Integrating Chemical Looping Gasification for Hydrogen Generation and CO$_2$ Capture in Pulp Mills

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Abstract

Emissions of CO_2 to the atmosphere are contributing to the global temperature rise. The industrial sector contributed to 20 % of the emissions and out of that, 6 % are generated from the pulp and paper industry. To limit the temperature increase below 1,5 °C, the emissions not only need to be reduced but also negative emissions should be generated from different sectors. The purpose of this study is to realize the implementation of Chemical Looping Gasification (CLG) to separate CO_2 (for permanent storage) in an energy-efficient way while co-generating H_2 as well as electricity.

Process analysis was carried out to investigate the possibility of substituting the multi-fuel boiler in a typical pulp mill with a CLG process. Process models for the CLG, heat recovery and electricity generation process were developed using Aspen Plus and Aspen HYSYS. The process was analysed for different design conditions (temperature, autothermal condition, air flow, oxygen carrier flow) in the CLG process.

It was found that in a typical pulp mill producing 800 000 adt per year, 375 kg CO_2/adt (14 % of total emissions from the process) can be inherently separated for storage to achieve negative emissions, if the multi-fuel boiler is replaced with a CLG unit. This process will also be able to generate 360-504 kWh/adt H_2 depending on the design conditions in the CLG process. Heat recovered from the CLG unit can be utilized in capturing approximately 13 % additional CO_2 from other sources in the pulp mill. Process analysis for different design conditions in CLG (temperature, airflow, oxygen carrier flow) have been presented. The key performance indicators were CO_2 capture rates, H_2 generated and net electrical output from the process.

Sammanfattning

Utsläpp av CO_2 till atmosfären bidrar till ökningen av globala temperaturer. Industrisektorn står för 20 % av utsläppen och utav dessa kommer 6 % från pappers- och massaindustrin. För att lyckas minska den globala temperaturhöjningen till under 1,5 °C hjälper det inte bara att minska utsläppen. Även negativa utsläpp måste genereras. Syftet med denna studie är att undersöka implementeringen av CLG för att separera CO_2 på ett energieffektivt sätt och samtidigt generera H_2 och elektricitet.

Processanalyser genomfördes för att undersöka möjligheten att implementera CLG-processen till ett typiskt massabruk. Processmodeller togs fram för att undersöka CLG, värmeåtervinning samt elektricitetsgenerering. Processmodellerna utvecklades med hjälp av Aspen Plus och Aspen HYSYS. De framtagna modellerna analyserades sedan med avseende på olika designparametrar inom CLG-processen.

På ett typiskt massabruk som producerar 800 000 adt varje år kan 375 kg CO_2/adt separeras och då uppnå negativa utsläpp, genom att byta ut multi-fuel förbrännaren med en CLG process. Den framtagna processemodellen skulle också kunna generera 360-504 kWh/adt av H_2 beroende på de designparametrar som används för CLG-processen. Enligt modellen kan värme som återvinns från processen användas för att fånga upp ytterligare 13 % av CO_2 från andra delar av bruket. Processanalys för olika designparametrar inom CLG systemet så som temperatur, luftflöde och flödet av syrgasbärare har presenterats. Nyckeltalen som undersöktes var den mängd CO_2 som kunde fångas upp, mängd H_2 genererad samt överskottet av elektricitet som produceras när multi-fuel förbränningen byts ut mot en CLG-process på ett typiskt massabruk.

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Contents

Acronyms

adt air dried tonne. ii, iii, 5, 22, 25–27, 30–33, 35–38

AR Air Reactor. 11, 13, 14, 16–20, 23–25, 27–36, 38

BECCS Bio Carbon Capture and Storage. 1, 2, 5, 6, 9, 10

CCS Carbon Capture and Storage. v, 1–7, 9–11, 34, 37

CCU Carbon Capture and Utilization. 9, 39

CLC Chemical Looping Combustion. 2, 12, 13, 20, 21, 25, 36–39

CLG Chemical Looping Gasification. ii, iii, v, 2, 3, 12–14, 16, 20, 21, 25, 27, 30, 36–39, 44

CLOU Chemical Looping Oxygen Uncoupling. 13

CLPs Chemical Looping Processes. 2, 11, 12

CLR Chemical Looping Reforming. 14

FR Fuel Reactor. 11–17, 19–21, 23–25, 27, 28, 30, 32, 35–37

GHG Green House Gases. 1

iG-CLC in situ Gasification Chemical Looping Combustion. 13

KPI Key Performance Indicator. 26

MEA Monoethanolamine. 3, 7, 10, 20, 25, 32–35, 37, 38

MT Metric Tonne. 5

MTPY Metric Tonne Per Year. 5

NETs Negative Emission Technologies. 1, 5

OC Oxygen Carrier. 2, 11–18, 20, 23, 27, 38

PSA Pressure Swing Adsorption. v, 7, 14, 16, 17, 19, 20, 23–25, 30, 36

RR Reduction Reactor. 16, 17, 19, 20, 23–25, 28–30, 36

WGS Water Gas Shift. v, 7, 14–16, 18–20, 23–25, 30, 31, 36

Nomenclature

ΔH_r Heat of reaction

ΔH_{vap} Heat of vaporization

λ Oxygen-to-fuel ratio

C_p Specific heat capacity

n_i Moles of species i

S/B Steam-to-biomass ratio

T Temperature

kWh Kilo watt hour

m Mass

Q Heat

W Work

1   Introduction

In today's society, there is an invariable problem with industries consuming huge amounts of fossil energy and emitting Green House Gases (GHG). Carbon dioxide (CO_2), is the single most common GHG and it keeps increasing due to the world's large use of fossil fuels.[1] Today about 20 % of the total global GHG are emitted by the industrial sector.[2] Furthermore, in 2018 around 80 % of the energy used globally was produced using fossil fuels and it is estimated to still be the major source of energy in 2050.[3] These large emissions of CO_2 are a contributor to the increase in global temperatures.[4] To be able to limit the increase of global temperatures below 2 °C by 2050, a 50 % reduction of the emission of CO_2 has to be achieved.[5] Moreover, the Paris Agreement aims to restrict the increase of temperature to less than 1,5 °C.[6] To make it possible to reach the goals of reducing emissions, renewable energy sources will play a large role. One of the most promising options to replace the use of fossil fuels is the implementation of biomass for the production of renewable energy. Biomass is a renewable carbon-neutral fuel which can be used for various processes. It is known for being more reactive than fossil fuels and has a high content of volatiles which makes it suitable for conversion reactions.[7] To succeed in limiting the rising global temperature below 1,5 °C the implementation of Negative Emission Technologies (NETs) is necessary. Regardless of whether solar and wind power is increased to convert renewable energy, it will most likely still be necessary to capture CO_2 to reach the goals of mitigation of CO_2. The implementation of Carbon Capture and Storage (CCS) has the potential of mitigating over 50 % of carbon emissions within one century. By coupling the use of biomass as a fuel with CCS, Bio Carbon Capture and Storage (BECCS), it will be possible to achieve negative emissions to meet the climate targets.[8]

The pulp and paper industry is one of the most energy-intensive industries and it contributes to around 6 % of the industrial energy consumption globally.[4] In Europe, Sweden and Finland are the main producers of pulp to be used in paper production, that are also taking the lead in working towards de-carbonizing the pulp and paper industry. These industries use a high amount of electricity as well as primary energy for production, with 10,80 MWh/tonne of paper produced in 2017.[9] However, they also produce a significant amount of biogenic energy as a by-product of the process. In 2020 Swedish pulp and paper industry produced 6,6 TWh of electricity.[9] This is due to the efficient use of side streams for energy conversion within the plant. The pulp and paper industry also does emit CO_2, however, they have the potential of reducing the total amount of CO_2 in the atmosphere.[9] The majority of the CO_2 emissions from the pulp and paper industry originates from the pulping process, rather than the paper making. Regarding different pulping methods, the Kraft process emits around 2,1 million tonnes a year of CO_2.[4] Within the Kraft process, the main sources of emissions are from the recovery boiler, the lime kiln and the multi-fuel boiler. The recovery boiler is used for the regeneration of the cooking chemicals used in the pulping process while the multi-fuel boiler is used to burn residual biomass for energy generation. Both the recovery boiler and the multi-fuel boiler are fueled with bio-based fuel and therefore, the majority of the CO_2 that is released, around 75-100 % , is biogenic. The lime kiln is used to regenerate the lime used for the cleaning of the cooking

chemicals.[4]

One solution to decrease the amount of CO_2 being emitted from the pulp and paper industry is the implementation of CCS. CCS relates to separating, capturing, transporting and storing of CO_2 emissions from a fixed point source.[1] Since the pulp and paper industry mostly emits biogenic CO_2, BECCS can be utilized which would then possibly, result in negative emissions.[2] An implementation of CCS has the potential to act towards a major reduction in the CO2 being emitted. More than half of the emissions globally could be reduced within one century. Whereas BECCS has been seen as a solution for compensating for the emissions from industries where it is still hard to reduce CO_2 being emitted. [8] However, there is as of now no incentive within the European Union for industries to implement negative emissions.[4]

CCS can be broadly classified into three categories, namely, post-combustion, pre-combustion and oxy-fuel combustion capture. However, amongst the several methods for capturing CO_2 one of the most promising with regards to cost reduction as well as its low energy penalty is the Chemical Looping Processes (CLPs).[4] Within these processes, a metallic Oxygen Carrier (OC) is oxidized with air to provide oxygen to a combustion or gasification reaction, where it is reduced again. The OC is circulated between the reactors and is oxidized and reduced multiple times. These processes also have the potential to produce heat, electricity and syngas while inherently capturing the CO_2 emitted. This can be achieved both through combustion and gasification reactions with the Chemical Looping Combustion (CLC) and Chemical Looping Gasification (CLG) processes where the CLG process also has the possibility to generate H_2.[10]

H_2 can be used for energy or converted for the production of fuels and within industries. Furthermore, it is considered an efficient energy carrier with a great possibility to contribute to a solution for climate change and develop a sustainable energy system. If the H_2 can be generated from renewable sources (green hydrogen) it will also be a clean energy carrier and a carbon-free energy source.[11] However, today the majority of the H_2 used is still produced using fossil fuels, with a majority of the fuel being natural gas that is reformed to H_2. To reduce emissions and produce green H_2 there is a large focus on renewable paths for production. One process with great potential is the gasification of biomass, where the product would be syngas containing H_2. However, even this process has its limitations and the energy efficiency needs to be increased as well as the yield of the H_2 produced. This could be achieved by integrating the production with other processes. One possible route is CLPs, which could help increase the H_2 content in the produced gas while inherently capturing any CO_2 generated from the process.[12] This is the process investigated in this thesis, the implementation of CLG in a pulp and paper making process, by substituting the multi-fuel boiler, to reduce the emissions of CO_2 while inherently producing H_2 as well as recovering heat for steam and electricity generation.

1.1 Aim

The aim of this thesis is to investigate the possibilities of implementation of a Chemical Looping Gasification (CLG) to substitute the multi-fuel boiler in a pulp and paper making process. The goal of implementing the CLG process is to generate electricity while simultaneously producing H_2 and inherently separating the CO_2. For the suggested process, various design conditions (temperatures and flows of reactant materials) should be examined to see how much of the desired products can be recovered. Another aim is to see whether the process can be designed in an auto-thermal manner to reduce the need for an external energy source. Furthermore, this work also analyses the amount of steam that can be generated from the residual heat and if this steam could be used for a Carbon Capture and Storage (CCS) process using a Monoethanolamine (MEA) based absorption process. The use of a MEA capture unit would then be to capture the CO_2 from the other sources at the pulp and paper mill, for example: CO_2 in the exhaust gases from the recovery boiler.

2 Background

This section of the report focuses on the background to the need for CCS in the pulp and paper industry as well as the technologies existing today. Future possibilities of capturing techniques will also be presented.

2.1 Pulp and Paper Mill

The pulping process starts with the preparation of raw materials where the trees are debarked and chipped. Next, there is the wood pulping, before the bleaching and then on to the paper process.[13] For the most part, the primary material used for paper making is wood and it is usually delivered in the form of logs. These logs are then debarked and chipped into the desired size for further use. The chips go through a screening to make sure the size is correct for their purpose, the larger chips are re-cut while the ones that are too small can be used directly for fuel in energy conversion. The same goes for the bark as well as the sawdust from the debarking process.[14] This step, along with the rest of the pulping process can be seen in Figure 1 which schematically shows the different parts of a pulping process and how they relate to each other.[4]
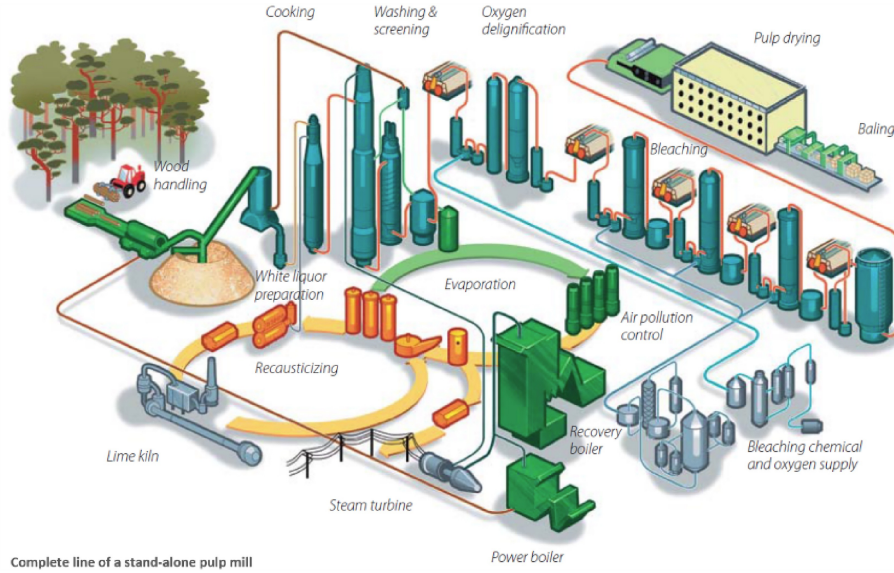
Figure 1: Simplified pulp mill process scheme. [15]

Next, the chips are sent to the pulping process, where they are separated into fibres. In the Kraft pulping process, which is the most common process, the chipped wood is cooked in an aqueous solution containing sodium hydroxide, (NaOH) and sodium sulfide, (Na_2S) called white liquor. This procedure is performed at high pressure and temperature. The Kraft process is the dominating pulping process due to its efficient chemical recovery. After the cooking step the pulp as well as the residual cooking

liquid, often referred to as weak black liquor, are separated and the weak black liquor is recovered. The pulp is washed and then sent for bleaching. The recovery of weak black liquor is done by firstly concentrating the solution to obtain strong black liquor which is then combusted in the recovery boiler. The organic compounds within the black liquor are combusted and since the black liquor, with up to 68 % solids, has a high energy content the energy is recovered. The inorganic molten salts from the recovery boiler are collected and dissolved to form a solution called green liquor, which contains mainly sodium sulfide and sodium carbonate. Next, the sodium carbonate is reacted with calcium oxide (lime) to regenerate the NaOH and form calcium carbonate. Calcium carbonate is then precipitated and dried in the lime kiln to recover the lime which is then recycled in the process. After this, the cooking chemicals Na_2S and NaOH, called white liquor, can be recovered and used in the Kraft process again.[14]

The multi-fuel boiler also called a power boiler, is used for the combustion of residual bark from the wood preparation as well as sludge from the on-site wastewater plant and other residues. These waste products are combusted to generate additional steam for different parts of the pulping process. Since both the recovery boiler and the multi-fuel boiler uses biogenic fuel, these have the capacity to become carbon sinks if the biogenic CO_2 emitted can be captured using CCS.[4] A reference pulp mill producing 800 000 air dried tonne (adt)/year have the following emissions from the various sources in a pulp mill that are presented in Table 1 and in total they add up to 2 162 336 Metric Tonne Per Year (MTPY).[4]

Table 1: CO_2 emissions from a reference pulp mill. Remade from [4]

	Unit	Recovery boiler	Multi-fuel boiler	Lime kiln
Biogenic CO_2	MT/adt	2,053	0,376	0,166
Fossil CO_2	MT/adt	-	-	0,108
Total CO_2	MT/adt	2,053	0,376	0,274

2.2 Carbon Capture Technologies

Even though the emissions of CO_2 are proven to affect global warming they still increase each year. One way to reverse that trend is by capturing the emitted CO_2. Carbon capture, however, faces many challenges moving forward. With the huge amount of CO_2 emissions around the world, CCS is needed on an equally large scale to be able to affect the net amount of CO_2 in the atmosphere.[3] To make an even larger difference for the mitigation of CO_2 implementation of Negative Emission Technologies (NETs) are required. One way to achieve negative emissions are to implement Bio Carbon Capture and Storage (BECCS), where the CO_2 captured is from biogenic sources[10], as illustrated in Figure 2, showing the concept of negative emissions compared to fossil or neutral emissions.[4] This would then help to not only reduce the emissions but instead make them negative. The potential for implementation of BECCS ranges from various industries as well as power plants. A potential issue

seen for the use of BECCS is the increased use of land for the generation of biomass, however, using residuals and biogenic waste shows great possibilities. In countries that already use large amounts of biomass, like Sweden, implementing BECCS could be a viable solution.[10] However, CCS has not always been seen as a permanent solution, it has been seen as a technology to be used until other solutions for mitigation of CO_2 can be achieved.[8] At the same time, BECCS has also been considered for compensating for industries where emissions are harder to cut down or where capture is more difficult. Nevertheless, the implementation of BECCS could help Sweden reach carbon neutrality by the year 2045.[8]
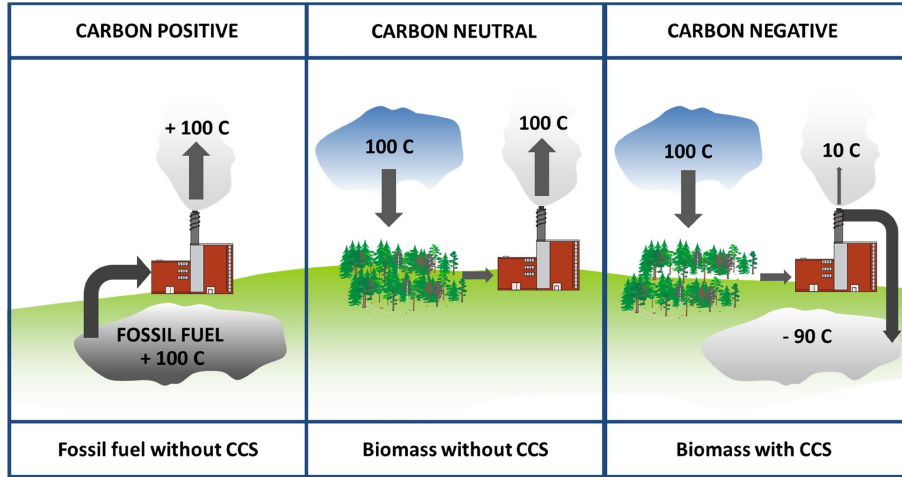

Figure 2: Concept of fossil, neutral and negative emissions.[4]

Since there are various sources of CO_2 emissions with origins from different processes, there are different conditions of the flue gasses that need to be considered (temperature, pressure, composition etc) for its capture. The amount of CO_2 emitted from the source also plays a role since the concentration of CO_2 determines the design conditions in the capture process. Capturing CO_2 from a large point source is proven easier than capturing it from various smaller sources with lower concentrations. For separation from multiple smaller sources both the cost and required energy for separation will increase. Furthermore, since CCS is an extremely energy-intensive and costly process, this will then lead to a higher plant cost as well as a decrease in the efficiency of the plant.[3] Within the CCS process, capturing, transporting and finally storing the CO_2, the actual capturing is by far the most energy-heavy part and it could stand for over 50 % of the overall cost. Close to half of the emitted CO_2 originates from scattered smaller sources which will be harder to capture while the other half are from larger sources such as industries. Due to this, there will have to be research done on various capturing methods since there is no one process that can satisfy every need.[3]

There are several technologies regarding CCS, with the three most common types being, post-

combustion, pre-combustion and oxy-fuel combustion.[16] Depending on from which source the CO_2 is being captured different technologies can be applied and there are various ways of later separating the CO_2. The separation of CO_2 can be done in several ways, by absorption, adsorption, using membranes and cryogenic distillation, to mention some. The absorption separation can be achieved both with chemical or physical absorption and the CO_2 is separated in an absorption/desorption process. Another possible process is adsorption where the molecule adheres to a surface. For this to be successful, the adsorbent should have a high CO_2 selectivity. The cryogenic distillation separates the gasses by condensing them and therefore, the CO_2 can be separated as a liquid which would benefit the transportation and storage part of CCS. [1]

2.2.1 Post-combustion

The post-combustion capture technology is, as the name tells, capturing the CO_2 after the fuel has been combusted and it is then separated from the flue gases.[16] Since the post-combustion technique is applied after combustion it has the possibility to be retrofitted into an already existing plant.[5] Since combustion is often done with air, the separation technologies used for post-combustion capture have the main focus on separating the CO_2 from an N_2-rich flue gas.[3] When using post-combustion technologies, the flue gas stream usually has a low concentration of CO_2. Therefore, a strong solvent is needed to separate the CO_2, as well as a large amount of energy for regeneration of the solvent for further use.[1] Today the most used method is separation by chemical absorption using an amine solvent, with the most developed one being Monoethanolamine (MEA). After the CO_2 is absorbed by the solvent it is removed using a regeneration process where differences in temperature and pressure are the driving force. The solvent can then be reused for further separation of CO_2. This is considered the most energy-demanding part of CO_2 separation and improving the regeneration could increase the efficiency of post-combustion separation. When using amines for the chemical absorption one has to be aware of the O_2 content in the flue gas since high concentrations of O_2 can start to degrade the amines. This could however be controlled by the addition of inhibitors.[5]

2.2.2 Pre-combustion

Another possible technology for CCS is the pre-combustion capture, where the CO_2 is then captured before any combustion reaction. For this process, the fuel is reformed to syngas which is purified through a Water Gas Shift (WGS) reaction to produce CO_2 and H_2.[16] To generate an even cleaner syngas without any nitrogen compounds present, an air separation unit can be integrated before the reforming process. However, the separation of air is an energy-intensive process.[5] In the pre-combustion process, carbon fuel is converted to carbon-less fuel and the chemical energy in the carbon is converted to chemical energy within H_2. CO_2 can be separated in various ways from H_2, such as adsorption, and absorption as well as by using membranes.[1] One possible way to separate the H_2 from CO_2 is using Pressure Swing Adsorption (PSA), an adsorption/desorption process driven by pressure changes.[5] Compared to post-combustion capture, there is a higher concentration of carbon in the flue gasses when using a pre-combustion process which is beneficial for separation. The gas

is also contained at a higher pressure which reduces the energy needed for compressing the gas after separation for transportation, which is also beneficial for separation.[1] The separated H_2 can then be combusted and sent through a turbine to generate electricity.[3]

2.2.3 Oxyfuel-combustion

The oxy-fuel combustion capture uses a stream of nearly pure O_2 for a combustion process where the O_2 is generated from an air separation unit. Combustion with pure O_2 will generate a flue gas with a much higher CO_2 content than from combustion with air, which is beneficial for the separation of the CO_2. After cleaning and washing the flue gas it will consist mainly of CO_2 and steam. The remaining CO_2 can then be separated by condensing the steam. The un-reacted O_2 is also recycled back to the combustion chamber to decrease the content of O_2 in the flue gas while continuously providing O_2 to the combustion. However, combustion using pure O_2 requires a higher combustion temperature and therefore, some modifications might be required for the steam generator.[5] Furthermore, due to the high temperatures there is also a need for materials with tolerance for high temperatures. These are often more expensive which will lead to higher investment costs in order to implement the process. To decrease the reactor temperature, a part of the flue gases can be recirculated back to the reactor. [3] To reduce the amount of flue gas leaving the system, a high purity O_2 is necessary. The most common method for separation of air to receive the O_2 is cryogenic air separation which is performed at temperatures below -180 °C. Furthermore, a large amount of energy is required for the air separation and due to this the efficiency of the process will decrease. [5]

2.2.4 Transport and Storage of CO_2

After the CO_2 has been successfully separated there is a need for efficient transportation as well as a storage site where the gas can be stored for an indefinite future.[1] There are several ways to transport the separated CO_2, using pipelines, trucks, trains or ships. When deciding the way of transport there are several things to consider, such as the distance of transportation, the geographical area where the transportation is taking place, under what conditions the CO_2 should be transported in as well as the transported volume. If the transport will require a discontinuous route this needs to be considered so that intermediate storage is feasible. For smaller amounts that do not need to be transported a larger distance, trucks or trains are a suitable choice. For these transportation methods, CO_2 is transported in pressurized vessels.[5] For larger amounts that should be transported further, transportation through a pipeline is preferred. If the CO_2 however is transported over water, ships are the best option. Before transportation, it is important that the CO_2 is free of contaminants and moisture since this can affect the chemical and physical characteristics of the gas and cause corrosion to the vessels or pipes used for transportation. As mentioned, the CO_2 can be transported in various forms such as gas, liquid or supercritical fluid. Transporting CO_2 as a liquid or supercritical fluid is most preferred since the mass-to-volume ratio is lower than for a gas.[3]

The final storage of CO_2 should be able to hold the gas for an indefinite future by being gas-tight. The

depth should not be less than 800 m for the storage to be secure. The different options include both onshore and offshore solutions such as saline aquifers, which are geologically deep porous rock layers. At these conditions, the CO_2 can dissolve into the rock formation water and become mineralized. Another suitable solution is using depleted reservoirs from oil or natural gas.[5] One offshore storage is located deep beneath the North Sea bed, the Norwegian project Sleipner. It has been active for over 20 years and the CO_2 is stored in an underground saline formation. An important safety concern that has to be considered when storing CO_2 is the risk of leakage. There is both the risk of a large leakage due to a failure of the system as well as a gradual leakage. The leakage of CO_2 has to be negligibly small otherwise it could be dangerous since the CO_2 is lighter than air. This could potentially be harmful to the environment as well as living creatures. Therefore, the potential risks of any leakage need to be thoroughly considered beforehand.[3]

Another approach with great opportunities, besides storage for emitted CO_2, is Carbon Capture and Utilization (CCU). In contrast to CCS, the CCU process aims at capturing the CO_2 but rather than storing it, utilize it. The CO_2 can be used as a starting material for many applications such as fuel production or as a building block molecule for chemical processes. Today it is already used for processes such as the production of carbonated drinks and as a solvent for separations or extractions in industries. CO_2 is also considered a "green solvent" and can be used to replace other, more toxic, organic solvents. Another possible application for captured CO_2 is to use the molecule in the storage of renewable energy. This can be done by using renewable electricity to react CO_2 and H_2 into methanol. Hence, the CO_2 becomes a source to be used to store energy by reacting it into a material with potential for high energy capacity.[3] By using the CO_2 for manufacturing of different products, it is important to consider the lifespan of the product. A product with a long lifespan would bind the carbon for a longer time and in that way temporally decrease the net amount of CO_2 in the atmosphere. However, some possible products have a shorter time where the carbon is bound, such as urea fertilizer.[5] Something to not forget is that CCU should not be considered as a solution to replace the storage of CO_2. However, if the CO_2 used in CCU is from a biogenic source the products produced would at least be carbon neutral.[3]

2.3 Possibilities of implementing CCS at a pulp and paper mill

The possibilities of implementing BECCS in the pulp and paper industry could yield a great opportunity for reduction of CO_2 emissions. Implementation of BECCS in Swedish industries is also estimated to contribute to reaching the net-zero emissions by 2045.[8] The energy required for capturing and compressing the CO_2 could potentially be supplied by the excess energy produced at the mill.[15] However since BECCS is an energy-intensive process it will increase the energy demand of pulp and paper mills at the same time as being costly to implement. These plants often work as energy exporters by burning by-products as well as waste from the plant. The implementation of BECCS to the plant could lead to a higher energy demand for the plant and then importing energy might instead become necessary. By disregarding the possibility of export of energy from a pulp mill, between 30-90

% of the emitted CO_2 could be captured using only the on-site produced energy.[2] Due to the increased demand for energy at the mill, the demand for biomass to burn for the extra required energy demand will then also increase. This could eventually affect the total supply of biomass, opening up the question of whether we should be leaving the forest as it is or using it as biomass for BECCS. However, the total amount of forest in Sweden has increased over the last years, therefore, sustainable use of the biomass from the forest could be possible. It should then also be noted that the fuel used for energy generation from biomass is usually residues and waste from handling of the wood.[17] It is also likely that BECCS would be costly for pulp and paper plants to implement since there are several diluted point sources of CO_2 emissions from the plant. This complex configuration, compared to one larger more concentrated point-source, will cost more to enforce while requiring more energy. When considering BECCS as a process to reach negative emissions it is also necessary to apply a cradle-to-grave perspective to make sure all emissions are accounted for. Thereby also considering the eventual emissions from the preparation of the biomass as well as the transportation to final storage. If those sectors were to emit more CO_2 than what is captured using BECCS, it can not in the end be considered negative emissions.[2]

An example of implementing CCS (BECCS) at an existing pulp and paper plant was done for two plants in Finland, one Kraft pulp mill and one integrated pulp and board mill.[4] In these particular plants, the emissions from the recovery boiler, multi-fuel boiler and the lime kiln were considered. Different scenarios were investigated regarding the energy consumption of the plants as well as the implementation of a CCS unit. The evaluated case used a post-combustion CCS with MEA-based separation process at both the stand-alone pulp mill and the integrated mill with assumed capture of 90 % of the emitted CO_2. The flue gasses from the different sources of emission were also assumed to be mixed before capturing the CO_2, therefore, not considering capture from the streams individually. For the case with the stand-alone pulp mill, the excess steam generated on-site would be sufficient to generate the energy required to run the CCS unit. The largest amount of steam would be required for capturing the CO_2 emitted from the recovery boiler since this is the largest source of emissions out of the three that were considered. Moreover, for the integrated pulp and board mill, which consumes more energy for production, an auxiliary boiler would be needed to reach up to 90 % capture. The possibilities for retrofitting CCS to a pulp and paper mill will also be case-specific and aspects such as the amount of CO_2 as well as excess steam should be taken into consideration.[4] An economic feasibility study was also performed for the example. This showed that without any economic incentives for the owners to reduce the emissions the implementation of a CCS plant retrofitted to a pulp mill will not be economically feasible. As of today, there are no taxes on biogenic CO_2 emissions since these are considered neutral. However, there is also no credit for negative emissions whereas, there would be an increased cost for retrofitting CCS to the plant. To compensate for the cost of implementing CCS, 60-70 €/t CO_2 as a negative emissions credit is needed for the stand-alone Kraft pulp mill and even higher for an integrated mill. However, the cost of CO_2 avoided could be decreased by the co-production of chemicals such as H_2 or methanol.[15]

2.4   Chemical Looping Technologies

The methods mentioned above for capturing CO_2 require a large amount of energy, so finding an alternative solution is desirable. One possible route to take is finding another, less energy-intensive way to supply the O_2 for combustion of the fuel, to generate a process similar to oxyfuel-combustion. Separation and capture of CO_2 while using pure O_2 in the process can be achieved in another way, namely, chemical looping. With Chemical Looping Processes (CLPs) the O_2 for the combustion reaction is supplied in the form of metal oxides that act as Oxygen Carrier (OC). The process usually takes place in a two-reactor system. The metals are oxidized in an Air Reactor (AR) using air and after supplying the O_2 to the Fuel Reactor (FR) they are reduced and can be re-oxidized, in a circulating manner, as shown in Figure 3.[5] Using this technology, no additional step of O_2 separation from the air is required as is the case for the oxyfuel-combustion. Moreover, the temperature of the process can be noticeably lower for the chemical looping than for the oxyfuel process.[3] Another advantage of using CLPs is that the air is never in contact with the fuel and therefore the produced gas after the reaction is not containing any N_2. Hence, the fuel only reacts with O_2. CLPs has a low energy penalty since it inherently separates CO_2. The oxidation of the metal used as OC is exothermic and the heat generated in the AR can be used to drive the reaction in the FR. Furthermore, it has the potential for cost reduction for CCS technologies and the CO_2 avoidance cost is estimated to be lower than for other CCS processes. This is partly due to reduced electricity cost as well as the possibility to produce steam for electricity, H_2 or other valuable products from the process. Overall, the CLPs show great prospect for CO_2 separation for transport and storage with regard to the low energy penalty associated with it.[10]
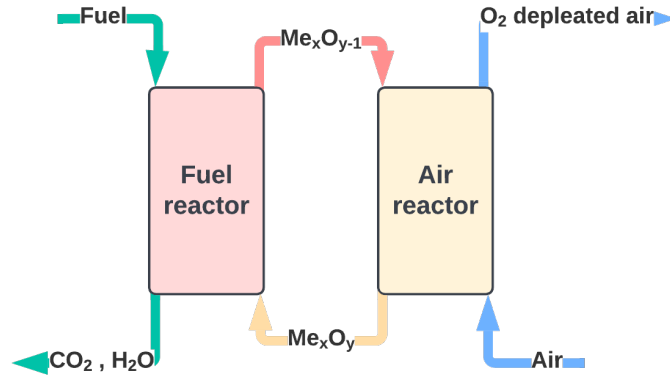

Figure 3: Simplified schematic showing the basic concept of CLPs. Figure remade from [10].

There are several different technologies regarding CLPs as well as versatile choices of fuel. The process can be customized for gaseous, liquid or solid fuels. Two of the main processes using solid fuel, such

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as biomass, are Chemical Looping Combustion (CLC) and Chemical Looping Gasification (CLG). Depending on the desired end products from the process, different design conditions, configurations of the reactors, OCs and source of biomass can be used in the CLPs.[10] For CLPs the most common reactor setup consists of a two-reactor system, however, a three-reactor system is usually used when H_2 is one of the desired products. For the three-reactor setup, the third reactor is usually a steam reactor where the syngas is produced. Depending on the wanted outcome of the process even more complicated reactor setups can be designed.[18] Moreover, different reactor types can also be used, fluidizing bed reactors, moving bed reactors or packed bed to mention some. Factors such as the reactivity of the OC or the scale of the process can determine the best reactor set-up to be used. There are many aspects to consider when designing the system, for the generation of heat and electricity, for example, woody biomass is a suitable choice while sewage sludge or algae is not preferred due to the high moisture content in these fuels. However, for H_2 production both options are possible fuels, the fuels with higher moisture will in the gasification reaction supply water to increase the yield of H_2. Generally, the CLC process is the preferred one for heat/electricity generation while CLG is considered for the production of syngas or H_2.[10]

The main challenge and cornerstone in the CLPs is finding suitable OCs. The OC could consist of a binary oxide such as copper, nickel, iron or manganese. It should be able to transfer bulk O_2 rapidly and have a high reactivity both to the O_2 and the fuel at the same time as it should withstand the conditions required for combustion as well as have a resistance to being reduced and oxidized various times.[19] For the OCs it is possible to use natural minerals but also synthetic carriers can be used.[10] Using a supporting material together with the oxygen carrier could increase the reactivity of the OC. The supporting material should be inert and be able to withstand high temperatures. The knowledge about OC is more widely spread regarding CLC in contrast to CLG. To use the same materials in both processes could show to be a problem since the more reducing environment during CLG could impact the performance of the metals and more research on appropriate OC for the CLG process is necessary.[20] However, one material found suitable for use in CLG is NiO, the material has a high capability for oxygen transfer as well as reactivity for both the reduction and oxidation reaction.[21] Other important design conditions regarding chemical looping technologies include temperature, steam-to-biomass ratio (S/B) and oxygen-to-fuel ratio (λ).[22] In CLG, steam is used as the gasifying agent, therefore, the S/B ratio is important to see the amount of steam per weight of dry biomass fuel that is required.[20] The oxygen-to-fuel ratio is defined as the amount of O_2 that actually reacts in the reactor with respect to the stoichiometric amount that would be required to reach total combustion.[22]

The flue gasses from a CLPs have a significant thermal energy value and therefore have great potential for energy recovery. Moreover, the gas needs to be cooled down and liquefied for transportation to storage. It is therefore important to integrate an efficient energy conversion into the process to recover the energy within the system.[12] The energy required in the FR for the endothermic reactions can be

supplied from the hot metal OC transported from the exothermic AR. This would then avoid the need for adding external heat to the process. The amount of heat generated from the AR is related to the amount of O_2 transferred from it to the FR. It is, therefore, necessary to find the optimal conditions to design in an auto-thermal state.[22]

2.4.1   Chemical Looping Combustion

During the Chemical Looping Combustion (CLC) process, a metal oxide working as an OC, transfers the necessary amount of O_2 to the combustion reaction. As mentioned previously, the CLC process usually consists of a two-reactor setup with one AR and one FR. In the AR the metal is oxidized with air and then sent to the FR. There, the fuel is combusted with the O_2 delivered from the OC, which is reduced. The OC is re-oxidized and the OC is circulated between the two reactors to continuously deliver O_2 to the combustion reaction.[10] As mentioned before, there is no N_2 present in the fuel reactor, the flue gas from the combustion reaction in the FR will therefore consist mainly of CO_2 and H_2O. The H_2O is in the form of steam and can then be separated by lowering the temperature and condensing the steam. Therefore, the separation and capture of the CO_2 is relatively easy to handle.[3]

The CLC process is highly fuel flexible and can be conducted with gaseous, liquid or solid fuels. Gaseous fuel is the most easily used since the gas can be injected and act as a fluidizing agent while reacting with the solid OC. In the same manner, liquid fuels can be introduced directly to the reactor.[19] However, there is one problem specifically regarding the use of solid fuels in the CLC process, the solid-solid contact between the solid fuel and the OC. To deal with this problem one solution is the direct gasification in the FR. The solid fuel is then gasified within the FR and the produced syngas reacts with the solid OC for the combustion reaction. During the combustion of the syngas, it is transformed to CO_2 and H_2O. A small part of the flue gas is then recirculated back into the FR again to act as gasifying agent for further reactions. This sort of CLC process is called in situ Gasification Chemical Looping Combustion (iG-CLC).[23] Another option for handling the problem with solid-solid interactions is using special OCs with the ability to release gaseous O_2 inside the FR, these OCs are called Chemical Looping Oxygen Uncoupling (CLOU).[23] When using CLOU the solid fuel is reacting directly with gaseous O_2 that is un-coupled from the metal in the FR and the reaction taking place is similar to the combustion with air. The benefit of this is that the reaction is taking place in the absence of N_2 and it will generate non-diluted flue gases.[10]

2.4.2   Chemical Looping Gasification

Looking at the CLG process instead, the fuel is gasified instead of combusted when in contact with the metal oxide material in the FR. The reduced OC is then oxidized in the AR in the same manner as for CLC. However, in this process, the goal is to partially oxidize the fuel and not to fully combust it, like for the CLC process.[19] In gasification, which is a thermo-chemical process, the carbon-containing fuel is converted to combustible synthesis gas at high temperatures. The syngas produced is usually

containing, CO, CO_2, H_2O and H_2.[18] The gasification process shows great characteristics to produce high-quality syngas, however, the technology used today has the problem of high energy demand for generating the high purity O_2 required to produce a high-quality syngas.[21] CLG with biomass as fuel shares the potentials of biomass gasification to reduce CO_2 emissions but without the gas separation of air which is energy-intensive.[10]

Most of the reactions taking place within the FR are endothermic and therefore, the process requires a large amount of energy. However, this can then be supplied by the highly exothermic reactions in the AR and transferred to the FR by the hot OC.[7] To succeed with the production of syngas it is required for the oxygen delivered by the OC to be below the stoichiometric amount to not achieve complete combustion.[10] This means the oxygen-to-fuel ratio (λ) needs to be below 1 to not achieve complete combustion.[22] Therefore, the transport of O_2 to the fuel reactor has to be moderated, which can be controlled by the amounts of carrier material used in the system.[19] However, at the same time, the system must have an adequate amount of O_2 transferred for the process to be auto-thermal and not in need of an external energy source. Meaning the degree of combustion has to be optimized for both product yield and to keep the process auto-thermal. The CLG process can be used for solid fuels if the desired product from the chemical looping is H_2 or syngas for further use. Other fuels, such as gases or liquids, are also possible but the process is then referred to as CLR. Syngas as a product from CLG will have a higher heating value since the gas will not be diluted with the N_2 from the air.[10] High-quality syngas could for example be used for the production of fuel through the Fisher-Tropsch process.[22]

If H_2 is the required product, the syngas produced within the FR can be sent to a WGS reactor to convert the CO and H_2O to CO_2 and H_2, to maximize the yield of H_2. A pre-combustion method for capturing the CO_2 should be implemented and the H_2 gas can be separated using a PSA unit.[10] The PSA unit has the possibility to recover 99.99 % pure H_2, however, only up to 85 % of the H_2 can be recovered and the rest is mixed with the off-gasses.[24] These off-gasses consist mainly of CO_2 and H_2, but also un-reacted CO and CH_4.[25] One possibility for the recovery of pure CO_2, for capture, is using the off-gasses from the PSA for combustion and form a purer CO_2 stream. The combustion of residual H_2 would also generate steam. The steam can be condensed to separate it from the CO_2, which can then be captured. This would make it possible to recover heat from the hot stream as well as ease the separation of the CO_2.[24]

It has been shown that the oxygen-to-fuel ratio (λ) has one of the largest impacts on the results from CLG. For a study using a two-reactor system with pine sawdust as fuel, a synthetic iron-based OC, temperature of 940 °C as well as the steam-to-biomass ratio (S/B) of 0.6, the increase of λ was investigated. It was shown that an increase from λ=0.21 to 0.58 generated an increase in both CO_2 and H_2O generation and a decrease in CO and H_2. Both the amount of CO and H_2 were halved and this is due to the higher O_2 content in the fuel reactor, driving the process towards a higher degree of

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combustion. It was found that a value of 0.3 for λ is required for the process to be auto-thermal, with this oxygen-to-fuel ratio, 37 vol% H_2, 21 vol% CO and 34 vol% CO_2 could be achieved. The same study showed that an increase in the S/B ratio would yield a higher H_2 content in the produced gas, and CO_2 content would also increase while CO decreased.[20] Another study investigated a process using a Ni-based OC and biomass in the form of rice straw.[21] In this experiment, NiO was used together with silica sand as the bed material to help transport heat to the FR. It was shown that a minimum amount of NiO content at 20 wt% is required to generate a stable temperature for the gasification reactor. However, the amount of OC also affected the syngas yield negatively, increasing the NiO content in the reactor generated a lower yield. Therefore, a NiO content of 30 wt% was deemed optimal for syngas production. As mentioned before, this study also showed that an increase in S/B ratio generated a higher syngas yield as well as a higher H_2 content in the produced gas. Lastly, it also showed that for temperatures over 750 °C a decrease in H_2 concentrations could be noticed due to the WGS equilibrium reaction being favoured for the generation of CO and H_2O.[21]

3 Process Description

This section will present the different steps of the proposed process in detail. The conditions of the different units as well as the reactions taking place will be presented.

3.1 Chemical Looping Gasification Process

The proposed process for this thesis is a Chemical Looping Gasification (CLG) process composed of a three-reactor system for capture of CO_2 as well as production of H_2 and recovery of energy in the form of electricity. The proposed process is meant to be able to replace the multi-fuel boiler for energy generation at a pulp and paper mill while simultaneously producing H_2 and capturing the CO_2 from the gasification of biomass without any additional energy having to be added to the system. The system, as can be seen in Figure 4, is consisting of an Air Reactor (AR), Fuel Reactor (FR) and Reduction Reactor (RR) combined with Water Gas Shift (WGS) and a Pressure Swing Adsorption (PSA) unit. A metal Oxygen Carrier (OC) is circulated between the three reactors supplying O_2 to the reactions. The fuel for the process is woody biomass residue from a pulp mill and the OC used is Ni/NiO. The desired products from the process are the captured CO_2, recovered heat from hot streams for steam generation as well as a pure stream of H_2.
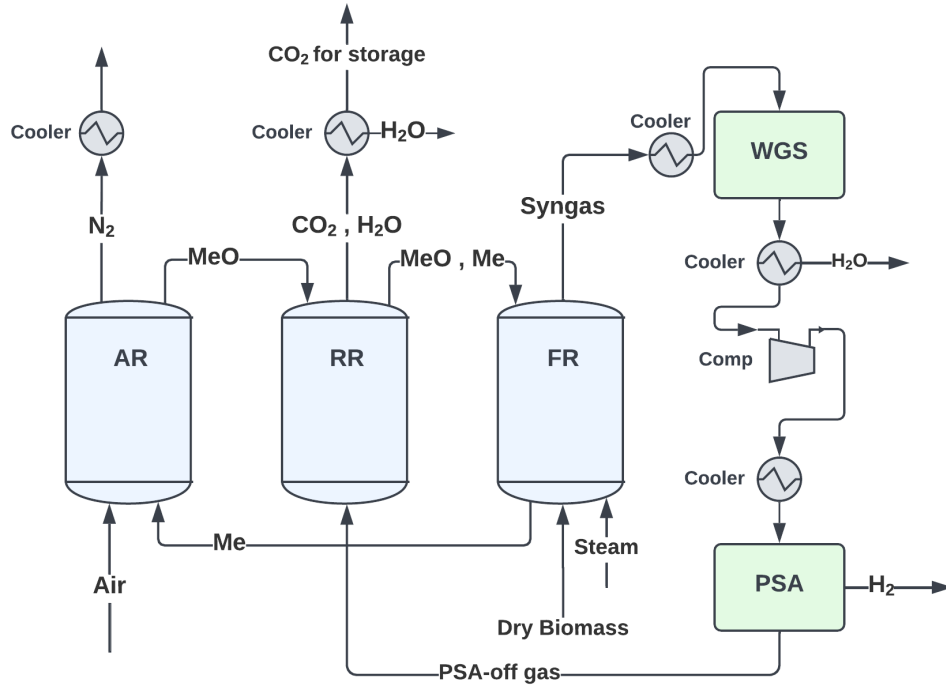

Figure 4: Simplified process scheme of the proposed process of CLG.

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3.1.1 Air reactor

Looking at the AR firstly, where the metal is oxidized to a metal oxide using air. The air enters the reactor with the use of a blower at ambient temperature and pressure while the reduced metal entering the reactor is at a temperature of 850 °C. The air and metal are entering the reactor at a ratio to maintain the AR temperature at the same time as ensuring that the system is designed in an auto-thermal manner. The O_2 in air is separated by oxidizing the metal OC, as can be seen from reaction 1[10]. For this specific process, the metal used is Ni and the reaction taking place can be seen as reaction 2 below. The hot N_2 stream from the separation of air is sent through a cooler where the energy is recovered, the cold stream can then be vented. The oxidation of the Ni OC is an exothermic reaction and heat is produced within the AR which will lead to an increase in the temperature of the metal. The hot OC leaves the AR at an elevated temperature and is transferred to the RR.

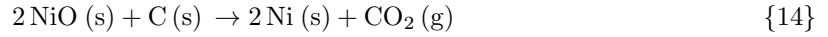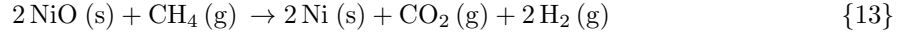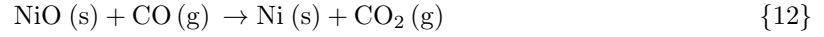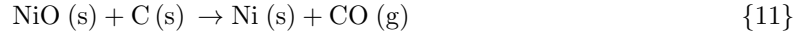$$2\,Me_xO_{y-1} + O_2 \rightarrow 2\,Me_xO_y \qquad\qquad \{1\}$$

$$2\,Ni\,(s) + O_2\,(g) \rightarrow 2\,NiO\,(s) \qquad\qquad \{2\}$$

3.1.2 Reduction reactor

Within the RR, a combustion reaction is taking place. The oxidized metal leaving the AR enters the RR to provide O_2 to the combustion of PSA off-gases, consisting of CO_2, CO and H_2. The CO and H_2 both react with the oxygen in the OC according to reaction 3 to form the combustion products, consisting of H_2O as well as CO_2. The outlet stream from the RR consists of all the emitted CO_2 leaving the system. By condensation of the steam, the CO_2 can be separated and sent to storage and the heat from the hot stream can be recovered. Only part of the NiO is consumed and reduced during the combustion in the RR and since not all the OC is reduced there is a mixture of metal and metal oxide leaving the RR and is transferred to the FR.

$$2\,NiO\,(s) + H_2\,(g) + CO\,(g) \rightarrow 2\,Ni\,(s) + CO_2\,(g) + H_2O\,(g) \qquad\qquad \{3\}$$
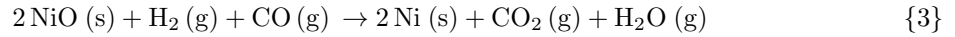
3.1.3 Fuel reactor

In the FR, the OC is used to provide oxygen to the gasification of biomass, which is performed at a temperature of 850 °C. Before the biomass enters the FR it is dried to reduce the moisture content. The NiO is reduced back to Ni while the biomass is being gasified. Besides the OC, 2 bar steam generated from a steam cycle within the system is added as a gasifying agent as well as to increase 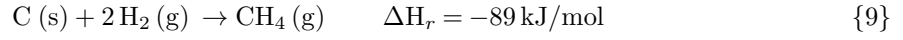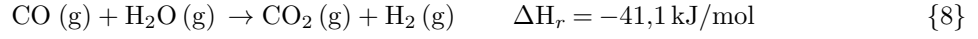the H_2 yield in the produced gas. There are multiple reactions taking place in the FR, as seen in reactions 4-11. The first one being the devolatilization of biomass, reaction 4 where the biomass transforms into char, tar and volatiles (CO_2, H_2O, H_2, CO and CH_4.[20] Furthermore, the char will react to form syngas according to reactions 5-6[20] as well as reaction 9[12] while the volatiles are reacting according

to reactions 7 and 8[20]. The desired product leaving the reactor is syngas, consisting of CO_2, CO, H_2 and H_2O.

$$\text{Biomass} \rightarrow \text{Char} + \text{Tar} + \text{Volatiles}\,(CO_2, H_2O, H_2, CO, CH_4) \qquad \Delta H_r > 0 \qquad \{4\}$$

$$C\,(s) + H_2O\,(g) \rightarrow CO\,(g) + H_2\,(g) \qquad \Delta H_r = 131{,}3\,\text{kJ/mol} \qquad \{5\}$$

$$C\,(s) + CO_2\,(g) \rightarrow 2\,CO\,(g) \qquad \Delta H_r = 172{,}4\,\text{kJ/mol} \qquad \{6\}$$

$$CH_4\,(g) + H_2O\,(g) \rightarrow CO\,(g) + 3\,H_2\,(g) \qquad \Delta H_r = 206{,}1\,\text{kJ/mol} \qquad \{7\}$$

$$CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g) \qquad \Delta H_r = -41{,}1\,\text{kJ/mol} \qquad \{8\}$$

$$C\,(s) + 2\,H_2\,(g) \rightarrow CH_4\,(g) \qquad \Delta H_r = -89\,\text{kJ/mol} \qquad \{9\}$$

$$NiO\,(s) + CH_4\,(g) \rightarrow Ni\,(s) + CO\,(g) + 2\,H_2\,(g) \qquad \{10\}$$

$$NiO\,(s) + C\,(s) \rightarrow Ni\,(s) + CO\,(g) \qquad \{11\}$$

$$NiO\,(s) + CO\,(g) \rightarrow Ni\,(s) + CO_2\,(g) \qquad \{12\}$$

$$2\,NiO\,(s) + CH_4\,(g) \rightarrow 2\,Ni\,(s) + CO_2\,(g) + 2\,H_2\,(g) \qquad \{13\}$$

$$2\,NiO\,(s) + C\,(s) \rightarrow 2\,Ni\,(s) + CO_2\,(g) \qquad \{14\}$$
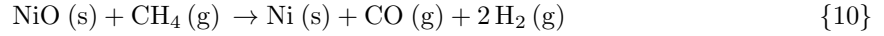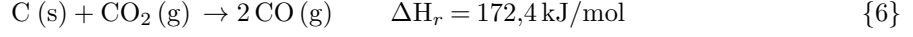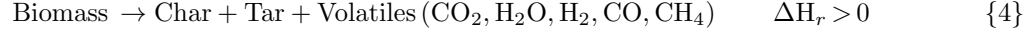
As can be seen from reactions 4-9, both exothermic and endothermic reactions take place during the gasification, however, the net reaction in the reactor will be endothermic.[20, 12] During the gasification all the NiO is reduced back to Ni, as seen in reactions 10-14. Then the reduced OC is sent back to the AR to be oxidized by air to be regenerated and used further in the process. Syngas, on the other hand, is sent to a heat exchanger to be cooled down to 200 °C. The energy from the hot stream is recovered before the syngas continues to the WGS unit to increase the composition of H_2 in the gas.

3.1.4   Water Gas Shift (WGS) and Pressure Swing Adsorption (PSA)

Within the WGS, which is designed as a low temperature WGS at 200 °C, the CO and H_2O are reacting to form CO_2 and H_2 to increase the H_2 yield from the system, according to reaction 15[20]. Due to the exothermic nature of the WGS reaction, the stream leaving the WGS will have an increased temperature and needs to be cooled down once again. This time it is cooled to 25 °C and within the cooler, the residual un-reacted water remaining after the WGS reaction is condensed and separated. The heat recovered during the cooling of the gas is used to generate 5 bar steam within the steam cycle unit seen in Figure 5. The gas, now containing mainly CO_2, H_2 and low amounts of CO, is then sent through a compressor working at a polytropic efficiency of 85 % and is pressurized to 20 bar. During pressurization, the temperature increases and therefore, the pressurized gas is once again in need of cooling down to 25 °C. Next, the pressurized gas mixture is sent through the PSA unit to separate pure H_2 from the mixture of gases. High-pressure H_2 is retrieved from the PSA with a separation efficiency of 85 % of the H_2 and the un-separated residue is leaving the PSA with the rest of the off-gases. The PSA off-gases consist of CO_2, residual H_2 as well as un-reacted CO from the WGS and leaves the PSA at atmospheric pressure and 25 °C. The off-gases are then all sent to the RR for combustion and the final separation of CO_2.

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g) \qquad \Delta H_r = -41{,}1\,\text{kJ/mol} \qquad \{15\}$$

3.1.5   Steam generation

There are four hot streams where energy can be recovered from the system. The hot N_2 stream leaving the AR, the hot syngas stream leaving the FR, the stream of syngas leaving the WGS and lastly the hot stream consisting of mainly CO_2 and steam leaving the RR, as can all be seen in Figure 5.
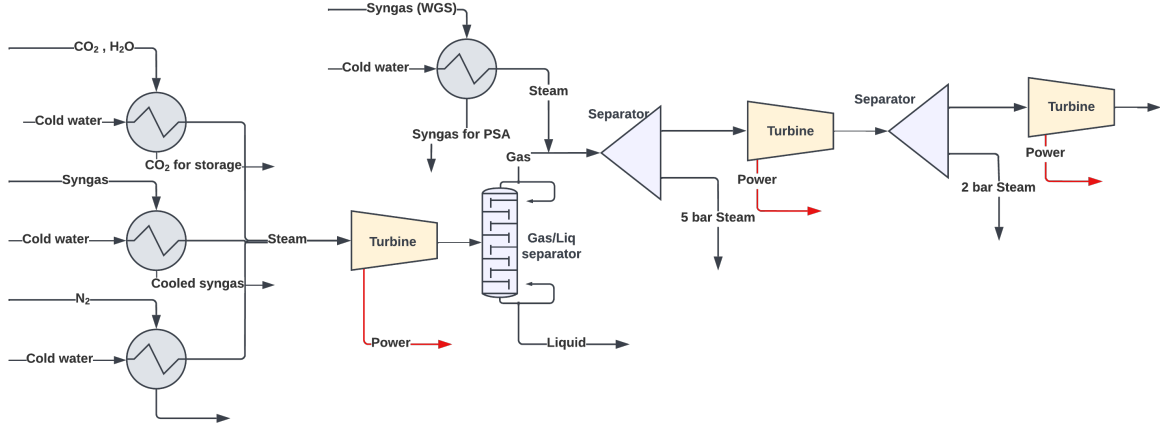

Figure 5: Simplified process scheme of the steam cycle.

Three of these streams, the N_2, FR syngas as well as the RR flu-gas are all cooled down using heat exchangers that are fed with 35 °C water at 92,2 bar (to account for the pressure drop). The syngas is to be cooled down to 200 °C for further use in the WGS as mentioned above. The other two streams, containing N_2 and CO_2 and H_2O mixture are both cooled down further. The steam from the three heat exchangers, now at a pressure of 92 bar, is then mixed before it is sent to a turbine. For the first turbine in the system, the pressure is lowered to 5 bar. From the turbine, energy is generated and recovered, as seen by the red arrows in Figure 5. The stream leaving the WGS is cooled using 36 °cooling water at 5 bar to generate additional 5 bar steam. The steam is then added to the same stream as the steam from the other sources, see Figure 5.

Next, the liquid fraction of the stream is separated and the gaseous part is sent to a separator. In the separator, the 5 bar steam can be separated for potential use. One possible area of use is utilizing it in a post-combustion unit using MEA for CO_2 capture of the remaining emissions generated at a pulp mill, namely, the recovery boiler as well as the lime kiln. The steam not used for additional CO_2 capture is sent through another turbine, this time to be lowered to 2 bar. Part of the 2 bar steam is recovered and sent back to the FR to be utilized as a gasifying agent in the reaction. The energy generated from the 2 bar turbine is recovered. Lastly, any residual steam left is sent through the last turbine where the pressure is set to 0,06 bar and the energy generated from the turbine is once more recovered. The energy generated within the steam cycle can be utilized in other parts of the process, such as for the compressing of the CO_2, CO and H_2 mixture prior to the PSA unit and for driving the blower used to transport the air into the AR.

A three-reactor system with the addition of a combustion step for the PSA-off-gases has previously been investigated for natural gas.[24] However, the analysis of the proposed process for a CLG system with an RR which is fueled with biomass, as in this project, is not explored to the same degree. The implementation of this process in a pulp and paper mill is also considered a novelty of this project.

3.1.6 Chemical looping combustion vs gasification

Another process was also considered, as a comparison to the CLG process. This process is instead based on the CLC process. The system is based on the same setup as for the principal system in the project, with an AR and a FR, however, without the RR, see Figure 6. In the same manner as for the CLG process, the air and metal are delivered to the AR for oxidation of the metal. However, the ratio between air and metal is varied to promote a combustion reaction taking place rather than the gasification reaction desired for the main process. The metal is oxidized and sent to the FR where the biomass is combusted and the OC is reduced. The flue-gas from the FR will for this process consist of mainly CO_2 and H_2O, which is then cooled down to condense out the water and to prepare the CO_2 for capture. Furthermore, from this suggested process there are only two streams where it is possible to recover heat, the hot N_2 stream leaving the AR as well as the CO_2 and H_2O stream leaving the FR. These are sent to the steam cycle unit which have the same design conditions as the system

mentioned above. However, no 2 bar steam is required as gasifying agent for the FR, therefore, more steam can be used for energy conversion into electricity in a steam turbine.
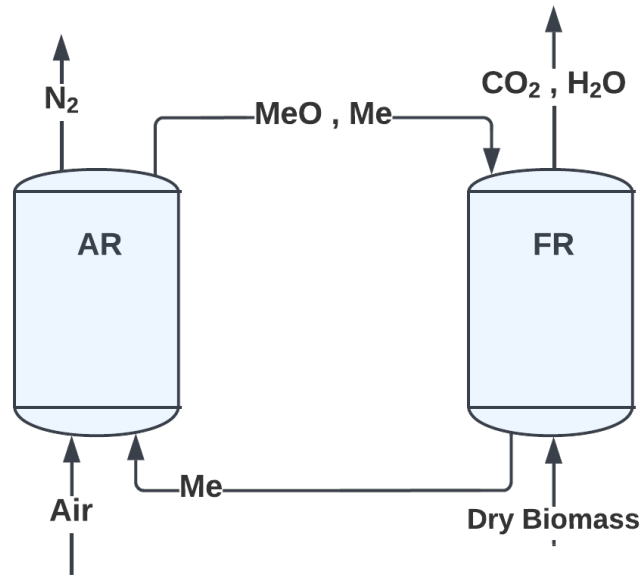

Figure 6: Simplified process scheme of the CLC process used for comparison to the CLG system.

4 Methodology

The methodology section of the report will go through how the project was conducted. It includes the methodology as well as the assumptions considered for the analysis. It will also go through how the process models/simulations were developed.

4.1 Mass and Energy balance

The first step in order to solve the questions of the project was to perform a mass balance. This was conducted on the basis of 100 kg biomass/h being sent into the system. The biomass composition was taken from literature [26] and the molar flows of the biomass components entering the system were calculated. Looking at the different units of the system seen in Figure 4, atom balances were produced for all the elements present in the various units, according to equation 1, where n_i is the number of moles of component i entering or leaving the units. Values of oxygen-to-fuel ratio (λ) and steam-to-biomass ratio (S/B) were taken from the literature [20] and integrated into the calculations. From this, the molar flows of all the streams within the system were calculated. The results from the mass balance were then used as input for the following simulations of the energy balances for the process. Note, however, that these values were used as a guideline for the inputs to the simulations performed and were later varied to satisfy the conditions of the system.

$$n_i(in) = n_i(out) \tag{1}$$

The energy required for the drying of biomass was not considered within the simulations and therefore the amount of heat required for the drying was calculated separately, using equation 2.

$$\Delta Q_{drying} = (mC_p\Delta T)_{biomass} + (mC_p\Delta T)_{water} + (m\Delta H_{vap})_{water} \tag{2}$$

Where ΔQ is the heat required to add to the system [kJ], m is the mass [kg], C_p is the specific heat capacity [kJ/kg K], ΔT is the temperature difference [K] and ΔH_{vap} is the heat of vaporization [kJ/kg].

Since the calculations in this work were all made based on 100 kg dry biomass/h entering the system, the units were later converted to be applicable for a reference pulp mill. This was done by using values of emissions from Onarheim [4] to back-calculate the amount of dry biomass required to produce 1 air dried tonne (adt) of pulp. Using this, all the results obtained were converted to the unit of per adt of pulp produced.

4.2   Process medelling

The next step of the project was to conduct an energy balance over the entire system using process models. Most of the process models of the proposed process were conducted using Aspen Plus, however, Aspen HYSYS was also used for part of the system simulations. The part of the process simulated using Aspen Plus included the AR, RR, FR, WGS and the PSA unit. The gasification reaction taking place in the FR was simulated using the Peng-Robinson with Boston-Mathias method while the AR, RR, WGS and the PSA were all simulated using the Predictive Redlich-Kwong-Soave equation-of-state method. All the simulations regarding the proposed process were conducted for four different temperatures of the AR, 900, 1000, 1100 and 1200 °C. Process flowsheets of all the simulations can be found in the Appendix in section 7.1.

For the process model of the gasification of biomass (FR), the simulation used was remade from a previously made study [26], however, the relevant steps for the suggested process for this project were added to the existing process flow sheet. In this model, the first step was to transform the non-conventional biomass into its smaller components, this was done using an RYield reactor in Aspen Plus. The biomass compositions used in the simulations are found in Table 2. Next, the components were sent to the gasification reactor, which was simulated using an RGibbs reactor where the biomass components are reacted with the OC and steam. The composition of the produced syngas from the FR was then used as input in the other simulation sheet for reaction within the WGS reactor.

Table 2: Biomass composition used for simulations. Taken from [26]

Ultimate analysis (dry basis)	wt%	Source
C	51,19	[27]
H	6,08	[27]
O	41,3	[27]
N	0,2	[27]
S	0,02	[27]
Cl	0,05	[27]
Ash	1,16	[27]
Proximate analysis (dry basis)		
Volatile matter	80	[28]
Fixed carbon	18,84	[26]
Ash	1,16	[27]
Moisture	20	[29]

The AR was simulated as an RGibbs reactor at atmospheric pressure and the heat duty was set to 0, no heat left the system meaning it works adiabatic. The inlet streams of Ni and air were both varied to that the outlet temperature of the NiO leaving the reactor would be at the desired temperatures of 900, 1000, 1100 and 1200 °C. Next, the RR was also simulated using an RGibbs reactor in the same

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manner as the AR. The amount of Ni/NiO leaving the RR was used as input for the simulation of the FR. For the WGS reactor an REquil reactor was used and the WGS reaction (see reaction 15) was specified as an equilibrium reaction. The compressor used was a polytropic compressor using ASME with a polytropic efficiency of 85 % .[30] The PSA unit was simulated as a black box with the yield of separation of H_2 being specified using an equation from [24]. Any cooling in the system was done using heat exchangers. Since this system, as previously seen in Figure 4, was simulated in two different Aspen files, one for the FR and one for the remaining reactors, the results from one model were used as input in the other. To get more accurate results, the process models were run various times while continuously updating the input values for both models until the results reach a constant value.

Moreover, the steam cycle was instead simulated using Aspen HYSYS, with the Peng-Robinson method being applied. Firstly, heat exchangers were used for any cooling of gasses, and turbines were used to lower the pressure and generate electricity, all with a polytropic efficiency of 80 % .[24] Separators were used to separate the vapour and liquid phases from each other and to separate any steam used elsewhere.

To decide the net electricity generation of the system the electricity used within the system was subtracted from the electricity generated from the steam cycle. The electricity used within the system is considered as the amount needed to blow the air into the AR as well as the electricity required to run the compressor used for compressing syngas before the PSA unit. The required electricity was calculated for all the different temperature cases considered in the simulation trials and from that the net electricity generation could be decided.

4.2.1 Sensitivity

A sensitivity analysis was performed as following.

- How much electricity that can be produced from the steam cycle was investigated by varying the amount of steam sent for use in the additional post-combustion MEA capture process. This was achieved by alternating the amount of 5 bar steam retrieved from the steam cycle from 0 % to 100 % . This was done after determining how much 2 bar steam was required for the FR and then calculated based on the residual steam. For every temperature of the AR (900, 1000, 1100,1200 °C), the difference in the generated electricity amount was investigated.

- The impact of the amount of air used in the AR relative to the amount of metal used was also investigated. For a constant metal flow, the airflow was both increased and decreased by 25 % to see the effect of the ratio between metal and air entering the system. For both cases, the impact of temperature within the AR, as well as the design conditions of the system and the composition of the produced gas, was investigated.

- Simulation models of the process were altered and used for simulations of a combustion reaction instead. For this trial the AR was designed in the same manner, the FR was altered to favour the combustion reaction while the RR, WGS and PSA were all removed. The steam cycle was designed in the same manner however no recovery of either 5 or 2 bar steam was considered. This was done to compare the suggested implementation of an CLG process to the implementation of an CLC process.

4.3 Limitations

- The only source of biomass considered was woody biomass.

- All results generated are based on Simulations made in Aspen Plus and Aspen HYSYS.

- No other method of capturing CO_2 from the multi-fuel boiler were considered other than CLG and CLC.

- Additional MEA-based capture was considered when recovering steam from the system.

- No indirect emissions were considered.

4.4 Assumptions

- The system is assumed to be at steady-state.

- The FR was only designed at 850 °C.

- The AR, RR and WGS were all assumed to have a heat duty of 0.

- All the carbon entering the system through the biomass was assumed to be converted to either CO_2 or CO, no char, tar or higher hydro-carbons was considered to be produced in the system.

- All N_2 is leaving the system and no contact between the fuel and the air occurs.

- The compressor working to compress the syngas gas before PSA is designed at a polytropic efficiency of 85 % . [30]

- All turbines in the steam cycle simulations are designed at a polytropic efficiency of 80 % . [24]

- The PSA unit separated 85 % of the H_2, calculated from formula from [24].

- The CO_2 emissions from the pulp mill in Onarheims article [4], are the same as for the suggested process in this report so that converting the unit to adt pulp could be done.

- Any deterioration of the metal was not considered.

4.5 Key Performance Indicators

There are three interesting Key Performance Indicator (KPI) considered for this project.

- CO_2 captured (kg CO_2/adt pulp)

- H_2 generated (kWh H_2/adt pulp)

- Net electricity generated (kWh/adt pulp)

The first two of these can be generated directly from the process models. However, the net electricity generation can be calculated using eq. 3, from the generated electricity from the steam cycle and the electricity required for the blower and compressor.

$$Net\ Electricity\ Generation = Electricity\ Generated - (Electricity_{Blower} + Electricity_{Compressor}) \quad (3)$$

With the knowledge of how much CO_2 has the possibility of being captured as well as how much the net electricity generation is, it is possible to compare with other CO_2 capture processes proposed for the pulp and paper industry.

5   Results & Discussion

This section of the report will go into the results of the project. Results from the different various simulations will be presented and discussed as well as the sensitivity analysis performed. The reference case of the simulation study was to investigate the performance and conditions of the CLG system for four temperatures of the AR. The temperatures tested were 900, 1000, 1100 and 1200 °C. For these four cases, the required inputs, as well as resulting outputs of the system, were determined.

Firstly, for the different reference cases, the inlet flows of air and metal were varied to generate the desired temperatures within the AR, this showed that an increased metal flow would generate a lower reactor temperature while an increased air flow would the generate a higher reactor temperature. The final amounts of air and metal used for the four base cases can be found in Table 3. Looking at Figure 7 it can be seen that the required amount of metal increases significantly when designing for a lower temperature within the AR. These values were chosen based on the desired temperatures of the AR as well as to make sure the system could be designed auto-thermal. The amount of metal to keep the system auto-thermal decreased at higher temperatures. Since the temperature of the metal entering the FR is higher for that case, less metal is required to keep the system auto-thermal. However, when lowering the design temperature in the AR, more metal is needed to transfer the required heat to the FR to keep the system auto-thermal. Having the system auto-thermal was assured by making sure the energy required for the decomposition reactor in the simulations was lower than the heat of the gasification reaction driven by the hot OC. The energy required for the decomposition of biomass was taken from the Aspen Plus simulation and was 352 kWh/adt, which is lower than all the Q_{FR} values seen in Table 3. Meaning that for the desired temperatures, the air and metal flows shown in Table 3 fulfil the condition of keeping the system auto-thermal.

Table 3: Inlet variables of the simulations for the four base cases examined in the project. Showing both metal into the AR as well as the FR.

T_{AR}	Me_{in}	Air_{in}	Me_{FR}	MeO_{FR}	Q_{FR}
°C	kg/adt	kmol/adt	kg/adt	kg/adt	kWh/adt
900	33 488	25	32 953	681,3	352,8
1000	11 024	26,6	10 438	745,7	356
1100	6552	28,3	5915,7	809,7	358,9
1200	4659	30	3972,9	873,3	361,9

It can be seen from Figure 7 that the amount of metal used in the system to keep it auto-thermal increases greatly when designed for lower oxidation temperatures, more metal is then required to transport heat to the reaction and is not acting as an OC. The required amount of air within the system increases to be able to reach the higher desired temperatures of the AR, as seen by Figure 8.
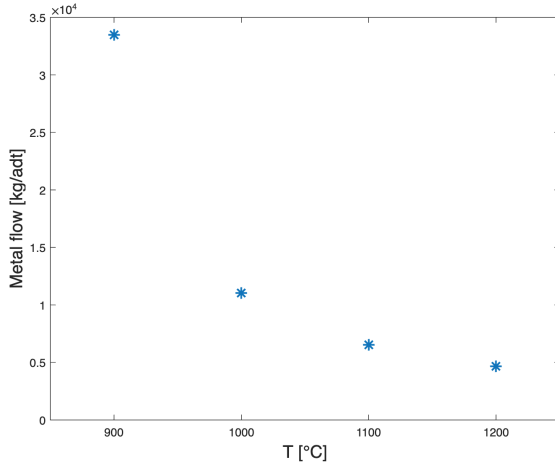
Figure 7: Amount of metal entering the AR for the different base case temperatures.
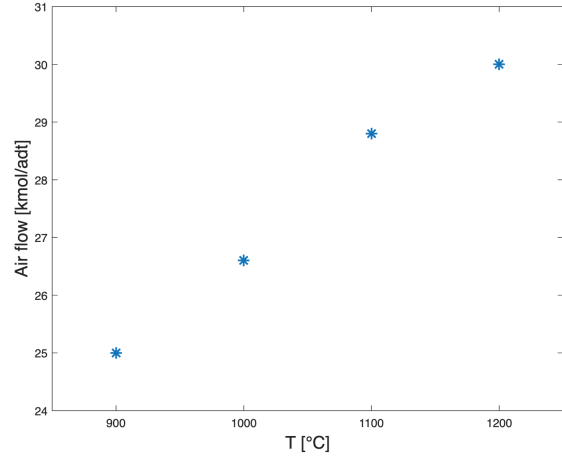

Figure 8: Amount of air entering the AR for the different base case temperatures.

Therefore, a higher O_2 content will be present in the AR, which leads to a larger part of the metal being oxidized. However, one goal of the process was also to produce H_2. A larger amount of metal being oxidized will in turn lead to a higher O_2 content in the FR. This will affect the composition of the syngas produced, as can be seen from Table 4. It can be seen from the composition that the H_2 and CO content decreases with an increased oxidation temperature, while the H_2O and CO_2 content increases. This can be seen more clearly in Figure 9. A higher conversion towards H_2O and CO_2, entails that there is a larger degree of combustion taking place within the FR, which is due to the amount of metal oxide increasing and more O_2 can react with the fuel.

Table 4: The composition of syngas for the four reference cases.

Compound	$\mathbf{T}_{AR}$			
mole %	900 °C	1000 °C	1100 °C	1200 °C
H_2O	0,525	0,545	0,565	0,584
CO_2	0,192	0,200	0,208	0,215
CO	0,080	0,072	0,065	0,057
H_2	0,202	0,183	0,163	0,144

Moreover, a higher temperature within the AR will generate higher temperatures in the RR as well as the FR and therefore higher temperatures of the different hot streams leaving the system. With a higher temperature of the streams being cooled down within the steam cycle a larger amount of steam can be generated. Table 5 shows the conditions of three of the streams used for steam generation. The fourth one is the syngas leaving the FR, which was designed at a temperature of 850 °C regardless of the AR temperature and which composition can be found in Table 4. Since the airflow is increased
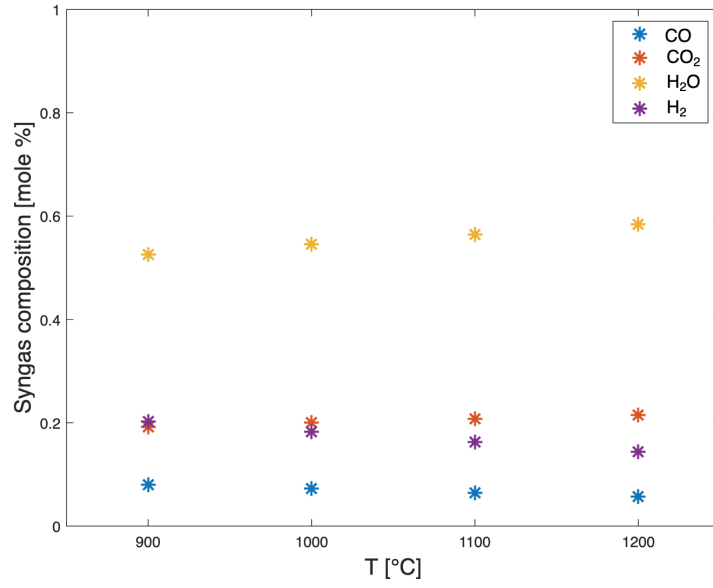
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Figure 9: Composition of the syngas produced for the four bases case temperatures.

to generate a higher oxidation reactor temperature, the flow of N_2 leaving the reactor will increase as well as the temperature of that stream, as seen from Table 5. As can be seen, the temperatures of the stream leaving the RR also increases with the increasing AR temperature.

Table 5: Input values for the steam cycle simulations with the composition of the streams.

	$\mathbf{T}_{AR}$	$\mathbf{T}_{stream}$	**CO**	**CO$_2$**	**H$_2$O**	**H$_2$**	**N$_2$**
	°C	*°C*	*mole %*	*mole %*	*mole %*	*mole %*	*kg/adt*
	900						
RR flu-gas		890	0,0055	0,8606	0,1332	0,0007	-
N$_2$		900	-	-	-	-	552,4
Syngas (leaving WGS)		285	2,85	373,9	255,2	17,8	-
	1000						
RR flu-gas		968	0,0071	0,8702	0,1221	0,0007	-
N$_2$		1000	-	-	-	-	589,2
Syngas (leaving WGS)		277	2,17	374,9	270,3	16,1	-
	1100						
RR flu-gas		1044	0,0086	0,8801	0,1107	0,0006	-
N$_2$		1100	-	-	-	-	626,0
Syngas (leaving WGS)		269	1,63	375,8	285,4	14,4	-
	1200						
RR flu-gas		1118	0,0101	0,8903	0,0991	0,0005	-
N$_2$		1200	-	-	-	-	662,9
Syngas (leaving WGS)		261	1,20	376,5	300,4	12,7	-

A higher temperature of the streams used for steam generation as well as an increased flow of N$_2$, entails a larger energy generation from the steam turbines, which can be noticed in Table 6 as well as Figure 11, showing the increasing electricity generation with increasing oxidation temperature. Table 6 below shows the results of the electricity generated from the steam cycle as well as the amount of H$_2$ generated and the CO$_2$ that can be captured. The energy outputs shown are with the assumptions that the required steam for the FR gasification is recovered, however, recovering steam for the hypothetical use within a post-combustion capture unit was not considered.

As seen previously, the highest H$_2$ generation is achieved for an AR temperature of 900 °C, which is shown clearly in Figure 10. This follows from the higher content of H$_2$ in the syngas which leads to more being possible to separate in the PSA unit. It can also be seen in Table 6 that the amount of CO$_2$ with the potential of being captured does not vary much for the different cases. The amount of CO$_2$ with the potential of being captured by implementing the CLG process instead of the multi-fuel boiler is almost 14 % of the total emissions generated from the reference mill.

Table 6: H_2 generated, CO_2 captured as well as the electricity generated from the steam cycle.

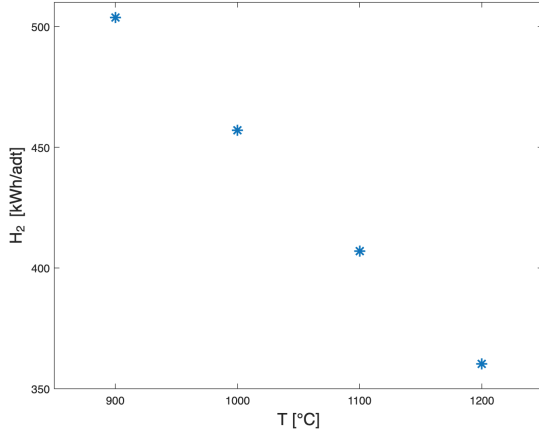| $\mathbf{T}_{AR}$	$\mathbf{H}_{2,sep}$	$\mathbf{H}_{2,sep}$	$\mathbf{CO_2}, sep$	**Electrical energy**
$°C$	kg/adt	kWh/adt	kg/adt	kWh/adt
900	15,1	503,7	375,9	174
1000	13,7	457,0	375,3	190
1100	12,2	407,0	374,7	207
1200	10,8	360,3	374,1	253

Figure 10: H_2 produced for different temperatures of the oxidation within the AR.
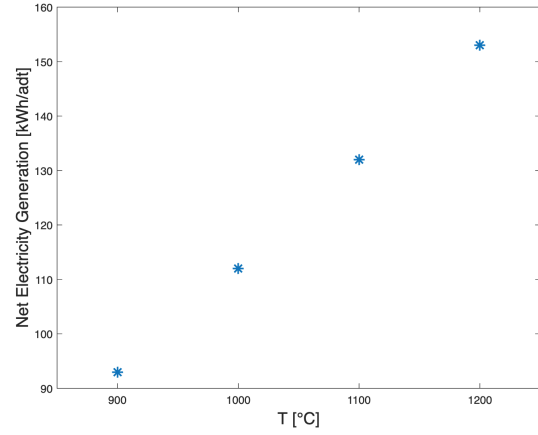

Figure 11: Net electricity generated for the four base cases considered.

Regarding the consumption of electricity, the considered areas were the compressor used to compress the syngas to 20 bar as well as the blower used to transfer the air into the AR. Out of the two, the largest amount was consumed by the compressor while a smaller part was consumed by the air blower. What can be noticed is that the amount of electricity required for compression of the syngas decreased with the increase of temperature, even though the gas is compressed at 25 °C in all cases. The reason for this can therefore be explained by the composition of the syngas leaving the WGS reactor, at the higher design temperatures the syngas contains a larger fraction of H_2O. In the cooler where the gas is cooled down to prepare for compressing that H_2O is condensed. Therefore, the total amount of gas being compressed is lower when being designed for a higher temperatures of the AR. Regarding the amount of electricity generated as well as the amount consumed, the net generation could be decided and can be seen in Table 7. The total amount consumed was higher for the case with a lower AR temperature and decreased as the temperatures investigated increased. Due to this the total net generation of electricity shows a large difference for the case with an AR temperature of 900 °C than the one at 1200 °C.

Energy (heat) was also assumed for the drying, the amount required was 44 kWh/adt pulp produced.

However, this was not considered while looking at the net generation of electricity since this would occur before the biomass enters the system designed in this project. Another energy-intensive process not considered when calculating the net generation of electricity is the amount required to compress the separated CO_2 to prepare it for transportation and storage. However, the required amount would be 41,6 kWh/adt, and as can be seen, this number is lower than the net generation for all four base case temperatures, presented in Table 7. Meaning, that the compression of CO_2 can also be conducted by using the electricity generated from the system.

Table 7: Net generation of electricity from the system.

T_{AR}	Generation	Blower	Compressor	Total Consumption	Net Generation
°C	kWh/adt	kWh/adt	kWh/adt	kWh/adt	kWh/adt
900	174	-9,04	-72,24	-81,28	93
1000	190	-9,64	-68,43	-78,07	112
1100	207	-10,24	-64,64	-74,88	132
1200	224	-10,85	-60,87	-71,72	153

There is a clear difference in the net amount of electricity generated for the cases with the highest and lowest AR temperature. However, since the case of 900 °C generates more H_2 than the case at 1200 °C, a trade-off between the amount of electricity generated to the amount of H_2 produced has to be considered. Depending on the desired products from the process the system could be adapted to favour either electricity or H_2 generation. Moreover, the H_2 could be considered a more valuable product than electricity with various possible applications.

5.1 Sensitivity analysis

For the sensitivity analysis, different variables during the gasification were altered to see how that would effect the simulation results.

Within the steam cycle simulations, the amount of steam sent to be used for post-combustion capture using MEA-based absorption system was varied to see the resulting difference in electricity generation from the system. The amount of 2 bar steam recovered for the FR was kept constant for all temperatures while the amount of residual steam was determined and from that 10 - 100 % were recovered for MEA-based capture. The results of this analysis are shown in Table 8 with the flow of steam being sent to use for capture and the amount of energy recovered for both cases.

Table 8: Sensitivity analysis of electricity generation for different amounts of steam recovered from the steam cycle.

900 °C	Unit		
% to MEA-based capture		10	100
Steam flow	*kg/adt*	53,5	534,6
Electricity generated	*kWh/adt*	166,0	96,2
1000 °C			
% to MEA-based capture		10	100
Steam flow	*kg/adt*	59,3	593,1
Electricity generated	*kWh/adt*	181,2	103,5
1100 °C			
% to MEA-based capture		10	100
Steam flow	*kg/adt*	65,4	653,7
Electricity generated	*kWh/adt*	197,1	111,3
1200 °C			
% to MEA-based capture		10	100
Steam flow	*kg/adt*	71,7	717,0
Electricity generated	*kWh/adt*	213,7	119,4

It can be seen from Table 8 that the energy generated from the steam turbines decreases with an increased amount sent for CO_2 capture using post-combustion capture with MEA-based capture, which is to be expected. What can also be noticed is that the difference in the amount of energy produced when sending 10 or 100 % of the remaining steam, is largest for the case of AR temperature of 1200 °C. This can be seen more clearly in Figure 12. For that case the difference in recovered energy is over 90 kWh/adt while for the case with AR temperature of 900 °C the difference between sending 10 and 100 % is not even 70 kWh/adt. Meaning that for a higher temperature of the stream entering the steam cycle, more energy is lost when part of that steam is recovered for a post-combustion MEA-based unit.

Table 9: Net generation of electricity from the system when recovering 100 % of the remaining steam.

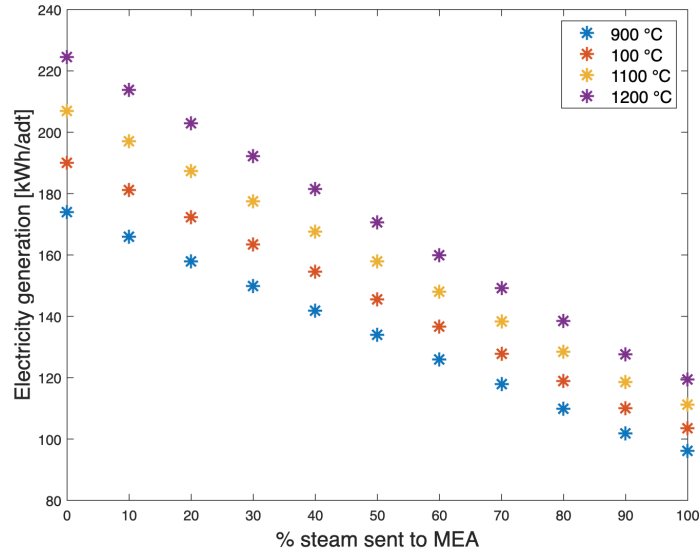| T_{AR}	Net Generation
°C	*kWh/adt*
900	14,9
1000	25,4
1100	36,4
1200	47,7

Figure 12: Electricity generated depending on the amount of steam recovered from the steam cycle.

Moreover, the net electricity generated for the case when 100 % of the steam is recovered can be seen in Table 9. The net electricity generated for the case at 900 °C can be seen to be considerably lower when recovering all of the residual steam from the system. Here it can then be noticed that the energy required to compress the CO_2 for transport is only contributed for the case with the AR temperature of 1200 °C. However, the recovered steam has the possibility of being utilized for post-combustion CCS. Regarding this, the total capture of an entire pulp mill has the potential of being increased considerably. Table 10 shows the amount of CO_2 that could be captured by utilizing the steam in an MEA post-combustion capture process as well as the total amount that can be captured and how much of the total emissions that would be. It can be seen that when recovering all the accessible steam from the system over 25 % of the total emissions from the reference plant could be captured. The trade-off would then be between the electricity generation and capturing more CO_2. Since more steam is accessible when the AR is designed at 1200 °C, it has a greater possibility of capturing a larger part of the residual CO_2 emissions from the mill. This opens up another trade-off regarding the H_2 generated as well as the additional capture of CO_2. All of these factors have to be considered when deciding which design temperature to use for the AR as well as how much steam to use for either electricity generation or CO_2 capture.

Table 10: Amount of CO_2 that could be additionally captured when recovering steam for post-combustion capture using MEA.

T_{AR}	Additional capture	Total capture	Total capture
°C	kg/adt	kg/adt	%
900	317,1	693	25,6
1000	351,8	727,1	26,9
1100	387,7	753,4	27,9
1200	425,3	799,4	29,6

Furthermore, the influence of the airflow, as well as the ratio between air and metal entering the reactor, were investigated. By using the same amount of metal required for reaching the temperatures used for the base case, the airflow was varied. Firstly, for all four temperatures, the airflow was increased by 25 % to see the effect of this on the system. Next, the airflow was decreased by 25 % to see how that would change the outcome of the simulations. The result of these changes are shown in Table 11 as well as Figure 13.

Table 11: Sensitivity analysis regarding the air flow into the AR and the effect of temperature and system conditions.

	T_{AR}	Me_{in}	Air_{in}	Q_{FR}	$H_{2,sep}$	CO_2, sep
	°C	kg/adt	kmol/adt	kWh/adt	kg/adt	kg/adt
+25 %						
	912	33 488	31,2	493,5	9,8	375,8
	1033	11 024	33,3	491,6	8	375
	1152	6552	35,4	491,7	6,2	374,3
	1269	4659	37,4	491,1	4,4	373,7
-25 %						
	888	33 488	18,7	213	20,4	376
	965	11 024	20	218,8	19,3	375,6
	1045	6552	21,2	224	18,2	375,1
	1125	4659	22,5	228,2	17,1	374,7

As anticipated, the temperature within the AR increased compared to the base case when the airflow was increased. In the same manner, the reactor temperature decreased when lowering the inlet airflow. For the case with an increased flow the reactor temperature for the last case, the one with a base case of 1200 °C reaches up to 1269 °C. The increase in temperature of the AR will additionally affect the heat of the gasification reactor and more heat than required for the decomposition of biomass will be available. Therefore, in the case of increased airflow, some heat integration would be required to minimize heat losses. Furthermore, the amount of H_2 generated at a higher airflow will decrease as a higher airflow means more metal being oxidized and therefore more metal oxide entering the FR. More O_2 present for the gasification will drive the reaction towards a higher degree of combustion and therefore, less H_2 conversion. The highest amount that could be generated when increasing the
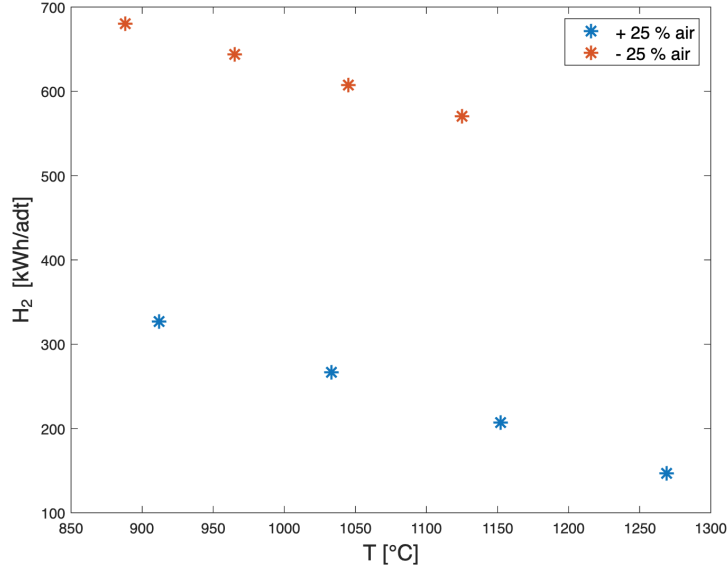
Figure 13: H_2 generated when varying the inflow of air.

airflow is just above 300 kWh/adt, when designed at an AR temperature of 900 °C, which is lower than for all cases considered in the base simulations.

Moreover, whilst looking at the case with a decrease in airflow there is less metal being oxidized leading to a lower degree of combustion within the FR and therefore, a larger amount of H_2 can be retained from the process. Here almost 700 kWh/adt could be generated when the system was designed for 900 °C. Looking at Figure 13, the difference in how much can be generated when increasing and decreasing the airflow is presented. However, for the case with lower airflow, the heat within the FR decreases. The values of Q_{FR}, seen i Table 11, are all lower than the value of 352 kWh/adt required for decomposition of biomass. What this means is that for the cases with a lower airflow the system is no longer designed auto-thermal and external energy would be required for the gasification reaction to take place. Since the proposed process for this project should work without external energy the case with a lower airflow is not a viable option as an energy-efficient CLG system. This shows the importance of finding the optimal design conditions and the effect of inflows of air and metal to have a high H_2 production while still having an auto-thermal system.

Lastly, the simulations were altered to model a CLC process. The AR was simulated in the same way while the steam gasifying agent to the FR was removed. The whole RR as well as the WGS and PSA units were also removed from the system. The combustion case was simulated at an AR temperature of 1000 °C. However, with a higher air-to-metal ratio since the combustion reaction is the favoured reaction during the CLC process.

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Table 12: Comparison between the performance of CLC and CLG processes.

$\mathbf{T}_{AR}$	$\mathbf{Me}_{in}$	$\mathbf{Air}_{in}$	$\mathbf{Me}_{FR}$	$\mathbf{MeO}_{FR}$	$\mathbf{CO}_2, sep$	**Electricity**	**Net electricity**	$\mathbf{H}_2, sep$
$°C$	kg/adt	$kmol/adt$	kg/adt	kg/adt	kg/adt	kWh/adt	kWh/adt	kWh/adt
(CLC) 1000	34 320	83,2	32 269	2610	375	252,6	174,5	0
(CLG) 1000	11 024	26,6	10 438	745,7	375,3	190	112	457,0

The inflows used for air and metal can be found in Table 12, which also shows the electricity generation as well as the net electricity generated from the CLC case, compared to the same values when designing the CLG unit for 1000 °C. It can be seen that the electricity values are considerably higher in the CLC case than for the CLG process. For the CLC process all the flue gases leave from the FR and are cooled down, no syngas is produced and no H_2 is separated from the gaseous stream. Therefore, a larger flue gas stream at a high temperature can be cooled down and used for the steam cycle to generate electricity. From the steam cycle, no steam is required to be recovered for the gasifying agent and it is assumed no steam is sent for the CO_2 capture using post-combustion with MEA. The CLC is beneficial if the main goal of the system is energy generation, however, no H_2 is produced from the system. Looking at the amount of CO_2 captured it is the same as for the previous cases which show they are all possible solutions for the implementation of CCS.

6 Conclusion

This thesis evaluated the implementation of a Chemical Looping Gasification (CLG) unit to replace the multi-fuel boiler for energy generation at a pulp mill. It shows great potential.

Integrating the CLG unit would make it possible to generate both electricity and high purity H_2 while simultaneously separating CO_2. Depending on the desired product, the inlet design conditions of the process can be varied to either favour the generation of H_2 or to favour the electricity generation. When designing the Air Reactor (AR) at 900 °C the highest H_2 conversion can be achieved with 15,1 kg H_2/adt being generated. While the highest net electricity generation is achieved at 1200 °C and reached 153 kWh/adt. For all temperatures considered, approximately the same amount of CO_2, 375 kg/adt, could be separated and prepared for permanent storage.

The steam used to generate electricity has the potential of being used to capture additional CO_2 from the pulp mill. By sending all accessible steam for the case of 900, 1000, 1100 and 1200 °C, to be used for post-combustion capture using MEA, an additional 317,1 (11,7 %), 351,8 (13,0 %), 387,7 (14,3 %) and 425,3 (15,7 %) kg/adt of CO_2 could be captured, respectively. However, this would mean a lower electricity generation from the system which would lead to the electricity required for compression of the CO_2 would not be generated from the system for the three lower temperature cases.

Change in the air flow showed the importance of the ratio between inlet air and OC flow. A higher air-to-metal ratio could lead to less conversion of H_2 while a lower ratio could instead lead to the system no longer have the possibility to design in an auto-thermal manner.

Lastly, the implementation of a CLC unit instead of the proposed CLG process would yield a higher electricity generation. Moreover, by using the steam for CO_2 capture rather than electricity generation, it would increase the possibility of capturing a larger part of the CO_2 from another part of the mill. However, the implementation of a CLC unit would remove the possibility to generate H_2 from the system.

6.1 Future Recommendations

To further continue the work on the implementation of a CLG process for energy-efficient separation of CO_2, there are various routes to take. Below follows some future recommendations to continue the research regarding this topic.

- More research on the most appropriate OC could be conducted to make it possible to increase the H_2 and electricity conversion.

- To run the system for various design conditions, since not all design conditions were considered in this thesis.

- In the future, a laboratory experiment to confirm the results generated from the simulations is required.

- Another aspect not considered in this thesis is the economic assessment of the process. This is crucial to consider to explore the cost and economic possibilities of integrating CLG/CLC it into a pulp mill.

- Lastly, seeing that the process generates N_2, H_2 and CO_2, it would be interesting to look into the possibility of CCU.

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7 Appendix

7.1 Aspen Flowsheets

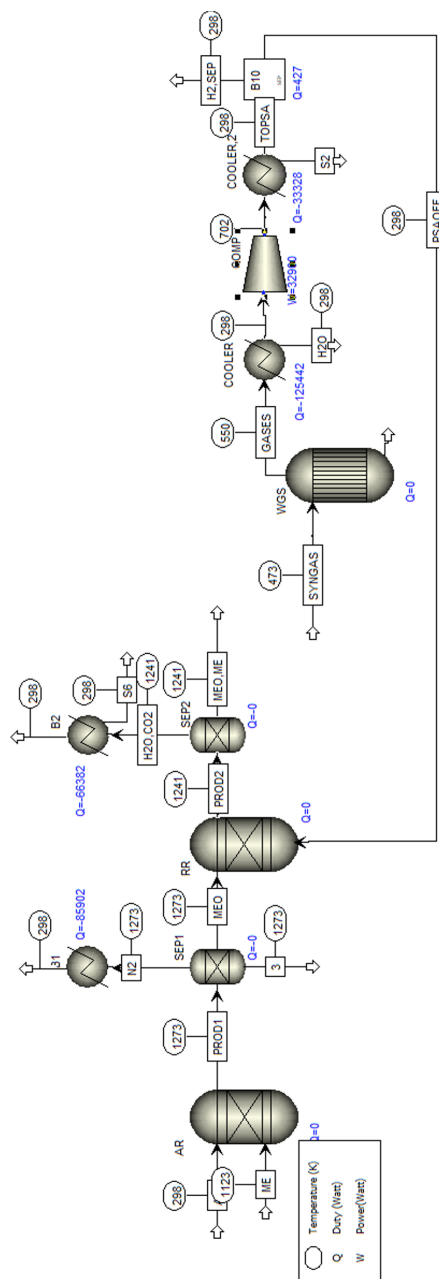**Figure 14:** Aspen Plus flowsheet showing the CLG system simulations.

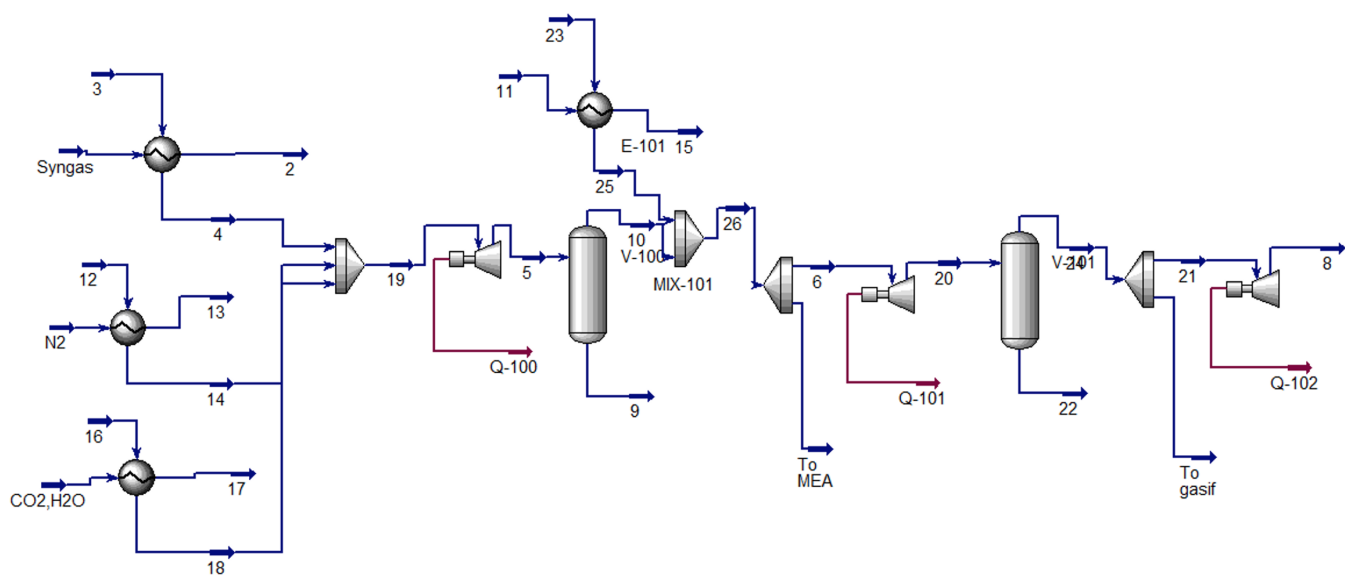**Figure 15:** Aspen Plus flowsheet showing the gasification simulation.

Figure 16: Aspen HYSYS flowsheet showing the steam cycle simulations.