



NTNU – Trondheim
Norwegian University of
Science and Technology

Utilization of Low Temperature Heat in Coal based Power Plants

Elmir Sisic

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Supervisor: Truls Gundersen, EPT

Norwegian University of Science and Technology
Department of Energy and Process Engineering



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Preface

This master project is part of the BIGCCS program at SINTEF and Norwegian University of Science and Technology (NTNU). The work was carried out at the Department of Energy and Process Engineering at the Faculty of Engineering Science and Technology.

Abstract

Carbon Capture and Storage aims at capturing and storing carbon emissions from large point sources underground. One of three main ways of implementing CCS is in coal based power plants is the pressurized oxy-combustion, an advanced form of oxy-combustion. There are different approaches in designing the heat cycle with CCS. Included in the design is the acid condenser, a heat exchanger which utilizes the low temperature and latent heat of the flue gas for preheating purposes.

The objective of this master thesis is to determine the maximum amount of power generated by a CO₂ power cycle using the mentioned heat available in the acid condenser. This alternative will be compared to other means of utilizing the low temperature heat, i.e. for preheating purposes in the primary steam cycle.

Acknowledgements

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Contents

| | |
|--|------|
| List of figures..... | VII |
| List of tables..... | VIII |
| Nomenclature..... | IX |
| 1. Introduction..... | 1 |
| 1.1 Motivation | 1 |
| 1.2 Objectives | 2 |
| 1.3 Thesis organization | 3 |
| 2. Background | 4 |
| 2.1 CO ₂ Emission..... | 4 |
| 2.2 Carbon Capture and Storage (CCS)..... | 5 |
| 2.3 Oxy-Combustion..... | 7 |
| 2.4 Low temperature heat recovery | 7 |
| 2.5 CO ₂ and Organic Rankine cycle (ORC) | 7 |
| 3. Oxy-combustion technology in coal-based power plants | 9 |
| 3.1 Introduction | 9 |
| 3.2 Rankine power cycle with oxy-combustion | 9 |
| 3.2.1 Air Separation Unit (ASU)..... | 10 |
| 3.2.2 Combustor | 11 |
| 3.2.3 CO ₂ Compression and Purification Unit (CPU)..... | 12 |
| 3.3 Pressurized oxy-combustion | 13 |
| 3.3.1 Introduction | 13 |
| 3.4 Rankine Cycle with pressurized oxy-combustion..... | 14 |
| 3.4.1 Process description..... | 14 |
| 3.4.2 Air separation unit (ASU)..... | 15 |
| 3.4.3 Pressurized combustor..... | 16 |
| 3.4.5 Heat recovery steam generation unit | 16 |
| 3.4.6 Power island | 16 |

| | |
|--|----|
| 3.4.7 CO ₂ Compression and Purification Unit..... | 17 |
| 3.5 Advantages of the pressurized oxy-combustion..... | 19 |
| 4. Utilization of low temperature heat for power generation..... | 20 |
| 4.1. Waste heat utilization..... | 20 |
| 4.2 Organic Rankine Cycle (ORC)..... | 20 |
| 4.3 Carbon dioxide as working fluid..... | 21 |
| 4.4 Low temperature heat in the pressurized oxy-combustion steam cycle..... | 22 |
| 4.5 Methodology..... | 22 |
| 4.6 Steam Rankine cycle with pressurized oxy-combustion – Baseline Case..... | 23 |
| 4.6.1 Process description..... | 23 |
| 4.7 Case 1: Low temperature CO ₂ Rankine cycle..... | 25 |
| 4.7.1 Process description..... | 26 |
| 4.7.2 Results and discussion..... | 27 |
| 4.8 Case 2: Low temperature CO ₂ Rankine cycle with recuperation..... | 28 |
| 4.8.1. Process description..... | 29 |
| 4.8.2 Results and discussion..... | 29 |
| 4.9 Case 3: Low temperature CO ₂ Brayton cycle with recuperation..... | 31 |
| 4.9.1 Process description..... | 32 |
| 4.9.2 Results and discussion..... | 32 |
| 4.10 Conclusion..... | 34 |
| 5. Further work..... | 37 |
| 6. References..... | 38 |

List of figures

- Figure 1 Line plot of global mean land-ocean temperature index, from 1880. to present, NASA Goddard Institute for Space Studies
- Figure 2 Illustration of Carbon capture approaches
- Figure 3 Simple configuration of an oxy-combustion power plant
- Figure 4 SO₂ concentrations in the combustor using a given type of coal in the process ^[33]
- Figure 5 Schematics of the Rankine power cycle with pressurized oxy-combustion
- Figure 6 Double flash compression and purification unit with intercooling [432]
- Figure 7 Schematics of the steam cycle case [?]
- Figure 8 Complete schematics of the steam and CO₂ cogenerated cycle
- Figure 9 CO₂ Rankine cycle configuration in Aspen HYSYS®
- Figure 10 Schematics of the CO₂ Rankine cycle with recuperation
- Figure 11 Schematics of the Brayton cycle with recuperation
- Figure 12 Comparative results of cycle performances
- Figure 13 Pump energy demands
- Figure 14 The CO₂ cycle contribution to net power generation and system efficiency
-

List of tables

| | |
|---------|---|
| Table 1 | Atmospheric concentrations of GHG from pre-industrial period to 2005. ^[17] |
| Table 2 | Properties of Carbon Dioxide |
| Table 3 | Steam cycle performance |
| Table 4 | Flue gas composition |
| Table 5 | CO ₂ Rankine cycle - data summary |
| Table 6 | CO ₂ Rankine cycle with recuperation - data summary |

Nomenclature

| | |
|------|------------------------------------|
| GSG | Greenhouse gas |
| CCS | Carbon Capture and storage |
| HRSG | Heat Recovery and Steam Generation |
| TIT | Turbine Inlet Temperature |
| TIP | Turbine Inlet Pressure |
| ORC | Organic Rankine Cycle |
| QGCS | Gas Quality Control System |
| ASU | Air Separation Unit |
| MAC | Main Air Compressor |
| DCA | Direct Contact Aftercooler |
| PPU | Pre-Purification Unit |
| FGD | Flue Gas Desulfurization |
| SCR | Selective Catalyst Reduction |
| HPT | High Pressure Turbine |
| IPT | Intermediate Pressure Turbine |
| LPT | Low Pressure Turbine |
| MAHE | Main Acid Heat Exchanger |

Chapter 1

1. Introduction

1.1 Motivation

Massive industrialization in the early 20th century led to increased emissions of greenhouse gases into the atmosphere that are incurred primarily by the combustion of fossil fuels and various industry processes. Just during the 1970s a general environment friendly approach was created as negative climate impacts due to the CO₂ and other GHGs started to take their toll. Increased concentrations of greenhouse gases has led to the creation of the greenhouse effect, which results in an increase in global average air and ocean temperatures.

Thermal power plants that use fossil fuel as primary heat source contribute 1/3 of the global carbon dioxide emissions. Besides CO₂, various volatiles and heavy metals like mercury are also released into the atmosphere. Because of growing power demand, a constant increase of thermal power plants is inevitable and a parallel increase of greenhouse gas emissions is expected. Thereby existing and future plants have to be adapted to new limits of greenhouse gas emission that assure a sustainable environment. To achieve this goal, we need to make great efforts in designing and improving technologies which reduce greenhouse gas emissions while being economically and technologically viable. One option is to implement Carbon Capture and Storage (CCS), a process that successfully removes over 90% of CO₂ from large point flue gas sources and still providing relatively high net plant efficiency.

My home country, Bosnia and Herzegovina, possesses large reserves of different types of coal and the share of coal based power plants in the total Installed Electricity Production Capacity is 43%, where the rest 57% share belongs to hydroenergy. Total installed power is 3659 MW and additional power plants and units are being built, thus it is of very importance to ensure that the present 43% installed energy production capacity are environmental friendly. Therefore, presenting the opportunities of CCS with oxy-combustion and further development is a big step towards achieving this goal.

1.2 Objectives

The Rankine steam cycle with pressurized oxy-combustion enables the recovery of the sensible and latent heat of flue gas. Flue gases generated during the combustion process pass through a series of heat exchangers where the high temperature heat is recovered and used to superheat the working fluid. Low temperature heat left in flue gas can be recovered for further power generation. By utilizing this heat, the overall fuel heat recovery is maximized, leading to increased plant efficiency and decreasing plant emission. The low temperature heat left after the main heat transfer process passes additionally through one heat exchanger, the acid condenser, where the heat is recovered to such an extent that water contained in the flue gas starts to condense, thereby recovering the sensible and latent heat which would otherwise be rejected from the system as waste. The “bonus” heat is generally used to preheat the feed streams, thus reducing turbine bleeding leaving more steam for the power generation process. But, the acid condenser potential is not utilized in an efficient way by the steam cycle because of the quality of the heat. It results in a slight increase of power generated compared to the amount of heat recovered.

So, rather than utilizing the acid condenser heat for preheating purposes, an alternative is to use it to drive a separate low temperature CO₂ Rankine cycle. The main objective is to determine the amount of energy generated by the mentioned cycle and compare it to the results of utilizing the same heat source for preheating purposes in the steam cycle.

1.3 Thesis organization

The thesis consists of four major chapters. The first one reserved for the introductory section. The second shortly addresses the topics background, waste heat recovery, greenhouse gas emission and countermeasures. Emphasis is placed on the contribution of fossil fuel based power plants to the overall global emissions. As a method of mitigating emissions the implementation of Carbon Capture and Storage is introduced. Different approaches of implementing CCS into a power cycle are presented, focusing on the oxy-combustion mode.

The third chapter shortly describes the atmospheric oxy-combustion integration from a technological aspect. An advanced variety of oxy-combustion, the pressurized oxy-combustion, is briefly described in the same chapter introducing every installation unit and describing the process from a thermodynamic point of view in order to better understand the nature of the Rankine steam cycle implementing this CCS approach. Advantages of the pressurized oxy-combustion are also presented compared to the atmospheric counterpart.

The final chapter is the research part of the master thesis. It focuses on simulating the recovery of low temperature heat left from the baseline steam cycle by different low temperature CO₂ engines. The methodology and simulation processes are briefly described, results are presented and compared to the results from the baseline steam cycle utilizing sensible and latent heat for preheating purposes rather than for power generation. Comments, diagrams and final conclusions are presented in this chapter regarding the CO₂ cycle performances and contribution to the total power generation of both steam and CO₂ cycle. Also, Organic Rankine Cycles (ORC) are considered as an alternative to the CO₂ cycle. The chapter ends with the suggestion for further work regarding the whole cogenerated system.

Chapter 2

2. Background

2.1 CO₂ Emission

Human activities results in emission of four long-lived greenhouse gases (GHG): Carbon dioxide CO₂, methane CH₄, nitrous oxide N₂O and halocarbons (gas containing fluorine, chlorine or bromine). The concentrations of the mentioned GHG have significantly increased since the industrialization from 1750. Atmospheric concentrations of CO₂ and CH₄ in 2005 exceed by far the natural range over the last 650,000 years ^[17]. Increased CO₂ concentrations from a pre-industrial value of about 280 ppm to 379 ppm in 2005 are primarily cause by fossil fuel use. The CO₂ radiative forcing, which impacts the overall absorption, scattering and emission of radiation within the atmosphere and at the Earth's surface, increased by 20% from 1995 to 2005, the largest change for any decade in at least the last 200 years ^[17]. The positive or negative total radiation forcing alters the energy balance of the climate system. The increment of the global atmospheric GHG concentrations is shown in table 1.

| Greenhouse gas | Pre-industrial | 2005 | Units |
|------------------|----------------|------|-------|
| CO ₂ | 280 | 379 | ppm |
| CH ₄ | 715 | 1774 | ppb |
| N ₂ O | 270 | 319 | ppb |

Table 1. Atmospheric concentrations of GHG from pre-industrial period to 2005. ^[17]

Carbon dioxide (CO₂) is the most important anthropogenic GHG. Its annual emissions have grown between 1970 and 2004 by about 80%, from 21 to 38 gigatonnes (Gt), and represented 77% of total anthropogenic GHG emissions in 2004. The rate of growth of CO₂-eq emissions was much higher during the recent 10-year period of 1995-2004 (0.92 GtCO₂-eq per year) than during the previous period of 1970-1994 (0.43 GtCO₂-eq per year) ^[17]. The increment has come primarily from the energy, transport and industry sector, while the emission growth from agriculture, deforestation and residential sector has been growing at a slower rate. It is likely that there has been significant anthropogenic warming over the past 50 years, and in contrast it is extremely unlikely that global climate change of the past 50 years can be explained without external forcing and very likely that it is not due to known natural causes alone^[17]. Figure 1 shows the Line plot of global mean land-ocean temperature index, 1880 to present, with the base period 1951-1980.

World energy-related CO₂ emissions rise from 30.2 billion metric tons in 2008 to 35.2 billion metric tons in 2020 and 43.2 billion metric tons in 2035—an increase of 43 % over the projection period. Coal, the most carbon-intensive fossil fuel, became the leading source of world energy-related carbon dioxide emissions in 2004.

It provides the largest share of world electricity generation, around 40 % of total generation in 2008, and the anthropogenic emissions of CO₂ result primarily from the use of fossil fuels. Worldwide energy-related carbon dioxide emissions associated with the consumption of coal accounts for 39 percent of total emissions in 1990, 43 percent in 2008. Global carbon dioxide emissions from coal were 13.0 billion metric tons in 2008 ^[19].

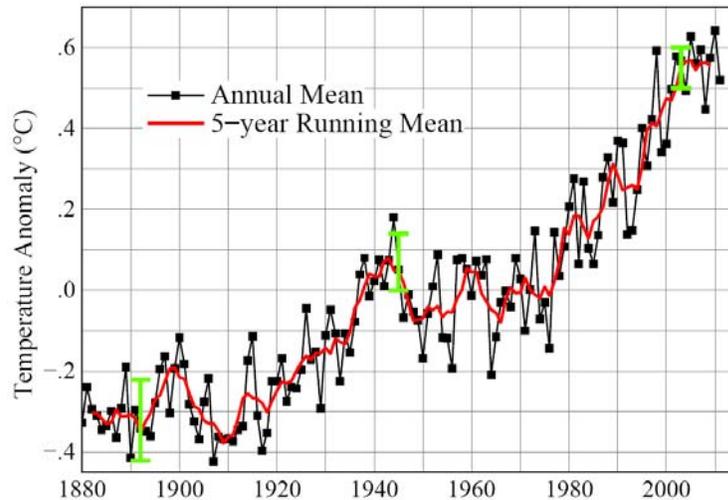


Figure 1, Global Annual Mean Surface Air Temperature Change [18]

Having concerned the importance of GHG emission and the role of CO₂ emission contributed by the combustion of coal, it is of very importance to mitigate CO₂ emission from the largest stationary CO₂ sources, the coal based power plants. The methodology which is used to limit emission is called Carbon Capture and storage.

2.2 Carbon Capture and Storage (CCS)

Since coal and gas-based power plants represent the biggest stationary CO₂ emitters, implementing CCS in these facilities is of vital importance. CCS technology represents capturing CO₂ (that would otherwise be released into the atmosphere) from large point sources, liquefying it and transporting it via pipelines or tankers to permanent geological storage formations. Proven CCS technologies can capture up to 90% CO₂ from the flue gases ^[10]. Storing fluids underground has been already used in the oil industry for enhancing oil recovery. With CCS, it could be possible to continuously use fossil fuels as primary energy source while mitigating global climate change.

A complete CCS system is a combination of various technologies and components which are already used in other applications. CCS has three major approaches towards implementing:

1. Post combustion – where CO₂ from flue gases is chemically extracted after the combustion of coal

2. Pre combustion – where integrated coal gasification combined cycle (IGCC) technology is used in order to gasify the coal and thereby producing hydrogen H_2 and CO_2 , which are more easily extracted than in post combustion.
3. Oxy-Combustion - where N_2 is separated from air thus leaving concentrated O_2 to combust with the coal, producing flue gas with mostly CO_2 , H_2O and minor impurity content.

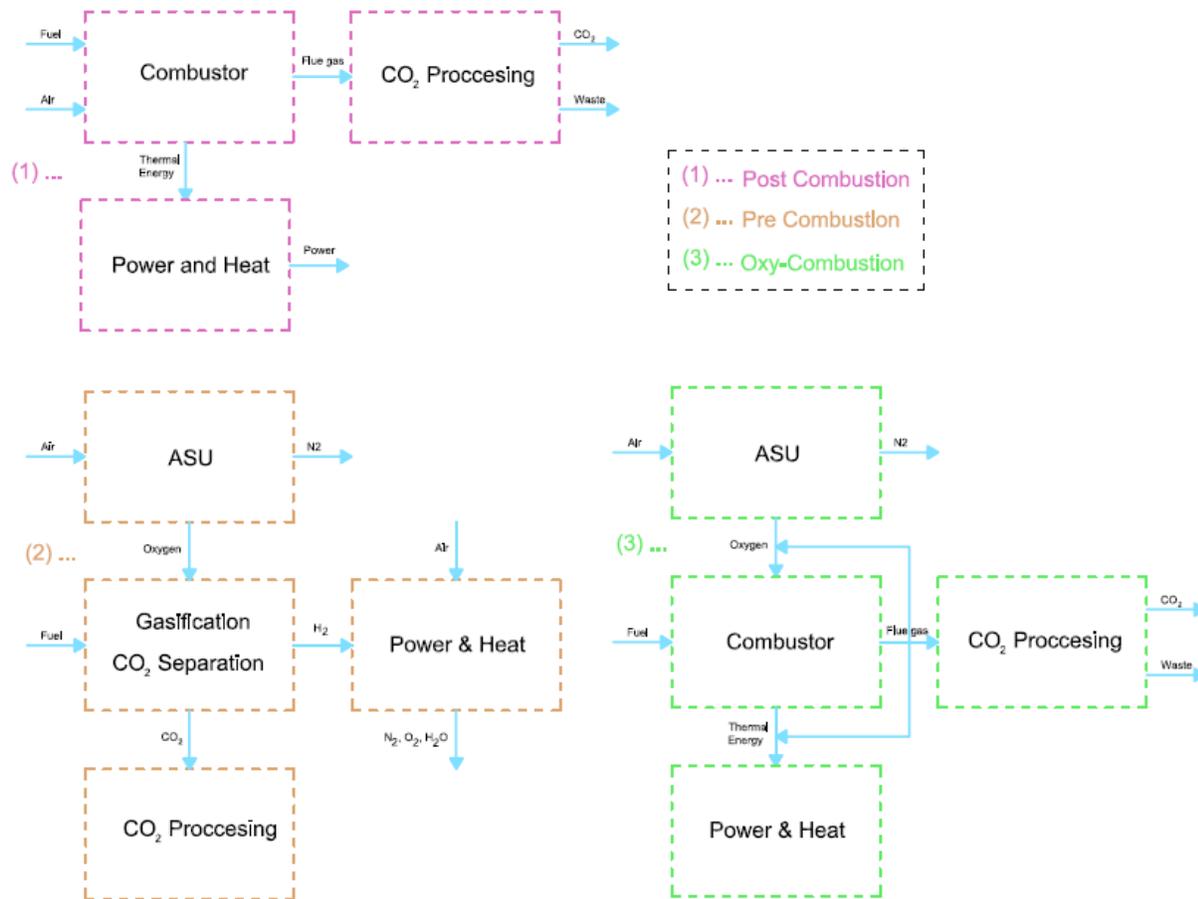


Figure 2. Illustration of Carbon capture approaches

Implementing CCS and mitigating climate change comes at a cost. All approaches require energy for the CCS process, thereby increasing plants own energy demand. In addition, CCS still faces many challenges towards successful use: commercial deployment (installation of infrastructure and maintenance costs) and providing secure CO₂ transportation and storage location.

2.3 Oxy-Combustion

Concerning the increasing greenhouse problem, oxy-combustion has been a subject of research in the last three decades and has emerged as one of the three most common technologies for the CO₂ capture process. Moreover, oxy-combustion has been researched as an alternative for reducing NO_x emissions in fossil fuel power plants. For implementing oxy-combustion in coal based power plants additional cycle units are required. The whole process is based on separating the nitrogen from the air, leaving only pure oxygen to combust with the coal thereby changing the flue gas to a different chemical composition which is more adaptable for CO₂ removing. High water content is present in the generated flue gas which in an advanced version of oxy-combustion can be recovered as latent heat, thereby maximizing energy recovery from the fuel.

All necessary auxiliary unit of oxy-combustion require energy to run and the penalty related to CCS for oxy-combustion coal based power plants is 10%. It is expected that in the near future the energy penalty will be decreased to 6% and the oxy-combustion technology to be commercialized by 2020 ^[4]. The world first full scale demonstration of an oxy-combustion power plant was in 2008. in Schwarze pumpe, Germany. Until now, two more plants have been built.

2.4 Low temperature heat recovery

Low-grade heat recovery implies the recovery of thermal energy from fluid streams that are the result of an industrial or any other process that would otherwise be unexploited and rejected as waste. In conventional thermal power plants, flue gases are yielded at relative high temperatures that are above the condensation point of acid compounds contained within. This however means that the full potential of flue gas heat is not utilized for power generation purpose thus negatively impacting the plant efficiency. Concerning the current environmental regulations limiting CO₂ emissions, energy recovery processes have become an important issue. The thermal energy contained in the flue gases cannot be utilized in an economical and practical way by standard power engines such is the steam Rankine cycle. New established technologies like Rankine cycle that use organic or non-organic working fluids utilize the low temperature heat in a more efficient way, thus in the it end reducing the amount of fuel burned or from a different point of view, gaining more power at the same fuel consumption rate.

2.5 CO₂ and Organic Rankine cycle (ORC)

Steam cycles are generally used for high temperature heat source, but when it comes to low grade heat recovery, the first choice is the Organic Rankine Cycle (ORC). ORCs have the ability to transform thermal energy from low temperature heat sources to useful work. This is possible

because of the thermodynamic properties of the working fluid. Unlike water, organic working fluids have much lower boiling points which enables steam generation at lower temperatures which is eventually used to drive the turbine in the expansion process. Moreover, organic compounds have advantages in the fields of heat transfer and cycle performance due to their molecular structures.

Just like organic compounds, carbon dioxide or CO_2 which is categorized as a non-organic compound, can be used as working fluid in low temperature power engine. Compared to water, carbon dioxide has distinguished performance in the heat transfer processes and cycle performance, especially while operating in the supercritical region. Therefore, it is of very significance to exploit the possibilities of the use of CO_2 as working fluid in the Rankine power cycle.

Chapter 3

3. Oxy-combustion technology in coal-based power plants

3.1 Introduction

Nitrogen represents approximately 80% of the air commonly used for combustion, and serves to dilute flue gas CO₂ content to less than about 15% for pulverized coal-fired boilers and other thermal heat recovery systems. Post-combustion capture process is designed to separate the relatively dilute CO₂ from the bulk flue gas nitrogen, thus making it difficult and costly to remove CO₂ by scrubbing methods. In oxy-combustion processes, the bulk nitrogen is removed from the air before combustion. The resulting combustion products will have CO₂ content around 90% (dry basis), which is a concentration increased by a factor of about 3.5 times compared to air firing. By concentrating CO₂ in the flue gas, it is more easily utilized or disposed. If regulations and geochemistry permit, the raw, dehydrated flue gas may be stored directly without further purification. Otherwise, the flue gas impurities (predominantly O₂, N₂, and Ar) may be removed by reducing the flue gas (at moderate pressure) to a temperature at which the CO₂ condenses and the impurities do not. Increasing CO₂ flue gas concentration also means that all other constituents are similarly increased. Unless removed in the process, even high quality coals (low sulfur and low moisture content) will produce significantly higher concentrations in the flue gas potentially adversely affecting boiler corrosion and combustion.

In the oxy-combustion process pulverized coal combusts in a mixture of recirculated flue gas and oxygen, rather than in air. The typically 95 % concentrated oxygen is provided by an air separation unit (ASU) which uses auxiliary power to drive the air compressors, representing the primary energy cost. The process is based upon a widely by industry used technology for separating oxygen from air by distilling liquid oxygen at cryogenic temperatures. This approach enables oxygen production in high quantities with oxygen purity around 95%. Another method is the membrane air separation which provides oxygen concentrations above 99% but in lower quantities [4]. For oxy-combustion of coal, typically 95% - 97% concentrated oxygen streams are used. More oxygen streams are used as secondary or tertiary combustor inputs at each coal fired burner or elsewhere to further enhance combustion and reduce hazardous compounds.

Although the flue gas properties of an oxy-combustion boiler differ from air intake counterparts, it is found that existing coal fired boilers, with adjusting proper recycle ratio and without changing heat transfer areas, can be converted into an oxy-coal combustion boiler, having as result only a small impact on fuel efficiency.

3.2 Rankine power cycle with oxy-combustion

Besides standard coal based power plant components, the oxy-combustion system also includes additional major components:

- Air Separation Unit (ASU) – The unit which provides concentrated oxygen product used for the combustion stage
- Combustor/Gas Quality Control System (GQCS) – These components are nearly the same as the components in corresponding air intake counterparts
- CO₂ Compression and Purification Unit (CPU) - processes the CO₂ to an transport ready state

A simple illustration of a coal based oxy-combustion power plant is shown in figure 3.

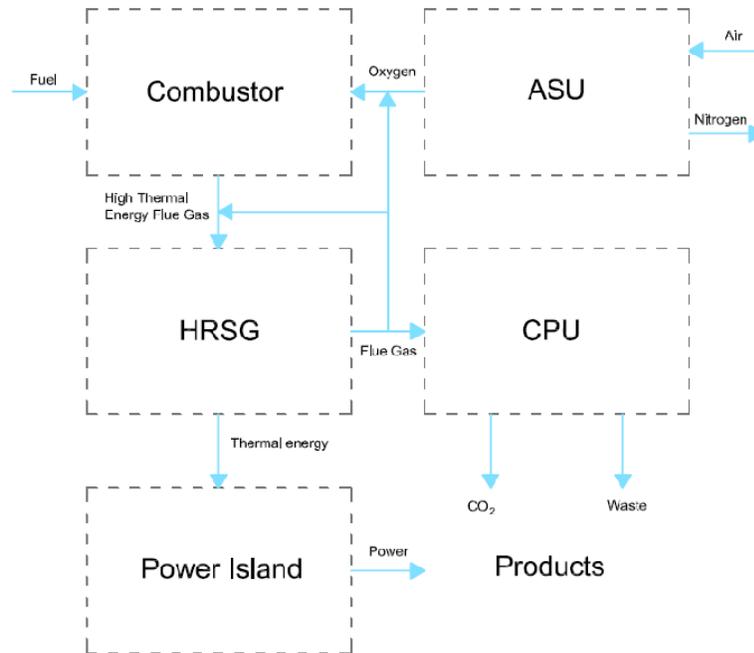


Figure 3. Simple configuration of an oxy-combustion power plant

3.2.1 Air Separation Unit (ASU)

Oxygen production is possible in several ways. For generation of high capacity oxygen streams, the cryogenic air distillation process is used, which is also the most frequently used method for large quantity oxygen production. Besides this one, there are also membrane and chemical air separation, adsorption methods, water splitting and chemical looping air separation.

3.2.1.1 Cryogenic Air Separation [1]

The air is typically compressed to 5-6 bar in the main air compressor (MAC) with water coolers. The compressed air is cooled down in the direct contact aftercooler (DCA). The H₂O, CO₂, and other impurities in the air are removed in the pre-purification unit (PPU) to avoid ice formation or explosion hazards. The purified air is cooled down to its dew point in the main heat exchanger (MHE) and fed to the bottom of the HP column. The air is crudely separated. The crude liquid O₂ (CLOX) is extracted from the bottom of the HP column and fed to the middle of the LP column after subcooling and expansion. The N₂ from the top of the HP column is condensed against the boiling O₂ at the bottom of the LP column. The condensed N₂ is used as liquid reflux

for the two columns. The O_2 product is extracted from the top of the HP and LP column. The products (O_2 and N_2) are heated in the main heat exchanger. The N_2 product may pass through the PPU for the regeneration of adsorbents or the DCA for cooling water.

Various cryogenic air separation cycles have been developed in the past 100 years targeting on different products, energy consumption, and capital cost. An argon column may be added for the production of argon and other products with high purities. A third column or dual boilers can be used to reduce the irreversibilities in the LP column, e.g. the oxyton cycle. The pumped liquid O_2 cycle has been used for the production of high pressure O_2 instead of the gaseous O_2 compression cycle for the reason of safety. The reversion heat exchangers were substituted by the front-end purification systems for the removal of impurities. Other improvement measures focus on the equipment. The plant size is increasing to a maximum 5000 tone O_2 per day. The energy consumption has been reduced significantly in the past century and is being further reduced. However, cryogenic distillation is considered as an energy intensive technology for O_2 production. This is the main incentive of the development of other air separation technologies.

3.2.2 Combustor

As mentioned, the combustion process takes place in a different gas environment in comparison to the air combustion process. Main oxy-combustion flue gas components are CO_2 and H_2O . Part of them (up to 80 %) is recirculated in order to control the combustion temperatures and flue gas temperature prior entering the HRSG unit. In the re-burn process, the quantity of fly ash and flue gas components such as SO_x , HCl , HF , NO_x are reduced. The extraction point from where flue gas is extracted is placed past the electrostatic precipitator (ESP) and flue gas desulfurization (FGD) unit (if coal with high sulfur content is used), thereby decreasing the sulfur and ash amount flowing into the combustor. As a negative consequence, this leads to an increase of flue gas processed in the FGD and ESP. In the other hand, recirculating decreases the amount of NO_x compounds in the flue gases, thus NO_x may transform into N_2 during this process.

CO_2 has a higher heat capacity and gas emissivity than N_2 . In order to maintain the same adiabatic flame temperature (AFT) during the combustion process, the concentration of O_2 is typically higher than that in the air fired combustor, around 30 %. The SO_x and NO_x concentrations are also higher, but since implementing oxy-combustion reduce the amount of flue gas generated by around 80 %, overall NO_x emission is reduced by 50 %, SO_x by 33 %. The condensation in the ducts and absorption by ash which is later removed in the ESP also contribute to the mentioned percentage value.

Thermal formation of NO_x in the burner is reduced because of the lack of N_2 , which in some cases annul the need for catalytic flue gas treatment. Because of the different chemical composition, oxy-combustion flue gas properties impact heat transfer, corrosion and erosion characteristics, which should be used in consideration during plant retrofit or designing stage.

Concerning the Gas Quality Control System (QGCS,) it treats the gas outside the recirculation loop minimizing cost due lower net gas flow.

3.2.2.1 SO_x Control

During the oxy-combustion process, sulfur originated from the fuel converts to SO₂ and SO₃ in traces, just like in the air-combustion counterparts. Besides coal and oxygen, flue gas is recycled into the combustor, which already contains SO_x component, and the overall sulfur concentration in the combustor is increased. The SO_x concentration in the mentioned recycle loop must be kept below the level which leads to excessive gas-side tube corrosion. For low sulfur coals a desulfurization of the flue gases within the recycle loop is not necessary, thus the SO_x concentrations are sufficiently low [11]. This is not the case with high sulfur coal, therefore a desulfurization may be necessary to keep SO_x concentrations below 2000 – 3000 ppmv range (values above force excessive corrosion) [11].

SO₂ removal includes processes applied in the recycle loop like limestone injection, wet and dry desulfurization. Figure – shows the reflection of the SO₂ concentrations in the combustor as SO₂ removal is applied inside the recycle loop at diverse extents.

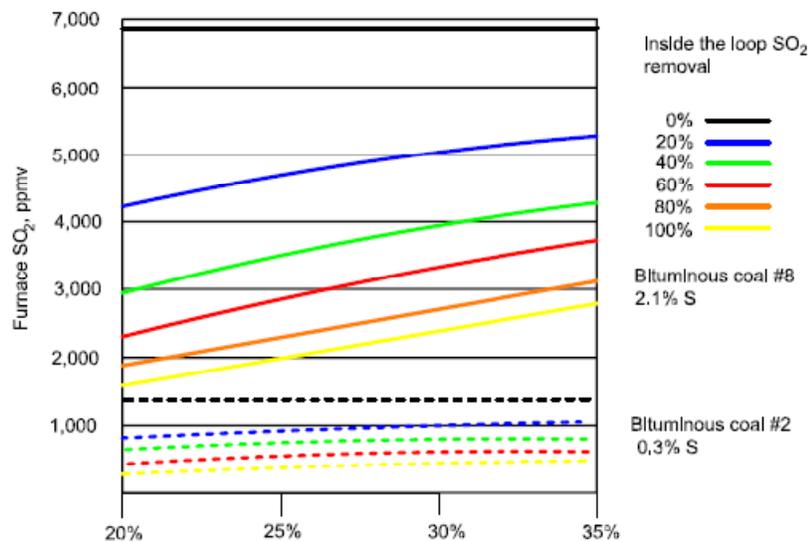


Figure 4. SO₂ concentrations in the combustor using a given type of coal in the process [13]

3.2.2.2 NO_x control

The NO_x forming during the oxy-combustion process is possible because of the presence of nitrogen. Just like in the case of sulfur, nitrogen originates only from coal, since only oxygen separated from nitrogen enters the combustor and burners. By recycling flue gas, formed NO_x particles are again exposed to the burning mechanism and are in the most part destroyed. Therefore, it is likely unnecessary to install NO_x removal technologies in a contrast to air-fired combustors.

3.2.3 CO₂ Compression and Purification Unit (CPU)

The main purpose of the CO₂ compression and purification unit is to separate CO₂ from the diluents (Ar, O₂, and N₂) and trace contaminants (SO₂, SO₃, NO, NO₂, CO, etc.) which represent 10-30 % of the flue gas composition [22]. At first, flue gas entering the CPU will be cooled and compressed to an intermediate level pressure, including deep drying. If environmental regulations permit, the raw CO₂ product may be compressed, transported and stored directly in geological reservoir without any purification treatment, avoiding the need for a CPU, therefore

reducing power consumption, installation and maintenance costs. Otherwise, the raw CO₂ product has to undertake a partial distillation process where compound with lower dew points than CO₂ (O₂, N₂, and Ar) are separated from the entering product CO₂ and vented. Gases with dew point higher than CO₂ (SO₂, NO₂) will eventually condense with the product CO₂.

To meet specifications for CO₂ transport, impurities (H₂O, N₂, O₂, Ar, SO₂) must be removed. The molar fraction of CO₂ in the flue gas is typically around 70 %, and in the purification process, a CO₂ product with more than 95 % purity must be reached. CO₂ is transported in a supercritical phase (in the end improving transport efficiency), and impurities affect this state by making difficult reaching and maintaining it.

In presence of water and oxygen, SO₂, NO_x and Hg can be removed by compressing the CO₂ product in a sour environment. At lower pressure levels (10-15 bars), SO₂ forms sulfur acid H₂SO₄, and at higher levels (up to 30 bars) NO_x forms nitric acid HNO₃, which further reacts with Hg. Impurities H₂O, O₂, N₂ and Ar have lower boiling points than CO₂ and are separated in a flash or distillation process at sub-ambient temperatures and pressure. Prior this step, in the CO₂ compression stage, most of H₂O is removed, and the remaining O₂, N₂ and Ar are removed in an auto-refrigeration separation process. In the end, CO₂ purity is around 97 % which meet potential environmental requirements. If high quality coals are used in the combustion stage, low NO_x burners, flue gas desulfurization (FGD) and selective catalytic reaction (SCR) installations may not be needed.

3.3 Pressurized oxy-combustion

3.3.1 Introduction

Oxy-combustion is an innovative and perspective way to reduce emissions in a coal fired power plants. A further step toward higher plant net efficiency is to pressurize the oxy-combustion chamber. As mentioned before, by removing N₂ from the combustion process, CO₂ is generated in higher concentrations, affecting the overall burning environment because of different chemical and physical properties between those two gases.

Lei Chen, Marco Gazzino, Ahmed F. Ghoniem, investigated the flow field and combustion characteristics of a pilot scale coal-water slurry (CWS) oxy-fuel combustor at elevated pressure^[12]. The characteristics of oxy-fired combustion were compared with the air-fired combustion. Results show higher specific heats of CO₂ and H₂O lower combustion temperatures by around 200 K and thereby delaying ignition of coal. Because of this, radiation levels in comparison to air-fired counterparts are lower though gas absorption levels are higher. Atmospheric oxy-combustion process requires processing of air and flue gas, executed by ASU and CPU. Both auxiliaries, in order to operate, use energy, thereby increasing plants own energy demand which affects overall plant efficiency. Besides, in this process latent enthalpy of flue gas is wasted, as it has high water concentration. Consequently, pressurized oxy-combustion has been investigated as alternative to mitigate negative oxy-combustion impacts.

Hong, Chaudhry, Brisson, Gazzino, Field, ^[13] presented a study in which pressurized oxy-combustion is implemented into a Rankine cycle. Higher combustor pressure raises flue gas dew point and the corresponding available latent enthalpy thus increasing heat recovery from the flue gas. Moreover, the bleeding from high and low pressure turbine stages is thereby decreased. A deaerator and a high pressure acid condenser are necessary to implement the pressurized case.

Leaving the condenser at state 1, condensate is pressurized by the first of two feedwater pumps to state 2 and enters the acid condenser, where on the other side flue gas enters at state 20, leaves at 21. As a result of convective heat transfer, flue gas latent heat is recovered, thereby preheating condensate to state 3, which subsequently recuperates more heat from combustor walls to state 4 then entering the deaerator at 10 bars, leaving at state 5. Feedwater stream is further pressurized by the second feedwater pump to a supercritical state and regeneratively heated to state 6. At this state, feedwater enters the Heat Recovery Steam Generator (HRSG) where it is superheated to 600°C at 250 bars, state 7, after which it expands in the high pressure turbine (HPT). A part of the expanding steam is bled from the turbine to be injected into the pressurized combustor to atomize the slurry particles. Across the HRSG and power island, there are two more steam reheating processes to 620°C at different pressures, state 9 and 11, after which it expands in the intermediate and low pressure turbines (IPT, LPT) respectively. After leaving the LPT, steam liquefies in the condenser, and the process repeats.

On the gas side of the power cycle, the air separation unit (ASU) provides an oxygen stream (state 13) which is mixed with the recycled flue gas (state 19), entering the pressurized combustor at state 14 and taking part in the combustion process. The flue gas stream exits combustor at 1550°C, state 15. State 16 represents flue gas stream that was cooled down by recycled flue gases (state 18) to a temperature 800°C. Now it enters the HRSG, and is being cooled down to state 17 by the entering streams 6, 9, and 11, which are, as mentioned before, superheated during this process. From state 17, one part of flue gas is recycled, the other part (state 20) passes the acid condenser (state 21) to deliver the low temperature and latent heat. Afterwards, the flue gas stream is processed in the compression and purification unit (CPU), having capture ready (22) and exhaust streams (23) as products.

3.4.2 Air separation unit (ASU)

The air separation unit (ASU) has a significant impact to the overall plant net efficiency because of the huge energy demands, “consuming” up to 15 % of gross power production^[13]. Product oxygen stream has a purity of 95 % and above, which afterwards mixes with the recycled flue gas that contains SO₂, SO₃, NO_x and HCl formed during the combustion process. Thereby, the oxygen delivery temperature must be high enough to avoid condensation of these acid compounds while mixing with the flue gas. The base case described in the study, sets oxygen stream delivery temperature to 200°C at a pressure of 10 bars. The ASU's air compressor operates at 5.5 bars. The Air compression work represents the major energy loss in the separation process. Specific energy of producing oxygen for commercial purposes is 0.244 kWh/kg-O₂, 0.247 kWh/kg-O₂^[13].

Since the air separation unit pressurizes the oxygen to higher pressure levels compared to the atmospheric oxy-combustion, the overall compression work is higher, which results in increased power demand of the ASU. But the mentioned pressure elevation will eventually have a positive impact in the lower gas flow stages.

3.4.3 Pressurized combustor

It is known that fossil fuels in presence of pure oxygen combusts at high temperatures. The stoichiometric combusting of coal in a pure oxygen environment reaches temperatures up to 3500 °C. The technology developed by ITEA supported by ENEL^[14] uses a certain amount of colder recycled flue gas premixed with pure oxygen, which is inserted into the combustor to maintain combustion temperature to more acceptable values ranging at 1400-1600 °C. Heat transfer from the combustor to the environment is inevitable. Therefore this heat may be used for preheating purposes.

For example, the data obtained from the study^[13] showed that 26.1 % (by mass) of flue gas is recycled to achieve target combustion temperature of 1550 °C, with 2% combustor heat loss used for preheating the feedwater stream. Coal is supplied in a coal-slurry form of 0,35kg_{H₂O}/1kg_Σ. The amount of oxygen injected into the combustor is adjusted in such way that the exiting raw flue gas contains 3% oxygen on a molar basis. Besides, bleeding steam from HPT is injected to atomize coal-slurry particles, with a mass flow rate set to 1/10th of coal mass flow.

3.4.5 Heat recovery steam generation unit

The temperatures of the gas entering the exiting HRSG must be kept in an appropriate range. Because of the high pressure, the acid dew point is now higher compared to the atmospheric oxy-combustion counterparts. Also the presence of NO_x and SO_x compounds higher additionally flue gas dew point relative to water condensation point. Therefore, the exiting temperature must be kept high enough to not cross the acid dew point and thus avoid hot corrosion and oxidation. Flue gas inlet temperature must be adjusted in such way, that after the heat transfer process in the HRSG, it meets the required exiting temperature. The inlet temperature is adjusted by mixing the raw high temperature flue gas exiting combustor with a certain amount of cooled recycled flue gas that is extracted after HRSG, forming a recycle loop as shown in the figure 5. The flue gas remained after extraction, passes the acid condenser transferring latent heat used for preheating purposes.

For example, 800/260 °C HRSG flue gas temperature drop was used in the study, while recycling 61.9 % (by mass) amount of flue gas extracted after the HRSG unit.

3.4.6 Power island

The high pressure feedwater stream, after passing through the HRSG, is superheated. Leaving HRSG the now superheated steam polytropically expands in the high pressure turbine stage transforming thermal energy into useful work. Afterwards, this process is repeated in the intermediate and low pressure turbine stages as well. The stream exiting the turbine is again reheated in the HRSG, prior expanding in the intermediate pressure turbine. After one more reheat and expansion process to low pressure, the steam eventually condenses in the condenser by cooling it down with water to the saturation temperature.

In conventional Rankine power cycles, preheating the feedwater is accomplished by extracting a part of steam that is expanding in the turbine. The amount of steam extracted depends on the steam enthalpy as well as feedwater parameters and feedwater target temperature. The available latent heat in the acid condenser is recovered and utilized for preheating purposes, as shown in figure 5 where the feedwater was preheated. Otherwise, like in

the atmospheric oxy-combustion, the latent heat would be rejected from the cycle as waste heat, and further turbine steam extraction would be inevitable to achieve target feedwater temperature, thus decreasing the amount of steam mass flow left for power generation. A crucial unit that contributes the establishing of an optimized thermal balance is the deaerator. After recovering heat in the acid condenser and combustor, feedwater stream enters deaerator with an increased temperature. According to saturation conditions, deaerator pressure level determines exit feedwater temperature. Therefore, operating pressure of the deaerator has to be high enough to keep the exiting water temperature higher than the incoming stream temperature.

3.4.7 CO₂ Compression and Purification Unit

The main purpose of the CO₂ compression and purification unit is to purify the CO₂ by remove impurities, in the end concentrating the CO₂ to over 90 %. The amount of flue gas left after the extraction past the HRSG enters the acid condenser where much of the water vapor consisted in the flue gas is condensed. The rest of the flue gas enters the CO₂ compression and purification unit. A schematic of the CPU is shown in figure 7. The flue gas enters with impurities that have to be removed prior transport and the final storing. Besides CO₂, the entering flue gas consist of SO₂, NO_x, Hg, O₂, N₂, Ar and water vapor that has not been condensed in the acid condenser. Those compounds are removed in two separate stages in the compression and purification process:

1. I stage -removal of SO₂, NO_x, and Hg
2. II stage -removal of H₂O, O₂, N₂, and Ar

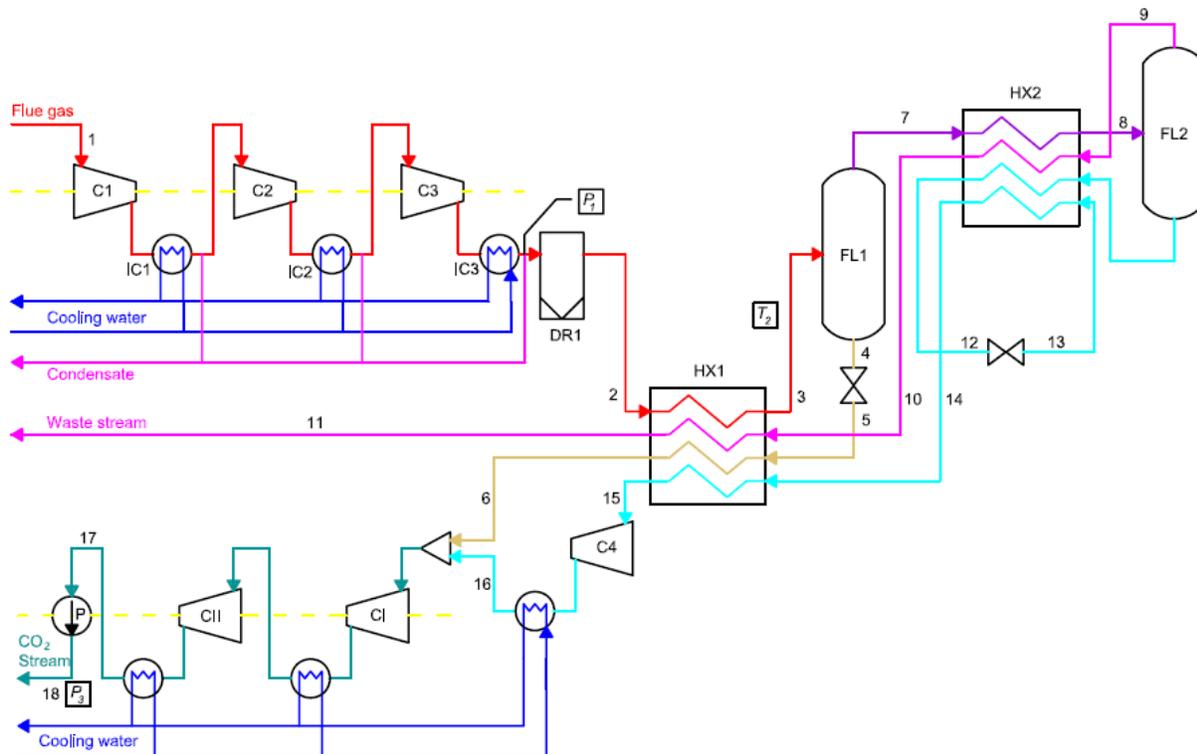
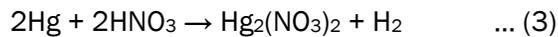
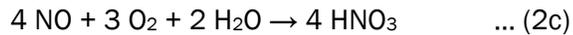
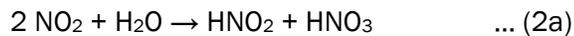


Figure 6. Double flash compression and purification unit with intercooling [13]

3.4.7.1. Process description

As shown in figure 7, the CPU is an auto-refrigerated system with two flash columns. The CO₂ after processing leaves the CPU in a supercritical state with a CO₂ concentration around 95 % by mass. Flue gas enters the first intercooled multi stage compression train in which it is pressurized to state p₁. After each compression, the gas passes through an intercooler where it is cooled down by the circulating cooling water. Every intercooler is equipped with a condensate trap to avoid inlet of formed droplets to the next compression stage. The removal of SO_x, NO_x and Hg occurs in this phase. These compounds can be removed in the presence of water and oxygen, during the compression process. The type of chemical transformation that occurs depends on the operating pressure. At lower pressure levels (10-15 bars) SO₂ reacts with water and oxygen forming sulfuric acid (1). At higher levels (30 bars) NO_x compounds which represent nitrogen monoxide NO and nitrogen dioxide NO₂, react as shown in equation 2.



NO forms directly nitric acid when reacting with water that is present in the flue gas, unlike NO₂ which besides nitric acid forms nitrous acid HNO₂, that eventually decomposes as shown in equation 2b and forming NO, which in the end again reacts with water and oxygen to form the acceptable nitric acid. The hazardous mercury Hg from the flue gas now reacts with the newly formed nitric acid forming mercury II salts, a less toxic compound (equation 3). The final reaction products contained in the condensate are extracted from the stream by the condensate trap and transported away from the system. The impurities O₂, N₂ and Ar have lower saturation points than CO₂ and are removed by liquefying the CO₂. The separation process takes place in a flash column having as product liquid CO₂ stream and a gaseous stream that contains impurities and still a smaller CO₂ content, because of which it undergoes a second separation process.

After the first compression and removal process, the flue gas enters the dehydration plant where the water content is reduced to 20 ppm ^[13] to avoid ice formation due to sub-ambient operation temperatures in the upcoming units. Entering the first heat exchanger, flue gas is partially condensed to temperature T₂ prior entering the first flash column where the gaseous part dilute in CO₂ is again partially condensed in the second multi stream heat exchanger to a temperature around - 54.5 °C ^[13]. The stream afterwards enters the second flash column in which the stream is separated into a rich CO₂ liquid stream and poor CO₂ vapor stream with high impurity content. Both streams re-enter the both of the heat exchangers to function as cooling agents, where afterwards the vapor stream rich in impurities leaves the CPU as waste stream. Before entering the second heat exchanger, the CO₂ rich stream passes through an adiabatic

throttle, expands and re-enters a second time the second heat exchanger. Both CO₂ liquid streams from the flash columns eventually connect to one CO₂ concentrated single stream and are being compressed to a supercritical state in a two stage compression unit. The supercritical dense fluid is now further pressurized by a pump to state p_3 which represents the transport & store state.

The condensate and waste stream represent the only exhaust of the coal based power plant implementing the pressurized oxy combustion. Generally, the concentration of CO₂ in the product stream should be higher than 90 %, though there is an option of reaching 99.9 % purity by a distillation process, but the energy cost increases by 1-35% [1]. The flue gases in the pressurized oxy-combustion case already enter the CPU at elevated pressure, unlike the atmospheric case where they enter at near ambient pressure. As a result, the CPU's compression work is reduced due to the lower compression ratio, in the end positively affecting the plant net efficiency.

3.5 Advantages of the pressurized oxy-combustion

By utilizing latent heat of water from flue gas passing through the acid condenser, overall recovery of the fuel's heating energy is increased. Raising flue gas pressure elevates the flue gas dew point thereby recovering more latent enthalpy of the water which is used for preheating purposes, thus avoiding further turbine steam extraction and leaving more steam mass flow for power generation. For comparison, data obtained from the study [13] show that flue gas dew point had elevated from a temperature of 70 °C (atmospheric case) to 150 °C at flue gas pressure of 10 bars and an decrease of 20.1 [kg/s] in turbine steam bleeding, a drop from 32 to 11.9 [kg/s]. The negative contribution comes from the air separation unit. Unlike the atmospheric case, oxygen must be delivered to the combustor at elevated pressure thus increasing compression work in the ASU. By combusting fuel at pressure higher than ambient, air leak into the combustor is avoided, unlike the atmospheric counterpart with the negative pressure gauge. Therefore, the amount of flue gas that has to be processed in the downstream part is slightly reduced decreasing fan and CPU energy demand. The combustor yields flue gases that pass the heat recovery steam generation unit including the acid condenser. A part of flue gas is recycled to cool down the high temperature raw gas exiting the combustor and to mix with the oxygen stream from the air separation unit. In order to extract and recycle flue gas exiting HRSG, fans are required to overcome the pressure drop across the HRSG and duct lines. Since the whole gas side is already pressurized, less fan work is required compared to the atmospheric case where the compression ratio is higher. The same positive impact is present in the CO₂ compression and purification unit (CPU), where the compression ratio is also decreased. Moreover, a big part of flue gas water content has been already liquefied while passing through the acid condenser, reducing flue gas mass flow that has to be processed in the CPU.

Taking into consideration higher energy demand of the air separation unit (ASU) and benefits of less energy demand of flue gas recycle fans, reduced CPU compression work, high-pressure flue gas latent heat recovery and less turbine steam extraction, the pressurized oxy-fuel combustion net efficiency and power generation exceed the one in the atmospheric counterpart. A lower parasitic power demand of the auxiliaries by 11.8 MWe, achieving net plant efficiency of 33.5% (HHV) or 34.9% (LHV) therewith exceeding efficiency values of conventional air-fired or oxy-combustion power engines [13].

Chapter 4

4. Utilization of low temperature heat for power generation

4.1. Waste heat utilization

Energy intensive industrial processes such as cement kilns, steel mills, glass furnaces, refineries release hot flue gases which thermal energy can be utilized by established technologies for power generation. Concerning the day-to-day rising fuel prices and energy dependence, it is important not to waste any feasible energy rich byproduct. The waste heat is often a result of process inefficiency and the inability of the existing process to recover the excess energy. Roughly a third of energy consumed by the industry is rejected as thermal losses to the environment [3]. Most of the energy wasted is of low quality and cannot be utilized by high temperature power engines in a way to be economical and practical justified. Only power generation from waste heat with higher temperatures (i.e. 260°C and above) is economically feasible, in contrast to low temperature waste heat with temperatures above 150°C [3]. But the emerging technologies like the use of organic and non-organic Rankine cycles are beginning to lower the temperature limit on which the economical feasibility depends.

Just as in the mentioned industrial sectors, conventional fossil fuel power plants discharge flue gas with a temperature that is above the condensation point of containing acid compounds. This reduces the plant efficiency by not recovering the whole energy potential of the fuel. Steam Rankine cycle can be utilized for waste heat sources greater than 260°C, whereas the organic and nonorganic counterpart is limited to 150°C [3]. The later use organic or non-organic working fluids that achieve better efficiencies at lower temperatures due to the lower boiling points, higher vapor pressure and molecular mass compared to water.

4.2 Organic Rankine Cycle (ORC)

Organic Rankine cycles use carbon-based compounds, hydrocarbons and their derivatives as working fluid. The selection of the fluids depends on the heat source type and temperature. Organic working fluids can operate at limited temperature ranges, from 82°C to 288°C (180-550°F) [3]. For recovering low grade heat, fluids with much lower boiling points than water have to be used. The efficiency of the heat transfer is crucial because of the low temperature. Organic fluids present flammability hazards, so direct heat exchange from a high temperature heat source is generally avoided. With their physical and chemical properties, organic fluids are used in low temperature ranges for recovery of waste heat to convert it into useful work which is then used for power generation. An advantage is the long operational life of the cycle components due to the characteristics of the working fluid that unlike steam is non-eroding and non-corroding for valve seats tubing and turbine blades.

Organic compounds are based on a covalent carbon-hydrogen bond and the difference between each working fluid is characterized by chemical and physical properties. Boiling point, critical point, molecular mass, specific heat, heat transfer characteristics and so on impact the overall selection of the working fluid. Optimum fluid performance depends on the temperature and pressure range in which they operate, heat source type and the system objective [15]. Each organic fluid has different impacts on component size, work output, heat transfer area thus

defining the net plant efficiency. There is no fluid that satisfies all criteria and positively impacts all cycle figures, so the selection in the end also depends on the system objective itself.

4.3 Carbon dioxide as working fluid

Carbon dioxide is a colorless, odorless, non-combustible compound with a molecular structure $O=C=O$. It is non-toxic gas, which under normed conditions is used as an inert gas. It is classified as non-organic. Detailed CO_2 specifications are shown in table 3 [4].

| Item | Symbol | | Unit |
|---|------------|------------------------------|------------|
| Molecular weight | M_{CO_2} | 44,011 | kg/kmol |
| Molecular normvolume | V_{mn} | 22,263 | $m^3/kmol$ |
| Specific gas constant | R_{CO_2} | 0,1889 | kJ/kgK |
| Density of gas (0 °C , 101,3 kPa) | ρ_n | 1,977 | kg/m^3 |
| Relative density of the gas (0 °C,101,3 kPa) | D | 1,529 | |
| Critical temperature | t_{crit} | 31 | °C |
| Critical pressure | p_{cri} | 73,83 | bar |
| Critical density | ρ | 466 | kg/m^3 |
| Sublimation point | t | -78,9 (p=0,981 bar) | °C |
| Triple point | t_t | -56,6 (p=5,18 bar) | °C |
| Temperature of disintegration | t_d | =>1200 °C at rate 0,032 vol% | |

Table 2. Properties of Carbon Dioxide

Respecting other working fluids, the high density and volumetric heat capacity makes the CO_2 more “energy dense” thereby having an positive impact on the size of all cycle components (such as turbine, heat exchanger, pump) without losing performance^[6]. Dostal ^[7] compares supercritical CO_2 turbines to steam turbines and indicates that CO_2 turbomachinery is very compact and highly efficient with simpler single-stage designs more adaptable to inlet/outlet piping. Due to the heat transfer performance of CO_2 in the supercritical region, it provides a better match to the heat source temperature profile compared to the heat transfer process with other working fluids. The heat transfer in the acid condenser (which is the heat source of the cycle) from the flue gas to the supercritical CO_2 permits simpler, more robust construction of the condenser. Another advantage of the use of supercritical CO_2 reflects on the positive impact to cycle piping and installation. CO_2 proved to be a clean, non-scaling and non-fouling fluid, and if it maintained in a dry condition, it is also non-corrosive as well ^[6]. Therefore, unlike water, CO_2 does not need to be conditioned prior using in the power cycle. Besides, the cycle inertness is decreased compared to steam Rankine cycles due to the shorter potential CO_2 heat up and time to power the cycle to operational parameters.

Unlike organic working fluids CO_2 has the ability to also operate at high temperature ranges, where it is at a supercritical state with superior heat transfer characteristics. Due to the thermal stability and non-flammability of CO_2 , direct heat exchange from high temperature sources is possible, permitting to achieve high fluid temperature which influences the cycle efficiency.

4.4 Low temperature heat in the pressurized oxy-combustion steam cycle

The average global efficiency of coal-fired plants is currently 28% compared to 45% for the most efficient plants [9]. For successful removing impurities and hazardous compounds from flue gas generated by plants, auxiliary units are required that “consume” a significant part of gross energy produced thus impacting efficiency. One approach is to utilize Carbon Capture and Storage (CCS) technologies, like the pressurized oxy-combustion power cycle described before.

One of the add-ons necessary to fully implement pressurized oxy-combustion is an acid condenser, which enables recovery of latent heat of water contained in the flue gas. This heat, as described before, could be used in preheating purposes like preheating the boiler feedwater. Rather than utilizing the low temperature heat available in the acid condenser for preheating purposes, an alternative is to use a low temperature heat engines like the CO₂ Rankine cycle to generate additional power. Carbon dioxide (CO₂) possess chemical and physical characteristics that enables steam generation in lower temperature ranges which is later used in the steam expansion process to transform thermal energy into useful work.

During the pressurized oxy-combustion process, flue gases are yielded out from the combustor at high temperatures that are consequently first cooled down by the recycled flue gas to an intermediate temperature state, and secondly, heat from flue gas is transferred to power cycle’s working fluid in the heat recovery steam generation (HRSG) unit. Leaving HRSG, flue gases enters acid condenser where the low temperature and latent heat recovery occurs. The acid condenser represents the actual heat source in the low temperature CO₂ Rankine cycle. Parameters of flue gas prior entering acid condenser are obtained from an existing PhD document. Therefore, the mentioned two power engines, pressurized oxy-combustion power cycle and low temperature CO₂ Rankine cycle are in one way cogenerated and their summarized power output represent the total net power generation.

The goal is to determine the maximum amount of power generated by CO₂ Rankine cycle utilizing low temperature heat from the acid condenser, and compare results to other means of utilizing the low temperature heat available in the flue gases, i.e. for preheating the oxygen or feedwater stream in the pressurized oxy-combustion Rankine cycle.

4.5 Methodology

In order to successfully accomplish the research, a simulation of the mentioned low temperature CO₂ power cycle is necessary. Therefore, all calculations are executed in the Aspen HYSYS® V7.3 simulations environment. Based upon literature, the equation of state that fits best to this research is the Peng-Robinson (PR) equation of state, thus it most accurately describes the state of matter under the given set of physical conditions. Other alternatives are the Lee-Kesler-Plocker (LKP) and Span-Wagner (SW) equation of state.

Some of the initial simulation input data are known: flue gas parameters presented before, cooling fluid inlet temperature (water at $t_w=18.2^\circ\text{C}$). To improve cycle net efficiency, all cycle installation efficiencies were set to up-to-date efficiencies over 90% [13]. Besides, it is also assumed that no heat leak occurs in the heat exchanging units. The heat transfer is adjusted upon pinch point or minimum approach value of 3°C to further enhance the heat recovery. Also,

thereby ending the heat recovery tract. Further, flue gas enters the CPU in which it is being processed to achieve the transport ready conditions.

On the steam cycle side, the condensed water is pressurized by the first electric pump to 22 bars and preheated in the main acid condenser and low pressure feedwater heater (LP-FWH). A deaerator then removes any impurities before the feedwater continues the preheating in the high pressure feedwater heater (HP-FWH). After passing the second pump that is driven by a low pressure condensing turbine supplied by steam at 9.4 bars pressure, the feedwater enters the HRSG unit at 325 bars and a temperature 310 °C, achieving TIT of 600 °C and TIP of 280 bars. Upon expansion in the high pressure turbine, steam is reheated to 610 °C at 50 bars to be again expanded continuously in the intermediate and low pressure stages. At each stage, steam is extracted to supply the regenerative feedwater heaters and the turbine-driven pump. Following the expansion depleted steam is condensed at 0.05 bars and 32 °C. The overall steam cycle utilizing pressurized oxy-combustion performance is listed in table 4.

| Item | | Units |
|---------------------------|--------|--------|
| Fuel energy input, LHV | 1610.9 | MWth |
| Condenser duty | 899.7 | MWth |
| ST shaft power | 807.5 | MW |
| ST-Gen losses | 15.3 | MW |
| Gross electric power | 792.2 | Mwe |
| Steam cycle aux. | 6.8 | Mwe |
| ASU power req. | 148.4 | Mwe |
| Boiler island aux. | 24.9 | Mwe |
| CPU power req. | 33.7 | Mwe |
| Total auxiliaries | 213.8 | MW |
| Net electric power | 578.4 | MW |
| Net plant efficiency, LHV | 35.9 | % |
| Net plant heat rate, LHV | 10026 | kJ/kWh |
| Net plant efficiency, HHV | 34.5 | % |
| CO ₂ emissions | 21 | g/kWh |

Table 3. Steam cycle performance

Oxy-combustion provides the possibility of utilizing the latent heat available in the flue gas which cannot be efficiently converted into useful work in a high temperature power engine. The heat recovered in the acid condenser lacks in quality compared to the heat recovered in the HRSG unit which is utilized at an acceptable efficiency. Every additional MW recovered in the HRSG results in an increase of 0.5 MW power generated, while just 12 % of the same energy added in the acid condenser is converted into power. The low utilization factor is due to the quality of heat recovered in the acid condenser.

This fact justifies the need of exploring additional alternatives of utilizing the heat from the acid condenser in a more efficient way. One approach, on which this master thesis focuses, is to determine the amount of energy generated by a low temperature heat engine utilizing the available acid condenser heat. The proposed engine is a CO₂ Rankine cycle where the cycle heat addition occurs in the acid condenser.

CO₂ has a low boiling point thus it is not difficult and energy consuming to achieve the gas phase. But, in the other hand, CO₂ can only be liquefied at relative high pressure when concerning the cooling fluids properties. Therefore, the CO₂ low pressure expansion is not simulated in this case, rather the expansion process occurs in a single stage turbine from super- to subcritical pressures.

Since the acid condenser (in the simulation referred as main acid heat exchanger) heat is not utilized in the steam cycle in preheating purposes, it will reduce the gross power generation of the steam cycle. The task of the CO₂ low temperature cycle is to generate power to overcome the mentioned loss and additionally increase gross power and therefore utilizing the acid condenser potential in a more efficient manner.

4.7.1 Process description

CO₂ condensate, at state 1, enters the feed pump, in which it is pressurized to high pressure supercritical state 2. Afterwards, it passes through the main heat exchanger. Here occurs the CO₂ phase change from liquid to gas, on the account of recovered flue gas high temperature and latent heat (heat addition). On the other side, flue gas, now with much of the water condensed, flows to the compression and purification unit (CPU). After leaving the acid condenser at state 3, which represent the turbine inlet pressure (TIP) and turbine inlet temperature (TIT), CO₂ polytropically expands in the turbine to a subcritical pressure, converting thermal energy to useful work, which is used to drive the power generator. Upon expansion, the CO₂ at state 5 enters condenser, in which it is liquefied by cooling down the CO₂ to saturation temperature, using water as cooling fluid. Exiting the condenser at state 1, the process repeats.

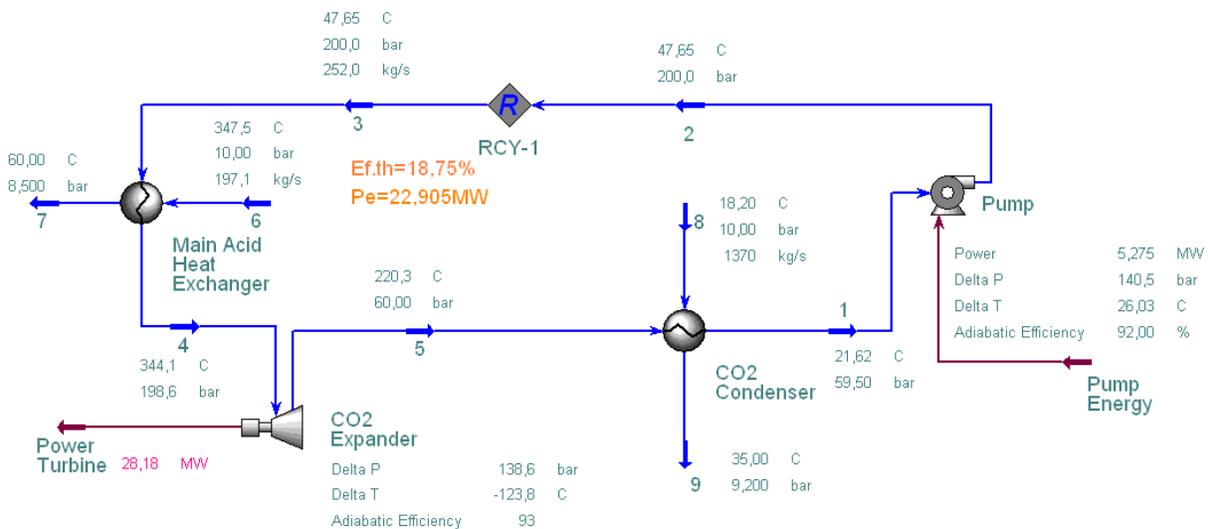


Figure 9. CO₂ Rankine cycle configuration in Aspen HYSYS®

4.7.2 Results and discussion

As described, CO₂ changes pressure from sub- to supercritical, making this cycle a transcritical one. The turning points between those two states are:

- feed pump – in which CO₂ is pressurized way over the supercritical pressure p_k , including temperature rise due compression over t_k
- expander – where CO₂ expands to subcritical pressure

CO₂ operating pressure is set so that maximum power generation is achieved. Since the available cooling water temperature is 18.2°C, it implies that CO₂ could only expand to a pressure with a corresponding saturation temperature at least 3°C higher than cooling water temperature, to meet the minimum temperature approach (pinch point) of condenser. On the other hand, the pressure at which CO₂ is pressurized is determined by the net power generation. So a trade-off between gross power output and pump power “consumption” was the key element in calculation of the cycles maximum operation pressure. Best results were obtained at a 200/60 bars pressure ratio. The CO₂ main acid heat exchanger outlet temperature, in this case also referred as turbine inlet temperature TIT, is adjusted to maximum possible outlet temperature while concerning the pinch point. To do so, CO₂ mass flow had to be adjusted to achieve target TIT.

$$W_{\text{exp}} = m_{\text{CO}_2} \cdot (h_4 - h_5) \text{ [MW]} \quad \dots(4)$$

As shown in equation (4), both CO₂ mass flow and inlet enthalpy (as a function of temperature) impact power output in the expander. Concerning the limited low temperature heat source, giving the priority to increase CO₂ TIT rather than mass flow, resulted in higher power output and net efficiency in comparison to the opposite case. Based on this fact, CO₂ TIT was adjusted to the maximum value, and the corresponding CO₂ mass flow came out of it. Cooling water enters condenser at a temperature $t_{\text{cwin}}=18.2^\circ\text{C}$. To assure that no environmental impacts exist due to heat rejection, cooling water outlet temperature must remain under a certain value, depending on the environmental conditions itself. In this case, an outlet temperature of $t_{\text{cwo}}=35^\circ\text{C}$ was selected. The amount of water needed for the CO₂ liquefying process depends on CO₂ inlet temperature and mass flow, and the cooling water inlet temperature.

Well known is the fact that every power cycle operating at high pressure and temperature reaches high efficiency. Concerning the carbon dioxide low enthalpy value at lower temperatures, it was expected that cycle efficiency reach low values comparing to high temperature cycles. In this case, a net thermal efficiency of $\eta_{\text{th}}=18.75\%$ was reached, while generating net power $P_{\text{net}}=22.905\text{ MW}$. All simulation data of CO₂ Rankine cycle data is shown in table 6.

Of course, there are ways of improving cycle efficiency like increasing TIT and TIP, lowering condenser pressure, preheating feedstreams and steam reheating. Maximum TIT in this case is already achieved, while lowering the condenser pressure is not possible due to the cooling water inlet temperature. Steam reheating is not justified because of the high CO₂ turbine outlet temperature after expanding into the high pressure region.

| Item | | | Units | |
|---|-----------|--------|---------|----------------|
| Heat input (acid condenser duty) | 122.10 | | MW | |
| Condenser duty | 99.24 | | MW | |
| ST shaft gross power | 28.18 | | MW | |
| CO ₂ Pump power req. | 5.27 | | MW | |
| Net power gen. | 22.90 | | MW | |
| Net plant efficiency | 18.75 | | % | |
| Stream No. | flow kg/s | T (°C) | p (bar) | Vapor Fraction |
| 1 | 252.0 | 21.26 | 59.50 | 0.00 |
| 2,3 | 252.0 | 47.65 | 200.0 | 0.00 |
| 4 | 252.0 | 344.20 | 198.5 | 1.00 |
| 5 | 252.0 | 220.50 | 60.0 | 1.00 |
| 6 | 197.1 | 347.50 | 10.0 | 1.00 |
| 7 | 252.0 | 60.00 | 8.60 | 0.75 |
| 8 | 1371.0 | 18.20 | 10.0 | 0.00 |
| 9 | 1371.0 | 35.00 | 9.20 | 0.00 |
| Main acid heat condenser | | | | |
| Minimum approach | | | 3.264 | °C |
| Tube side pressure drop | | | 1.400 | bar |
| Shell side pressure drop | | | 1.500 | bar |
| Tube side Δt (CO ₂) | | | 296.4 | °C |
| Shell side Δt (Flue gas) | | | 287.5 | °C |
| CO ₂ Condenser | | | | |
| Minimum approach | | | 3.423 | °C |
| Tube side pressure drop | | | 0.500 | bar |
| Shell side pressure drop | | | 0.800 | bar |
| Tube side Δt (CO ₂) | | | 198.7 | °C |
| Shell side Δt (Flue gas) | | | 16.8 | °C |
| Adiabatic efficiency | | | | |
| Turbine | | | 93 | % |
| Pump | | | 92 | % |

Table 5. CO₂ Rankine cycle data summary

The only possibility that remains is to utilize CO₂ heat available after expansion for preheating the CO₂ condensate. Since CO₂ expands to a state $p_5=60$ bar and $t_5=220.5^\circ\text{C}$, significant heat rejected occurs in the CO₂ condenser. As a consequence of preheating, the CO₂ condensate temperature prior entering the main heat exchanger would be increased over the desirable 60°C . This approach will be presented in the upcoming cases.

4.8 Case 2: Low temperature CO₂ Rankine cycle with recuperation

As a method of improving cycle efficiency, heat recuperation has been added to the first case. In case 1, heat available in the stream after CO₂ expansion was rejected in the condenser. Instead of rejecting, part of the available heat in this case is used to preheat CO₂ condensate stream to highest possible temperature, while respecting the 3°C pinch in the heat exchanger (recuperator). With this approach, a huge part of heat remains in the cycle, which would otherwise be rejected into the environment. Thermal efficiency of the cycle directly depends on the amount of heat rejected, less heat rejected means higher cycle efficiency.

4.8.1. Process description

The cycle configuration differs from the first case just in one added heat exchanger, the recuperator, as shown in figure 11. Flue gas parameters, operation pressure and the cooling fluid properties, unit efficiencies and pressure drops are maintained the same as in case 1. Condensate at state 1 is pressurized to a supercritical state 2, whereupon it enters the recuperator. After the heat exchange process, now at state 3, CO₂ feed stream passes through the main heat exchanger. Complying with the pinch methodology, CO₂ is heated to state 5, which represents TIT/TIP parameters. Afterwards, CO₂ polytropically expands in the turbine to state 6 and then enters the recuperator. Expanded CO₂ vapor transfers part of heat energy to the incoming low temperature CO₂ feedwater stream state 2. Upon leaving recuperator at state 7, CO₂ gas is liquefied in the condenser by cooling it down to the saturation temperature. Afterwards, the process repeats.

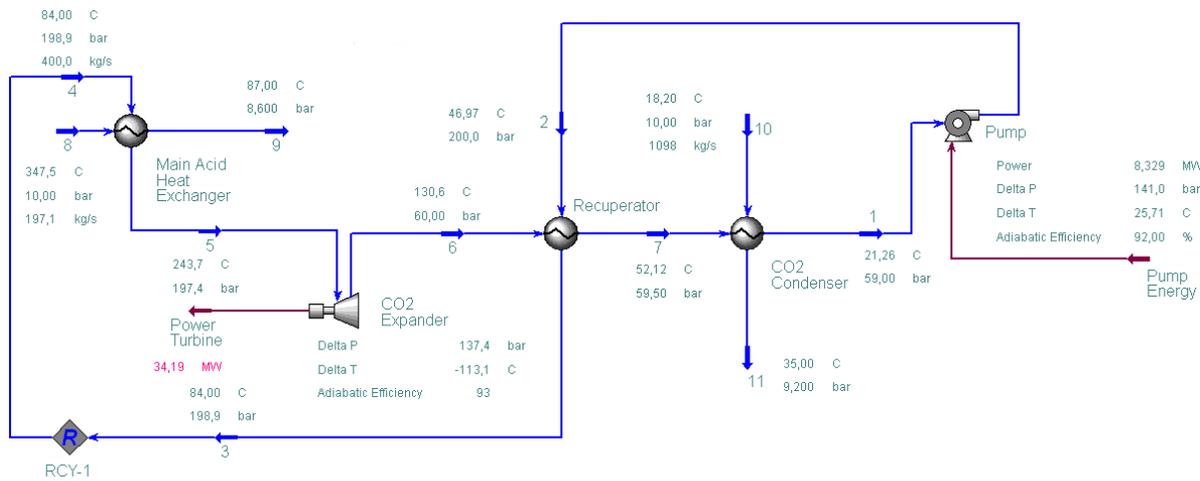


Figure 10. Schematics of the CO₂ Rankine cycle with recuperation

4.8.2 Results and discussion

Results show a significant increase both in net thermal efficiency and power generation by utilizing recuperation. Increased CO₂ feed stream temperature t_5 prior entering main acid heat exchanger has an impact on the flue gas outlet temperature $t_{f_{exit}}$, which has to be at least 3 °C higher than t_5 . The balance between CO₂ mass flow rate and TIT is set in such way to achieve maximum power generation rather than high efficiency. Applying low scale optimization, best results were obtained at a CO₂ mass flow of $m_{CO_2}=400$ kg/s, whence comes the related TIT. Pressure ratio throughout the cycle was kept the same as in the first case. As a result of preheating CO₂ feedstream, less heat is “sent” to the condenser, thereby decreasing the amount of heat rejected and cooling water needed for CO₂ liquefying process. This led to an increase both in efficiency and power generation. HYSYS calculated a decrease of cooling water mass flow by 273 kg/s or 19.91 %, while keeping same water temperature ratio of 18.2/35 °C. Thermal net efficiency increased significantly from $\eta_{th1}=18,75\%$ to $\eta_{th2}=24,56\%$, while power generation increased by 2,96 MW or 12.92 % compared to power generated in the first case of $P_1=22,905$ MW. Complete cycle data is summarized in table 6.

| Item | | | Units | |
|----------------------------------|-----------|--------|---------|----------------|
| Heat input (acid condenser duty) | 105.30 | | MW | |
| Condenser duty | 74.47 | | MW | |
| ST shaft gross power | 34.19 | | MW | |
| CO2 Pump power req. | 8.33 | | MW | |
| Net power gen. | 25.86 | | MW | |
| Net plant efficiency | 24.56 | | % | |
| Stream No. | flow kg/s | T (°C) | p (bar) | Vapor Fraction |
| 1 | 400.0 | 21.26 | 59.0 | 0.00 |
| 2 | 400.0 | 46.97 | 200.0 | 0.00 |
| 3,4 | 400.0 | 84.00 | 198.9 | 0.00 |
| 5 | 400.0 | 243.70 | 197.4 | 1.00 |
| 6 | 400.0 | 130.60 | 60.0 | 1.00 |
| 7 | 400.0 | 52.12 | 59.5 | 1.00 |
| 8 | 197.1 | 347.50 | 10.0 | 1.00 |
| 9 | 197.1 | 87.00 | 8.6 | 0.79 |
| 10 | 1098.0 | 18.20 | 10.0 | 0.00 |
| 11 | 1098.0 | 35.00 | 9.2 | 0.00 |
| Main acid heat condenser | | | | |
| Minimum approach | | | 3.000 | °C |
| Tube side pressure drop | | | 1.400 | bar |
| Shell side pressure drop | | | 1.500 | bar |
| Tube side Δt (CO2) | | | 260.5 | °C |
| Shell side Δt (Flue gas) | | | 159.7 | °C |
| CO2 Condenser | | | | |
| Minimum approach | | | 3.065 | °C |
| Tube side pressure drop | | | 0.500 | bar |
| Shell side pressure drop | | | 0.800 | bar |
| Tube side Δt (CO2) | | | 30.86 | °C |
| Shell side Δt (Flue gas) | | | 16.80 | °C |
| Recuperator | | | | |
| Minimum approach | | | 5.150 | °C |
| Tube side pressure drop | | | 0.500 | bar |
| Shell side pressure drop | | | 1.100 | bar |
| Tube side Δt (CO2) | | | 78.49 | °C |
| Shell side Δt (CO2) | | | 37.03 | °C |
| Adiabatic efficiency | | | | |
| Turbine | | | 93 | % |
| Pump | | | 92 | % |

Table 6. CO₂ Rankine cycle with recuperation - data summary

The flue gas exit temperature of $t_{fgexit}=60^{\circ}\text{C}$ was not achieved. In contrast, flue gas temperature was $t_{fgexit}=87^{\circ}\text{C}$. To achieve the preferable $t_{fgexit}=60^{\circ}\text{C}$ prior entering CPU, the related heat in the flue gas had to be rejected elsewhere beyond of the CO₂ Rankine cycle area.

4.9 Case 3: Low temperature CO₂ Brayton cycle with recuperation

The objective of this case is to determine the maximum amount of power generated by using a Brayton rather than the Rankine power cycle. In the means of configuration, only installation change compared to the second case is the replacement of the CO₂ feedstream pump with a multi-stage compression, as the working fluid CO₂ remains in gas phase throughout the whole thermal cycle, or restated, no phase change occurs. Brayton cycle configuration is shown in figure 11. As in the second case, recuperation is also introduced, thus increasing flue gas exit temperature $t_{f_{\text{gexit}}}$.

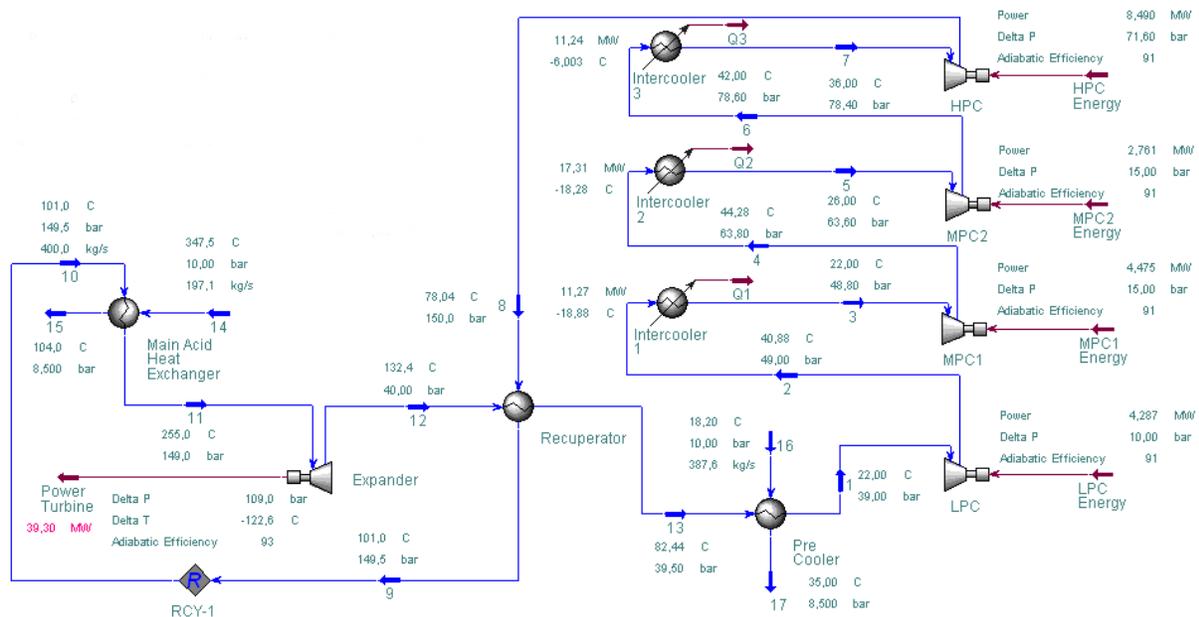


Figure 11. Schematics of the Brayton cycle with recuperation

The Brayton cycle consists of 4 major parts:

- Four-stage CO₂ compression with intercooling
- Recuperator
- Main Acid Heat Exchanger (MAHE)
- CO₂ Expander

To reduce the overall compression work, CO₂ specific volume is kept as low as possible during polytropic compression. This is achieved by maintaining CO₂ temperature to the lowest possible level near the saturation temperature prior entering the compressor, since specific volume is proportional to temperature. By dividing the compression process into stages, and cooling down CO₂ stream between them, the total compression work is reduced, thereby reducing the parasitic power demand. Moreover, the known process of preheating CO₂ feedstream in the recuperator prior entering MAHE additionally improves cycle performance.

4.9.1 Process description

Starting at state 1, CO₂ gas is compressed to state 2 by the first low pressure compressor (LPC). Afterwards, the CO₂ stream passes through an intercooler transferring at this point undesirable heat generated by the compression process, thus reducing CO₂ temperature at the inlet of the next compression stage. This process is repeated 3 more times passing through two intermediate and one high pressure compressor (IPC, HPC respectively). Now compressed to TIP, state 8, CO₂ is first preheated in the recuperator (state 9), then flowing through MAHE heated to final turbine inlet temperature TIT (state 11).

Moreover, as in previous cases, water contained in the flue gas already started to condense, so latent heat is recovered. The rest of the flue gases enter the CPU. CO₂ leaving MAHE expands in the turbine to state 12, in the end generating power, upon which it passes the recuperator to transfer part of heat energy to the incoming CO₂ feedstream. Now partially cooled down, CO₂ flows to the main precooler to be cooled down to final temperature prior entering the LPC to repeat the cycle process again.

4.9.2 Results and discussion

The pressure ratio at which the cycle operates was determined by net power generation. Pressure at which CO₂ expands is $p_{12}=40$ bar. Expanding to lower pressure significantly increases total compression work, especially the LPC work. Compressing CO₂ (as well as other gases) at low inlet/outlet pressure values is characterized by increased compression work, due to high compression ratio ε . This ratio is significantly smaller at higher pressure values, whence comes the decreased energy demand. Particularly in this case, expanding CO₂ to low pressure while not increasing TIT (thereby increasing CO₂ enthalpy) to a superheated value would only (due high compression work) result in very low net power generation.

Turbine inlet pressure was determined by the balance between power generated in the expansion process and power “consumed” in the compression stage. At low scale optimization, best results were obtained at CO₂ TIP value of $p_{TIP}=150$ bar, and a temperature/mass flow balance of $t_{TIP}=255.0$ °C, $m_{CO_2}=400$ kg/s. Cycle thermal efficiency reached $\eta_{th}=22,17\%$ while generating $P=19,427$ MW power. Higher thermal efficiency was accomplished but less energy produced compared to the baseline Rankine cycle case ($\eta_{th}=18,75\%$ $P=22,905$ MW) because of the lower cycle heat input in the MAHE. Flue gas temperature exiting MAHE was relative high $t_{fgexit}=104$ °C, so a huge amount of flue gas heat would have to be removed elsewhere.

| Item | | | Units | |
|--|-----------|----------------|---------|----------------|
| Heat input (acid condenser duty) | 87.14 | | MW | |
| Main precooler duty | 28.03 | | MW | |
| Turbine shaft gross power | 39.30 | | MW | |
| Compression power req. | 19.98 | | MW | |
| Net power gen. | 19.32 | | MW | |
| Net plant efficiency | 22.17 | | % | |
| Stream No. | flow kg/s | T (°C) | p (bar) | Vapor Fraction |
| 1 | 400.0 | 22.00 | 39.0 | 1.00 |
| 2 | 400.0 | 40.88 | 49.0 | 1.00 |
| 3 | 400.0 | 22.00 | 48.8 | 1.00 |
| 4 | 400.0 | 44.28 | 63.8 | 1.00 |
| 5 | 400.0 | 26.00 | 63.6 | 1.00 |
| 6 | 400.0 | 42.00 | 78.6 | 1.00 |
| 7 | 400.0 | 36.00 | 78.4 | 1.00 |
| 8 | 400.0 | 78.04 | 150.0 | 1.00 |
| 9,10 | 400.0 | 101.00 | 149.5 | 1.00 |
| 11 | 400.0 | 255.0 | 149.0 | 1.00 |
| 12 | 400.0 | 132.40 | 40.0 | 1.00 |
| 13 | 400.0 | 82.44 | 39.5 | 1.00 |
| 14 | 197.1 | 347.50 | 10.0 | 1.00 |
| 15 | 197.1 | 104.00 | 8.5 | 0.85 |
| 16 | 387.6 | 18.20 | 10.0 | 0.00 |
| 17 | 387.6 | 35.00 | 8.5 | 0.00 |
| Main acid heat condenser | | | | |
| Minimum approach | | | 3.0 | °C |
| Tube side pressure drop | | | 0.50 | bar |
| Shell side pressure drop | | | 1.50 | bar |
| Tube side Δt (CO ₂) | | | 154.00 | °C |
| Shell side Δt (Flue gas) | | | 243.50 | °C |
| Main Precooler | | | | |
| Minimum approach | | | 3.80 | °C |
| Tube side pressure drop | | | 0.50 | bar |
| Shell side pressure drop | | | 0.50 | bar |
| Tube side Δt (CO ₂) | | | 60.44 | °C |
| Shell side Δt (Flue gas) | | | 16.80 | °C |
| Recuperator | | | | |
| Minimum approach | | | 4.40 | °C |
| Tube side pressure drop | | | 0.50 | bar |
| Shell side pressure drop | | | 0.50 | bar |
| Tube side Δt (CO ₂) | | | 49.96 | °C |
| Shell side Δt (CO ₂) | | | 22.96 | °C |
| Intercooler | | Δp bar | Duty | |
| Intercooler Q1 | | 0.2 | 11.27 | MW |
| Intercooler Q2 | | 0.2 | 17.31 | MW |
| Intercooler Q3 | | 0.2 | 11.24 | MW |
| Adiabatic efficiency | | | | |
| Turbine | | | 93 | % |
| Compressors | | | 91 | % |

Table 7. CO₂ Brayton cycle with recuperation - data summary

4.10 Conclusion

All cases have been tuned for maximum net power output. The resulting cycle efficiency is not of priority since only the amount of power generated affects the power production and efficiency of the whole cogenerated system. The flue gas exit temperature of 60 °C was desirable but the power generated in the second case by not fulfilling the demanded temperature was of greater importance. Therefore, the second case, the CO₂ Rankine cycle with recuperation showed best performance as can be shown in figure 12.

The first case is configured in such way, so that all cycle heat rejection occurs in the CO₂ condenser, to achieve the desirable target flue gas temperature leaving the main acid heat condenser. In this way, the low temperature CO₂ Rankine cycle do not cause any negative impacts to the pressurized oxy-combustion cycle by “sending” high temperature flue gases to CPU. It is common that thermal efficiencies of low temperature cycles range from 10% to 20%, so high efficiencies were not expected. To reduce the negative impact on net cycle efficiency of non-isentropic compression and expansion, up-to-date unit efficiencies were set in the simulation environment. Net efficiency and power generation of all cases are presented in figure 12.

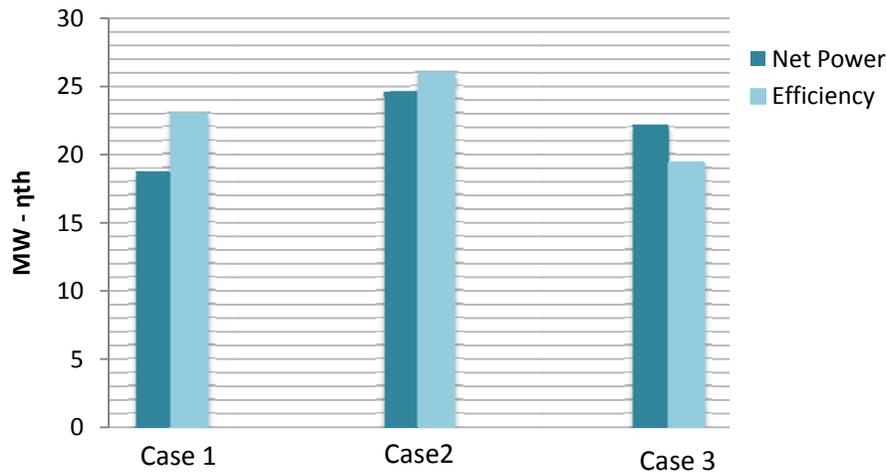


Figure 12. Comparative results of cycle performances

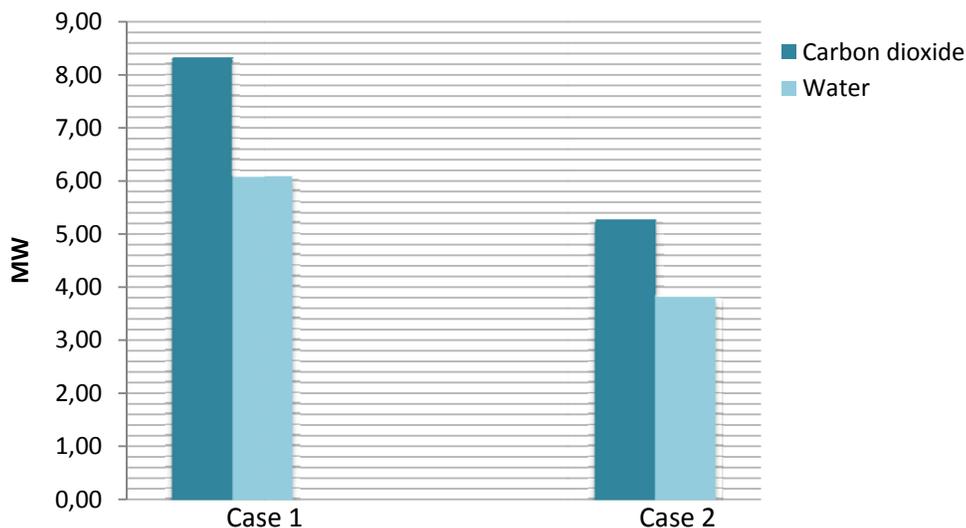


Figure 13. Pump energy demands

In both Rankine cycles (Case 1 and 2) the CO₂ feed pump consumed a significant part of the gross energy generated. In the first case, the energy demand was 5.275 MW or 18.718% of gross power, and in the second, 8.329 MW or 24.360%. This can be explained by the fact that the parameters of the CO₂ stream prior entering the feed pump were near the supercritical values, whereas the fluid becomes less dense while approaching p_k and t_k thereby increasing pump work. For comparison, pressurizing the denser water with the same parameters and pump efficiency, demands less energy as shown in figure 13.

As mentioned before, the objective was to use the available low temperature flue gas heat for power generation via a CO₂ Rankine cycle instead of preheating purposes in the pressurized oxy-combustion cycle, and then to compare the total net power generation in both cases. The steam cycle converts the low temperature heat from the acid condenser into power with low efficiency. Every MW of heat recovered by the steam cycle results in 0.12 MW of additional power generated. If assumed that the flue gas stream temperature after the acid condenser is 60 °C, which means that the flue gas temperature drop is 287.5 °C, than a total of 122,148 MW of low temperature heat would be available. This is the maximum amount of heat recoverable from the flue gas. Concerning the level of utilization by the steam cycle of 12%, it results in additional 14.66 MW of power generated.

The utilization level of the CO₂ Rankine cycle exceeds the steam cycles. In the best scenario, the second case generates 25.86 MW of power while utilizing even a lower amount of heat from the acid condenser. Therefore, having concerned the fact of power generation loss in the steam cycle due to the redirecting of low temperature heat to the CO₂ Rankine cycle and the resulting power generation, the net power generation has been increased by 11.02 MW. The contribution to power generation and efficiency of all three cases is showed in figure 14.

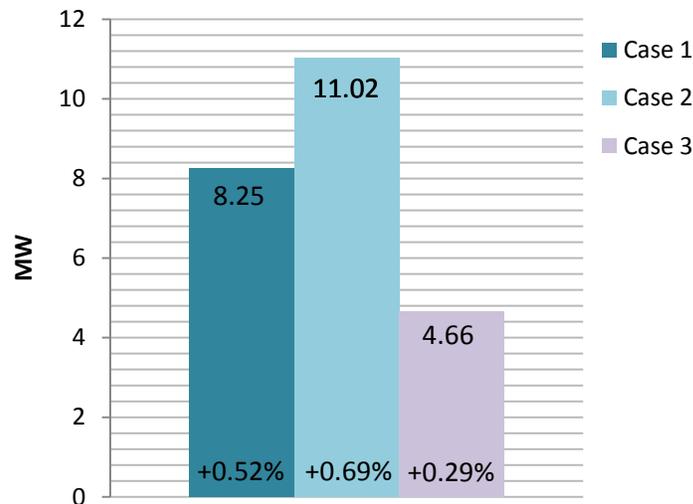


Figure 14. The CO₂ cycle contribution to net power generation and system efficiency

A crucial part in determining the cycle efficiency and power output had the temperature balance of the recuperator. It defined the amount of heat utilized in the main heat exchanger as well as the heat rejected from the cycle. Therefore, it was of importance to correctly balance the stream temperatures entering the recuperator so that the heat recovered from the main heat exchanger can be maximized, and heat rejected in the CO₂ condenser minimized. The recuperator stream temperatures are the result of a step to step analyzed simulation process in

which the temperatures have been set and changed in a one degree interval and the best stream temperatures have been chosen depending on the cycle net efficiency and gross power output that came out of it. The power required to transport the cooling water to the condenser was not included in the cycle performance calculations.

Despite the fact that the first case power cycle operated at higher pressure and temperature, the second case cycle performance surpass the performance of those in the first case. CO₂ mass flow in the second case was higher and still a relative high temperature could be achieved due to preheating. Following equation (5) exergy losses have been calculated in all heat exchangers of the two Rankine cycles. Total exergy lost in all heat exchangers of the first cycle was 12.05 % higher in comparison to the second case exergy loss.

$$\Delta E_{ex} = E'_{ex1} - E''_{ex1} + E'_{ex2} - E''_{ex2} = \Delta E_{ex1} + \Delta E_{ex2} \quad [W] \quad \dots(5)$$

$$\Delta E_{ex1} = q_{m1} \cdot [h'_{1} - h''_{1} - T_{env} \cdot (s'_{1} - s''_{1})] \quad \dots(5a)$$

$$\Delta E_{ex2} = q_{m1} \cdot [h'_{2} - h''_{2} - T_{env} \cdot (s'_{2} - s''_{2})] \quad \dots(5b)$$

With case number two, increase of total (steam and CO₂ cycle) net power production is established. To implement this approach in a commercial scale, additional economic research and pay-off period analysis is required. Trade off between the cost of installment and the investment return time has to be considered. The cost of materials, cycle installation, service and labor force changes with the day. Therefore, to determine the mentioned facts from an economical aspect, a detailed feasibility study would be necessary.

5. Further work

Concerning the master thesis content, the following studies would be relevant. Simulations could be carried out using a working fluid whose condensation pressure at the temperature of the cooling fluid is much lower than the one of carbon dioxide. Additionally, a detailed optimization could be done to further enhance the cycle performance. Detailed cost analysis would contribute to estimating the economic factors of the cogenerated high- and low-temperature power cycle.

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