NTNU
Norwegian University of
Science and Technology

Efficiency loss analysis for oxy-combustion CO2 capture process

Energy and Exergy analysis

Rengarajan Soundararajan

Innovative Sustainable Energy Engineering
Submission date: July 2011
Supervisor: Olav Bolland, EPT

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

Preface

The thesis is a part of my master's programme in Innovative Sustainable Energy Engineering (M.Sc) at the 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

Natural gas combined cycles with oxy-fuel combustion is expected to be an important component of the future carbon constrained energy scenario. An oxy-combustion power cycle enables the fuel to burn in a nitrogen free environment and thereby helps separate the CO_2 stream for storage. Depending on the oxygen source and purity, the CO_2 stream may need furthur purification via a purification unit (CPU) before compressing it to a high pressure for storage. The major energy penalty in this type of power cycle is the production of oxyen and the downstream purification to remove volatiles. It is this energy penalty which results in the cost of avoiding the CO_2 emissions to the atmosphere.

Cryogenic Air Separation Units (ASU) for oxygen production contribute to approximately 20% of the total energy penalty of such power plants. Oxygen Transport Membranes (OTM) for oxygen production offers a potential solution to reduce the energy penalty of oxy-combustion natural gas cycles. The energy penalties associated with OTMs are that membranes operate at high temperatures and require a sweep gas to establish an oxygen partial pressure difference between the feed and permeate streams. Further, while the Cryogenic ASU has minimum integration with the power process, oxy-combustion cycles with OTMs are tightly integrated with the power plant. Thus the contributions to efficiency penalty in an OTM-based cycles are distributed and not easily identified.

The objective of the thesis is to answer the question: *Where does the plant efficiency loss originate in oxy-combustion CO_2 capture process usinng Oxygen Transport Membrane as compared to one with cryogenic ASU?* The contribution of the work will be to highlight the losses at the sub-process and at the equipment level.

This work studies three different cases of oxy-combustion natural gas combined cycles (NGCC) with CO_2 capture. The baseline scenario, modified/improved scenario and the advanced scenario. The baseline scenario is a simple oxy-combustion NGCC power plant with ASU as the oxygen source. Various losses associated with this system are studied in detail. The modified/improved scenario involves analysis of possible modifications to the baseline case and applying the results inorder to improve the baseline case. The modified scenario is expected to have a better overall plant performance. The advanced scenario involves usage of OTM for oxygen production.

The power plants are simulated in Aspen HYSYS and plant mass and heat balances are calculated. Using the stream enthalpy, entropy and composition, we can calculate the stream exergy values. Control volumes help us analyse the component and sub-system exergy losses and arrive at the overall power plant exergetic efficiency. The baseline power plant scheme is found to have an exergetic efficiency of 47 percentage points with a thermal efficiency of 49.6 percentage, with capture.

The modified power plant scheme is obtained by increasing the gas turbine pressure ratio and this has a significant impact on the overall system design and hence the performance. The modified system has exergetic and thermal efficiency of 49 and 51 percentage points respectively. The advanced power plant with OTM, also called as the Advanced Zero Emissions Powerplant (AZEP) has an exergetic efficiency of 51 and a thermal efficiency of 53.4 percentage. In all the cases, the combustor where most of the fuel is burnt is responsible for majority of the exergy destruction.

There is potential for improving the ASU and thereby achieving a lesser specific oxygen production power and also due to system integration and other improvements, the overall oxy-combustion NGCC power plant is expected to play an important role in 5 - 10 years. Also as the working fluid is different from that of a normal air based power plant, significant work needs to be done in the gas turbine and compressor part. Also detailed cost estimations, reliability and flexibility studies, operability and safety related studies need to be carried out inorder to boost the confidence in oxy-fuel NGCC power plants and take it to the next phase.

Sammendrag

Forbrenning av naturgass i et kombinert gass-dampkraftverk ved forbrenning av rent oksygen (Oxy-fuel combustion) kan bidra til å senke CO_2 utslippet til atmosfæren. Ved ren oksygenforbrenning foregår forbrenningen uten nitrogen til stede. Den rene forbrenningen fører til enklere separering av CO_2 for lagring. Avhengig av oksygenkilde og kvalitet kan det være behov for videre rensing av CO_2 via en renseenhet (CPU) før gassen komprimeres for lagring. Produksjon av oksygen og nedstrøms rensing av CO_2 bidrar til storparten av energitapene i denne typen energiproduksjon. Det er også i disse energitapene kostnadene for å unngå CO_2 utslipp til atmosfæren ligger.

En kryogenisk luftsepareringsenhet står for rundt 20 % av det totale energitapet i denne typen kraftverk. Oksygentransportmembran (OTM) for oksygenproduksjon kan være et alternativ for å redusere energitap i denne typen prosesser. Energitapene i OTM oppstår pågrunn av høy driftstemperatur og krav til sweep gass for å oppnå partielltrykkdifferanse for oksygen over membranen. En luftseparasjonsenhet er i liten grad integrert i energiproduksjonsprosessen mens en OTM i stor grad vil vre en integrert del av energiproduksjonsprosessen. Energitapene i en OTM-prosess vil derfor være vanskeligere å identifisere. Målet med denne hovedoppgaven er å finne ut *hvor tapene i gass-dampkraftverk ved bruk av OTM oppstår sammenliknet med en prosess som bruker en luftsepareringsenhet.*

Arbeidet vil belyse tap i underprosesser og tap på komponentnivå. Tre ulike caser er undersøkt. En basis case, en forbedret/modifisert case og en avansert case. Basis casen er et enkelt gass-dampkraftverk med ren oksygenforbrenning hvor oksygenkilden er luftsepareringsenhet. Energitapene er studert i detalj. I den forbedrede casen inkluderes

en analyse av mulige modifikasjoner på basis casen og implementeres. Den forbedrede casen forventes å være en mer effektiv prosess en basis casen. Den avanserte casen bruker en oksygentransportmembran for oksygenproduksjon.

Energiproduksjonsprosessene er simulert i Aspen HYSYS og masse og energibalanser er gjort. Ved å bruke strømmenes entalpi, entropi og komposisjon, kan eksergiverdier finnes. Kontrollvolumer brukes for å analysere komponent eller underprosessers eksergitap, og til å finne prosessens totale eksergivirkningsgrad. Basiscasen har en eksergivirkningsgrad på 47 %, med en termisk virkingsgrad på 49,6 %, med CO_2 - fangst. Den modifiserte casen har et høyere innløpstrykk på gassturbinen, som har stor innvirking på prosessens design og ytelse.

Den modifiserte casen har en eksergivirkningsgrad og termisk virkningsgrad på henholdsvis 49% og 51%. Den avanserte casen med oksygentransportmembran også kalt AZEP (Advanced Zero Emissions Power plant), har en eksergivirkningsgrad på 51 og en termisk virkningsgrad på 53.4. I alle casene var det i forbrenneren hvor mesteparten av drivstoffet forbrennes mesteparten av eksergitapet oppsto. Det er potensial for forbedringer i luftsepareringsenheten og på grunn av dette å oppnå lavere spesifikt arbeid i oksygenproduksjonen og også på grunn av systemintegrasjon og andre forbedringer er gass-dampkraftverk med ren oksygenforbrenning forventet å ha en viktig rolle om 5-10 år. Siden det er et annet arbeidsfluid enn i vanlige luftbaserte gass-dampkraftverk mye arbeid gjenstår på gassturbin og kompressordelen. Detaljert kostnadsestimat, pålitelighets og fleksibilitetsstudier samt drift og sikkerhetsrelaterte studier må gjennomføres før ren oksygenforbrenning i gass-dampkraftverk kan tas til neste steg påveien til å oppnå tillit som utprøvd, pålitelig teknologi.

Acknowledgements

I would like to thank my supervisor, Prof. Olav Bolland for guiding me find the right people and resources in order to work with this master thesis. I'm thankful to Rahul Anantharaman (SINTEF), for helping me through out the project with inputs and clarification whenever required. Thanks to Toril Larssen in the administration department for helping me with fixing meetings with Olav, and other very essential errands with an ever smiling face!

Many thanks to Sultan Pwaga and other friends that helped me with my questions regarding Aspen HYSYS. Thanks to Terje Borlaug for translating the summary to Norwegian and Yasir Baig for sharing the much needed GT Pro keys at the right time.

Also I would like to thank my friends and family for moral support and being with me throughout the entire period which largely helped to concentrate on my work in the unpredictable Norwegian weather.

Also I would like to thank NTNU for all the resources and amenities such as computers, printers, softwares, books and other resources that helped me complete this project and learn a lot about my field of interest.

Rengarajan Soundararajan

Contents

List of Figures

List of Tables

Nomenclature

ΔG	Molar gibbs free energy of formation of the substance in kJ/kmol
$\dot{E}$	Exergy flow rate of a steady flow stream in kW
$\dot{E}^Q$	Exergy flow rate due to heat transfer in kW
$\dot{E}_0$	Chemical component of exergy flow in kW
$\dot{E}_e$	Outlet exergy flow rate in kW
$\dot{E}_i$	Inlet exergy flow rate in kW
$\dot{E}_k$	Kinetic component of exergy flow in kW
$\dot{E}_p$	Potential component of exergy flow in kW
$\dot{E}_{ph}$	Physical component of exergy flow in kW
$\dot{I}$	Irreversibility rate in kW
$\dot{m}$	Molar flow rate of the stream in kgmole/s
$\dot{Q}_r$	Heat transfer with reservoir r in kJ/s
$\dot{W}_x$	Work transfer in kW
ε	Specific exergy of the stream of substance in kJ/kgmole

ε^0	Standard chemical exergy of the substance in kJ/kmol
C_0	Bulk velocity of the stream in m/s
g_E	Acceleration due to gravity in m/s^2
h_i	Specific enthalpy of the stream in kJ/kgmole
P_0	Environmental reference pressure in Pa
P_{00}	Environmental partial pressure of an atmospheric gas in Pa
R	Gas constant in J/(kg K)
s_i	Specific entropy of the stream in kJ/kgmole-K
T_0	Environmental reference temperature in K
T_r	Temperature of the thermal reservoir in K
x_i	Mole fraction of ith component in the mixture
Z_0	Elevation above sea level in m

Chapter 1

Introduction

1.1 Motivation

Global energy demand is witnessing a sharper rise than ever before in the last few years. Although the recent financial crisis has reduced the demand for energy, the latter bounced back before even the economy started to recover fully and this is reflected in the price of commodities such as oil and gas. This can be attribured to the rise of new and emerging economies such as China, India and others. With signs of economic recovery in the west, global trade is set to witness new heights which will inevitably lead to more demand for energy and other natural resources.

Today, the global energy supply scenario is clearly dominated by fossil sources such as oil, coal and natural gas. Interest in fossil fuels can be attributed to several reasons such as their relatively cheap and abundant nature, proven technologies and hurdles in large scale development of other renewable energy sources such as solar and wind. As these natural resources are keen to the development of any country, there is an ever growing interest to secure these assets in order to ensure the supply. Countries such as China and India are investing in fossil resources abroad such as coal assets in Australia, Indonesia, South Africa and as a result of this, resource rich economies are witnessing a boom.

This leads us to the much talked about issue of the global warming. Burning of large amount of fossil fuels results in the increase in greenhouse gas concentrations in the atmosphere which inturn leads to human induced globbal warming. Research has shown that the recent warming pattern observed on the planet is largely man made! Because of the continued reliance on fossil fuels, the warming of the planet will only be accelerated and this could lead to serious climate related issues in the later part of this century.

Hence it is widely accepted that mitigation measures must be taken without delay, inorder to ensure a better future for the mankind. Although international efforts to curb greenhouse gases such as the Kyoto protocol has seen mixed responses, there is much more to be done both politically and technologically inorder to limit the emission of greenhouse gases into the atmosphere. Nuclear energy which was once considered to be emission free is facing many questions after the recent disaster in Japan. This may also lead to increase in fossil fuel usage. So, there is a need to make the fossil fuels cleaner inorder to limit the rise in global temperatures.

Norway, being an energy exporting nation has interest in developing technologies that make our energy ecosystem cleaner and better. Natural gas being the largest export commodity of norway is a relatively cleaner fossil fuel when compared to coal. At the same time, switching to natural gas from coal alone cannot be the only solution to the much bigger problem of global warming. Technologies such as carbon capture and sequestration (CCS) which essentially captures CO_2 emissions of a fossil fuel burning point source and stores in underground formation for a very long time, is required to achieve the reduction in greenhouse gas emissions. Due to the experience in the oil and gas industry, storage of CO_2 in sleipner formation for more than 15 years, Norway has both the technological leverage, economic support and political will to develop CCS technologies. It is worth mentioning that CCS is currently an expensive technology due to the penalties involved in capturing of CO_2 and also due to lack of a policy support.

By developing the CCS technologies, Norway can make its exports cleaner and not environmentally harmful. Also the depleted oil and gas reservoirs in the Norwegian continental shelf can be converted into large scale storage spaces for european emissions. Norway could also make use of the gas resources domestically and continue to export energy in the form of electricity, with lesser emissions. CCS being an expensive alternative for greenhouse gas mitigation, a lot of research needs to be done to reduce the penalty involved and to ultimately bring down the cost of commercial deployment of CCS technologies.

1.2 Objectives

The primary objective of this work is to study about the various losses in a system designed to generate electricity while emitting very little greenhouse gases into the atmosphere. The systems considered in this work are an oxy-fuel natural gas power plant with cryogenic ASU and one that employs an oxygen transport membrane (OTM) for oxygen production instead of an ASU. The technical details and the systems will be discussed later in detail.

The objectives can be summarised as follows:

1) To design a natural gas combined cycle power plant with CO_2 capture(commercial or near commercial technologies such as cryogenic

ASU) and quantify the various plant efficiency losses from the thermodynamic perspective.

2) To investigate any modifications possible to the design, inorder to improve the overall power plant performance.

3) To study the efficiency losses in an advanced power plant (with CCS) that employs technologies (OTM) that promises substantial benefits over todays available power plant technologies.

By studying the system from the thermodynamic point of view (second law analysis), we can answer the question "Where does the plant efficiency loss originate in oxy-combustion CO_2 capture process using oxygen transport membrane as compared to cryogenic ASU?"

1.3 Thesis organization and contribution

The thesis report contains seven chapters with analyses of three different power plant schemes. Chapter 2 gives a technical background relating to global warming and climate change, mitigation technologies including CCS and some insight into the oxy-combustion scheme studied in this report. Chapter 3 explains the methodology used to study the systems, tools and the theory behind the second law analysis. Chapter 4 has the baseline power plant scheme and discusses about the process design, thermodynamic assumptions and the results. Chapter 5 contains the modifications to the baseline power plant and results of the improved scheme. Chapter 6 has the design, thermodynamic assumptions and the analysis results of the advanced OTM based power plant. Final chapter has the short conclusion for this report.Results and discussion part is included in every chapter as every chapter is individual and the objective is not to compare three schemes. As the improved scheme is a modification of the baseline scheme, it is only natural to draw some comparisons to gain some perspective, although comparison of three schemes is not the main objective. The main objective is to locate and quantify the plant efficiency losses.

The main contributions of this master thesis are as follows:

1) The report guides the reader to the major factors/sub-systems within the scheme that are responsible for exergy destruction in an oxy-fuel power plant with CO_2 capture.

2)Process potential in terms of the overall capture plant efficiency can be obtained. This helps the reader to compare the oxy-combustion natural gas technology for power generation with other alternatives such as post/pre combustion natural gas/coal cycles.

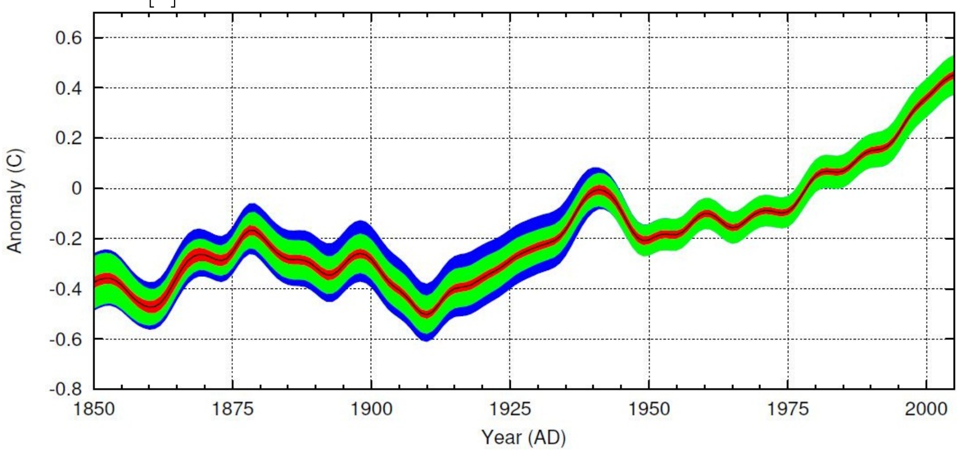
Chapter 2

Technical Background

2.1 Climate change and mitigation

2.1.1 The science behind

Figure 2.1: HadCRUT3 global temperature anomaly time-series. Brohan et al. [1].



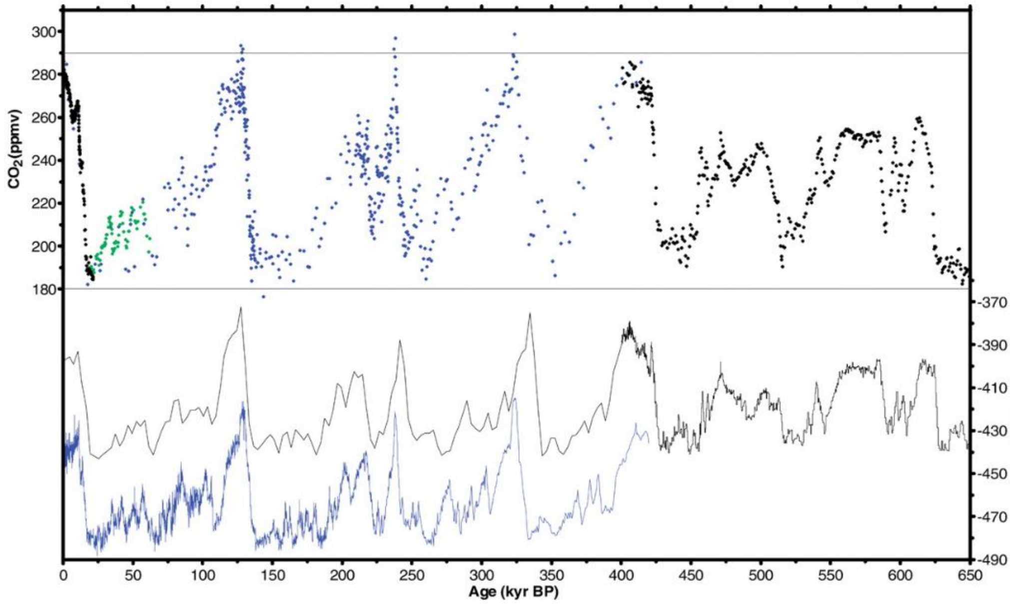
The solid black line is the best estimate. The red band covers the uncertainties caused by station, sampling and measurement errors, green band due to limited coverage and blue band adds the error range due to bias errors

Recent (from 1850) observations show unusual changes in the global climate. Eleven of the last twelve years (1995 to 2006) with the exception of 1996 - rank among the twelve warmest years on record since 1850. Three different global estimates all show consistent warming trends and there is also consistency between the data sets in their separate land and ocean domains, and between sea surface temperature and nighttime marine air temperature [2]. Also there are numerous anomalies observed in earths climate such as increase in tropospheric water vapour, changes in wind pattern, decreasing snow cover and much more [3].

From a palaeoclimatic perspective, the science is much more developed and credible than ever before. Studies indicate that there have been many changes in the climate in the past due to several factors. There are certain climate proxies through which it is possible to estimate the temperature and many other climate indicators into the past with reasonable accuracy. For instance, variations in deuterium from the air trapped within ice cores can be used to estimate the local air temperature [4].

The Earth's climate is determined by several factors such as the amount of solar radiation it recieves, reflection, absorption and emission of energy within the atmosphere and many other causes. The system is very complex and there are N number of factors that affect the energy budget of the earth and hence the mean global climate. Among the factors are the concentration of the greenhouse gases in the atmosphere which increases the radiative forcing by absorbing the outgoing radiation, aerosols that reflect the incoming solar radiation and hence result in some cooling effect and much more. We are more interested in the major factors that affect the energy balance and hence greatly influence the mean global climate of the earth.

Figure 2.2: A composite CO2 record over six and a half ice age cycles, back to 650,000 years B.P.-Siegenthaler et al. [4].



Based on our understanding of how the climate works and from the palaeoclimatic studies, it is possible to construct a climate model that can predict the global climate with reasonable and acceptable accuracy. The output from such models are inline with the observations from the studies. It is these kind of palaeoclimatic studies that show that there is something unusual with the earths climate in the recent industrial age. For instance, it has been found that atmospheric CO_2 concentration has lied within the range of 180 to 260 ppm by volume in the past 650,000 years before the present year [4]. This startling discovery can be taken as a proof that the latest climate anomalies are different and man-made.

One may ask that the climate models are man-made and that cannot predict the earths climate accurately. The climate models are constructed with the help of the understanding gained over the years from data collected from the climate proxies that give insight well into the past. Natural phenomenon such as solar variations, volcanic eruptions and other factors that are very rare and occur once in a very long time frame have been accounted by collecting and verifying data from multiple sources. The mathematical models are also validated extensively before using them to predict the climate. The models take care of almost all the natural factors.

The climate models predict climate taking the internal/natural factors and it is almost impossible to explain the recent changes in climate without external forcings (in this case, large scale greenhouse gas emissions). This shows that the recent climate change is largely man made.

More details on the climate models, model validation and attribution of the climate change can be found in chapter 8 and chapter 9 of the Working Group I (The Physical Science Basis) of the fourth assessment report (AR4 - IPCC) [5][6].

2.1.2 Greenhouse gas emissions and the climate

One of the major factors affecting the climate in this industrial era is the atmospheric greenhouse gases [6]. Some gases are produced due to natural phenomenon such as volcanic eruptions and some are only produced due to human activities. The contribution of each type of greenhouse gas to the global warming can be calculated using its atmospheric lifetime and the effectiveness of the gas in perturbing the radiative balance. Some greenhouse gases may stay longer in the atmosphere but have lesser effect on the climate whereas other gases may have a very short lifetime but a great effect on the climate.

Natural processes continuously remove and recycle these greenhouse gases from the atmosphere. The removal rate of each gas determines the atmospheric lifetime of the gas. This, combined with the rate of production of the gas will result in either increase or decrease in the concentration of the gas. Hence, if a greenhouse gas is produced at a rate which is substantially higher than the natural removal rate, it may result in dangerous increase in the atmospheric concentrations of the gas.

Due to human activities such as agriculture, combustion of fossil fuels and other industrial processes, a lot of greenhouse gases are released into the atmosphere. The principle of all those gases is carbon dioxide. Carbon dioxide being chemically stable, has a long life span and hence is well mixed and the average atmospheric concentrations can be measured from anywhere on earth.

Carbon dioxide is recycled by nature through the carbon cycle and hence it is continuously released and absorbed by several natural means such as vegetation, oceans etc... The increase in the atmospheric concentration of the gas indicates that the natural capacity of the earth to recyce the gas has been exceeded by the anthropogenic emissions. This trend of releasing a large amount of greenhouse gases into the atmosphere, if continued may cause rapid warming of the earth and hence may cause lot of climate related issues within the end of this century.

Climate change poses a lot of threat to water resources and availability, precipitation and wind pattern, can cause sea level rise, desertification to name a few. These changes are expected to cause significant economic and social burden to the people by causing frequent and severe floods, draughts and other extreme weather events [7]. The extent to which climate change affects the people depends on the geography and vulnerability of a particular region. Some regions maybe positively affected by climate change and other regions may be negatively affected.

2.1.3 Potential mitigation measures

There is a continued reliance on fossil fuels for energy production and this seems to continue or even increase in the future. Fossil fuels are projected to dominate the global primary energy supply scenario atleast until 2030 based on studies by the International Energy Agency [8]. Hence it is virtually certain that the atmospheric greenhouse gas concentrations (primarily CO_2) are set to increase dramatically over a short period of time. At the same time a lot of mitigation measures are suggested by the international community.

It can be argued that political measures are key to such mitigation measures, technological developments are also required to make the measures cost effective and reliable. For instance, a stable price for carbon can encourage the industries and power producers to reduce their emissions and at the same time availability of cheap alternatives to fossil fuels will also naturally steer the economy towards a low carbon energy scenario.

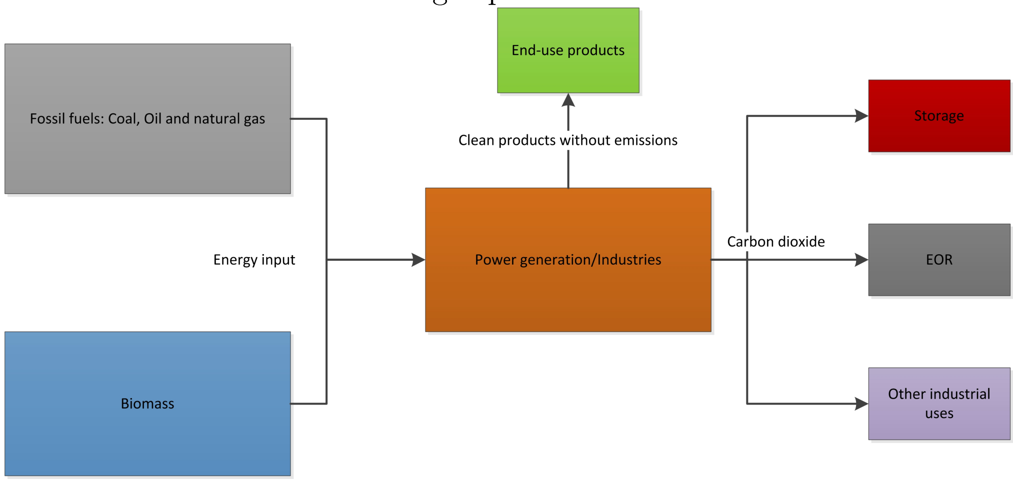
Each source of emission such as power generation, transport, agriculture holds varied potential and challenges for mitigation based on the cost of mitigation and other technical and non-technical issues. There is substantial potential available in the power generation industry for mitigation. As the electricity generation industry is dominated by fossil fuels and due to the cost of some alternate electricity generation technologies, there is a need to make the sector cleaner, i.e. There is a need to make fossil fuel based power generation more environmental friendly. The estimation of mitigation potential is complex in nature and can be found in detail in the report published by IPCC [9].

2.2 Role of CO_2 capture in mitigation

Carbon Capture and Sequestration (CCS) has been found to have an economic potential of 220 to 2200GtCO_2 cumulatively, which is equivalent to 15-55% of the cumulative worldwide mitigation effort until 2100 in most of the atmospheric CO_2 stabilization scenarios [10]. Moreover, inclusion of CCS in the mitigation portfolio is expected to bring down the total cost of stabilizing atmospheric CO_2 concentrations by 30% or more [10]. The technical potential for CCS is much more than the economic potential. Two interesting aspects of CCS is its compatibility with existing energy supply infrastructure and the potential to provide negative emissions when coupled with biomass.

Fossil fuels such as coal lock the carbon away from the atmosphere. Industrial processes and power generation that need energy for operation, access these fossil sources of energy and thereby release the carbon into the atmosphere. CCS processes capture the CO_2 while burning the fossil fuels for energy and transport it for either storage or Enhanced Oil Recovery (EOR). Storage is mainly geological storage or ocean storage aimed at locking the carbon away from the atmosphere. EOR is mainly aimed at producing oil that is difficult to extract. Also other methods such as mineral carbonation can be used to store CO_2 for sufficiently long time.

Figure 2.3: Schematic of the possible CCS system showin the source of carbon dioxide and the storage options.



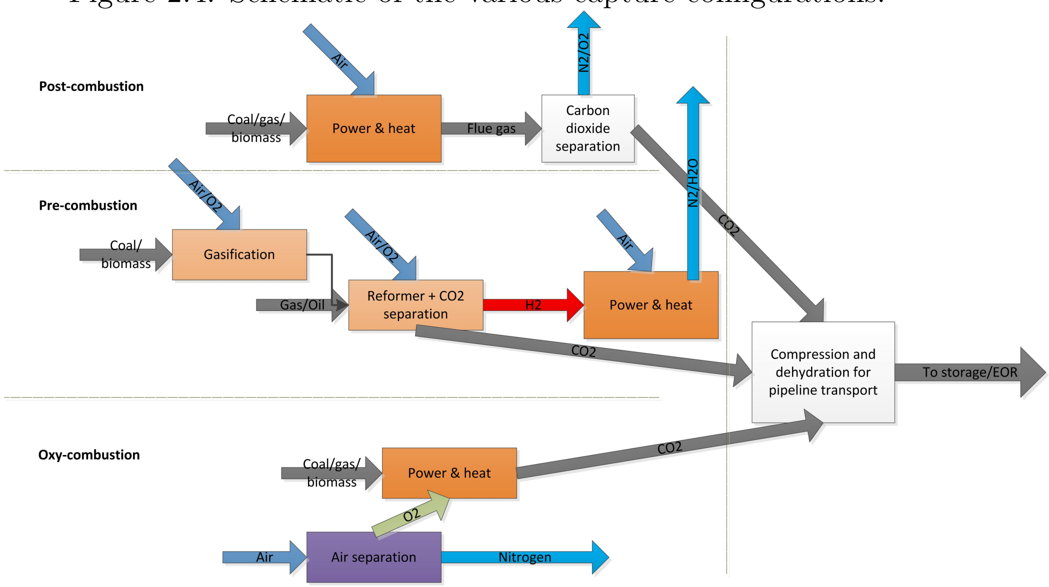
Although EOR will not offer a permanent storage option, it provides a source of income and thereby helps reduce the cost of capture and transport. Hence EOR may help kickstart the CCS technologies in the near future and the scheme may sustain itself when necessary regulatory framework is ready. As mentioned earlier, when coupled with biomass, CCS offers a unique way to remove CO_2 from the atmosphere and thereby results in negative emissions. The end use products from industries using CCS will be emission free. For instance, if coal power plants are enabled with CCS and the transport system is electrified, then the benefit will be manifold.

The technology for transport of CO_2 is matured whereas the technology for storage is also well developed due to the experience with the oil and gas industry. The technology for capture, which is the most expensive part of the CCS chain, is at various stages of development and needs much more research to bring the costs down. Also the regulatory framework needs to be developed. Geological potential for storage is believed to be available for large scale global storage of

CO_2 from the power and industrial sector.

There are mainly three different methods used to capture CO_2 from the source. They are post-combustion method that captures the CO_2 using chemical scrubbing (using amines) after burning the fuel, pre-combustion method that separates the carbon from the fuel before burning and the oxy-combustion method that burns the fuel in a nitrogen free environment so that the resulting flue gas will be rich in CO_2.

Figure 2.4: Schematic of the various capture configurations.



Post-combustion process involving amine solutions to scrub CO_2 from the flue gas is the most matured of all the capture technologies. There are detailed studies of cost estimations, and other optimizations studies available on this scheme [11].

Pre-combustion is particularly useful with biomass and hydrogen production. Integrated Gasification and Combined Cycle (IGCC) power plants are expected to play a major role as coal is abundant in nature and also due to potential synergies with biomass and large scale hydrogen production.

In this report, we discuss in detail about the oxy-combustion CO_2 (AKA oxy-fuel) capture scheme.

2.3 Oxy-fuel capture: description of subsystems

Since the focus of this report in oxy-fuel capture, the major components of such a system are described in this section.

Figure 2.5: Schematic of the generic oxy-combustion natural gas combined cycle.

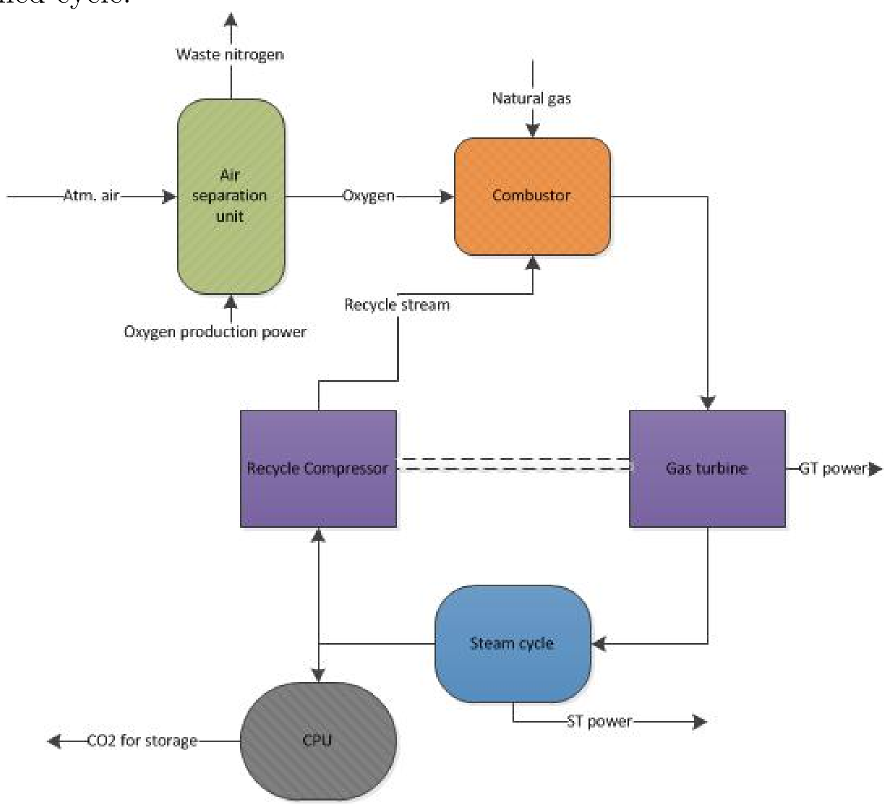


Figure 2.5 shows the general schematic of an oxy-combustion natural gas combined cycle with CO_2 capture and compression. The CPU in the figure is the CO_2 processing and compression unit that removes the volatiles such as nitrogen, oxygen and argon.

2.3.1 Oxygen production and purity

Oxygen production is the heart of any oxy-combustion process as it is the key step in achieving nitrogen free combustion. Also it is responsible for the major penalties incurred for the capture of CO_2.

Cryogenic distillation

Cryogenic air separation is the state-of-the-art technology for large scale production of oxygen. The process involves distillation of liquified air into its main components, namely nitrogen, oxygen and argon. As we are talking about large scale production of oxygen in the order of several thousand tons per day, the product specifications such as purity, delivery pressure and other conditions such as solid or liquid state has a bearing on both the capital cost of the Air Separation Unit (ASU) and also on the operation cost mainly in the form of energy requirement. Also, the ASU forms a substantial part of the overall plant and is responsible for a significant portion of the auxilliary power consumption.

As the main objective in going for an oxy-fuel combustion is to eliminate nitrogen, so as to enable easier separation of CO_2 from the flue gas, oxygen product purity plays an important role in the overall design of the plant. It is vital to choose an energy-optimal oxygen purity, usually in the order of 95-97%. Also, as the combustor pressure in a gas turbine combined cycle is in the order of 20-30 bars, oxygen delivery pressure is a major parameter in determining the overall plant efficiency.

Although oxygen production by cryogenic distillation of air is a commercially matured process, there have been many improvements over the time that has resulted in significant reduction in the specific oxygen production power and the trend is expected to continue in the future.

Oxygen Transport Membrane

Oxygen production by oxygen transport membranes is an emerging technology to produce oxygen in large scale which promises substantial savings in the specific oxygen production power. Although there are lot of challenges regarding the membrane technology, this particular technology for large scale oxygen production for power generation applications appears promising.

2.3.2 Oxygen combustion stoichiometry

Oxy-fuel combustion must ideally be carried out under pure stoichiometric conditions, but due to combustion requirements, there is a need to have an excess oxygen level in the combustor. This excess oxygen level increases the overall CO_2 capture penalty by requiring more oxygen flowrate from the ASU, as well as requiring more effort to remove volatiles from the flue gas resulting from the combustion.

2.3.3 Heat Recovery Steam Generator

The Heat Recovery Steam Generator is used to generate steam for the bottoming cycle by using the heat rejected by the gas turbine. The HRSG is nothing but a set of heat exchangers producing steam usually at three different pressure levels. The exhaust gas from the HRSG is taken to the stack where it is released to the atmosphere. In an Oxy-fuel cycle, involving CO_2 capture, major portion of the exhaust gas is recycled to the combustor and a part of the exhaust is tapped for processing and compression to pipelinne pressure which is then transported to the storage site. Eventhough the HRSG handles a gas stream that is different in composition than that of a gas stream from a regular gas turbine using air for combustion, there will not be a significant change in terms of the HRSG design for the Oxy-fuel cycles.

2.3.4 Compressor and Turbine

The compressor and the turbine used in the system is different from that of the usual gas turbine as it largely handles a different gas mixture. Hence, all of the thermodynamic parametres of the turbine and compressor are assumed. This type of gas turbine that runs primarily on a CO_2 rich gas is yet to be developed.

2.3.5 CO_2 purification and compression

The flue gas stream from oxy-fuel process, though rich in CO_2 will have other volatiles and impurities to be removed before conforming to the pipeline specifications for furthur storage or Enhanced oil recovery activities.

It is found that CO_2 concentration should be atleast 95% for pipeline transport [12]. A typical natural gas fuelled oxy-combustion process with recycle has a CO_2 concentration of around 75% with water, nitrogen, argon, oxygen and other impurities forming the rest. Presence of volatiles such as oxygen, nitrogen causes several issues such as increased power penalty for compression, overheating at injection point and so on. All these requirements and constraints make CO_2 purification system a necessity even for oxy-fuel processes.

A series of processes such as Seawater Flue Gas Desulphurization (SFGD), compression, cooling, and flashing or distillation is required to remove all of the volatiles and impurities. This adds to the overall penalty of the CO_2 capture and reduces the overall plant efficiency.

Chapter 3

Methodology

3.1 Process design and modelling

The power plant design was carried out with inputs from

1) Literature review
2) Discussions with Prof.Olav Bolland and Rahul Anantharaman (SINTEF)

The designs were developed within the process constraints considering practical issues. Some of the key design considerations include:

1) Oxygen purity and production power
2) Gas turbine pressure ratio and inlet temperature
3) Condensation of flue gas in the HRSG

Thermodynamic assumptions, steam pressure and temperature levels, equation of state and other essential design parametres were selected in accordance with the current technological development and industry standards. Design was discussed and verified with Prof.Olav

Bolland. The power plant was simulated in Aspen HYSYS (Version 7.2). The ASU was not simulated in detail in this work. Instead, the power required to produce the oxygen and the energy optimal oxygen purity was taken from the literature [13][14][15].

The HRSG design in the steam cycle was done in an indirect way as follows. The HRSG being the most complex part of the cycle, was designed using Thermoflow GT Pro and then the design was transferred to Aspen HYSYS for exergy calculations. Thermoflow GT Pro is a combined cycle power plant design software which can be used to design a HRSG of a steam bottoming cycle if the gas turbine was removed and the flue gas parametres are specified. In GT Pro, there was only limited flexibility in specifying the flue gas compositions and hence a flue gas different from that of the actual HYSYS stream was assumed to come up with the HRSG design. The flue gas composition assumed was similar to the original flue gas in terms of the specific heat capacity and hence would represent the actual case. As the HRSG involves only heat transfer and no other complex processes, the only process parameter that has to be same is the heat capacity (C_p).

The HRSG design transferred to Aspen HYSYS performed similar to that of the one in the GTPro. All the thermodynamic assumptions such as pinch temperatures, flue gas exit temperature and other parametres of the Aspen design was found to be inline with the GTPro specifications.

The CO_2 purification and compression unit (CPU) which is used to remove the volatiles and compress the CO_2 stream to pipeline specifications was also not designed in detail. Instead, the power required for the process is scaled from similar estimates found in the literature [12]. The flue gas parametres from a similar oxy-fuel natural gas combined cycle available in the literature was found to be similar to that of the stream in the process designed in this work and hence the purification and compression power required per kg of CO_2 stored was assumed to be same.

3.2 Exergy analysis

3.2.1 The concept of exergy

Traditionally, energy balances are used to assess the performances of engineering systems. Although they provide some information regarding the performance of the systems under consideration and enable us to compare and evaluate various designs, analyses just based on energy is not enough from the thermodynamic point of view. For instance, heat loss from a pipe carrying high temperature steam is not equivalent to the heat rejected by the condenser eventhough the quantity of energy could be the same. Also, the energy balances provide no information about internal losses such as losses in combustion, adiabatic throttling, heat transfer etc.. An energy balance on these processes would show these as perfect processes with no losses.

Some other criteria of performance is necessary in order to asses the thermodynamic perfection of these processes. Traditional analyses of the systems under the First law of thermodynamics provide limited information on the performance of the system, especially from the work point of view. Hence, a different analysis method based on the second law of thermodynamics, called the Exergy Method is necessary to locate and quantify the losses in the system under study. The loss of exergy or the irreversibility provides a measure of process inefficiency. Exergy of a steady flow stream can be defined as the maximum amount of work that can be generated by thermal interaction with the reference environment.

The concept of exergy heavily depends on the definition of the reference environment in which the system operates. The Environment is a very large body or medium in the state of perfect thermodnamic equilibrium. Any system outside the environment with a differnet pressure, temperature or a different chemical composition can be considered to have a potential to cause change by interacting with the environment. The natural environment consists of the atmosphere, the oceans and the earth's crust. The physical parametres and the composition of matter in these components of the environment forms the reference to the system under consideration.

In the *dead state*, the system is in mechanical, thermal and chemical equilibrium with the environment and hence cannot cause any more change or produce work by interacting with the reference environment. Hence, all the substances that form the conceptual environment are in their respective dead states and hence it is not possible to extract work from the components available from the environment. The exergy of atmospheric air is thus zero and no work can be extracted with just air unless it is heated or pressurised by some other inputs such as a fuel.

Exergy has many components such as kinetic, potential, physical, and chemical exergies. The kinetic and potential components of exergy are the kinetic and potential components of energies of the stream of substance, that are ordered forms of energy and hence fully convertible into work.

$$\dot{E} = \dot{E}_k + \dot{E}_p + \dot{E}_{ph} + \dot{E}_0 \tag{3.1}$$

$$\dot{E}_k = \dot{m}^{C_0^2}/_2 \tag{3.2}$$

$$\dot{E}_p = \dot{m} g_E Z_0 \quad (3.3)$$

where $\dot{m}$ is the mass flow of the stream, C_0^2 is the bulk velocity of the stream relative to the surface of the earth, g_E is the acceleration due to gravity and Z_0 is the altitude of the stream above sea level.

Physical exergy is equal to the maximum amount of work obtainable when the stream of substance is brought from its initial state to the environmental state defined by P_0 and T_0, by the physical processes involving only thermal interaction with the environment [17].

The physical exergy of a stream of substance can be naturally divisible into two components. The *thermal component* of the physical exergy is a result of the temperature difference between the stream and that of the environment whereas the *pressure component* of the physical exergy is a result of the difference in pressure between the stream and that of the environmental pressure. Hence, when a stream of substance at a high pressure and a high temperature is brought to the environmental state either by cooling at a constant pressure and then by isothermal expansion reversibly, the work extracted is the physical exergy of the stream. In fact, any combination of reversible processes can be used to access the thermal and the pressure components of the physical exergy and convert them into work reversibly.

$$\dot{E}_{ph} = \dot{E}_1 - \dot{E}_2 = \dot{m}[(h_1 - h_2) - T_0(s_1 - s_2)] \quad (3.4)$$

where h, s are the specific enthalpy and specific entropy of the substance respectively. The state 1 corresponds to the actual state of the stream and 2 corresponds to the environmental state temperature and pressure. T_0 is the temperature of the reference environment or the reference temperature.

Chemical exergy is equal to the maximum amount of work obtainable when the substance under consideration is brought from the environmental state to the dead state by processes involving heat transfer and exchange of substances only with the environment [17].

To assess the work potential of a stream of substance by virtue of the difference between its chemical potential and that of the environment, properties of the chemical elements comprising the stream must be referred to the properties of some corresponding suitably selected substances in the environment. The *reference substances* must be *in equilibrium with the rest of the environment.* A general scheme of *standard reference substances* for each chemical element and the chemical exergy values are provided by Kotas [17]. For instance, the chemical exergy of pure nitrogen in the environmental temperature and pressure is the amount of work obtainable when the stream of nitrogen is expanded reversibly from the environmental state (T_0 and P_0) to its partial pressure (P_{00}) in the atmosphere which is the reference environment for gaseous nitrogen. Then the expanded gas can be discharged through a semi-permeable membrane into the atmosphere.

In most of the engineering applications such as a power or a chemical plant, the stream under consideration is usually a mixture of more than one pure chemical component and hence there is a need to account for the loss of chemical exergy due to the mixing. This loss can be accounted as the reversible work required to separate and compress each of the N components of a mixture from their partial pressures in the mixture to the environmental pressure, reversibly and isothermally. The total work of compression per mole of an ideal gas stream is:

$$\sum_i [W_{xi}]_{REV} = RT_0 \sum_i x_i ln x_i \tag{3.5}$$

where x_i is the mole fraction of i^{th} component in the mixture. Hence, the total exergy of the stream will be the sum of physical and chemical exergy after accounting for the mixing exergy losses where the kinetic and potential components of exergy are usually neglected.

3.2.2 Stream exergy flows

Process simulations by HYSYS and GT pro provide the stream composition and properties for both the actual process and the environmental conditions. The stream composition and properties obtained from the simulations are then used in an in-house program to calculate the total exergy flow (MW) of each stream, using a method provided by Kotas [18][19]. The total exergy flow of every stream is the sum of physical and chemical exergy flows, less the mixing exergy losses. The mixing exergy losses are calculated at the actual stream conditions. In order to calculate the physical exergy of a stream, we need the molar flow of the stream, specific enthalpy and specific entropy of the stream at both actual (process) and at reference conditions (environmental). The environmental conditions for our case was that of the ambient conditions i.e Pressure 101,325 Pa, Temperature 15 ^0C and a Relative humidity of 60%.

As for the chemical exergy calculations, the stream composition is the data required along with the *standard chemical exergy* values of the pure components that are the constituents of the stream. Although the standard chemical exergy values are provided by Szargut [20], these values are calculated for the standard environmental conditions i.e for 25 ^{0}C (298.15 K), 1 atm (101,325 Pa) and 70% RH. As our process involves large scale separation of air gases (ASU), as suggested by Ertesvåg [21], it is appropriate to re-calculate the standard chemical exergy values of the pure components involved in our study, that have atmospheric references. Hence, we recalculated the standard chemical exergy values based on the air composition used in the simulation. Table 3.1 provides the updated standard chemical exergy values for atmospheric reference substances used in this analysis.

Every chemical substance has a reference substance in the environment using which the standard chemical exergy is calculated. For some substances, the reference is same as the substance itself and for other substances it could be different. Also there is a reference reaction and gibbs energy of formation based on which the standard chemical exergy values are calculated. For instance, the reference substance for CO_2 is the gas itself as it is a constituent of the atmosphere and hence the molar chemical exergy of pure CO_2 at environmental conditions is the reversible isothermal compression work required to compress one mole of the gas from its atmospheric partial pressures to the atmospheric pressure (eqn 2.5). In case of other chemical substances such as methane which are not a part of standard environment, the chemical exergy values are calculated as below:

$$\varepsilon^0{}_{CH_4} = -\ \Delta\mathrm{G} + \varepsilon^0{}_{CO_2} + 2\varepsilon^0{}_{H_2O} - 2\varepsilon^0{}_{O_2}$$

where ΔG is the molar gibbs free energy of formation of methane at environmental temperature and pressure.

Table 3.1: Updated standard chemical exergies

Component	**Standard chemical exergy kJ/kmol**
Nitrogen	616.86
Oxygen	3768.87
Carbon dioxide	19434.20
Argon	11225.10
Methane	833656.67
Propane	2153215.98
Water	11009.29
n-Butane	2805841.98
Ethane	1497312.41
n-Pentane	3460973.30
n-Hexane	4115449.29

Mixing exergy losses for all the streams were also calculated based on equation 2.5, which is based on the method suggested by Kotas [18][19].

$$\dot{E}_i = \dot{E}_{Phy} + \dot{E}_{Che} - \dot{E}_{Mix} \qquad kW \tag{3.6}$$

3.2.3 The exergy balance

Once we have all the stream exergy values, we can calculate the irreversibilities in the various components of our system. We need to define the control region of the component and then we need the various input and output streams to the component, work and heat interactions in order to make an exergy balance of the component. Unlike energy, exergy is actually destructible and hence there will be a difference between the exergy flow input to the system and that of the exergy flow output from the system in a real world scenario and that difference is the irreversibility rate. The magnitude of irreversibility rate defines the thermodynamic perfection of the system according to the second law. The exergy balance of a control region undergoing a steady-state process can be written as [17]:

$$\dot{E}_i + \dot{E}^Q = \dot{E}_e + \dot{W}_x + \dot{I} \tag{3.7}$$

$$\dot{E}_i = \sum_{IN} \dot{m}\varepsilon \tag{3.8}$$

$$\dot{E}_e = \sum_{OUT} \dot{m}\varepsilon \tag{3.9}$$

$$\dot{E}^Q = \sum_{in} \dot{Q}_r [{}^{T_r - T_0}/T_r] \tag{3.10}$$

3.2.4 Irreversibility rate

The exergy method [17] allows us to calculate the numerical value of process irreversibilities. The irreversibility can be divided into *internal irreversibilities* that includes friction, uncontrolled combustion, heat transfer over a finite temperature difference etc... and *external irreversibilities* that include mixing of gases into the atmosphere, loss of heat to the environment, etc... The definition of control region helps us calculate both forms of irreversibilities. By comparing the magnitudes of the irreversibility rates for the various plant components, one can see at a glance where the greatest losses occur and focus on the areas to be improved. But, just the value of irreversibility doesnt give us the potential for improvement in performance. The potential for improvement in a given component is determined by its irreversibility rate under a given set of conditions in relation to the minimum irreversibility rate possible within the limits imposed by physical, technological and economic and other constraints. This type of minimum irreversibility rate is called the *intrinsic irreversibility rate*. The difference between actual and the intrinsic irreversibility rate is the *avoidable irreversibility rate*.

$$\dot{I} = \dot{I}_{intrinsic} + \dot{I}_{avoidable} \tag{3.11}$$

Efficiency of some plant components can be readily improved by making a few modifications at a relatively low cost where as that of other components might be expensive. For instance, increasing the size of a heat exchanger may help in better utilizing the available heat streams but the increase in size must be economically justifiable. Some components may be more efficient when their complexity is increased, but that might come at some other costs such as increased operability issues or reduced availability. Hence, its always a trade-off between cost and thermodynamic perfection.

3.3 Control volumes and loss calculation

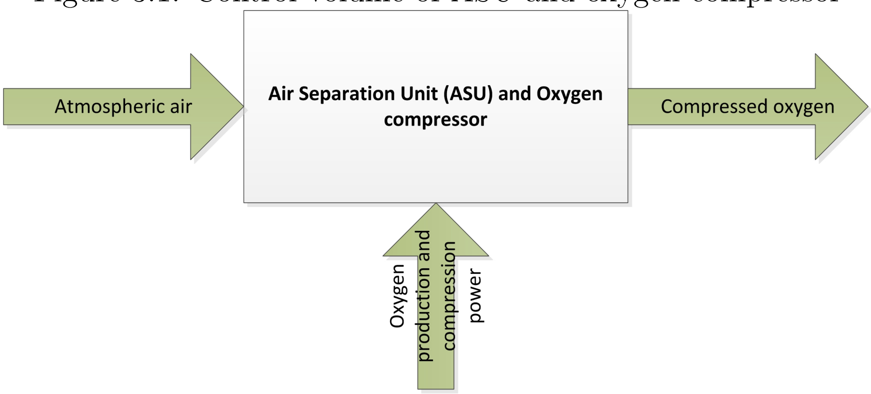
The process simulation provides us with the necessary parametres to calculate stream exergy values. After arriving at the stream exergy values, the control volumes for each component/sub-process is established with all the inputs and outputs defined. This helps us calculate the exergy losses in each of the component/sub-process, sum of which provides the total losses in the system. This inturn gives the exergetic efficiency of the system when all the inputs to the system are identified.

All the components/sub-processes are explained below in which the difference between sum of all the inputs and sum of all the outputs gives the irreversibilities.

ASU and oxygen compressor

The ASU and the oxygen compressor is taken as a single block with atmospheric air (contains no exergy) and the power as inputs. The output of the block is the compressed oxygen as per the assumed purity. The nitrogen stream produced by the ASU is not used anywhere in the system and hence considered as a waste (irreversibility). The irreversibility includes that of the ASU and that of the compressor along with the waste nitrogen stream.

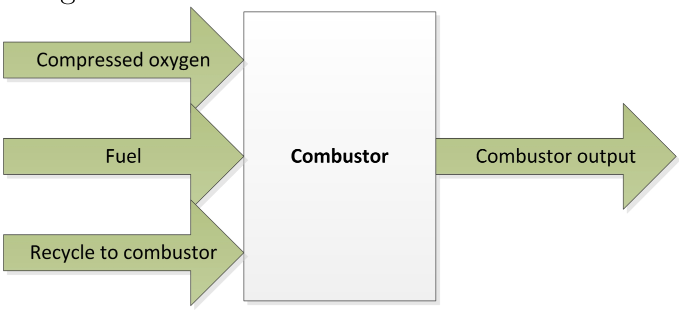
Figure 3.1: Control volume of ASU and oxygen compressor



Combustor

The control volume for the gas turbine combustor is shown below. Irreversibilities due to mixing, heat conduction, viscous dissipation, chemical reaction and others contribute to the overall entropy production in the combustion process. Combustor output is the hot gas resulting from the oxy-fuel combustion process that has to be cooled down before expansing in the gas turbine.

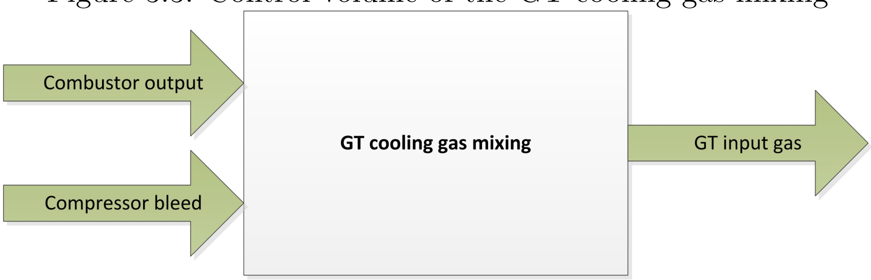
Figure 3.2: Control volume of the Combustor



GT cooling gas mixing

The gases out of the combustor are mixed with a bleed gas from the compressor to achieve the desired TIT. The exergy losses in this process are mainly due to heat comduction and mixing of gases which is inherently irreversible.

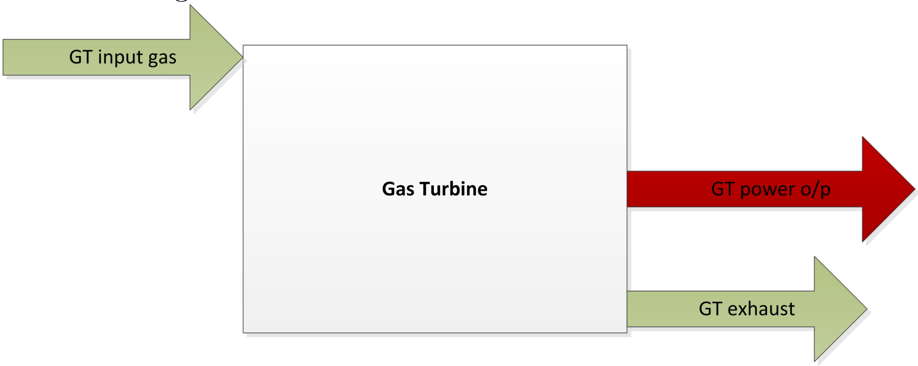
Figure 3.3: Control volume of the GT cooling gas mixing



Gas turbine

The hot gases are expanded in the turbine until the specified outlet pressure is reached. This generates the useful work and the irreversibilities are mainly due to the isentropic efficiency of the turbine. The turbine exhaust is not considered a waste as it is fed to the downstream steam cycle for additional power generation.

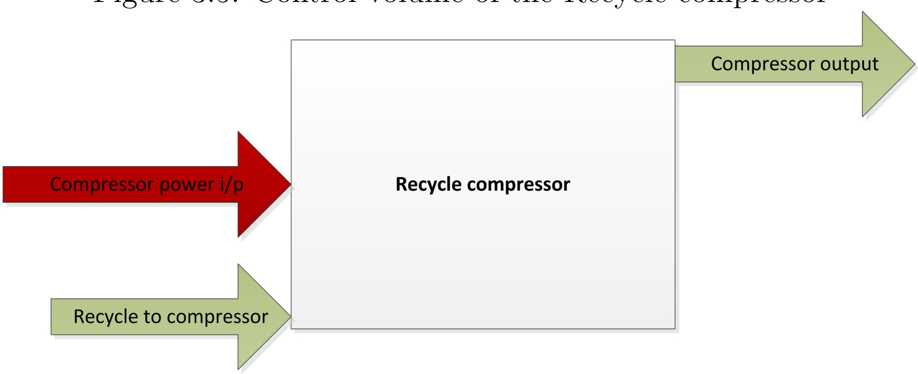
Figure 3.4: Control volume of the Gas turbine



Recycle compressor

The recycle compressor is the main compressor in the system that increases the pressure of the recycle stream to the desired level determined by the gas turbine pressure ratio. The exergy losses in the compressor are due to non-ideal (non-isentropic) compression of the gas stream. Work input to the compressor and the recycle stream are the inputs with the high pressure recycle being the output.

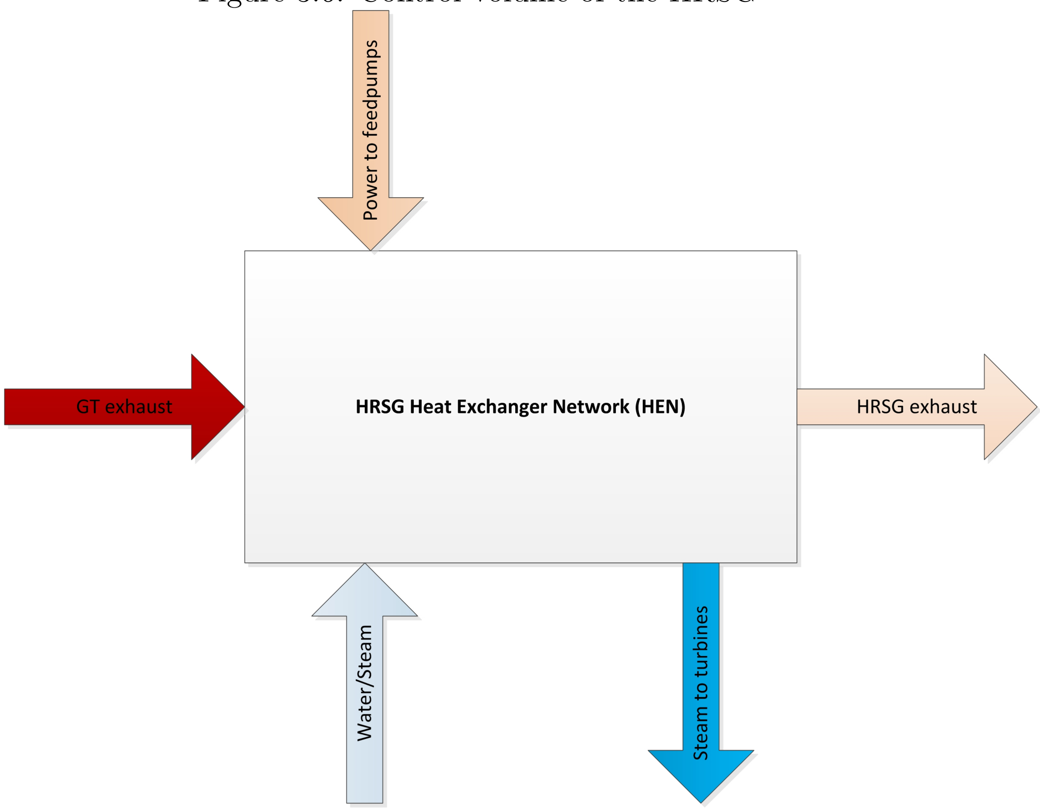
Figure 3.5: Control volume of the Recycle compressor



HRSG HEN

Heat recovery steam generator-Heat exchanger network is one of the main components of the steam cycle. Feedwater or steam inputs such as the cold reheat enters the HRSG and high quality superheated steam leaves the HRSG. On the gas side, the gas turbine exhaust enters at a very high temperature and leaves at a fairly low temperature. The main function of the HRSG is to produce steam by using the thermal exergy of the input hot gas. Hence, the irreversibility is mainly due to heat transfer between finite temperature difference. Also the HRSG exhaust is not considered as a loss in a closed cycle. But in a open cycle, where the HRSG exhaust is released to the atmosphere through a stack, the mixing exergy losses contribute to significant amount of exergy losses.

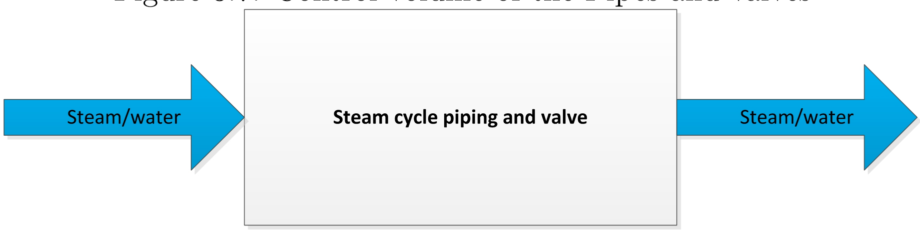
Figure 3.6: Control volume of the HRSG



Steam cycle pipes and valves

Although there is no major thermodynamic processes take place in the pipes and valves, they contribute to considerable losses due to their non-ideal nature. Pressure drops in steam pipes and valves are the major cause of irreversibility.

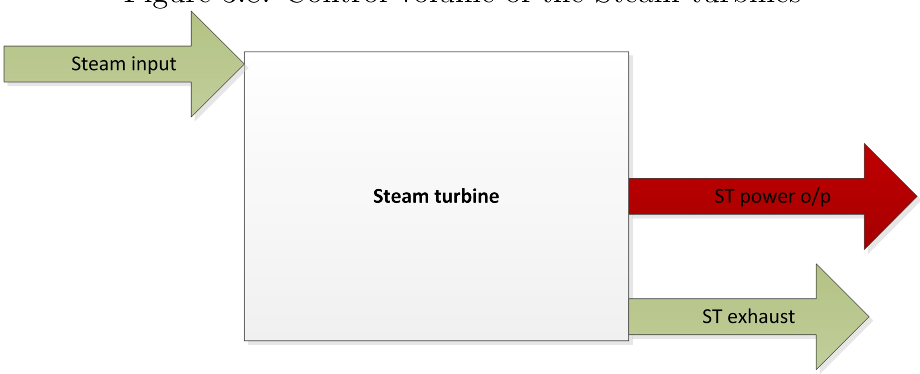
Figure 3.7: Control volume of the Pipes and valves



Steam turbines

Steam turbines expand the steam produced in the HRSG and generates power. Irreversibility in a steam turbine are due to non-isentropic expansion of the steam inside the turbine due to various factors.

Figure 3.8: Control volume of the Steam turbines



Balance of plant systems

The CO_2 purification and compression unit (CPU), the flue gas cooler after the HRSG which is used to cool the flue gas temperature, The steam turbine condenser and other system auxilliaries are considered as losses as these systems does not produce useful output. For instance, all the work input to the CPU is considered as a waste and similarly, the steam turbine conderser is dissipative in nature. Hence, all these systems have only inputs and no outputs. Other components such as the splits and the separators are considered lossless.

Part of the recycle stream separated for storage is also considered a loss in this analysis. The stream contains mainly carbon dioxide and hence containns a lot of chemical exergy. The thermomechanical exergy of the stream is low due to its low temperature and pressure.

Fuel being the main input to the power plant with make-up water and atmospheric air making up the rest. The main exergy output of the power plant is the net electricity output. This helps us to calculate the second law efficiency of the power plant. Also in this report, sum of all the individual component losses are verified to be the overall system loss.

The above method is used for the baseline case as well as the modified/improved case as both the systems are identical. For the AZEP case discussed in chapter 6, the system is different although many components such as the gas turbine, compressor, steam cycle components are similar.

Chapter 4

Baseline oxy-combustion natural gas combined cycle with Cryogenic ASU

In this chapter, an oxy-combustion natural gas combined cycle with cryogenic ASU is presented. The cycle contains a three pressure reheat HRSG.

4.1 Process description

4.1.1 GT cycle description

The flowsheet of the process is shown in figures 4.1 and 4.2. The process flow diagram for the whole case is divided into two parts, one each for the semi-closed gas turbine cycle and the steam cycle. Within the gas turbine cycle, the oxygen compressor is shown where as the oxygen source, the ASU is not displayed. Oxygen supply parametres are assumed instead of modelling the ASU in the process flow diagram.

Fuel input is assumed as a material stream avaialble at 70 bars. In the gas turbine cycle, the HRSG is shown as a cooler and the output gases of HRSG is fed to a separator unit after cooling to a very low temperature. Also, the CO_2 processing unit is not considered in the simulations.

The available oxygen at the assumed purity is compressed to the required pressure depending on the combustor pressure and the pressure drops associated with the pipes and nozzles. This compressed oxygen is fed to the combustor along with the fuel and the recycle stream from the compressor. The combustor outlet gases are at a temperature higher then the allowed maximum Turbine Inlet Temperature (TIT) and hence a bleed stream from the compressor is mixed to achieve the desited TIT. The hot gases expand in the turbine generating useful power and leaves at a low pressure but at a fairly high temperature. This high temperature exhaust enables us to use a Heat Recovery Steam Generator (HRSG) to produce steam and generate additional power. The flue gases from the HRSG is furthur cooled to condense the water content before extracting a part of the flue gas for processing and storage.

4.1.2 Steam cycle description

The steam cycle consists of three pressure levels and reheat for better efficiency. The steam cycle components including pumps, turbines and various heat exchangers like the economizers, boilers and superheaters are modelled assuming reasonable and industry accepted assumptions. The steam cycle major components including low temperature economizer (LTE), low, intermediate and high pressure economizers (LPE, IPE and HPE), boilers (LPB, IPB and HPB) superheaters (LPS, IPS and HPS), the reheat section (RH), pumps, turbines and condenser are shown in the figure.

In the steam cycle model, the steam turbine consists of four turbines with a HP, IP and two LP turbines. Majority of the HP turbine exhaust is extracted as cold reheat stream (CRH) and the inputs for IP turbine is a mixture of hot reheat, HP/IP crossover and leakages. Also there is an extraction of low pressure steam at 1.299 bar for deaeration. Make-up water is added to the condensate after pumping it to the deaerator pressure. Also the low temperature heat from the exhaust gas is recovered in the LTE to preheat the feed water before deaerator.

Figure 4.1: Baseline semi-closed gas turbine cycle

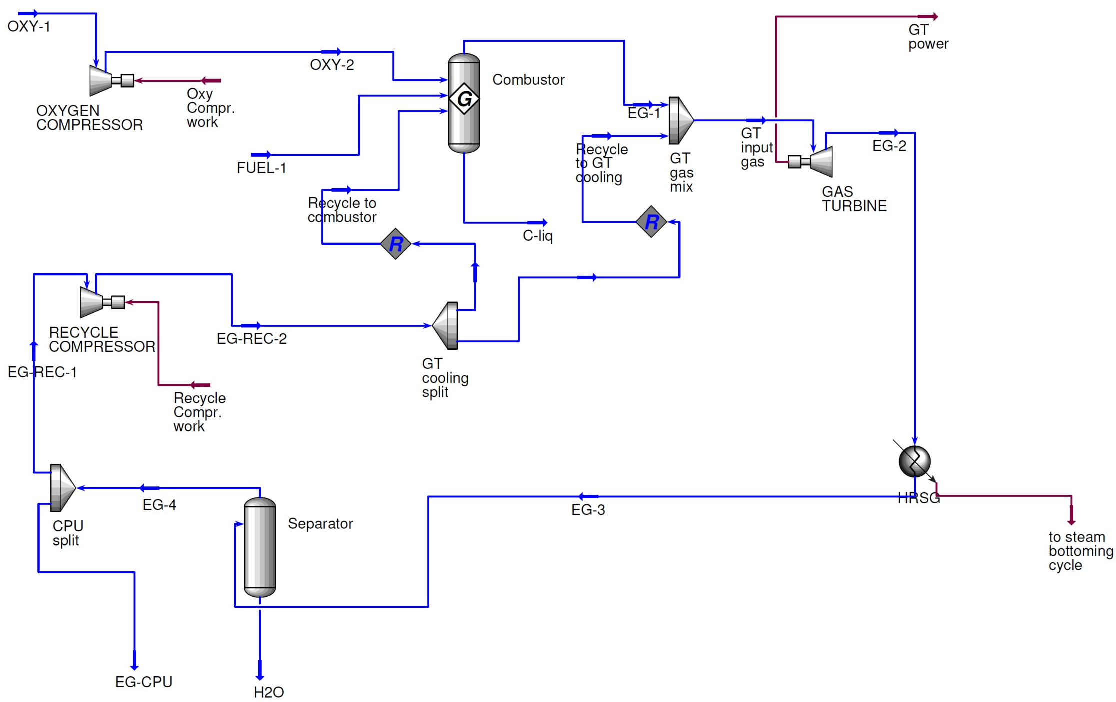
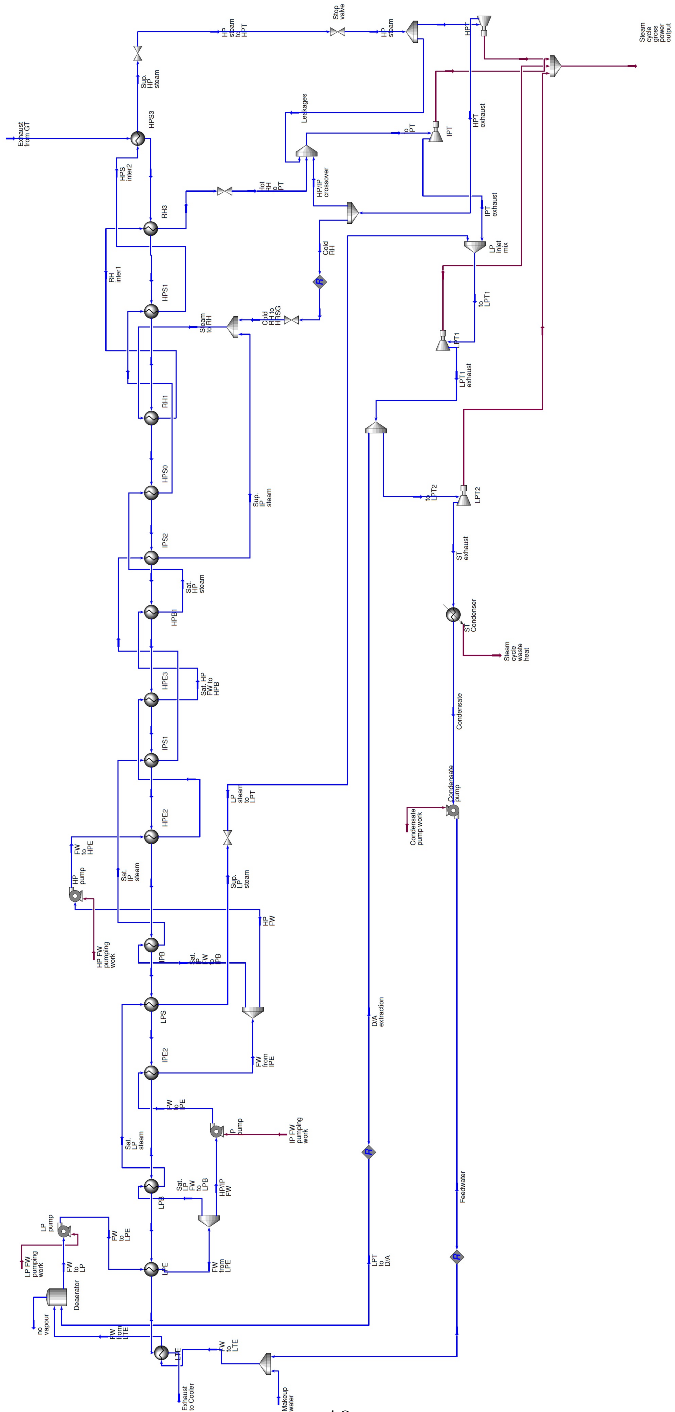


Figure 4.2: Steam bottoming cycle for the baseline GT cycle



4.1.3 Unit operation blocks

Gas turbine cycle

Oxygen compressor

The oxygen compressor is modelled as a single stage compressor with assumed polytropic efficiency using the Aspen HYSYS compressor block. No intercooling is used as the output of the compressor is directly fed to the combustor.

Combustor

The combsutor is modelled as a gibbs reactor available in the Aspen HYSYS.

Gas turbine

The gas turbine is modelled as an expander with a fixed polytropic efficiency and outlet pressure.

Separator

The separator used in the process separates the water content from the flue gas before recirculation. It is modelled using the Aspen HYSYS separator block.

Recycle compressor

The recycle compressor is a HYSYS compressor block with a fixed polytropic efficiency and a constant outlet pressure.

Steam cycle

Heat exchangers

All the heat exchangers excluding the condenser were modelled using the HYSYS shell and tube type heat exchanger. Assumptions include pressure drops on both the gas side as well as the water/steam side. Shell side was kept as the gas side where as the tube side was used for water/steam flows. Care was taken to ensure that the pinch and minimum approach temperature differences were not violated.

Deaerator tank

The deaerator tank was modelled using the Aspen HYSYS tank with the steam input extracted from the low pressure steam turbine.

Pumps

All the steam cycle pumps were modelled using the Aspen HYSYS pump with an assumed efficiency and constant head.

Steam pipes and valves

The piping for steam transport and other valves involved in the steam cycle are modelled using the valve unit operation block available in HYSYS with reasonably assumed pressure drop based on the pressure level of the steam being transported.

Steam turbines

All the four steam turbines were modelled using the Aspen HYSYS expander unit ops block with assumed overall isentropic efficiennty for each pressure level. Care was taken to ensure that the vapour fraction of the steam at the low pressure turbine outlet was satisfactory.

condenser

The steam turbine condenser was modelled as a cooler for simplicity.

4.2 Assumptions and practical constraints

4.2.1 Thermodynamic assumptions and other design input parameters

This section of the report provides a summary of all the design input parametres and assumptions involved in the design of the baseline case.

Table 4.1: Natural gas supply state, heating value and chemical composition

Parameter	**Unit**	**Value**
Temperature	^{o}C	15
Pressure	bar	70
LHV	MJ/kg	46.497
Composition		
CO_2	mol-%	2.000
N_2	mol-%	0.890
CH_4	mol-%	89.000
C_2H_6	mol-%	7.000
C_3H_8	mol-%	1.000
C_4H_{10}	mol-%	0.100
C_5H_{12}	mol-%	0.010
C_6H_{14}	mol-%	0.001

Table 4.2: Ambient conditions and air composition

Parameter	Unit	Value
Temperature	^oC	15
Pressure	bar	1.013
Relative humidity	%	60
Gas constant	J/(kg K)	288.16
Molecular weight		28.85
Composition		
N_2	Mole fraction	0.7730
O_2	Mole fraction	0.2074
H_2O	Mole fraction	0.0101
Ar_2	Mole fraction	0.0092
CO_2	Mole fraction	0.0003

Table 4.3: ASU data and assumed oxygen supply parametres

Parameter	Unit	Value
Temperature	^oC	15
Pressure	bar	1.2
Specific production power	MJ/kg_{O_2}	0.720
Composition		
O_2	mol-%	95
N_2	mol-%	2
Ar	mol-%	3

Table 4.4: Baseline case gas turbine cycle thermodynamic assumptions

Parameter	**Unit**	**Value**
Combustor data		
Pressure	bar	20
Pressure loss	%	3
Heat loss	%	0
Maximum outlet temperature	^oC	1365
Minimum outlet oxygen	mol-%	3
Air infiltration ratio	%	0
Gas turbine data		
Polytropic efficiency	%	91
Cooling ratio	%	15
GT pressure ratio	–	18.25
Max. Turbine Inlet Temperature	^oC	1250
Compressor data		
Recycle compressor		
Polytropic efficiency	%	91
Oxygen compressor		
Polytropic efficiency	%	87
Exhaust gas recycle data		
Exhaust gas cooler pressure drop	bar	0.01
EG cooler outlet temperature	^oC	28
Cooling water pump efficiency	%	75
Pump head	bar	2
Inlet temperature	^oC	18
Outlet temperature	^oC	28

Table 4.5: Steam cycle assumptions and parametres

Parameter	**Unit**	**Value**
Pressure levels		
LP steam	bar	5.2
IP steam	bar	23
HP steam	bar	165
Condenser	bar	0.048
Deaerator	bar	1.16
Temperature levels		
LP superheat	^{o}C	210
IP superheat	^{o}C	400
IP steam reheat	^{o}C	566
HP superheat	^{o}C	565
Condenser inlet	^{o}C	32.3
Turbine and pump efficiencies		
LP steam turbine isentropic efficiency	%	89
IP steam turbine isentropic efficiency	%	92
HP steam turbine isentropic efficiency	%	92
Efficiency of pumps	%	75
Pressure and temperature losses		
Hot-side HRSG pressure loss	bar	0.03
Cold-side HRSG pressure loss for each exchanger	%	3
Condenser pressure loss	%	3
Deaerator pressure loss	%	0
Temperature loss in HRSG	^{o}C	0
Minimum internal temperature approach		
Steam-exhaust gas	^{o}C	25
Boiling water-exhaust gas	^{o}C	10
Water-exhaust gas	^{o}C	10
Condensate-cooling water	^{o}C	3
Cooling water data		
Pump efficiency	%	75
Pump head	bar	2
Inlet temperature	^{o}C	18
Outlet temperature	^{o}C	28

4.2.2 Practical considerations

SCR and desulfurization

Selective Catalytic Reduction (SCR) for NOX control and desulfurization methods to remove sulfur from the fuel are not included in the simulation. As the assumed natural gas composition contains no sulfur and also as the NO_x produced during combustion is negligible (in the order of parts per billion), there is no need for the above emission control systems. However, based on the fuel, operating conditions, and the local emission regulations, one or both of the emission control systems might be necessary.

ASU and CPU

Air Separation Unit and CO_2 Processing Unit are not included in the simulation. Reasonable energy penalties available in the literature have been assumed to arrive at the overall efficiency of the plant.

Steam cycle considerations

The steam pipe pressure losses were assumed to be 7, 9 and 12 percentage for HP, IP and LP pipes respectively. The HRSG boilers are designed without considering the blowdown losses for simplicity purposes. However, the initial HRSG design with blowdown was compared with a modified design without blowdown and it was found that there is no substantial difference between the net power generated in the two cases.

Also it was found that extracting a low pressure steam from the steam turbine for feeding the deaerator instead of tapping it from the low pressure boiler resulted in a better steam cycle overall efficiency and hence the feature was included in the final design scheme.

As HRSG is the most important and complex to design part of the steam cycle, Thermoflow GT Pro was used to design the same and then the design was transferred to Aspen HYSYS. The HRSG design involves a complex and optimised arrangement of various heat exchangers and the steam mass flows. Also it is important to mention that, GT Pro was not fully flexible in accepting the flue gas composition and hence the flue gas composition used to arrive at the initial design in GT Pro would be similar to but different from that of the actual flue gas from the gas turbine semi closed cycle. Nevertheless, the analysis done in GT Pro helped in coming up with a steam cycle design including steam mass flows, heat exchanger placements, auxilliaries and an estimate of the steam cycle output and efficiency before transferring the design to HYSYS for exergy calculations. Also the GT Pro analysis helped in estimating the impact of blowdown and deaerator losses and helped optimise the system for maximum efficiency before finalising the design in HYSYS.

4.3 Results and discussion

4.3.1 Plant performance

Stream data such as temperature, pressure, composition and mass flow of key streams are presented in this section. Also key plant performance data such as power produced, auxilliaries, efficiency and other figures are also presented in table format.

The gas turbine and steam turbine power outputs presented in table 4.8 are calculated after considering the mechanical efficiency and generator efficiency of 99.6% and 98.5% respectively. Power consumption for steam cycle pumps are from HYSYS data adding the individual energy requirements of LP, IP and HP pumps. The cooling water pump power requirement is from GT Pro as GT pro estimates the cooling water parametres and flow accurately. The ASU power penalty is calculated from the assumed oxygen production specific power requirement of 0.72MJ/kg$_{O_2}$. The CPU power penalty is based on the estimate arrived by Pipitone et al. [12] for purification of a flue gas resulting from a similar oxy-combustion natural gas semi-closed cycle.

Table 4.6: Stream data for baseline case (Stream names from figures 4.1 and 4.2.).

	Temperature	**Pressure**	**Mass Flow**
Stream name	**^{o}C**	**bar**	**kg/s**
OXY-1	15.0	1.20	58.4
OXY-2	469.4	25.00	58.4
FUEL-1	15.0	70.00	14.6
EG-REC-2	324.1	20.00	505.4
EG-REC-1	28.0	1.02	505.4
EG-1	1364.7	19.40	502.6
EG-2	717.6	1.06	578.4
EG-3	28.0	1.02	578.4
EG-4	28.0	1.02	549.3
H2O	28.0	1.02	29.1
EG-CPU	28.0	1.02	43.9
GT input gas	1244.5	19.40	578.4
Steam cycle			
to HPT	565.2	160.90	95.3
to IPT	562.7	23.00	104.7
to LPT1	341.9	5.20	107.6
ST exhaust	32.3	0.04	105.8
Cold RH	305.5	28.40	94.2
Hot RH to IPT	567.2	23.00	100.8

Table 4.8: Overall plant performance

Parameter	**Unit**	**Value**
Gas turbine power	MW	398.8
Steam turbine power	MW	168.4
Gross power	MW	567.2
Exhaust gas compressor	MW	143.3
Steam cycle pumps	MW	2.9
Cooling water pumps	MW	2.4
Oxygen compressor	MW	25.6
ASU power penalty	MW	39.9
CPU power penalty	MW	16.2
Total power consumption	MW	230.3
Net power	MW	336.9
Chemical energy of fuel	MW	679.3
Net efficiency	%	49.6

While removing the volatiles in the CPU, some of the carbon dioxide is emitted to the atmosphere along with nitrogen and argon. This determines the CO_2 capture rate of the power plant. This capture rate or recovery rate is also determined by the purity of the oxygen available fromm the ASU. In our case, for an oxygen purity of 95%, the CO_2 capture rate is assumed to be 95% [12]. Although literature contains a lot of studies involving various configurations of O_2/CO_2 cycles, it is hard to compare it with our baseline case for obvious reasons such as sharp variations in assumptions.

Amann J.M et al. [24] have arrived at a net electrical efficiency of 51.3% points. Their power plant has many similarities with the baseline scenario such as the low GT pressure ratio, ASU and CPU power penalties and so on. At the same time, the cycle discussed in the study differs from that of our baseline case by using a recuperator, lower CO_2 recovery rate and other assumptions. This results in a slightly optimistic efficiency estimate of a little over 51 percentage points. Another study by Bolland and Mathieu [25] has arrived at a net plant efficiency of 45%. Their design uses a higher gas turbine pressure ratio, a two pressure HRSG and 100% CO_2 recovery rate.

4.3.2 Exergy flows and losses

Table 4.9 provides the exergy flow values of various key streams from the simulation in MW. This table contains physical and chemical exergy values of the streams as well as the mixinng exergy lossesl. There is no mixing exergy loss for water/steam flows in the steam cycle, as pure water is the working substance. Also we can notice that after combustion, the chemical exergy part of the fuel will be transferred to the physical exergy part of the combustor outlet gases. Similarly, we can observe many key exergy transfers associated with heat transfer, expansion/compression, variation of mixinng exergy loss due to change in composition and other losses from this table. All the stream names used in this table are from the process simulation and can be referred in the figures 4.1 and 4.2.

Table 4.9: Stream exergy flows for the baseline case

Stream Name	Physical Exergy	Chemical Exergy	Mixing Exergy loss	Total Exergy flow
GT cycle			*MW*	
OXY-1	0.74	7.14	1.01	6.86
OXY-2	24.35	7.14	1.01	30.48
FUEL-1	7.92	707.08	0.90	714.09
EG-1	638.36	214.77	27.47	825.66
GT input gas	649.37	246.31	30.69	864.98
EG-2	237.06	246.31	30.70	452.68
EG-3	0.77	246.31	21.20	225.87
EG-4	0.73	228.55	21.20	208.08
H2O	0.04	17.76	0.01	17.79
EG-CPU	0.06	18.28	1.70	16.65
EG-REC-1	0.67	210.26	19.50	191.43
EG-REC-2	135.03	210.26	19.50	325.79
Steam cycle			*MW*	
Makeup water	0.00	0.05	0.00	0.05
FW to LTE	0.22	64.64	0.00	64.86
FW from LTE	4.06	64.64	0.00	68.70
LPT to D/A	1.19	1.13	0.00	2.32
to LPT1	103.98	65.77	0.00	169.74
Cold RH	104.99	57.57	0.00	162.56
Hot RH to IPT	145.14	61.61	0.00	206.75
HP steam	156.82	59.93	0.00	216.75
ST exhaust	13.72	64.64	0.00	78.36
Condensate	0.21	64.64	0.00	64.86

Figure 4.3 shows the exergy destructon rate in the component/sub-process level. Flue gas cooler is not illustrated in the process flow diagrams shown in figures 4.1 and 4.2. It is a cooler present after the HRSG to reduce the flue gas temperature to a very low level, to condense the moisture content of the gas. ST aux. and losses includes the power consumed by the cooling water pumps of the condenser,

turbine mechanical and generator losses and other miscelaneous losses. Other plant Aux. and losses includes the gas turbine and recycle compressor mechanical losses, GT generator losses, and other losses such as power required for cooling water pump of the flue gas cooler. CO_2 purification losses are taken as the power required to purify and compress the slip-stream to the pipeline specifications for storage.

Figure 4.5 contains the exergy balance of the plant for the Plant exergy input of 714.15MW. The input exergy is distributed among the plant major losses, minor losses and the net power output. We can clearly see that the gas turbine combustor is the single component responsible for major part of the plant exergy destruction. Other components in the gas turbine cycle such as the turbine itself, the compressor and other components are fairly efficient.

Although ASU, the oxygen compressor and the CO_2 processing unit (CPU) are responsible for a significant loss of the fuel input exergy, their overall impact is still much lower than that of the combustor. Steam cycle losses are also significant and a closer look into the steam cycle losses reveals that there is a little potential for improvement. The H2O+CO2 in the figure 4.5 refers to the water removed from the flue gas stream and the part of flue gas stream taken for purification and compression. Both the streams are at very low temperature and pressure and hence contain less physical exergy. But the chemical exergy components of the streams are not negligible. But as the streams are not contributinng for power production, they must be accounted as losses.

After accounting all the losses in the plant and considering that the input fuel exergy is the major exergy input, the overall exergetic efficiency of the power plant (including the penalty for capture and compression of CO_2) stands at 47.2 percentage points.

Figure 4.6: Grassmann diagram for the baseline case

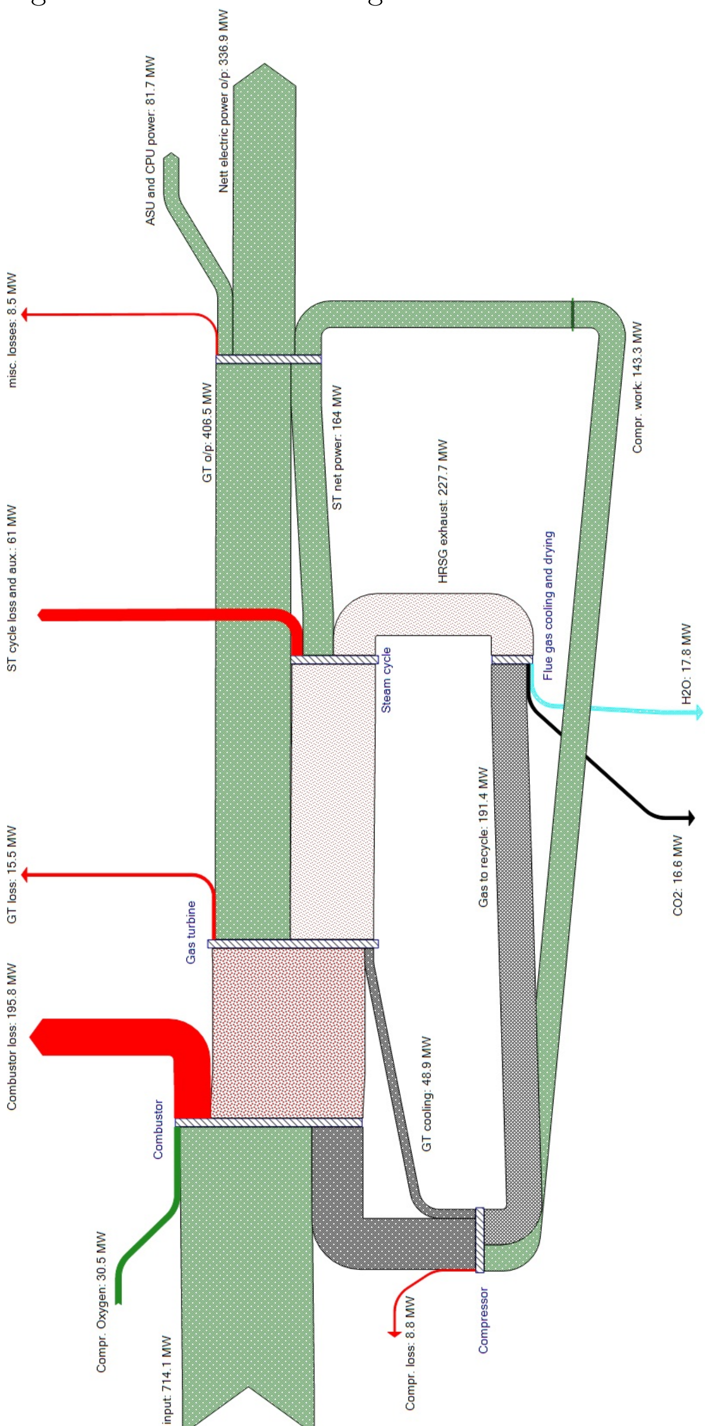


Table 4.7: Stream composition for baseline case (Stream names from figures 4.1.).

Stream	**OXY-1**	**FUEL-1**	**EG-1**	**GT input gas**	**EG-2**	**EG-4**	**H2O**	**EG-CPU**
Component	**Mole fraction**							
Nitrogen	0.020	0.009	0.036	0.037	0.037	0.041	0.000	0.041
Oxygen	0.950	0.000	0.030	0.031	0.031	0.035	0.000	0.035
CO_2	0.000	0.020	0.732	0.744	0.744	0.836	0.001	0.836
Argon	0.030	0.000	0.045	0.046	0.046	0.052	0.000	0.052
Methane	0.000	0.890	0.000	0.000	0.000	0.000	0.000	0.000
Propane	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	0.000	0.000	0.157	0.142	0.142	0.037	0.999	0.037
n-Butane	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Ethane	0.000	0.070	0.000	0.000	0.000	0.000	0.000	0.000
n-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Hexane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Figure 4.3: Irreversibilities in the baseline scenario

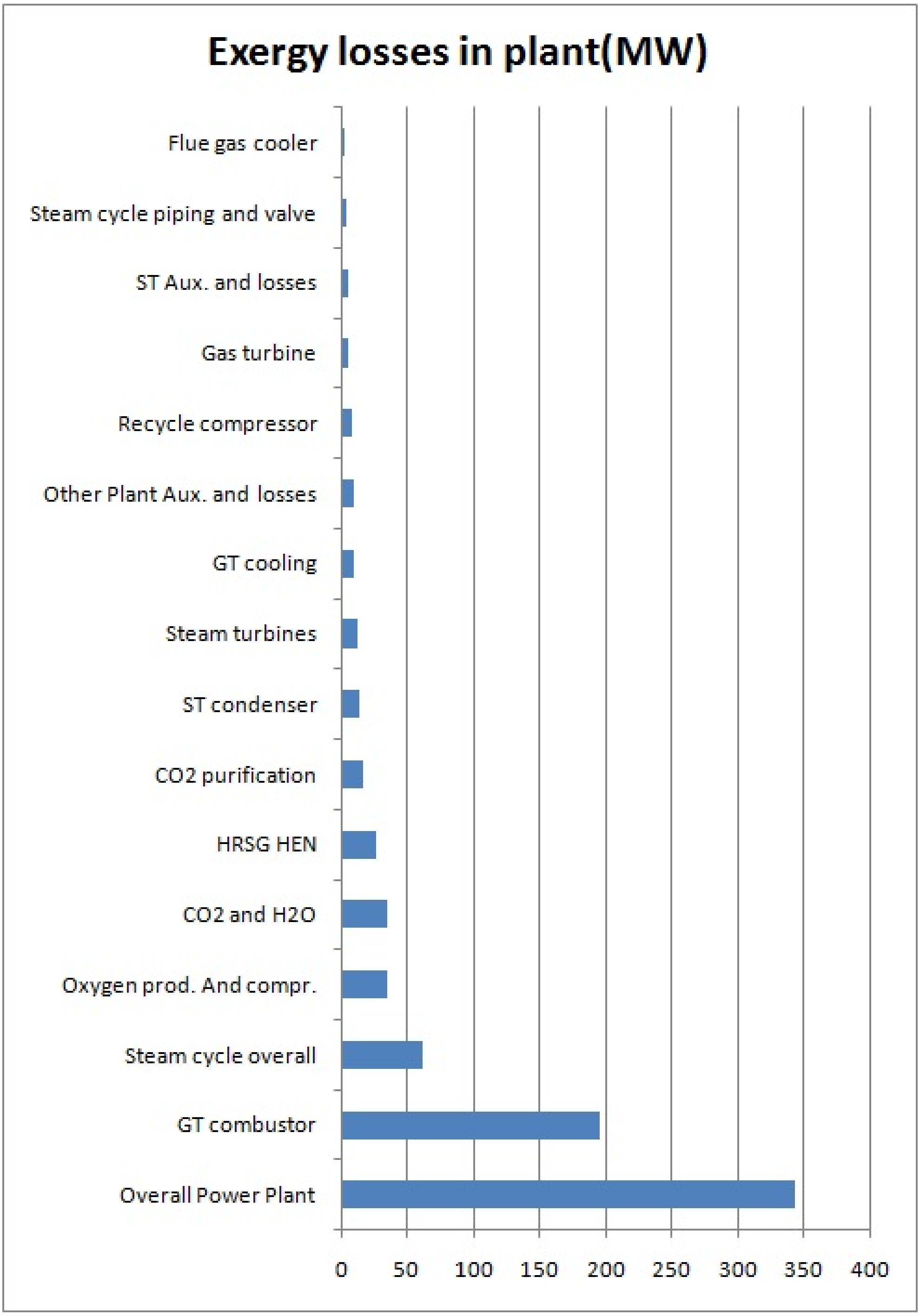


Figure 4.4: Share of the components in the steam cycle losses (Values in MW).

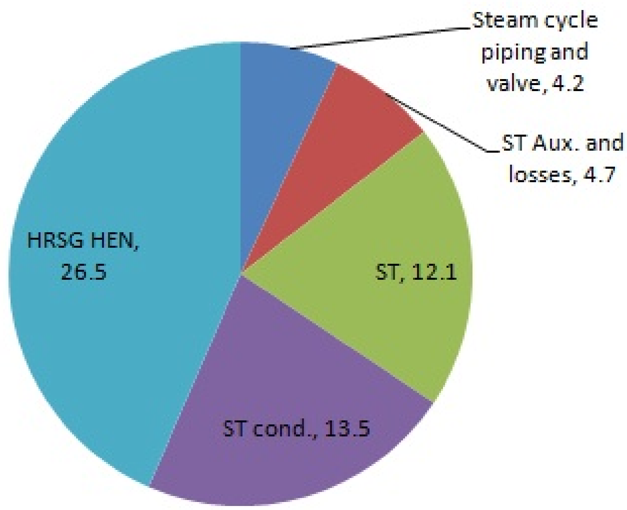
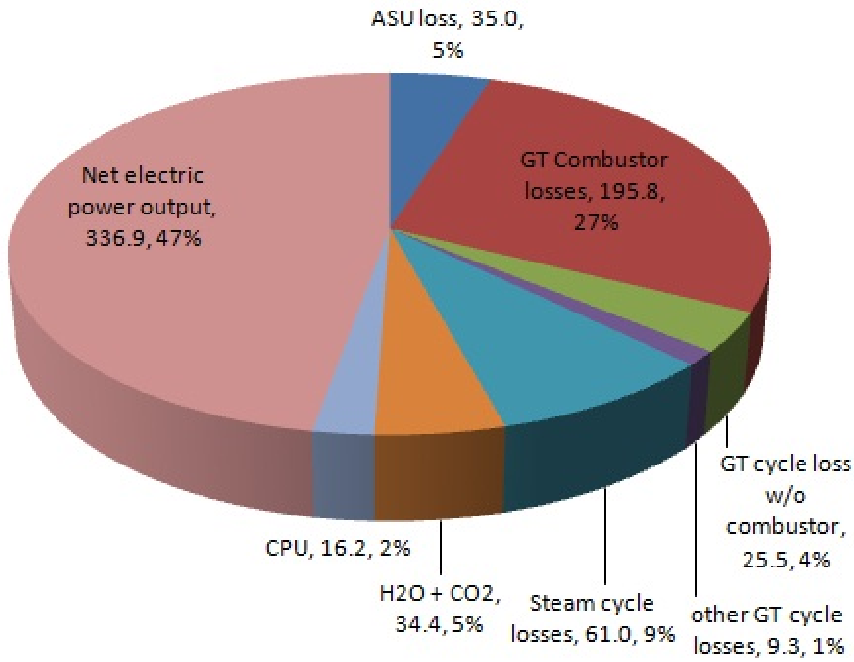


Figure 4.5: Exergy balance of the plant (Values in MW).



Chapter 5

Improved oxy-combustion natural gas combined cycle with Cryogenic ASU

5.1 Modifications to the baseline case

The baseline case discussed in Chapter 4 gives us some directions to proceed in order to improve the process and arrive at a modified case. For instance, the combustor is the single component in the whole power plant that is responsible for most of the fuel exergy loss. There are various reasons for loss of exergy during combustion. An analysis of entropy generation and exergy destruction during combustion by Nishida et al. [26] has found that entropy generation due to heat conduction is a major reason for exergy destruction during combustion along with chemical reaction and other factors. Hence, increasinng the feed temperature would result in reduced entropy generation. Preheating the fuel, oxygen or the recycle would achieve some reduction in entropy generation. Also there are other ways of modifying/improving the baseline process and making it more exergetically efficient. In this section, we present the modifications considered for the baseline case and the detailed results of the modifications finally applied.

GT pressure ratio

Gas turbine pressure ratio is an important parameter that can be modified in an oxy-combustion power cycle. As the pressure ratio affects major components in the system such as the compressor, turbine, the combustor and also the oxygen delivery pressure, it has a huge impact on the design of the overall system and on the efficiency. As the gas turbine and the compressor are going to use a working medium very different from that of air, they have to be designed from the scratch. Hence we have the flexibility to choose a pressure ratio very different from that of a normal air based gas turbines, if the new pressure ratio gives a better performance. In order to find a different pressure ratio that gives a better overall performance, a sensitivity analysis of the overall plant performance with respect to the gas turbine pressure ratio can be done.

GT outlet pressure

Varying the GT outlet pressure coule be one of the possible modifications that can be done to the plant. A higher gas turbine outlet pressure would result in a smaller HRSG thereby saving materials and space, but this would require a new and expensive HRSG set up rather than a more conventionlal HRSG (working at atmospheric pressure). Also, having a flue gas at an elevated pressure would certainly reduce the power required to purify the same to pipeline requirements. But having a HRSG at a higher than atmospheric pressure (10-20 bar) would be very expensive and hence this option is not considered in this report.

Oxygen purity, Trade-off between ASU and CPU penalty
This is probably the most discussed parameter when it commes to oxy-combustion power cycles for CO_2 capture. But in order to find the optimal oxygen purity required to achieve the best overall efficiency, we need detailed ASU and CPU scheme along with many other parametres such as the CO_2 specifications required for storage and enhanced oil recovery (EOR). Although ASU is a matured technology and it is possible to estimate the power requirements fairly accurately for various purity levels, other data required to carry out this study are not that easy to obtain. For instance, the CO_2 specifications for storage/EOR are not clearly defined and hence the results would be largely uncertain.

In this report, we assume both the ASU and CPU parametres to arrive at the baseline case and hence no modifications to oxygen purity is considered for this case. Oxygen purity, specific production power and CPU power requirements are all maintained same as that of the baseline case.

Steam cycle parametres
Various steam cycle parametres such as steam pressure levels, live steam temperature, or even going for a supercritical steam cycle can be considered as potential changes that can be applied in order to enhance the overall system efficiency. In this study, we have selected a sub-critical steam cycle with fairly high pressure and temperature levels. Based on discussions with professor Olav Bolland, the option of a supercritical steam cycle was ruled out owing to the size of the power plant (less than 300MW steam plant output). Hence, in this case, no steam cycle modifications were done.

Other process modifications

There are some other process modifications that could be considered such as intercooled compression of oxygen and preheating the recycle before feeding it to the combustor. Intercooling the oxygen reduces the power required to compress the oxygen, but at the same time increases the combustor exergy losses, resulting in an overall efficiency reduction. Preheating the recycle stream after the compressor would involve a heat exchanger which would be both expensive and bulky. Also, the heat exchanger must operate at fairly higher temperature range in the order of 500-700 degrees and hence, the option of preheating was also omitted.

5.2 Gas turbine pressure ratio sensitivity analysis

After evaluating all the possible modification options, it is evident that studying the effect of gas turbine pressure ratio on the overall plant efficiency would be a logical choice at this point. In order to carry out the sensitivity analysis, all the thermodynamic assumptions, fuel and air compositions, and other parametres such as TIT, compressor and turbine efficiencies, were kept constant and same as that of the baseline case. The oxygen pressure was taken as 2 bars more than the compressor outlet pressure in order to take care of the pressure drops involved in the pipes and nozzles.

Care was taken to maintain the combustor outlet oxygen concentration, gas temperature at the combustor outlet, etc... Assuming same compressor/turbine efficiencies for various pressure ratios may not provide accurate outputs, but it served the purpose by making the analysis simple.

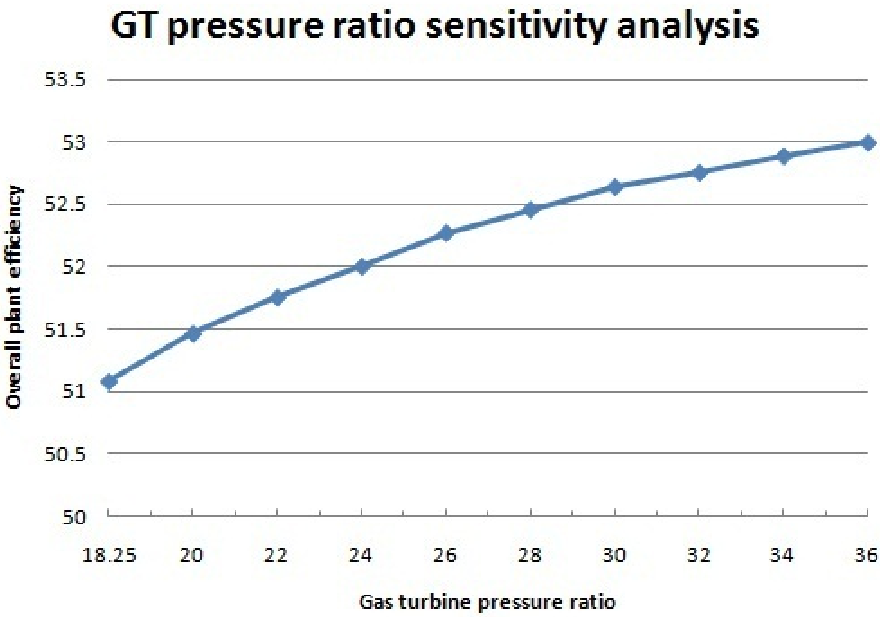
For each pressure ratio, the gas turbine cycle parametres such as power output, turbine exhaust temperature and gas flow are calculated by HYSYS. Then GT Pro was used to calculate the steam cycle parametres. The main inputs to steam cycle were the gas flow, temperature and composition. Just like the baseline case, the gas composition used in GT Pro was different from that of the HYSYS gas composition because of the GT Pro restrictions. This would result in a slight error, but the output from GT Pro was satisfactory enough to carry out the sensitivity analysis.

But for the exergy analysis part, the steam cycle was transferred completely to Aspen HYSYS to get the stream parametres. The main results from GT Pro was the steam cycle net power output and efficiency. With this we were able to come up with the overall power plant efficiency for various gas turbine pressure ratios (without CPU power). CPU power requirement will be same regardless of the pressure ratio.

As we can see from the figure 5.1, the overall power plant thermal efficiency (w/o including the CPU power requirement) increases with the increasing gas turbine pressure ratio. Also we can observe that the incremental gain in efficiency diminishes sharply after a pressure ratio of 32. By choosing a pressure ratio of 36, the overall plant energy efficiency can be improved by almost 2 percentage points over the baseline pressure ratio of 18.25.

One of the major practical constraints in going for a very high pressure ratio is the gas turbine blade cooling. Inclusion of a generic cooled model such as the one discussed by Jonsson and Bolland [27] would give better results. Also, as suggested by Fiaschi et al. [28], closed loop steam cooling can also be used for better performance of the cooled gas turbine. However, in this study, no cooling models are included and as a result, the peaking of the overall combined cycle power plant efficiency after a particular gas turbine pressure ratio is

Figure 5.1: Gas turbine pressure ratio sensitivity analysis



not clear. But the incremental benefits due to increasing pressure ratio keeps diminishing. In this study, simple cooling by the compressor bleed stream is assumed for all the pressure ratios.

5.3 Process description

The process itself is not much different from that of the baseline case with the main change being the gas turbine pressure ratio from 18.25 to 36. As a result of the increase in the compressor outlet pressure from 20 bar to 39.5 bar, the temperature of the gas at the outlet of the compressor increases. Hence the recycle gas flow increases substantially to 630 kg/s from 578 kg/s in order to maintain the combustor outlet temperature. Also the oxygen must be compressed to a pressure of 41.5 bar. But as the TIT is maintained, the turbine outlet temperature drops considerably from 713 degrees to 619 degrees centigrade.

The gases given as input to the steam cycle will now be more in terms of flow but at a lower temperature. The steam cycle configuration is also unchanged with all the thermodynamic parametres such as pressure losses, turbine and pump efficiencies, cooling water specifications maintained. Now more power is generated from the gas turbine cycle and the share of power generated by the steam cycle goes down.

Figures 5.2 and 5.3 shows the modified process in two parts similar to that of the baseline case. Figure 5.2 shows the gas turbine cycle whereas the figure 5.3 presents the flow diagram of the steam cycle.

Figures 5.2 and 5.3 shows the modified process in two parts similar to that of the baseline case. Figure 5.2 shows the gas turbine cycle whereas the figure 5.3 presents the process flow diagram of the steam cycle.

Figure 5.2: Modified semi-closed gas turbine cycle

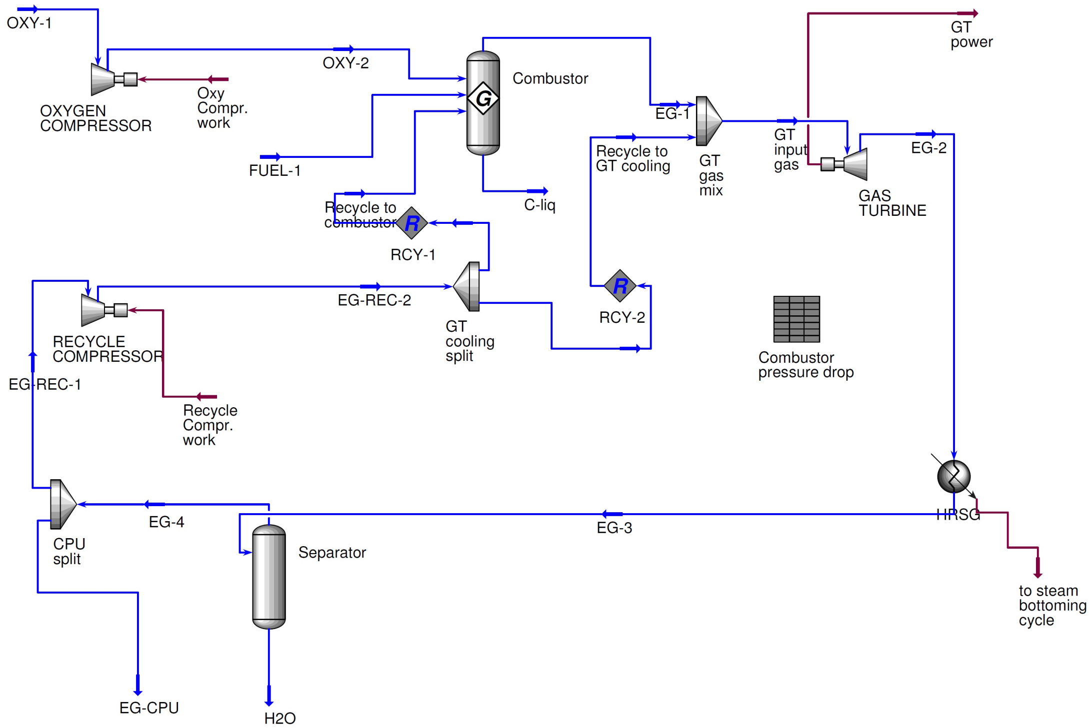
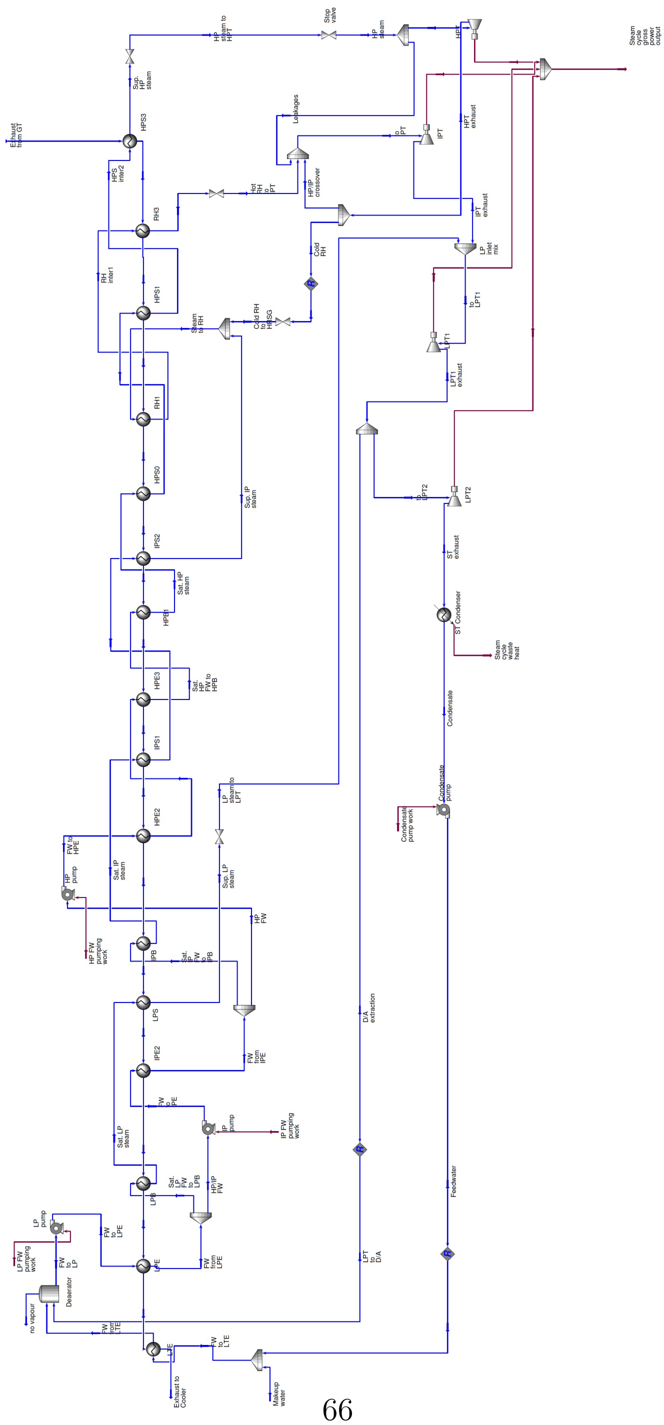


Figure 5.3: Steam bottoming cycle for the modified GT cycle



5.4 Results and discussion

The results of the simulation and the exergy calculations are presented in this section. As we can see from the figure 5.7, the increase in the GT pressure ratio has clearly improved the overall exergetic performance of the cycle by 2 percentage points. The thermal efficiency has also gone up by 1.4%.

5.4.1 Plant performance

Table 5.1: Stream data from the modified case (Stream names from figures 5.2 and 5.3.).

	Temperature	**Pressure**	**Mass Flow**
Stream name	^oC	**bar**	**kg/s**
OXY-1	15.0	1.20	58.4
OXY-2	584.7	41.45	58.4
FUEL-1	15.0	70.00	14.6
EG-REC-2	414.1	39.45	557.5
EG-REC-1	28.0	1.02	557.5
EG-1	1358.2	38.27	546.9
EG-2	619.1	1.06	630.5
EG-3	28.0	1.02	630.5
EG-4	28.0	1.02	601.4
H_2O	28.0	1.02	29.1
EG-CPU	28.0	1.02	43.9
GT input gas	1246.0	38.27	630.5
Steam cycle			
to HPT	565.2	160.90	70.1
to IPT	563.1	23.00	91.0
to LPT1	333.7	5.20	99.8
ST exhaust	32.3	0.05	98.1
Cold RH	305.5	28.40	69.2
Hot RH to IPT	567.2	23.00	87.8

Table 5.2: Stream composition for modified case (Stream names from figures 5.2.).

Stream name	**OXY-1**	**FUEL-1**	**EG-1**	**GT input gas**	**EG-2**	**EG-4**	**H2O**	**EG-CPU**
Component	**Mole fraction**							
Nitrogen	0.020	0.009	0.037	0.037	0.037	0.041	0.000	0.041
Oxygen	0.950	0.000	0.031	0.031	0.031	0.035	0.000	0.035
CO2	0.000	0.020	0.739	0.751	0.751	0.836	0.000	0.836
Argon	0.030	0.000	0.046	0.047	0.047	0.052	0.000	0.052
Methane	0.000	0.890	0.000	0.000	0.000	0.000	0.000	0.000
Propane	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.000
H2O	0.000	0.000	0.148	0.134	0.134	0.037	0.999	0.037
n-Butane	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Ethane	0.000	0.070	0.000	0.000	0.000	0.000	0.000	0.000
n-Pentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Hexane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 5.3: Overall plant performance for the modified case

Parameter	**Unit**	**Value**
Gas turbine power	MW	506.4
Steam turbine power	MW	144.4
Gross power	MW	650.8
Exhaust gas compressor	MW	211.2
Steam cycle pumps	MW	2.1
Cooling water pumps	MW	2.3
Oxygen compressor	MW	32.6
ASU power penalty	MW	39.9
CPU power penalty	MW	16.2
Total power consumption	MW	304.4
Net power	MW	346.4
Chemical energy of fuel	MW	679.3
Net efficiency	%	51.0

The overall power plant performance is actually better than that of the Amann J.M et al. [24]. The efficiency of the modified cycle is same as that of Amann J.M et al. [24] while recovering more CO_2 (95% instead of 85%).

5.4.2 Exergy flows and losses

Details related to the exergetic performance of the power plant are presented and discussed in this section.

When we analyse in detail, from figure 5.7, we can see that although oxygen is supplied at a much higher pressure and requires far more work than the baseline scenario, there is only negligible increase in exergy losses due to this additional compression. Also, as the CO_2 purification unit handles the same amount of gas flow with almost the same composition as that of the base case, there is no increase in the CPU penalty.

Due to the increase in the pressure ratio, the gas flows to the steam cycle from the gas turbine increases in volume but goes down in temperature and hence, the exergetic efficiency of the steam cycle increases. This increase is mainly due to the reduction in the exhaust gas temperature and the resulting reduction in the exergy loss due to HRSG heat transfer. Other steam cycle losses are almost same as that of the baseline scenario.

This leaves us with the gas turbine cycle components where major changes have taken place. Due to the rise in the compressor outlet pressure, the temperature of the recycle being fed into the combustor has increases and as a result of this, there is a substantial reduction in the combustor exergy losses. Although the total reduction in steam cycle exergy losses are compensated by the increased exergy losses in the other GT cycle components such as the compressor and the turbine, overall plant exergy losses are much lower than that of the baseline case. This is mainly due to the reduction in the combustor exergy losses.

This has ultimately resulted in the overall improved performance of the power plant with exergetic efficiency of 49%.

Table 5.4: Stream exergy flows for the modified case

Stream Name	**Physical Exergy**	**Chemical Exergy**	**Mixing Exergy loss**	**Total Exergy flow**
GT cycle			*MW*	
OXY-1	0.74	7.14	1.01	6.86
OXY-2	31.05	7.14	1.01	37.18
FUEL-1	7.92	707.08	0.90	714.09
EG-1	710.20	233.21	29.36	914.05
GT input gas	732.19	268.00	32.88	967.31
EG-2	203.71	268.00	32.88	438.83
EG-3	0.83	268.00	32.88	245.61
EG-4	0.80	250.24	23.21	227.83
H2O	0.04	17.76	0.01	17.79
EG-CPU	0.06	18.28	1.70	16.65
EG-REC-1	0.74	231.96	21.52	211.18
EG-REC-2	199.94	231.96	21.52	410.38
Steam cycle			*MW*	
Makeup water	0.00	0.05	0.00	0.05
FW to LTE	0.21	59.94	0.00	60.15
FW from LTE	3.76	59.94	0.00	63.70
LPT to D/A	1.10	1.05	0.00	2.15
to LPT1	95.53	60.99	0.00	156.53
Cold RH	77.14	42.30	0.00	119.43
Hot RH to IPT	126.37	53.64	0.00	180.02
HP steam	115.84	44.27	0.00	160.11
ST exhaust	12.68	59.94	0.00	72.62
Condensate	0.20	59.94	0.00	60.14

Figure 5.4: Grassmann diagram for the modified case

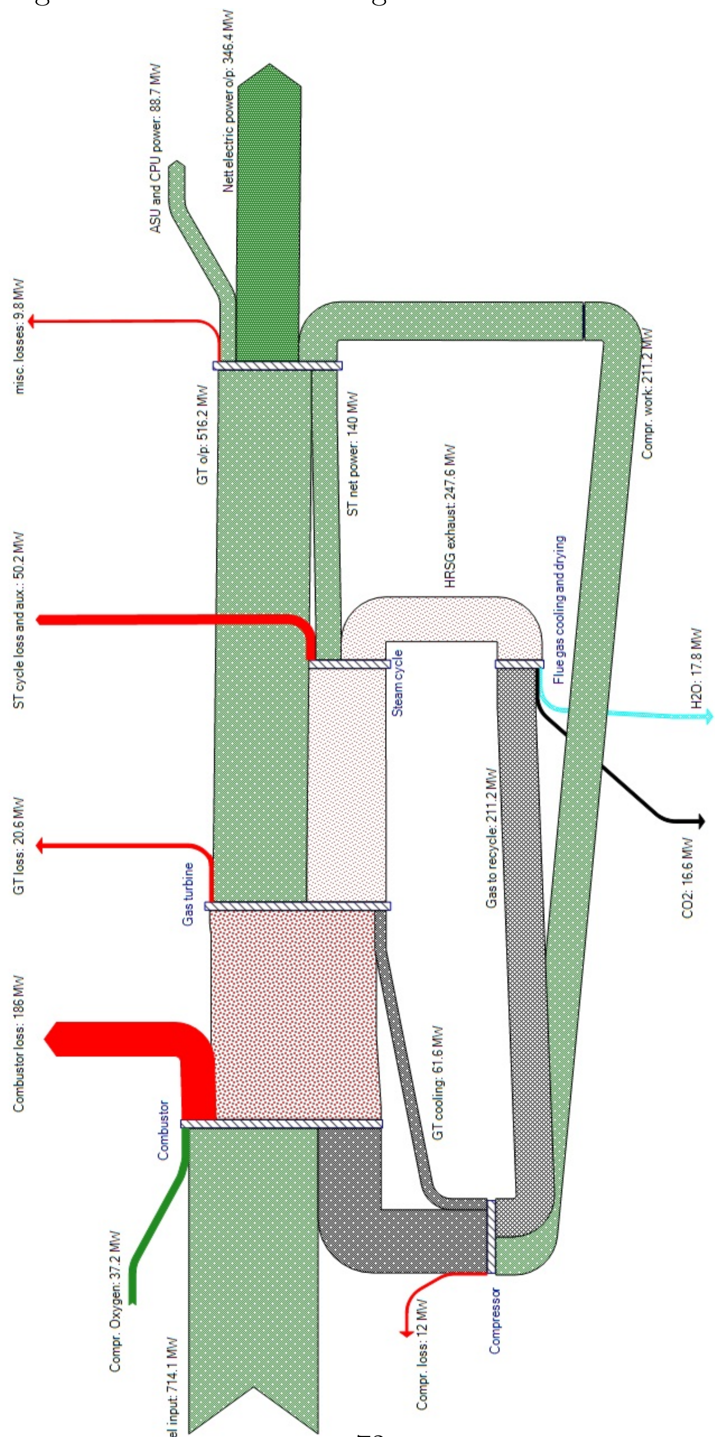


Figure 5.5: Irreversibilities in the modified scenario

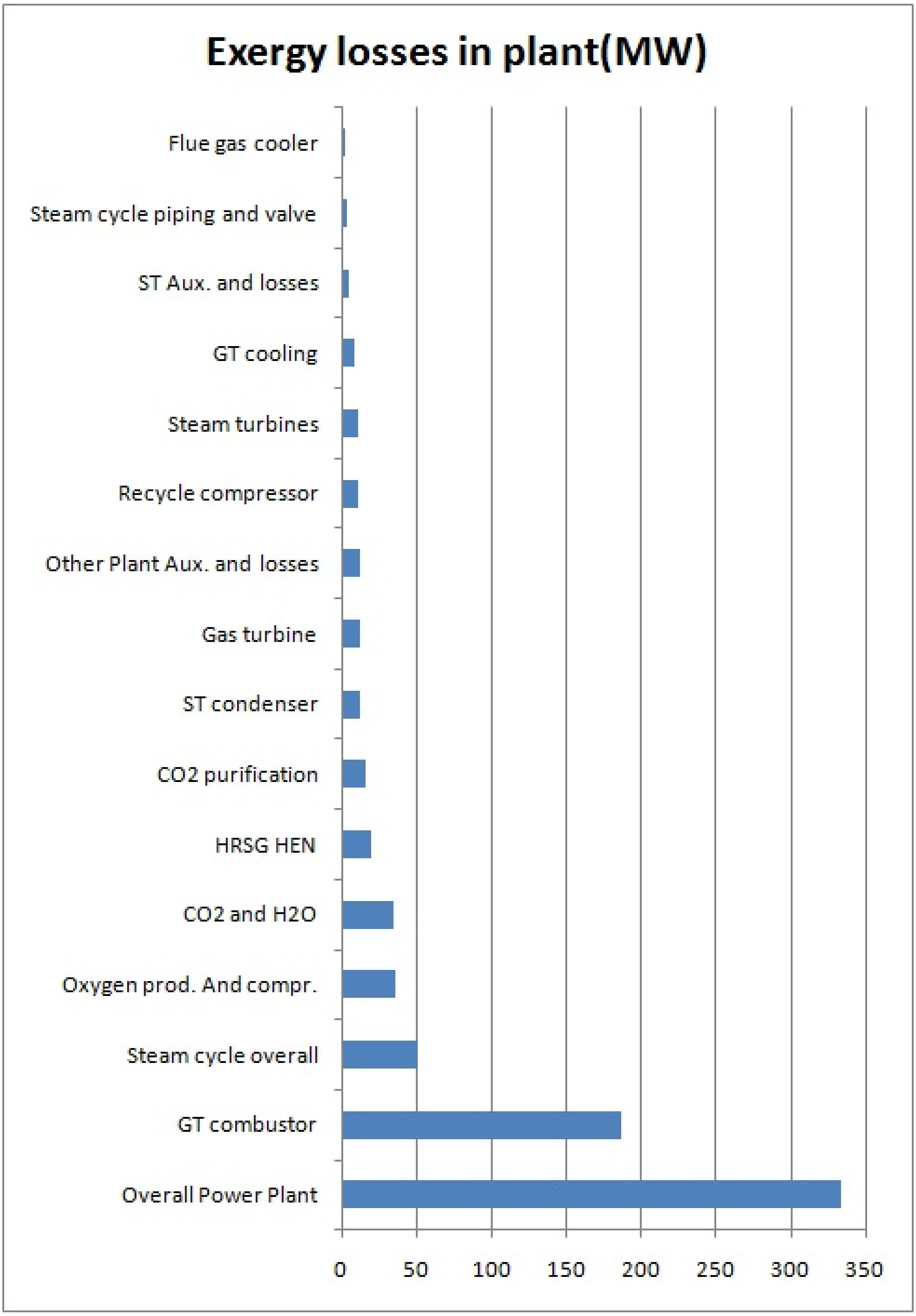


Figure 5.6: Steam cycle losses (all values in MW).

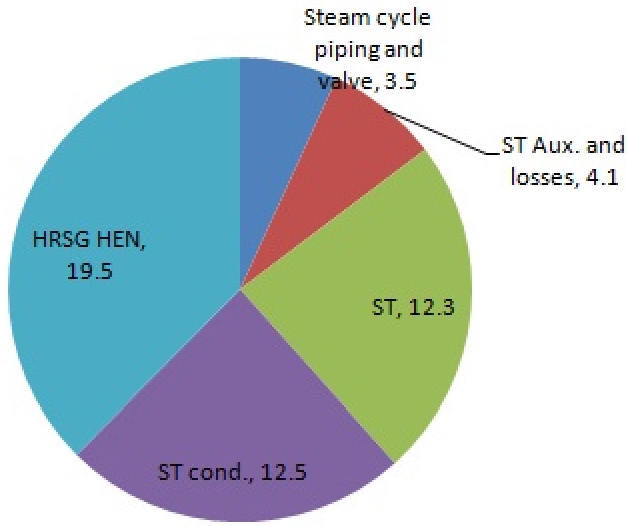
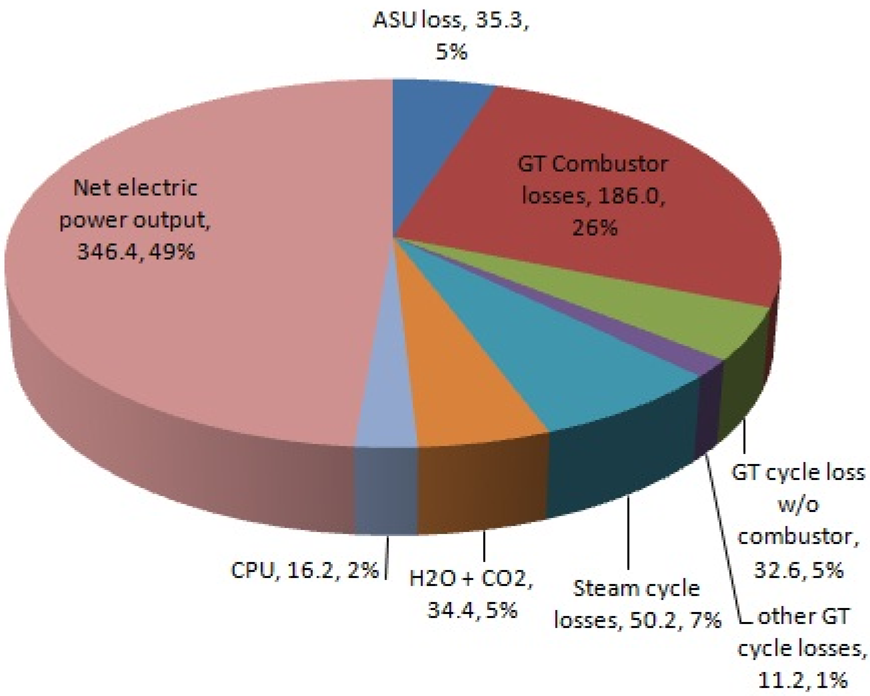


Figure 5.7: Exergy balance of the plant (all values in MW).



Chapter 6

Advanced OTM based natural gas combined cycle

In this chapter, an advanced concept for power generation with greenhouse gas removal is presented. The concept involves a Mixed Conducting Membrane (MCM) as a key element. The MCM separates oxygen from air and hence it is possible to achieve a very high overall efficiency, essentially by eleminating the need for an ASU and furthur downstream CO_2 processing. Although the concept sounds promising, there are many practical constraints and operational challenges involving membrane physical integrity, support stability and other issues [29]. Studying the exergy losses of such an advanced and complex system helps us understand the system more from a thermodynamic viewpoint.

6.1 Process description

The concept is called AZEP (Advanced Zero Emissions Power plant) is a gas turbine based power plant involving a membrane to separate oxygen from air and hence has a potential to reduce emissions in a less energy intensive way. The driving force for oxygen separation being the difference in partial pressure of oxygen between the fresh air and a sweep stream of the recirculated gas. Using the AZEP concept, 100% reduction of emissions is possible. Although we focus here on a concept that captures less than 100% of the CO_2 emissions for better overall efficiency.

6.1.1 The MCM reactor

The MCM reactor is showm in figure 6.1. The reactor replaces the normal combustion chamber in a conventional gas turbine power plant. The reactor essentially does the job of an air separation unit and a combustor combined together. Oxygen transport mechanism involves surface adsorption followed by decomposition into ions. Oxygen ions are then transported by occupying vacancies in the membrane structure. This enables nitrogen free combustion environment and thus eleminating need for ASU. Also heat from the combustion is transferred through the membrane to the oxygen depleted air.

6.1.2 Cycle description

Ambient air is compressed to the desired pressure in the gas turbine compressor and then fed to the MCM reactor. Oxygen available in the air is separated by the membrane and the depleted air is also heated at the same time. The air leaving the MCM reactor will contain less oxygen (14%) and will be at a very high temperature of around 1275 degrees. This air still contains enough oxygen to burn additional fuel in the sequential burner. On the other side of the MCM reactor, a recycle stream is circulated which is supplied with oxygen transported from the air.

Figure 6.1: Mixed Conducting Membrane reactor

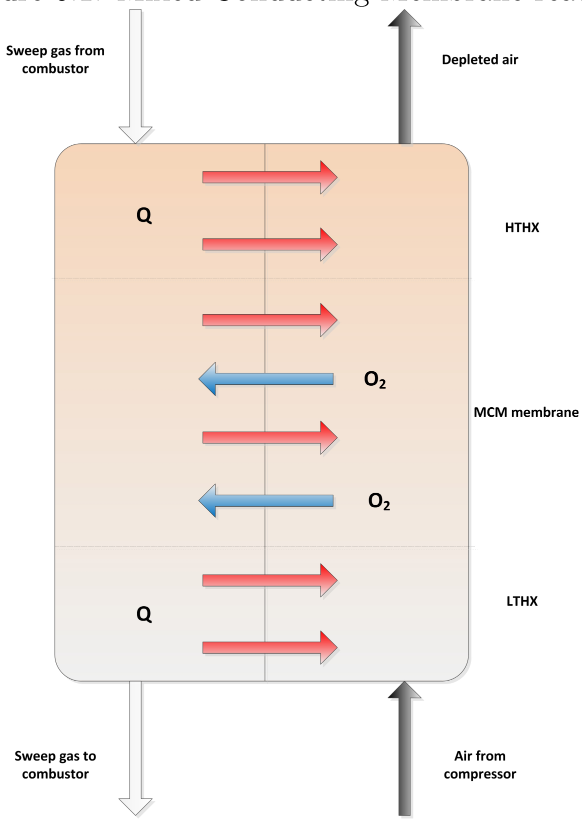
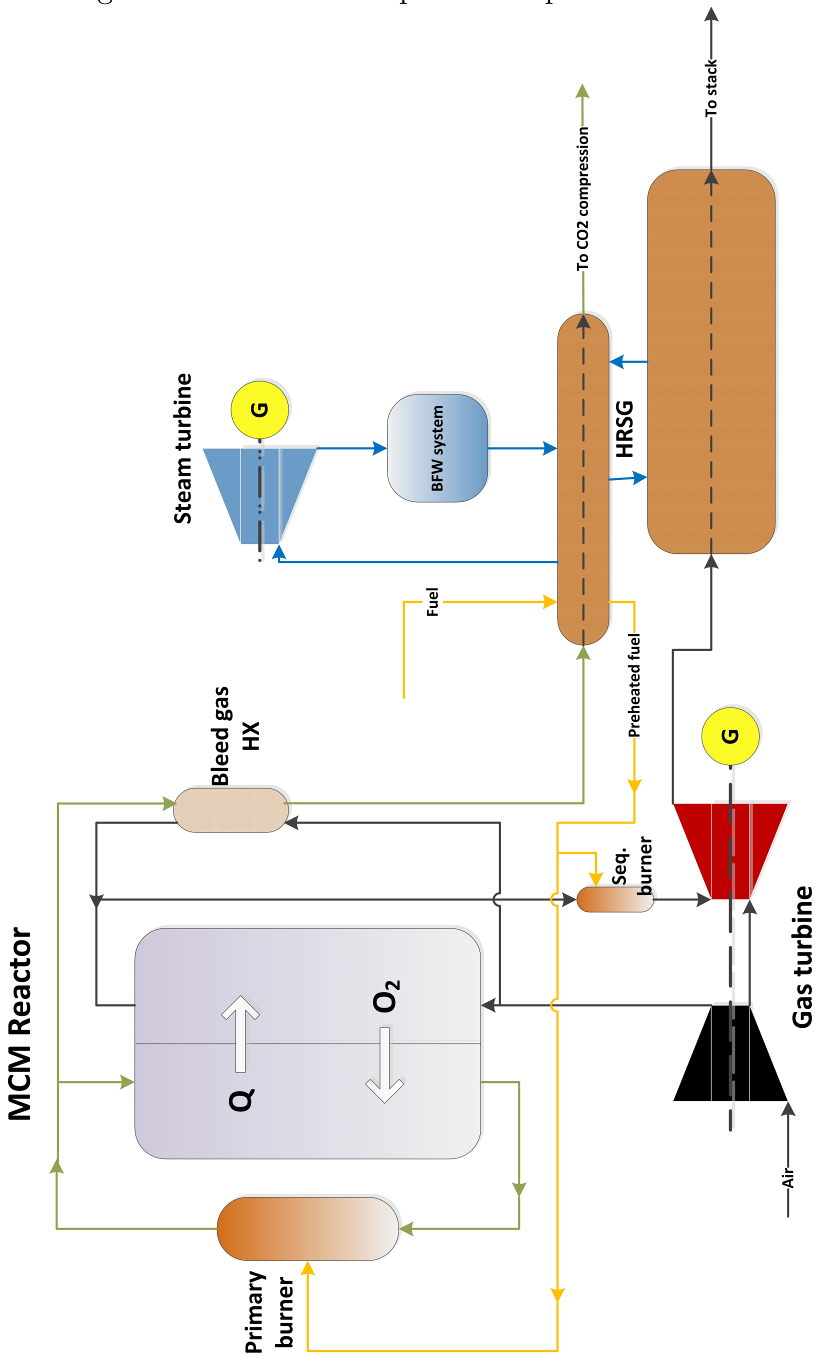


Figure 6.2: AZEP concept with sequential burner



The recycle feed, now enriched with oxygen enters the primary burner where most of the fuel in the system is burnt. A slip stream is taken out of the recycle for compression and storage. The recycle stream coming out of the primary burner then gives out heat to the depleted air and starts the cycle again. The slip stream which is at a very high temperature is cooled by heating a part of the compressed air from the compresser which then is mixed with the depleted air from MCM reactor. The depleted air is expanded in a gas turbine before entering the HRSG for steam production.

The slip stream which is rich in CO_2 and water vapour is also used to produce additional steam for the steam cycle apart from preheating the fuel. The slip stream must be furthur cooled down to condense most of the water vapour before compressing it to the pipeline specifications. There is no need for downstream purification in this case as the slip stream does not contain more volatiles than the allowed amounts for storage/EOR.

As additional fuel is burnt in the sequential burner, this concept does not capture 100% CO_2. The slip stream is at a fairly high pressure and hence the power required to compress the stream to pipeline pressure will be reduced a little. One other alternative is to use a bleed gas turbine to expand and produce additional power using the slip stream. But as the bleed gas turbine technology is not commercially matured, that option is not considered at this point.

The MCM reactor was modelled in Aspen HYSYS using two heat exchangers and a separator as shown in figure 6.3. The main steam cycle was modelled in Thermoflow GTPro which is shown in figure 6.4. Feedwater is extracted from the steam bottoming cycle and additional steam is produced while cooling down the slip stream (Bleed gas in the figure 6.3). High pressure steam produced is then expanded along with the main steam. Also part of the reheat, equivalent to that of

Figure 6.3: Process flow diagram of the AZEP concept (does not include the steam cycle)

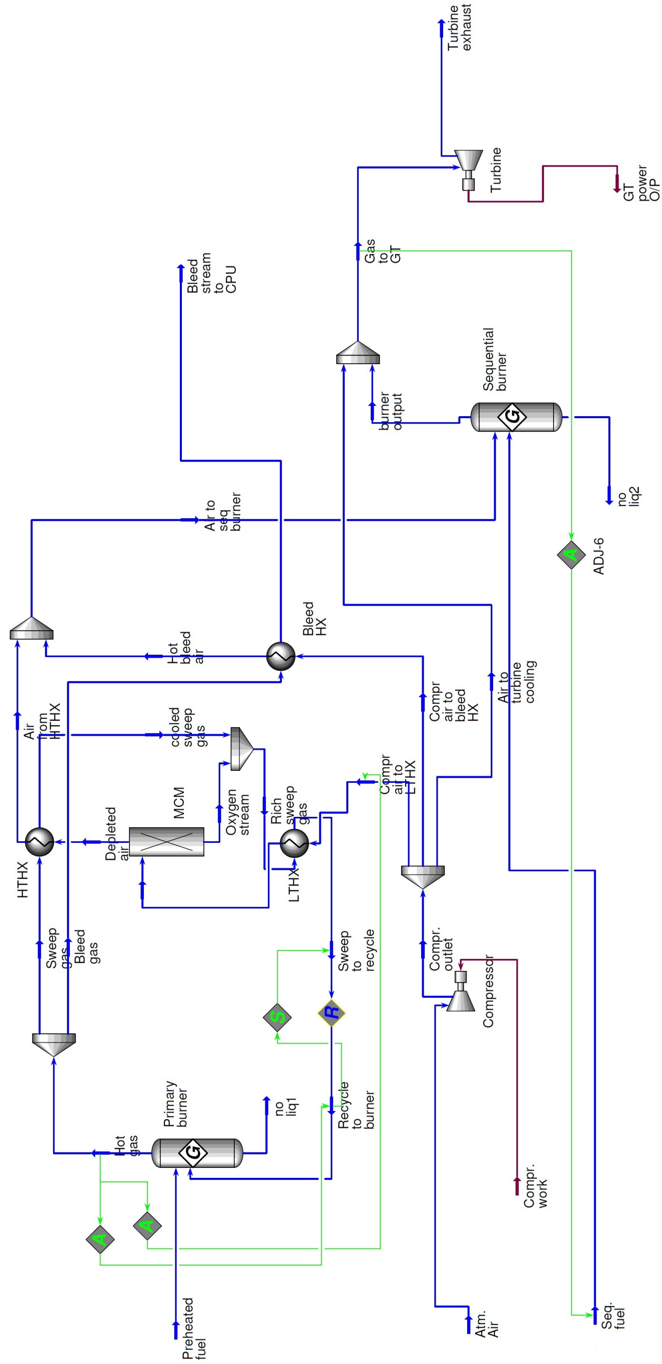
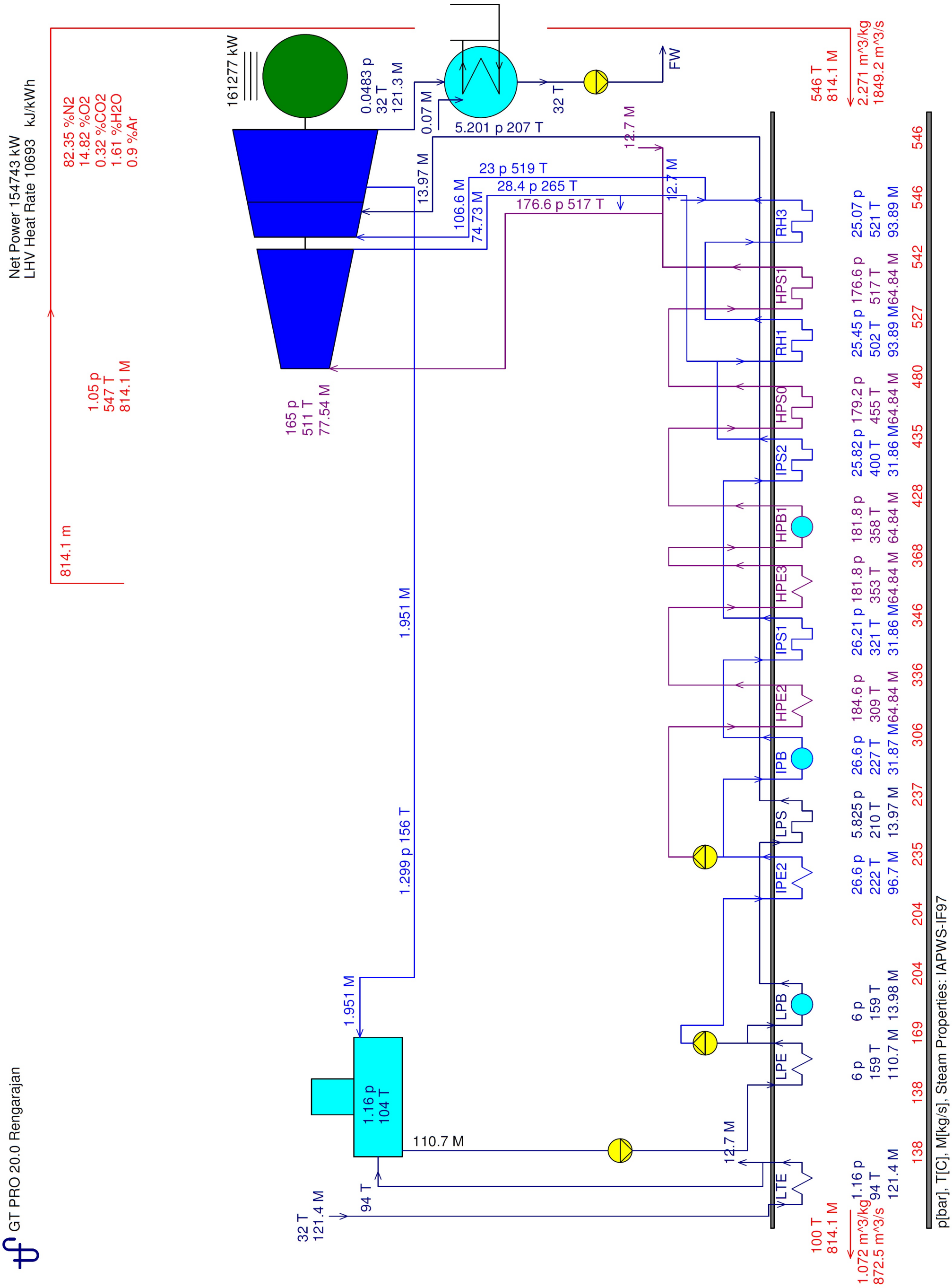


Figure 6.4: Steam cycle design for the AZEP concept



the additional steam added, is extracted and heated to reheat temperature using the slip stream. The cooling of slip strean and furthur downstream compression are not shown in the figures.

6.1.3 Unit operation blocks

The main gas turbine cycle alonng with the MCM reactor and the slip stream cooling part was modelled in Aspen HYSYS, whereas the steam cycle was modelled using Thermoflow GTPro. For simplicity, the steam cycle was not transferred completely to HYSYS. Only the major streams and extractions are transferred to HYSYS for exergy calculations.

Primary and sequential burners

Primary and sequential burners are modelled using the HYSYS Gibbs reactor.

MCM reactor

The MCM reactor is modelled using two shell and tube heat exchangers available in HYSYS and a separator. Oxygen transfer from the air side to sweep side is an important parameter while designing the MCM reactor as this parameter has a profound effect on the overall system performance. This is assumed as a fixed percentage of oxygen transferred from the air side to the sweep side.

Bleed HX

The bleed gas heat exchanger is modelled using the shell and tube heat exchanger unit availabe in Aspen HYSYS.

Air compressor and gas turbine

The air compressor and the gas turbine were modelled using HYSYS compressor and expander blocks respectively.

Slip stream cooler
The slip stream (Bleed gas) cooler which is used for fuel preheating and additional steam production is modelled using a LNG exchanger module in Aspen HYSYS with pressure drops similar to that of the steam cycle parametres.

6.2 Assumptions and practical constraints

6.2.1 Thermodynamic assumptions and design parametres

Thermodynamic assumptions used for the purpose of simulation are presented in this section. Natural gas supply state, composition and ambient conditions including air composition are same as that of the baseline scenarios and are available in tables 4.1 and 4.2.

All the steam cycle parametres such as the steam pressure levels, steam turbine isentropic efficiencies, HRSG hot side and cold side pressure drops and other losses, pumps, cooling mechanisms and condenser specifications are maintained same as that of the baseline scenario. Please refer to the table 4.5 for the thermodynamic assumptions of steam cycle. However, due to the temperature and mass flows of the turbine exhaust gas, the HP superheat has been reduced to 511 degrees and the reheat temperature has been reduced to 520 degrees centigrade.

Table 6.1: Thermodynamic assumptions and design input parametres for the AZEP power plant

Parameter	**Unit**	**Value**
MCM reactor data		
Primary burner outlet temperature	^oC	1295
Primary burner outlet oxygen	mol%	0.5
Bleed stream flow	%	14.77
Oxygen transport	%	38
Depleted air outlet temperature	^oC	1275
Air side pressure drop	bar	1
Sweep side pressure drop	bar	0
Gas turbine and compressor		
Compressor polytropic efficiency	%	91
Turbine polytropic efficiency	%	91
Turbine cooling	%	10
Bleed air	%	10
Sequential burner outlet temperature	^oC	1339
Turbine inlet temperature	^oC	1244
GT Pressure ratio	–	15.28
Compressor outlet pressure	bar	17.24
CO_2 compression		
Product pressure	bar	110

6.2.2 Practical considerations

Sulphur removal unit

The natural gas composition assumed in the simulation has no sulphur content and hence there is no need for a sulphur removal unit. In case of a natural gas stream with significant amount of sulphur, a sulphur removal unit after preheating of the natural gas is required.

NoX control

As the combustion takes place in a nitrogen free environment, there is no need for NoX control systems in the process.

Bleed gas cooling

The bleed gas is cooled and additional steam is produced. But as the bleed gas is mostly CO_2 and water, it is not being cooled below 180 degrees, as furthur cooling may cause corrosion in the HRSG unit. A separate cooler is used to cool the stream in order to condense the water content before furthur compression.

CO_2 compression

The CO_2 compression part of the process is not simulated and instead the power penalty for the same is calculated from the base case scenario of Pipitone et al. [12]. Our CO_2 stream has negligible volatiles and hence no furthur purification is required for both EOR/storage applications. Only compression to 110 bar is required with intermediate cooling and drying. Also as our bleed gas stream is at a higher pressure (16 bar), the power required for compression will be even lesser.

Integration with steam cycle

The gas turbine cycle is integrated with steam cycle by means of additional steam produced in the cooling process of the bleed gas stream (Slip stream). The steam cycle part is simulated in Thermoflow GT-Pro. Also the fuel stream is preheated to 400 degrees during the cooling of bleed stream.

6.3 Results and discussion

6.3.1 Plant performance

Key plant performance data such as the stream temperature, pressure mass flows and composition are presented in this section of the report. Table 6.2 contains the key stream data from HYSYS. The thermal efficiency of the power plant with CO_2 capture is found to be 53.4% which is inline with similar studies [13].

Table 6.2: Stream data for AZEP case (Stream names from figures 6.3.

	Temperature	**Pressure**	**Mass Flow**
Stream name	^{o}**C**	**bar**	**kg/s**
Preheated fuel	400.0	70.00	16.4
Atm. Air	15.0	1.01	873.9
Compr air to LTHX	407.8	17.24	699.1
Depleted air	950.0	16.74	638.0
Air from HTHX	1275.0	16.24	638.0
Sweep gas	1294.7	16.74	447.0
Rich sweep gas	989.0	16.74	508.1
Sweep to recycle	464.3	16.74	508.1
Hot gas	1294.7	16.74	524.5
Turbine exhaust	547.1	1.06	814.1
FW from LTE	93.8	1.16	12.7
HP steam	520.0	176.60	12.7
CRH in	264.0	25.82	12.7
HRH out	522.0	25.00	12.7
HRSG exhaust	100.5	1.03	814.1

Table 6.3: Overall plant performance of the AZEP cycle

Parameter	Unit	Value
Gas turbine power	MW	657.0
Steam turbine power	MW	161.3
Gross power	MW	818.3
Exhaust gas compressor	MW	362.2
Steam cycle aux.	MW	6.5
misc aux and losses	MW	0.4
CPU power penalty	MW	9.0
Total power consumption	MW	378.1
Net power	MW	440.2
Chemical energy of fuel	MW	824.6
Net efficiency	%	53.4

6.3.2 Exergy flows and losses

The exergy losses are distributed, owing to the complexity of the process. Major losses occur in the primary burner where most of the fuel is burnt. MCM reactor is fairly efficieny with only 3 percentage of the fuel exergy being lost in it. Other major components such as the gas turbine, GT compressor have losses similar to that of the baseline scenario. In this case, second major loss after the primary burner is the bleed stream that is taken for compression and storage.

The bleed stream is at a higher temperature of 179 degrees and hence contains significant physical exergy and also the chemical exergy of the stream is considered as a loss as no useful work is derived from it. The gases leaving the steam cycle main HRSG is also considered a loss. The gas stream will be depleted of oxygen and also at a very low temperature of 100.5 degrees and hence both physical and chemical component of exergy of the stack gas is not significant. The overall exergetic efficiency of the power plant with capture stands at

51 percentage points.

Table 6.4: Stream exergy flows for the AZEP case

Stream Name	Physical Exergy	Chemical Exergy	Mixing Exergy loss	Total Exergy
Unit		*MW*		
Preheated fuel	15.71	793.14	1.01	807.84
Atm. Air	0.00	44.80	44.80	0.00
Compr. outlet	340.58	44.80	44.80	340.58
Compr air to LTHX	272.47	35.84	35.84	272.46
Depleted air	522.07	28.64	27.82	522.89
Air from HTHX	717.92	28.64	27.82	718.74
Sweep gas	785.10	228.57	27.42	986.25
Rich sweep gas	628.40	235.76	41.25	822.91
Sweep to recycle	323.65	235.76	41.25	518.17
Hot gas	921.21	268.19	32.17	1157.23
Bleed gas	136.10	39.62	4.75	170.97
Bleed stream to CPU	68.77	39.62	4.75	103.64
Turbine exhaust	206.84	40.25	39.09	208.00
CRH in	13.38	7.75	0.00	21.14
HRH out	17.56	7.75	0.00	25.31
HP steam	19.24	7.75	0.00	27.00
FW from LTE	0.49	7.75	0.00	8.24
HRSG exhaust	10.23	40.25	39.09	11.39

The improvement in the overall power plant performance can be attributed to the MCM reactor which replaces the ASU in the conventional oxy fuel power cycles. The MCM reactor burns the fuel in a nitrogen free environment while consuming much less power than the ASU. CPU for this case is just a compression and drying unit rather than a purification unit.

The overall exergetic efficiency of 51% is inline with other similar studies availabe in the literature [30].

Figure 6.5: Irreversibilities in the AZEP scenario

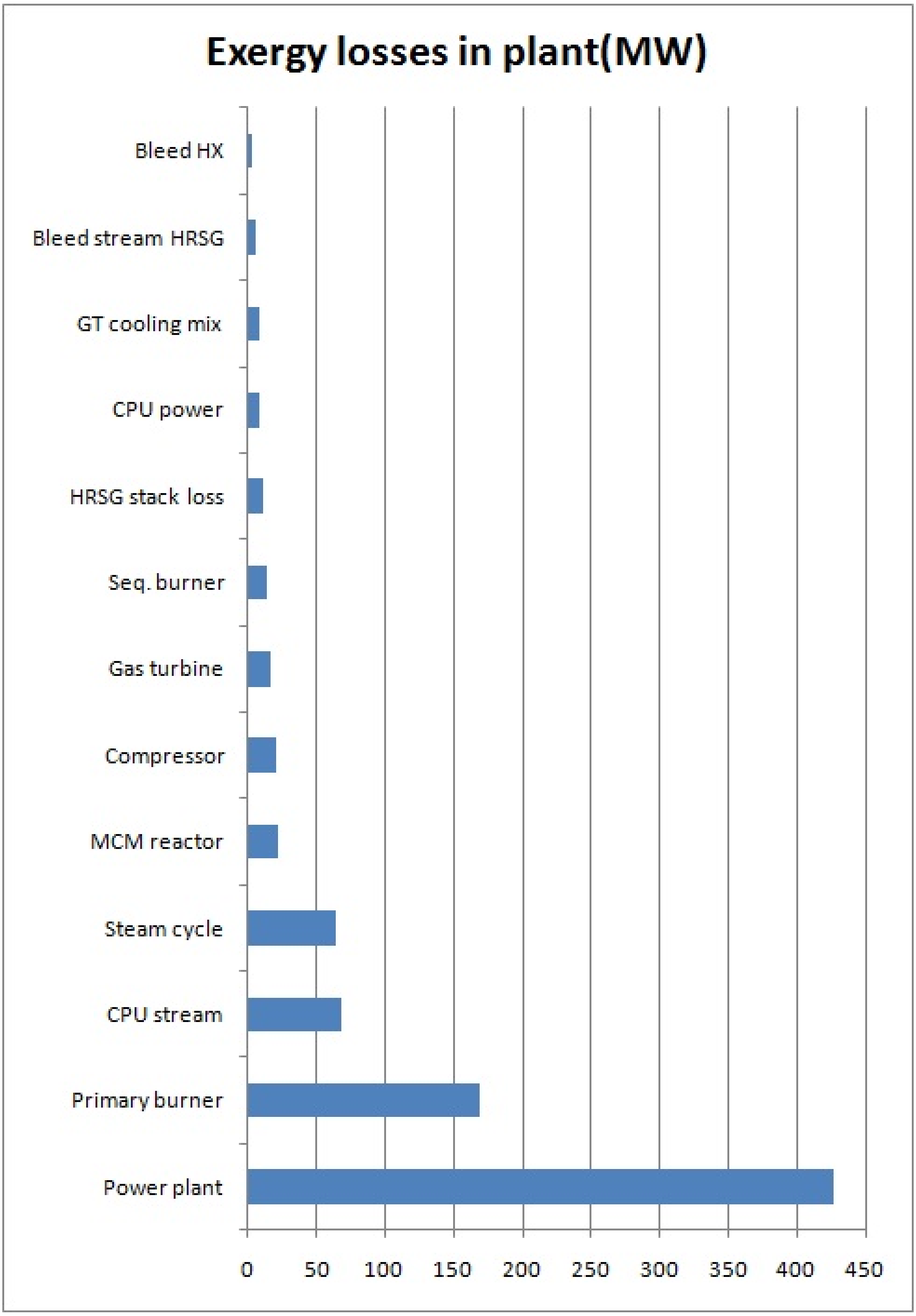
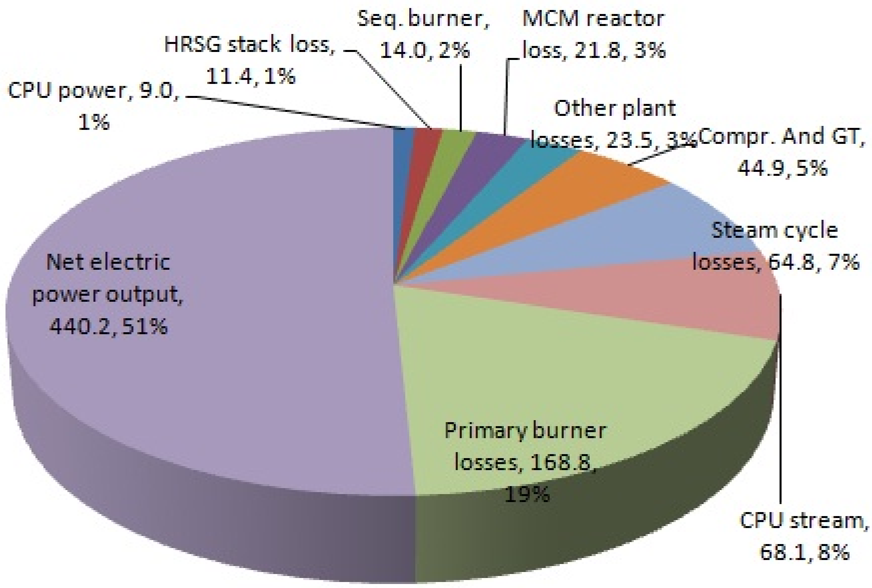


Figure 6.6: Exergy balance of the plant (All values in MW)



Chapter 7

Conclusion and further work

7.1 Conclusions

The design of oxy-combustion natural gas combined cycle power plants with two different technologies for oxygen production were studies in this work. Cryogenic ASU, being the most matured and commercially available technology, helped reduce the uncertainties and arrive at a power plant design that is more feasible. Whereas the AZEP concept using the Oxygen Transport Membrane was more efficient while having a lot of other practical issues to be reslved before commercialization.

The second law analysis of such systems throws light on the subsystems or components that are responsible for the major irreversibilities in the system. The study highlights that combustion of fuel is still the major source of irreversibility in the system. Increasing the gas turbine pressure ratio improves the power plant performance by improving the exergetic performance of the GT combustor.

7.2 Further work

The following studies would be relevant as far as the above systems are concerned. As the oxy-combustion natural gas technology itself is quite new, a RAMS (Reliability Availability Maintainability Safety) analysis can be carried out. Also dynamic analysis (transient) of the power plant along with off-design studies can be done. Detailed cost estimations can help policymakers understand the economic potential of these type of systems in mitigation of climate change.

Bibliography

[1] Brohan P, Kennedy J.J, Harris I, Jones P.D & Tett S.F.B. *Uncertainty estimates in regional and global observed temperature changes: a new dataset from 1850.* Journal of geophysical research, (2006) Vol. 111, D12106, 21 PP.

[2] Rayner N.A, Brohan P, Parker D.E, Folland C.K, Kennedy J.J, Vanicek M, Ansell T.J, & Tett S.F.B. *Improved analyses of changes and uncertainties in sea surface temperature measured in Situ since the mid-nineteenth century: The HadSST2 dataset.* Journal of Climate, (2006) Volume 19, Issue 3, 446-469

[3] Solomon, S., D. Qin, M. Manning, R.B. Alley, T. Berntsen, N.L. Bindoff, Z. Chen, A. Chidthaisong, J.M. Gregory, G.C. Hegerl, M. Heimann, B. Hewitson, B.J. Hoskins, F. Joos, J. Jouzel, V. Kattsov, U. Lohmann, T. Matsuno, M. Molina, N. Nicholls, J. Overpeck, G. Raga, V. Ramaswamy, J. Ren, M. Rusticucci, R. Somerville, T.F. Stocker, P. Whetton, R.A. Wood and D. Wratt, 2007: *Technical Summary. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[4] Siegenthaler U, Stocket T.F, Monnin E, Luthi D, Schwander J, Stauffer B, Raynaud D, Barnola J, Fischer H, Masson-Delmotte V, Jouzel J. *Stable Carbon CycleClimate Relationship During the Late Pleistocene.* Science 25 November 2005: 310 (5752), 1313-1317. [DOI:10.1126/science.1120130]

[5] Randall, D.A., R.A. Wood, S. Bony, R. Colman, T. Fichefet, J. Fyfe, V. Kattsov, A. Pitman, J. Shukla, J. Srinivasan, R.J. Stouffer, A. Sumi and K.E. Taylor, 2007: *Cilmate Models and Their Evaluation. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[6] Hegerl, G.C., F. W. Zwiers, P. Braconnot, N.P. Gillett, Y. Luo, J.A. Marengo Orsini, N. Nicholls, J.E. Penner and P.A. Stott, 2007: *Understanding and Attributing Climate Change. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[7] Parry, M.L., O.F. Canziani, J.P. Palutikof and Co-authors 2007: *Technical Summary. Climate Change 2007: Impacts, Adaptation and Vulnerability. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, M.L. Parry, O.F. Canziani, J.P. Palutikof, P.J. van der

Linden and C.E. Hanson, Eds., Cambridge University Press, Cambridge, UK, 23-78.

[8] World Energy Outlook 2009 Edition ISBN: 978-92-64-06130-9

[9] Barker T., I. Bashmakov, L. Bernstein, J. E. Bogner, P. R. Bosch, R. Dave, O. R. Davidson, B. S. Fisher, S. Gupta, K. Halsns, G.J. Heij, S. Kahn Ribeiro, S. Kobayashi, M. D. Levine, D. L. Martino, O. Masera, B. Metz, L. A. Meyer, G.-J. Nabuurs, A. Najam, N. Nakicenovic, H. -H. Rogner, J. Roy, J. Sathaye, R. Schock, P. Shukla, R. E. H. Sims, P. Smith, D. A. Tirpak, D. Urge-Vorsatz, D. Zhou, 2007: *Technical Summary. In: Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [B. Metz, O. R. Davidson, P. R. Bosch, R. Dave, L. A. Meyer (eds)], Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[10] IPCC, 2005: *IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change* [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp.

[11] Edward S.R, Chao C, Anand B.R. *Cost and performance of fossil fuel power plants with CO_2 capture and storage.* Energy Policy 35 (2007) 4444 - 4454.

[12] Pipitone G, Bolland O. *Power generation with CO_2 capture: Technology for CO_2 purification.* International Journal of Greenhouse Gas Control 3 (2009) 528534.

[13] Kvamsdal HM, Jordal K, Bolland O. *A quantitative comparison of gas turbine cycles with CO_2 capture.* Energy 32(1) 2007, 10-24.

[14] Bolland O, Undrum H. *A novel methodology for comparing CO_2 capture options for natural gas-fired combined cycle plants.* Advances in Environmental Research 7(4) 2003, 901-11.

[15] Kakaras E, Doukelis A, Giannakopoulos D, Koumanakos A. *Economic implications of oxyfuel application in a lignite-fired power plant.* Fuel 86(14) 2007, 2151-58.

[16] National Energy Technology Laboratory (United States). *Cost and performance baseline for fossil energy plants.* 2007 May 15 OSTI ID: 20905803 DOE/NETL–2007/1281 Research and Development Solutions, LLC (RDS) (United States); United States Department of Energy.

[17] Kotas T.J, *The exergy method of thermal plant analysis.* Krieger publishing company, Malabar Florida, 2nd Edition, 1995.

[18] Kotas T.J, *Exergy Concepts for Thermal Plant: First of two papers on exergy techniques in thermal plant analysis.* Int J. Heat & Fluid Flow (1980) Vol 2 No 3

[19] Kotas T.J, *Exergy Criteria of Perforniance for Thermal Plant: Second of two papers on exergy techniques in thermal plant analysis.* Int J. Heat & Fluid Flow (1980) Vol 2 No 4

[20] Szargut J, Morris D.R, Steward F.R, *Standard chemical exergy of some elements and compounds on the planet earth.* Elsevier Energy Vol. II, No. 8, pp. 733-755, 1986

[21] Ertesvåg S.I, *Sensitivity of chemical exergy for atmospheric gases and gaseous fuels to variations in ambient conditions.* Elsevier Energy Conversion and Management 48 (2007) 1983-1995

[22] Tranier J-P, Dubettier R, Perrin N. *Air separation unit for oxy-coal combustion systems.* 1 st International Oxyfuel Combustion Conference, Cottbus, 2009.

[23] Cohen H, Rogers GFC, Saravanamuttoo HIH. *Gas Turbine Theory.* Longman Group Limited, 4th Edition, 1996.

[24] Amann J.M, Kanniche M, Bouallou C, *Natural gas combined cycle power plant modified into an O_2/CO_2 cycle for CO_2 capture.* Energy Conversion and Management 50 (2009) 510521

[25] Bolland O, Mathieu P, *Comparison of two CO_2 removal options in combined cycle power plants.* Energy Convers. Mgmt Vol. 39, No. 16-18, pp. 1653-1663, 1998

[26] Nishida K, Takagi T, Kinoshita S. *Analysis of entropy generation and exergy loss during combustion.* Proceedings of the Combustion Institute, Volume 29,2002/pp. 869-874.

[27] Jonsson M, Bolland O, *Gas turbine cooling model for evaluation of novel cycles.* Proceedings of ECOS 2005, Trondheim, Norway

[28] Fiaschi D, Manfrida G, Mathieu P, Tempesti D, *Performance of an oxy-fuel combustion CO_2 power cycle including blade cooling.* Energy 34 (2009) 22402247

[29] Bredesen R, Jordal K, Bolland O, *High-temperature membranes inn power generation with CO_2 capture.* Chemical Engineering and Processing 43 (2004) 11291158

[30] Petrakopoulou, F., et al., *Exergoeconomic and exergoenvironmental evaluation of power plants includinng CO_2 capture*. ChemEngResDes(2010),doi:10.1016/j.cherd.2010.08.001