No N ₂ -99%”	°C	-12
Case “Aa-C/B-No N ₂ -95%”	°C	-12
Case “Aa-C/B- N ₂ -95%”	°C	-15
Case “Ac-C/B- N ₂ -99%”	°C	-15
* 90% RR without recirculation		
** Cycle A		
*** Cycle B		
**** When used with ASU and combustor to make up for the cooling penalty		

13 REFERENCES

- [1] Abad Alberto Mattisson Tobias, Lyngfelt Anders, Johansson M. *The use of iron oxide as oxygen carrier in a chemical looping reactor*. Fuel 86 (2006) 1021-1035
- [2] Abad Alberto, Mattisson Tobias, Lyngfelt Anders, Rydèn M. *Chemical looping combustion in a 300 W continuously operating reactor system using a manganese-based carrier*. Fuel 85 (2006) 1174-1185
- [3] Anheden Marie, Svedberg Gunnar . *Exergy analysis of chemical-looping combustion systems*. Energy Convers. Mgmt Vol 39. 1998
- [4] Aspelund Audun, Jordal Kristin. *Gas conditioning-The interface between CO₂ capture and transport*. International journal of greenhouse gas control 1 (2007) 343-354.
- [5] Aspelund Audun. Personal communication.
- [6] Austegard Anders and Barrio Maria. *Inert components, solubility of water in CO₂ and its mixtures and CO₂ hydrates*. Project memo, Sintef.
- [7] Bert Metz, Ogunlade Davidson, Heleen de Coninck, Manuela Loos and Leo Meyer. *IPCC Special Report on Carbon dioxide Capture and Storage*. IPCC, 2005
- [8] Brandvoll. Ø, Bolland. O. *Inherent CO₂ capture using chemical looping combustion in a natural gas fired power cycle*. ASME 2004.
- [9] Consonni Stefano, Lozza Giavanni, Pelliccia Giampaolo, Rossoni Stefano, Saviano Francesco. *Chemical-looping combustion for combined cycles with CO₂ capture*. Journal of Engineering for Gas Turbines and Power. (2006 Vol 128.)
- [10] Corbella Beatriz M., Palacios José María. *Titania-supported iron oxide as oxygen carrier for chemical looping combustion of methane*. Fuel 86 (2007) 113-122.
- [11] de Diego Luis F., García-Labiano Francisco, Gaya'n Pilar, Celaya Javier, Palacios Jose' M., Adanez Juan. *Operation of a 10 kWth chemical-looping combustor during 200 h with a CuO–Al₂O₃ oxygen carrier*". Fuel 86 (2007) 1036–1045
- [12] Ditaranto Mario. Personal communication.
- [13] *ESI New Entrants' Benchmark Report*, DTI ENERGY GROUP, March 2006
- [14] Hossain Mohammad M., de Lasa Hugo I. *Chemical-looping combustion for inherent CO₂ separation- a review*. Chemical Engineering Science 63 (2008)
- [15] IPCC. *Climate change 2007: synthesis report. Summary for policy makers*.

[16] Johansson Eva, Mattisson Tobias, Lyngfelt Anders, Thunman Hilmer . *A 300 W laboratory reactor system for chemical looping combustion with particle circulation*. Fuel 85 (2006) 1428-1438

[17] Jordal Kristin. Personal communication

[18] 1Kvamsdal Hanne M., Jordal Kristin, Bolland Olav. *A quantitative comparison of gas turbine cycles with CO₂ capture*. Energy 32 (2007) 10-24

[19] Kolbitsch Philipp, Pröll Tobias, Bolhar Johannes, Nordenkampf, Hofbauer Hermann. "Design of a Chemical Looping Combustor using a Dual Circulating Fluidized Bed Reactor System". Chem. Eng. Technol. 2009, 32, No. 3, 398–403.

[20] Leion Henrik, Mattisson Tobias, Lyngfelt Anders. *Solid fuels in chemical looping combustion*, Int. J. Greenhouse Gas Control (2007)

[21] Linderholm Carl, Mattisson Tobias, Lyngfelt Anders. Long-term integrity testing of spray dried particles in a 10 kW chemical looping combustor using natural gas as fuel. Fuel (2008).

[22] Linderholm Carl, Abad Alberto, Mattisson Tobias, Lyngfelt Anders. *160h of chemical looping combustion in a 10 kW reactor system with a NiO-based oxygen carrier*. International journal of greenhouse gas control 2 (2008) 520-530.

[23] Lyngfelt.A, B. Kronberger, J. Adanez, J.-X. Morin and P. Hurst. "The GRACE project. Development of oxygen carrier particles for chemical-looping combustion. Design and operation of a 10 kW chemical-looping combustor." Seventh International Conference on Greenhouse Gas Control Technologies Vancouver, Canada, September 5–9 (2004).

[24] Lyngfelt Anders, Leckner Bo, Mattisson Tobias. *A fluidized-bed combustion process with inherent CO₂ separation; application of chemical-looping combustion*. Ind. Eng. Chem. Res. 2005, 44, 546-556.

[25] Lyngfeldt Anders, Johansson M, Mattisson Tobias. *Chemical-looping combustion Status of development*. 9th International Conference on Circulationg Fluidized Beds. 2008

[26] Lyngfelt. A and Thunman H. Construction and 100 h of operational experience of a 10 kW chemical looping combustor". In: D. Thomas, Editor, Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO₂ Capture Project, Capture and Separation of Carbon Dioxide From Combustion Sources vol. 1, Elsevier Science, London (2005), pp. 625–646 (Chapter 36).

[27] Mattisson Tobias, Johansson Marcus, Lyngfelt Anders. *The use of NiO as an oxygen carrier in chemical-looping combustion*. Fuel 85 (2005) 736-747

- [28] Naqvi Rehan. Analysis of Natural Gas-Fired Power Cycles with Chemical Looping Combustion for CO₂ Capture. Doctoral thesis Trondheim, July 2006.
- [29] Pfaff Imo, Kather Alfons. “Comparative Thermodynamic Analysis and Integration Issues of CCS Steam Power Plants Based on Oxy-Combustion with Cryogenic or Membrane Based Air Separation”. Energy Procedia 1 (2009) 495–502
- [30] Paul Cho, Mattisson Tobias, Lyngfelt Anders. Comparison of iron-, nickel-, copper- and manganese based oxygen carriers for chemical-looping combustion. Fuel 83 (2003) 1215-1225
- [31] Ritz Oliver, MAN Turbo AG. Mail correspondence.
- [32] Richter, H.J and Knoche K.F. “Reversibility of combustion process” Efficiency and Costing-Second law analysis of processes. ACS Symposium series 235 page 71-85.
- [33] Ryu Ho-Jung, Jin Gyoung-Tae & Yi Chang-Keun. “DEMONSTRATION OF INHERENT CO₂ SEPARATION AND NO NO_x EMISSION IN A 50kW CHEMICAL-LOOPING COMBUSTOR: CONTINUOUS REDUCTION AND OXIDATION EXPERIMENT”. Korea Institute of Energy Research, Daejeon 305-343, Korea
- [34] Saravanamuttoo HIH, Rogers GFC, Coen H, Straznicky PV. *Gas Turbine Theory*. ISBN:978-0-13-222437-6
- [35] de Visser Erika, Chris Hendriks, Maria Barrio,, Mona J. Mølnvik, Gelein de Koeijer , Stefan Liljemark, Yann Le Gallo. *Dynamis CO₂ quality recommendations*. International journal of greenhouse gas control 2 (2008) 478-484.
- [36] Wolf Jens. CO₂ Mitigation in Advanced Power Cycles - Chemical Looping Combustion and Steam- based Gasification. Doctoral Thesis 2004, KTH - Royal Institute of Technology
- [37] Yunus A. Cengel & Michael A. Boles. *THERMODYNAMICS-AN ENGINEERING APPROACH. Fourth edition*. ISBN 0-07-112177-3