

Modelling of CO₂ capture using Aspen Plus for EDF power plant, Krakow, Poland

Vipul Gupta

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Supervisors : Prof. Ana Paula Vieira Soares Pereira Dias
Dr inż. Karol Sztekler

Examination Committee

Chairperson : Prof. Edgar Caetano Fernandes
Supervisor : Prof. Ana Paula Vieira Soares Pereira Dias
Member of the Committee : Prof. Ana Filipa da Silva Ferreira

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Note : This work was done in cooperation with EDF (Electricité de France) coal fired power plant located in Krakow (Poland), which provided samples to analyze, as well as information regarding the power plant operation.

Abstract

This work describes the functioning of the EDF CHP plant, Krakow, Poland and modelling of CO₂ capture unit. Aspen Plus simulation software was used for modeling of the reference thermal-steam cycle model of the power unit in EDF CHP plant, Krakow, Poland. Coal is combusted at the mass flow rate of 32.5 ton/h with boiler thermal efficiency of 212.4 MW. After the development of power unit model, CO₂ capture unit using the post combustion capture method was modelled. Aqueous monoethanolamine (MEA) is used as the solvent for absorption of CO₂ since it is highly reactive with CO₂ and CO₂ capture of 85% was envisaged in this model. The models were developed in order to integrate the power unit and capture unit. Integration relies on the most optimal arrangement for steam utilization from the power unit so that there will be minimum efficiency reduction of the plant. The results obtained from the simulation model provide the amount of CO₂ that is not emitted in the atmosphere and how much energy is utilized for capturing. Finally energy penalty imposed by CCS unit using aqueous MEA as solvent on the EDF CHP plant was estimated. About 65.3 ton/h of CO₂ was captured with energy penalty of 8.1 MW by flue gas compressor and 209 GJ/h by stripper re-boiler. Thermal energy consumed by re-boiler is about 3.2 GJ/ton CO₂, which is bit less than published literature data of 3.65 GJ/ton CO₂.

Modelou-se a captura de CO₂ para a central termoelétrica da EDF localizada em Cracóvia (Polónia). A central termoelétrica queima cerca de 32.5 ton/h de carvão produzindo 212.4 MW e o sistema de captura pretende remover 85% do CO₂ produzido. A unidade de combustão e a posterior captura de CO₂ foram modeladas usando o software Aspen Plus. A captura de CO₂ foi simulada usando modelos cinéticos de carbonatação de soluções aquosas de monoetanolamina. A integração, na central termoelétrica, da unidade de captura de CO₂ foi concebida de forma a otimizar o consumo do vapor de água produzido reduzindo assim a penalização energética da captura de CO₂. O consumo energético, após optimização, para a unidade de captura de CO₂ foi estimado em 8.1 MW (compressor do gás de exaustão) para 65.3 ton/h de CO₂ acrescido de 209 GJ/h no ebulidor do processo de stripping. O consumo energético global de 3.2 GJ/ton de CO₂ para a unidade de captura apurado é inferior ao valor médio referido na literatura (3.65 GJ/ton de CO₂).

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Nomenclature

Monoethanolamine	<i>MEA</i>
Methyl diethanolamine	<i>MDEA</i>
Diethanolamine	<i>DEA</i>
Carbon Monoxide	<i>CO</i>
Carbon Dioxide	<i>CO₂</i>
Hydrogen	<i>H₂</i>
Molecular Nitrogen	<i>N₂</i>
Nitrogen Oxides	<i>NO_x</i>
Nitrogen Dioxide	<i>NO₂</i>
Methane	<i>CH₄</i>
Sulphur	<i>S</i>
Sulphur Dioxide	<i>SO₂</i>
Sulphur Oxides	<i>SO_x</i>
Total Liquid Flow	<i>L</i>
Total Vapor Flow	<i>G</i>
Flue Gas	<i>FG</i>
Kilopascal	<i>kPa</i>
High Pressure	<i>HP</i>

Medium Pressure	<i>MP</i>
Low Pressure	<i>LP</i>
Net Calorific Value	<i>NCV</i>
Unit Operation Model	<i>UOM</i>
Vapor Liquid Equilibrium	<i>VLE</i>
Flue Gas Desulfurization	<i>FGD</i>
Carbon Capture and Storage	<i>CCS</i>
Green House Gas Emissions	<i>GHGE</i>
Intergovernmental Panel On Climate Change	<i>IPCC</i>
Organisation for Economic Co-operation and Development	<i>OECD</i>
Combined Heat and Power	<i>CHP</i>
Air Separation Unit	<i>ASU</i>

1.1 Thesis Motivation

Due to global warming and climate change there has been significant increased in efforts to reduce the green house gasses in the atmosphere. European union promised to reduce the green house gas emissions (GHGE) by 20-30% till 2020 compared to the levels of 1990[14].

One of the major green house gas in the atmospher is CO₂. Figure 1.1 shows that the CO₂ level in the atmosphere is continuously increasing. Also IPCC (Intergovernmental Panel on Climate Change) have said to reduce the global CO₂ emissions by 50-80% till 2050[15].

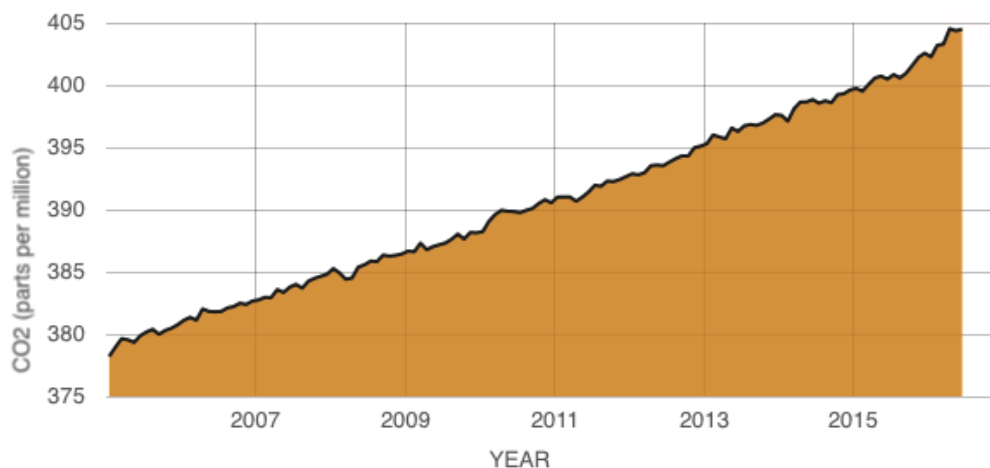


Figure 1.1: Plot of CO₂ level vs the time [1]

(Source: <http://climate.nasa.gov/vital-signs/carbon-dioxide/>)

About 20% of the energy consumption in Europe is in the form of electricity. And electricity demand has been increasing at the rate of 2% annually. About half of this electricity is produced by the fossil fuel based power plant. These power plants are the big sources of CO₂ emissions, so in order to reduce the GHG emissions from the power plants, CCS technologies needs to be introduced in the newer power plants or integration within old power plants[14].

CCS (Carbon Capture and Storage) is the process of separating the CO₂ from industrial and energy source, capture it before it enters into the atmosphere, and then transport the gas to storage location. CCS is not a new technology and it has been available for years. But the main problem arises from the cost involving CO₂ capture. It is more costlier to capture and transport the CO₂ compare to releasing it in the atmosphere. By implementing the CO₂

capture technology at the major source of CO₂ emissions into the atmosphere i.e coal fired power plants, cost for capturing can be reduced drastically.

1.2 Objective

The main objective of this thesis is to study the effect of integrating CO₂ capture unit in the EDF CHP plant, Krakow, Poland. The steam cycle of the power plant is modelled in Aspen Plus and the CO₂ capture unit is also modelled in the Aspen Plus. The objective is to integrate the CO₂ capture unit with the steam cycle and utilise the steam from the steam cycle for the energy requirement of the CO₂ capture unit.

The goal of the thesis is to discuss:

1. **Discuss about the world energy scenario.**
2. **Define the basic functioning of the coal fired power plant.**
3. **Modelling the CO₂ capture unit in Aspen Plus.**
4. **Integrating the CO₂ capture unit in power plant and estimating the energy penalty imposed by CCS system.**

1.3 Thesis Outline

The thesis is basically divided into 6 chapters.

Chapter 1. Introduction

Discuss the scope and motivation, objectives and outline of the thesis. This chapter discusses why CO₂ capture is necessary in order to control the global warming.

Chapter 2. Literature Review

Focuses on the green house gas emissions (GHGE) in the world, energy scenario around the world, fuel sources, fuel consumption around the world, CCS methods. In this chapter, emission around the world, which country has the highest emission is discussed, then energy consumption around the world is compared and pointed out which countries are consuming the most energy, further the fuel sources like coal, oil, gas and there reserved locations are discussed, then the basic CO₂ capture methodology like post combustion, pre combustion capture, oxyfuel combustion are discussed in brief, and finally the usage of CO₂ is discussed.

Chapter 3. EDF CHP Plant, Krakow, Poland Description

This chapter deals with the overview of the EDF CHP Plant, Krakow, Poland , power plant operation, units of power plant and their functionality, coal supply details, type of coal used, maintenance of the power plant and as well as environmental treatment issues are discussed here.

Chapter 4. Modelling and Simulation

Description of the modelling Work. In this chapter the Aspen Plus basics are described, then how the chemical absorption of CO₂ takes place is discussed. EDF CHP plant Steam Cycle is modelled and parameters like efficiency of turbines and power generated are discussed. CO₂ capture unit is modelled, material used for capture, properties of substance and parameters are discussed.

Chapter 5. Results and Analysis

Describes the results drawn from the Carbon Capture unit and how CO₂ Capture unit effects the plant efficiency.

Chapter 6. Summary and Conclusions

A brief summary of the entire work and conclusions are drawn from the available results in this chapter.

The literature reviewed is divided into 6 sections:

1. Emissions in the world.
2. World energy scenario.
3. Resources.
4. Consumption of fuel.
5. CO₂ capture methods.
6. CO₂ storage and Usage.

2.1 Emissions In The World

Global emissions of CO₂ has been significantly increased from 1990. In 1991 global CO₂ emissions were measured to be 22,000 million metric tons. Figure 2.1 shows that largest growth took place in Asia where the emissions almost doubled. Also there is huge increase in CO₂ in Africa and Middle East [2].

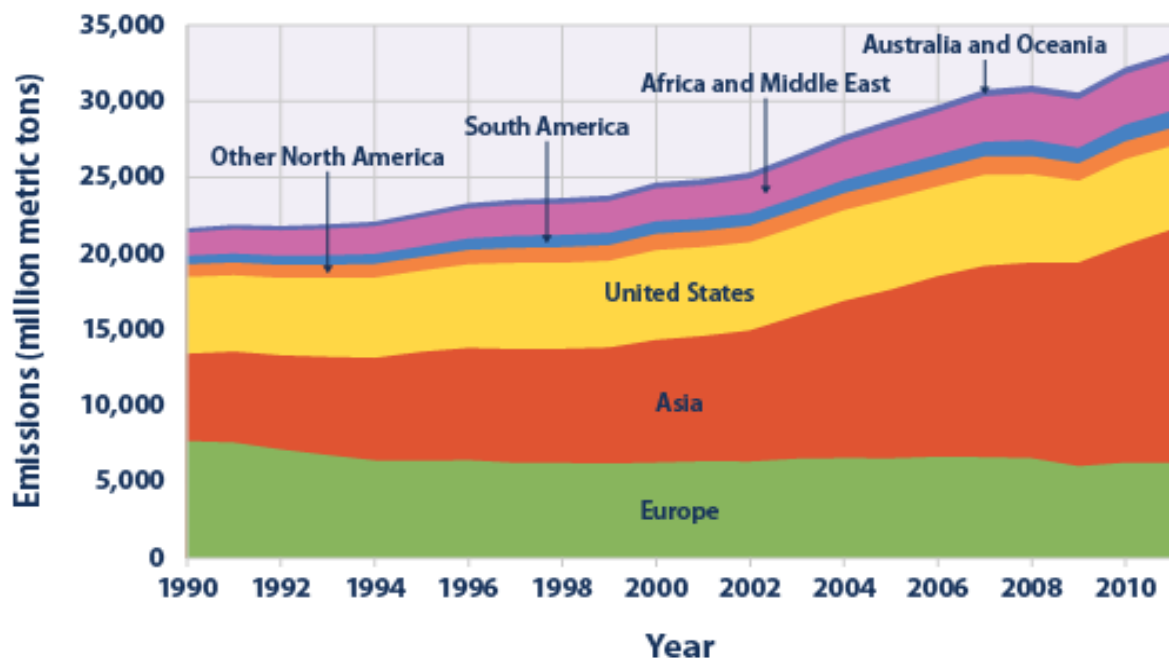


Figure 2.1: CO₂ Emissions Vs Year [2].

(Source: <https://www3.epa.gov/climatechange/science/indicators/ghg/global-ghg-emissions1.html>)

Economic growth of the country can be measured by amount of its CO₂ emission. As the country is more developed it will utilize more energy and the energy is produced and utilized at the cost of increase green house gases emissions in the atmosphere. Figure 2.2 shows that top 4 CO₂ emitting countries are China (28.03%), U.S (15.9%), India (5.81%) and Russia (4.79%). China emits more CO₂ compare to the total of next two countries U.S and India together. As the countries are developing, there energy utilization is also increasing and hence they are emitting more greenhouse gases. It can also be seen that India is now the third largest emitter of CO₂ leaving behind Russia, and this trend is going to continue in the future [3].

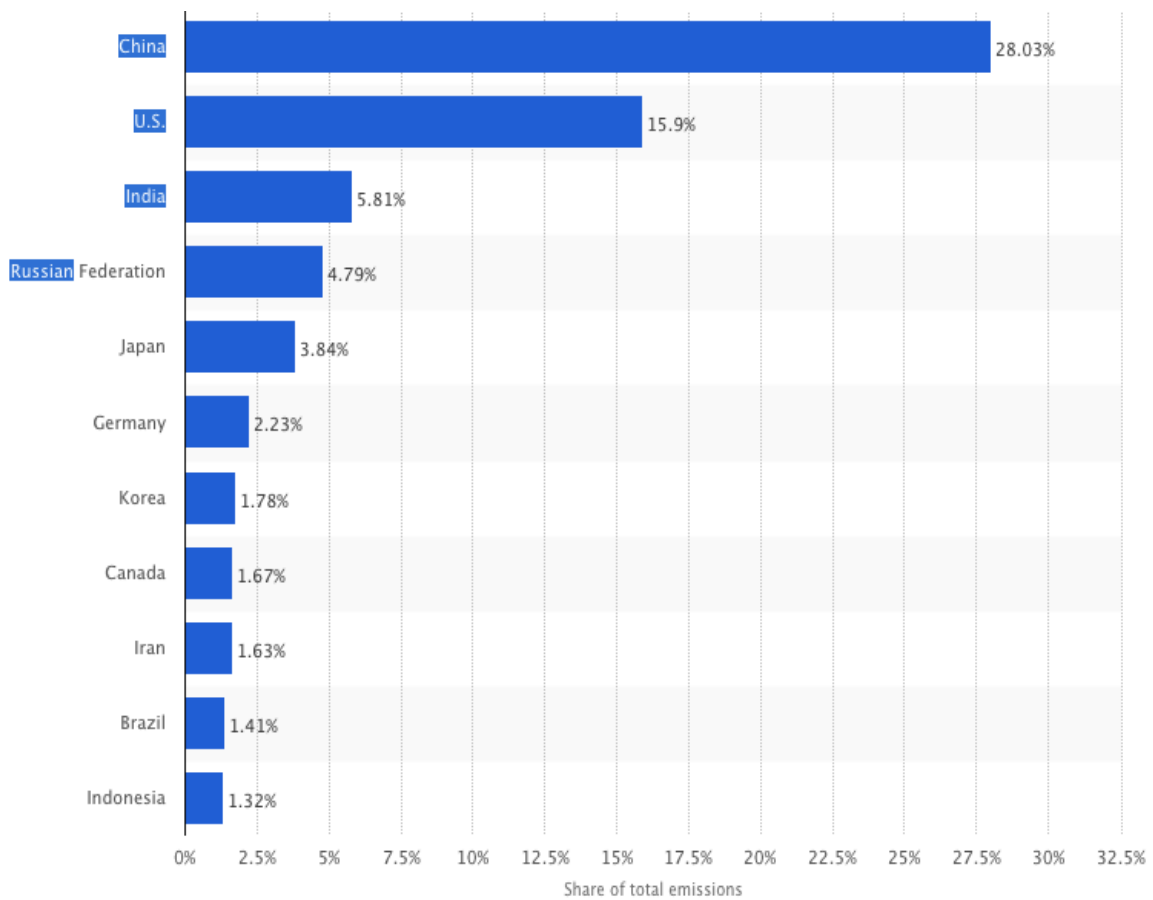


Figure 2.2: Share of total emissions per country [3].

(Source:[http://www.statista.com/statistics/271748/the-largest-emitters-of-CO₂- in-the-world/](http://www.statista.com/statistics/271748/the-largest-emitters-of-CO2-in-the-world/))

Comparing this data with the number of people living in a country one can see that US is the number one emitter of CO₂ per capita i.e 18 tonnes per person, while china emits 6 tonnes per person and India only emits 1.38 tonnes of CO₂ per person. This also shows how the emissions are directly related to the economic prosperity of a particular country [3].

2.2 World Energy Scenario

Energy is used daily for heating houses, cooking meals, transporting from one place to another, for entertainment, for running the industries. New advancements and developments are taking place each day. In 20th century desktops and laptops were introduced and now most of the work in offices is done on these devices. In 21st century mobile phone became famous and now more than half of the population of the world is using them..

Energy is needed by the world for economic development. But due to these reasons energy demand have been significantly increased from the past. The economies of countries like China and India are expanding significantly and there energy demand is also increasing.

Global demand for energy has been increased by about $1/3^{rd}$ from 2000-2014 in which china accounts for half of the increase. It is estimated that energy demand will be increased by 45% across non-OECD countries while demand in OECD countries will remain the same due to the increasing efficiency of how energy is utilized [5].

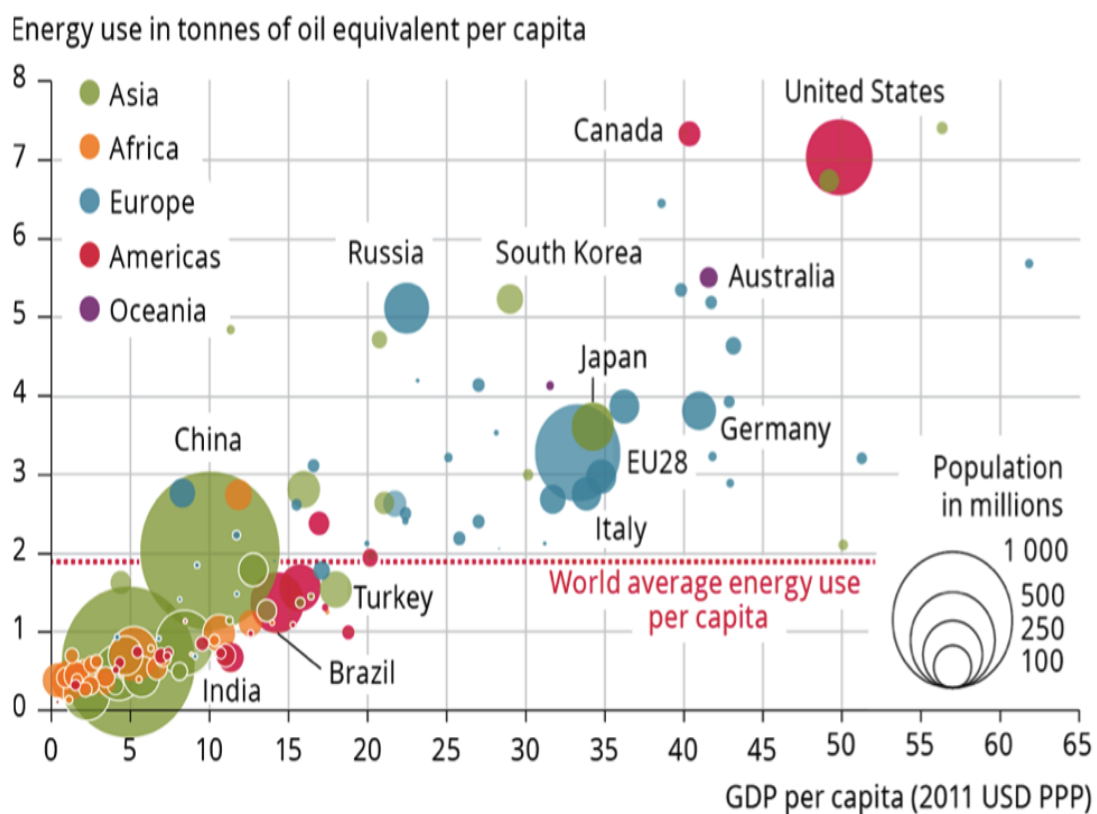


Figure 2.3: Correlation of energy consumption and GDP per person [4].

(Source: <http://www.eea.europa.eu/data-and-maps/figures/correlation-of-per-capita-energy>)

Figure 2.3 shows that even after having much less population United States being the highest consumer of energy and consumes much more energy compare to countries like China and India

which is due to fact that they have very low standards of living in these countries. World's average energy use per capita lies near to energy supplied by 2 tonnes of oil. But as the economies of China and India is expanding there is also more number of people moving from lower class to middle class family, there energy demand is also increasing proportionally [4].

Electricity plays a major role in day to day life, all the digital devices (mobile phones, laptops etc), industries, heating of houses, air conditioners, lightning require electricity. More than 35% of energy is used in the generation of electricity [4].

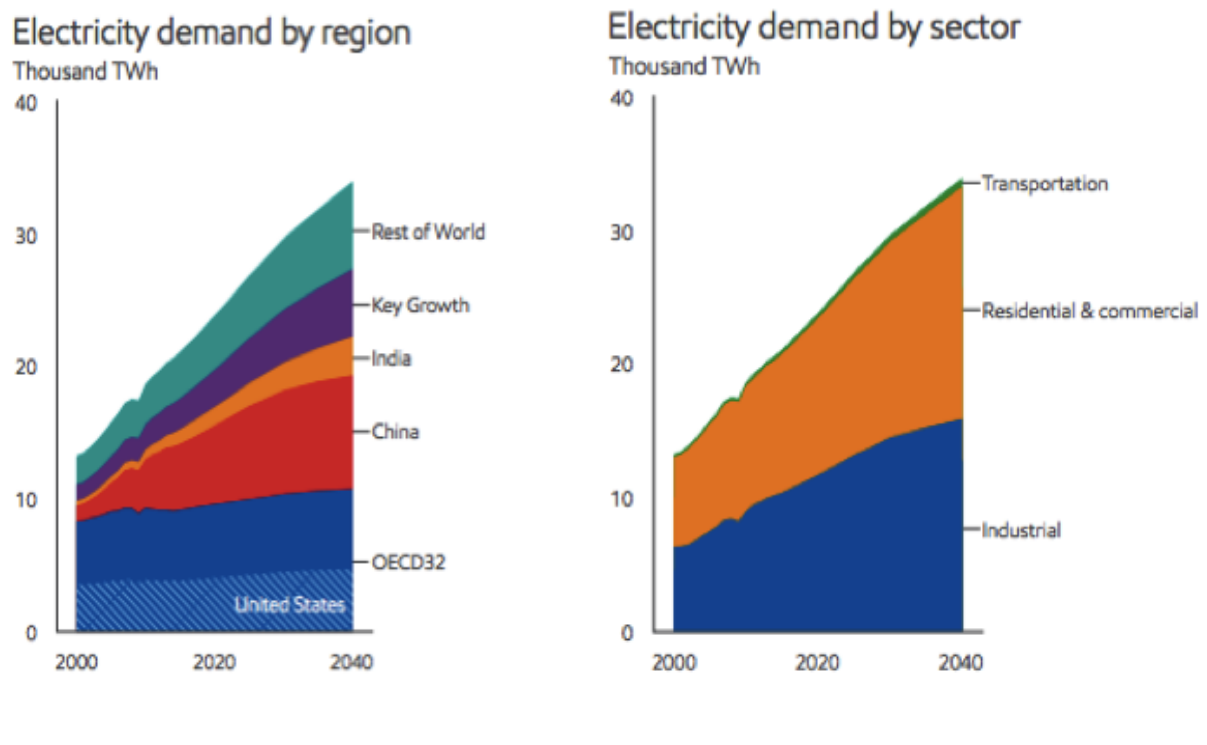


Figure 2.4: Electricity Demand By Region And By Sector [5].

(Source:<http://cdn.exxonmobil.com/media/global/files/outlook-for-energy/2016/2016-outlook-for-energy.pdf>)

Future trend of electricity demand shows that the demand for electricity is expected to rise for more than 65% from year 2014 to 2040 i.e about 2.5 times faster than overall energy demand. The growth of demand will mainly take place in non-OECD countries like China and India due to there increasing population and expanding economies. Electricity demand in India will rise by almost 185% by 2040. In 2014 almost 50% of the electricity is used in industrial sector and 50% in Residential and Commercial regions. It is estimated that industrial electricity demand will rise by 55%, while there will be rise of 70% in residential and commercial electricity demand from year 2014-2020. Demand of electricity for transportation will be doubled by 2020 [5].

Figure 2.5 shows how the electricity generation scenario will be changed by 2040, more cleaner

fuels and renewable energy will be used. Share of electricity generation by gas, wind, solar and nuclear will increase while share of electricity generation by coal will decrease. Share of electricity generation by coal is almost 40% in 2014 which will shrink to 30% by 2040. While wind and solar energy which provide about 4% of energy in 2014 will increase their share to 10% by 2040 [5].

Share of global electricity generation

Share of TWh

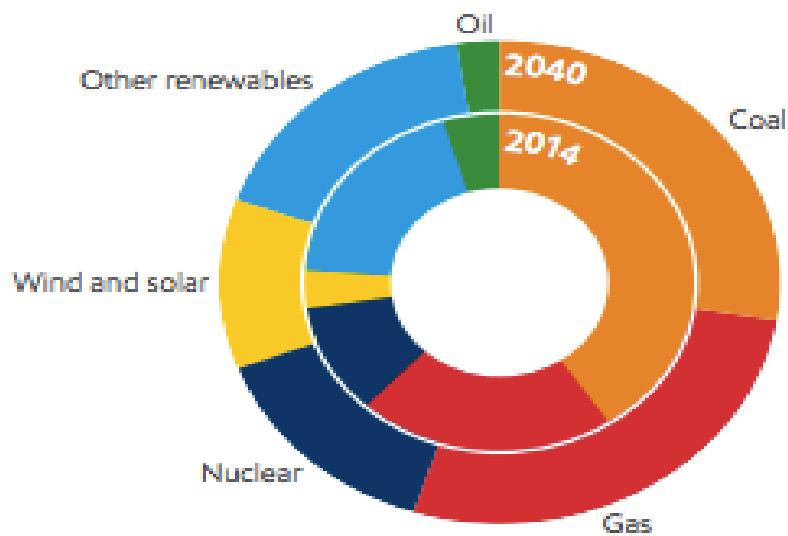


Figure 2.5: Share Of Global Electricity Generation in TWh [5].

(Source: <http://cdn.exxonmobil.com//media/global/files/outlook-for-energy/2016/2016-outlook-for-energy.pdf>)

Figure 2.6 shows the scenario of electricity generation by particular region of the world. It is believed that china will increase utilizing more nuclear, renewables and gas to generate. OECD countries will also shift from coal to gas, wind and Solar for electricity generation. On the other hand India will start utilizing about double the amount of coal by 2040 [5].

Electricity generation by region

Thousand TWh

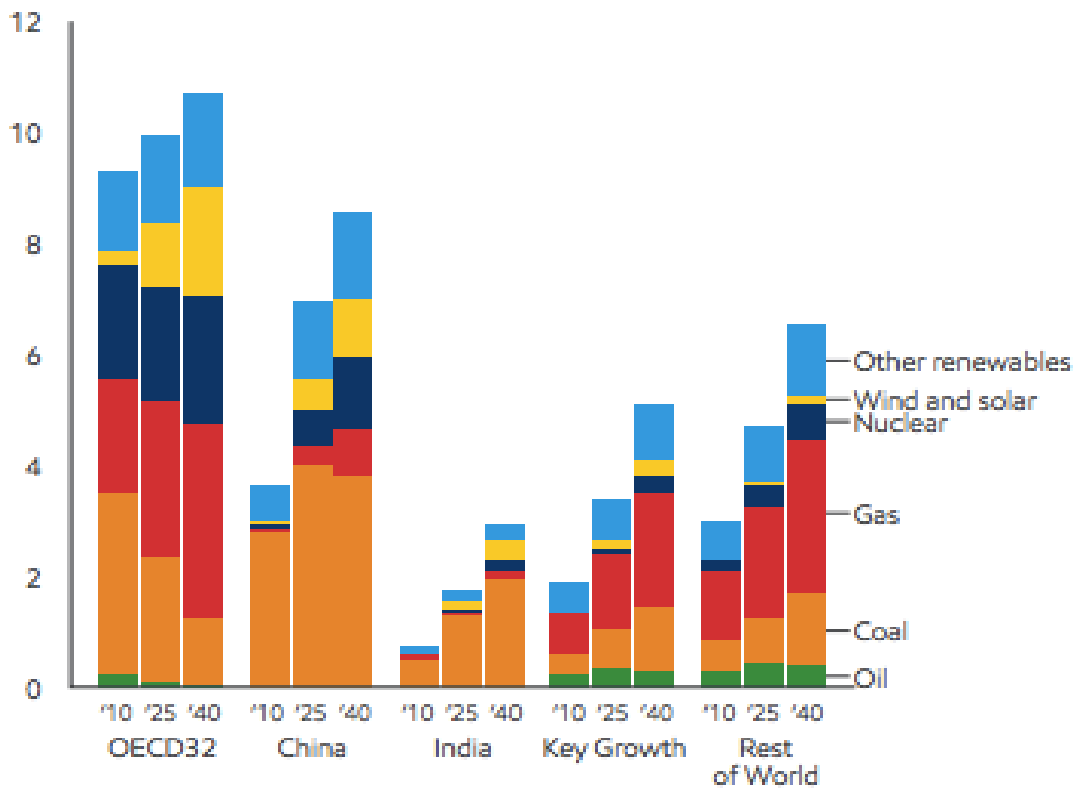


Figure 2.6: Electricity Generation By Region in TWh [5].

(Source: <http://cdn.exxonmobil.com//media/global/files/outlook-for-energy/2016/2016-outlook-for-energy.pdf>)

2.3 Resources

It has been forecasted that by the year 2040 oil, natural gas and coal will be providing about 80% of the energy demand of the world [16].

2.3.1 Oil Reserves

Total proved oil reserves in the world was 1118 billion barrels in 1994, which increased to 1366.2 billion barrels in 2004 and 1700.1 billion barrels in 2014. The current oil reserves by the end of 2014 that is 1700.1 billion barrels is sufficient to meet the oil demand for about 52 years. The OPEC countries have the major share of oil reserves which is about 71% of the total reserves, while oil reserve share of South and Central America has increased to 19.4% in 2014 from 7.3% in 1994. Major addition of oil reserves took place in Saudi Arabia adding about 1.1 billion barrels while largest decline came from the Russia where reserves fell by 1.9 billion barrels [6].

The country with highest oil reserve is Venezuela holding about 298 billion barrels of proven reserves. Venezuela is followed by Saudi Arabia which is holding about 268 billion barrels. For quite a long time it was believed that Saudi Arabia holds the highest share of oil reserves which was proven wrong in the last decade only [17].

Distribution of proved reserves in 1994, 2004 and 2014
Percentage

- Middle East
- S. & Cent. America
- North America
- Europe & Eurasia
- Africa
- Asia Pacific

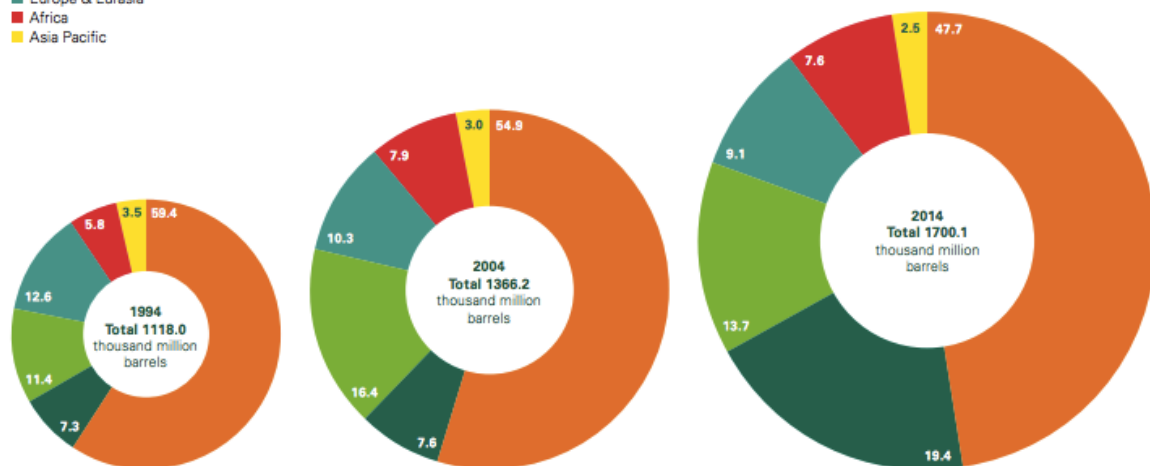


Figure 2.7: Distribution Of Proven Oil Reserves in 1994, 2004 and 2014 [6].

(Source: <https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf/>)

2.3.2 Natural Gas Reserves

Total proved gas reserves in the world was 119 trillion cubic metres in 1994, which increased to 156.5 trillion cubic metres in 2004 and 187.1 trillion cubic metres in 2014. The gas reserves are sufficient to meet the need of global demand for about 54 years. The gas reserve share of middle east has been increased from 38.2% to 42.7% from 1994 to 2014, while share of Europe and Eurasia has fallen from 34% to 31%. Russia and Iran hold the majority of Gas reserves in the world of about 32.6 and 34 trillion cubic metres respectively.[6]

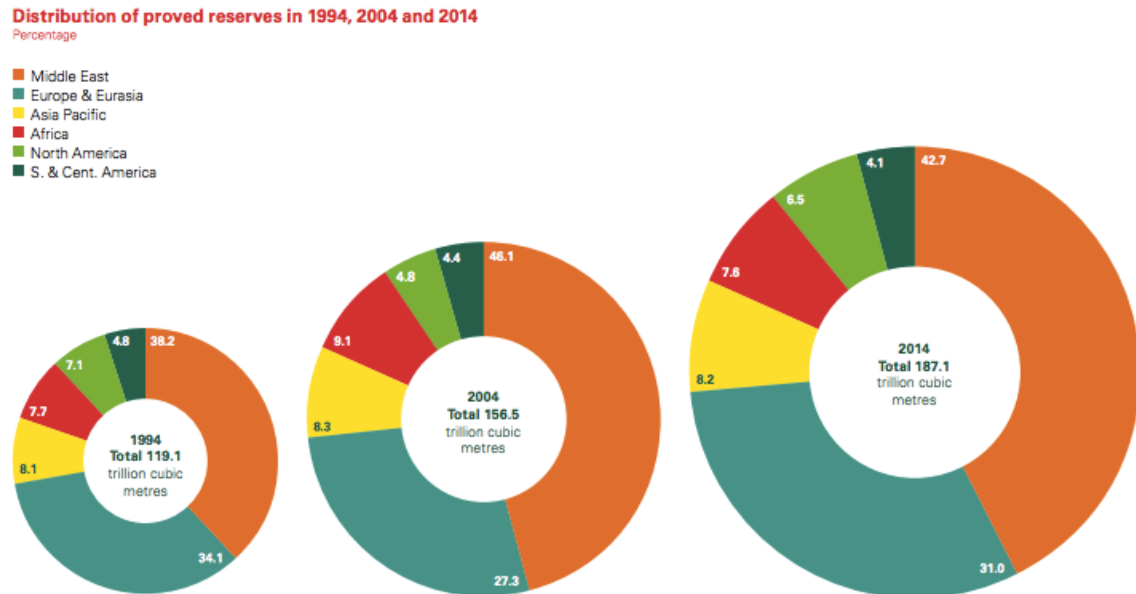


Figure 2.8: Distribution Of Proven Natural Gas Reserves in 1994, 2004 and 2014 [6].

(Source:<https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf/>)

2.3.3 Coal Reserves

Total proven coal reserves in the world was 1039181 million tonnes in 1994, which increased to 909064 million tonnes in 2004 and then decreased to 891531 million tonnes in 2014. These reserves are sufficient to meet the current global production demand for about 110 years while the oil and gas reserves are only able to meet the demand for 52 and 54 years respectively and hence it is more important to find a way to reduce the greenhouse gas emissions from coal fired power plant. [6]

Coal reserves are generally found in most of the countries around the world. The biggest reserves of coal are in Russia, USA, India and China.

Distribution of proved reserves in 1994, 2004 and 2014

Percentage

- Europe & Eurasia
- Asia Pacific
- North America
- Middle East & Africa
- S. & Cent. America

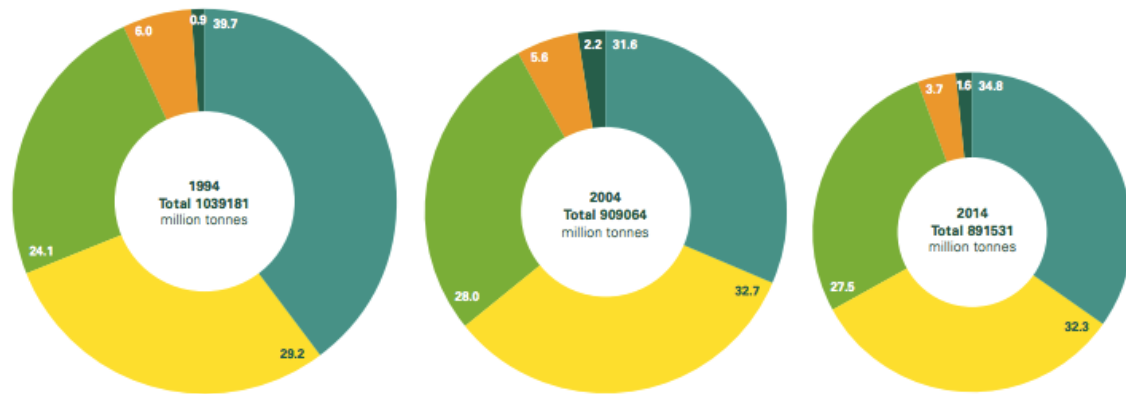


Figure 2.9: Distribution Of Proven Coal Reserves in 1994, 2004 and 2014 [6].

(Source:<https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf/>)

2.4 Consumption of Fuel

2.4.1 Oil Consumption

World oil production outnumbered the consumption in 2014 by 2.1 million barrel per day. Oil production has been increased by 2.1 million b/d while the consumption only increases by 840,000 b/d. Mostly the Non-OPEC countries like USA was reason behind the increase in production. The major oil consuming countries per capita are Saudi Arabia followed by USA and Canada [6].

Per capita consumption of Oil is directly related to the economic development of that country. Countries like Saudi Arabia, Canada and U.S consumed a high amount of oil per capita. While African Countries and Asian countries consumed a small amount of oil per capita. Still one third of the oil consumption take place in the Asian countries due to its huge population [6].

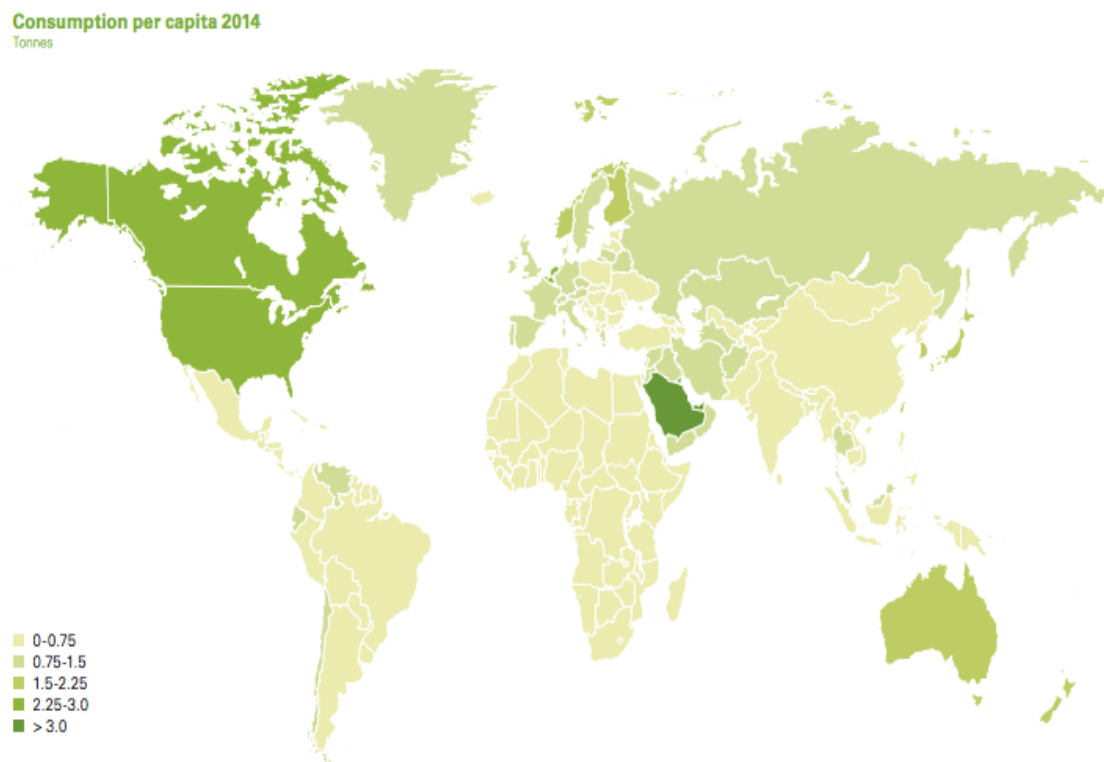


Figure 2.10: Consumption Of Oil per Capita 2014 [6].

(Source: <https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf/>)

2.4.2 Natural Gas Consumption

Natural gas production have been increased by about 1.4% in 2014 while the consumption has increased only by 0.4%. The largest increment in production of natural gas took place in United States (+6.1%) while largest decline in production took place in Russia(-4.3%). The

largest increment in consumption took place in United States(+2.9%) while largest decline took place in Europe(-11.6%). From the figure 2.11 we can see that the major natural gas consuming countries per capita are USA, Canada, Russia, Saudi Arabia and Turkmenistan [6].

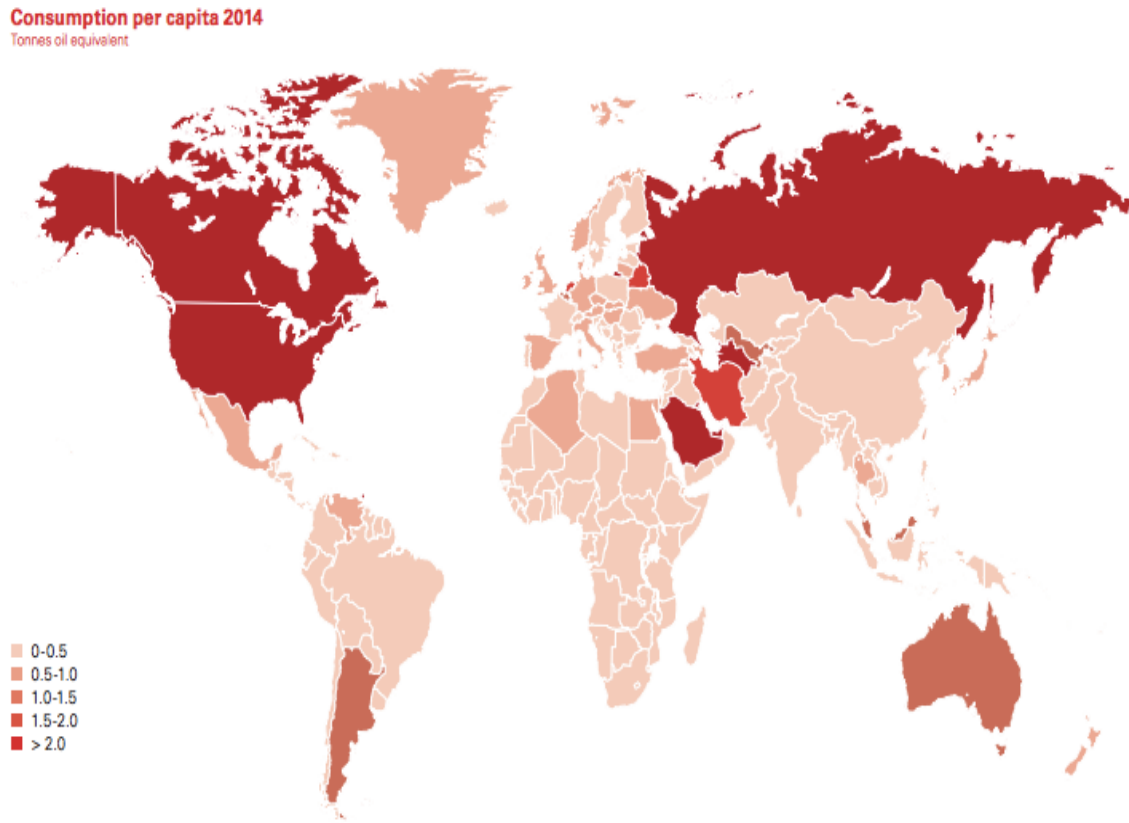


Figure 2.11: Consumption Of Natural Gas per Capita 2014 [6].

(Source:<https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf/>)

2.4.3 Coal Consumption

Coal production have been decreased by about 0.7% in 2014 while the consumption has increased by 0.4%. The largest increment in production of coal took place in India (+6.4%) while largest decline in production took place in China (-2.6%). From the figure 2.12 we can see that the major coal consuming countries per capita are USA, Australia, Poland, Kazakhstan and South-Africa [6].

Consumption per capita 2014
Tonnes oil equivalent

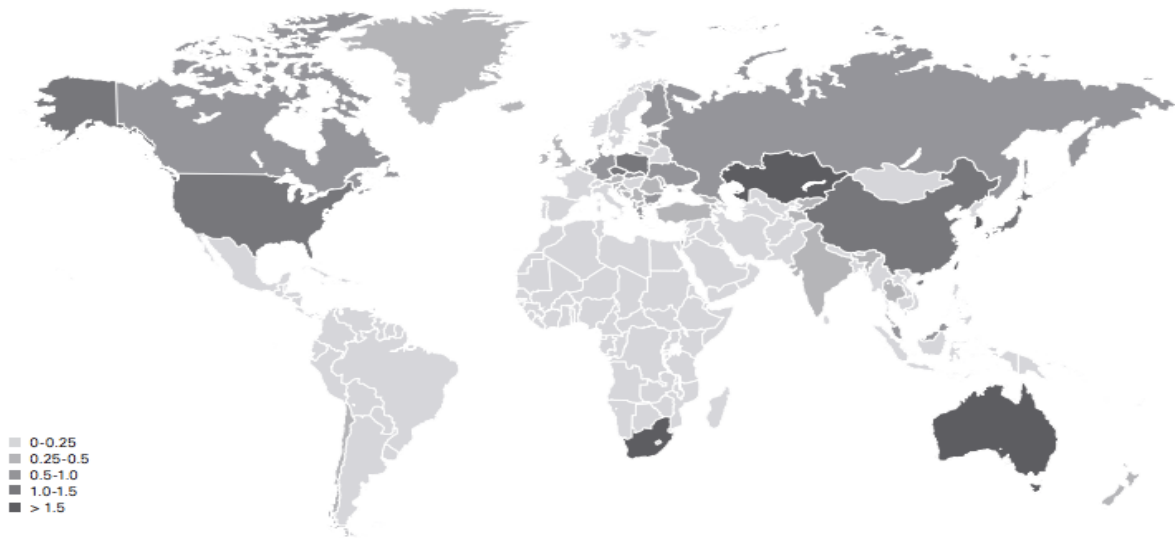


Figure 2.12: Consumption Of Coal per Capita 2014 [6].

(Source: <https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf/>)

2.4.4 Nuclear Energy Consumption

Nuclear Power consumption has been increased by 1.8% in 2014 compare to the 10 year average of -0.8%. The major contributing countries for increase in consumption were South Korea, China, France and North America [6].

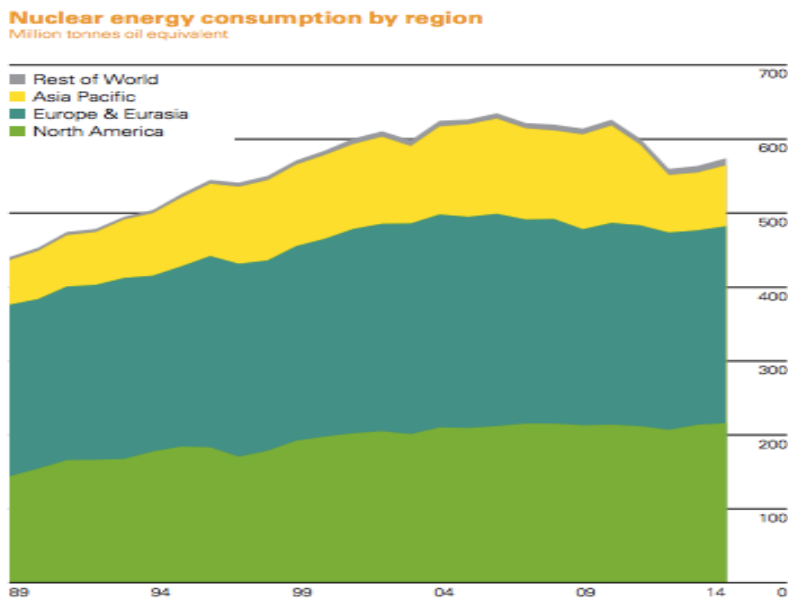


Figure 2.13: Nuclear Energy Consumption By Region [6].

(Source: <https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf/>)

2.4.5 Hydro Energy Consumption

Hydroelectric Power consumption has been increased by 2% in 2014 compare to the 10 year average of 3.3%. Most of the contribution was done by China which grew by 15.7% [6].

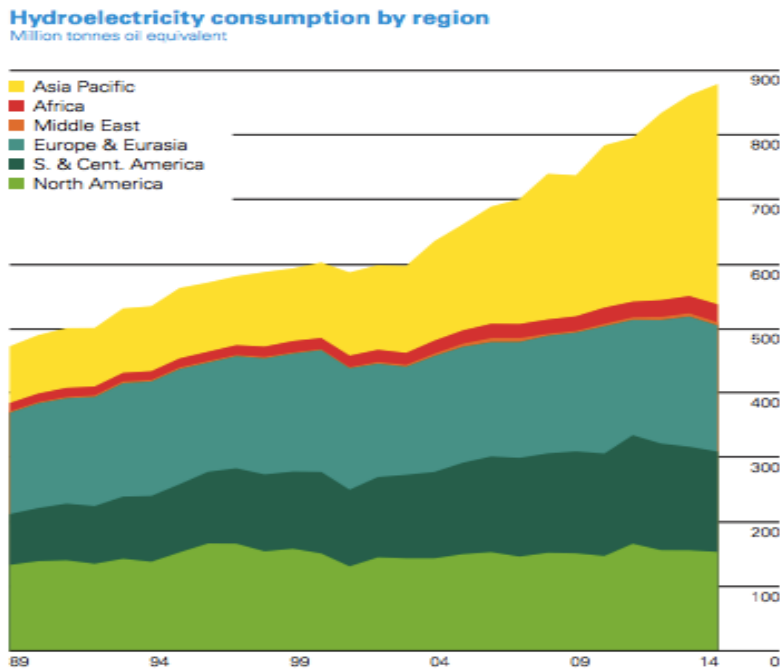


Figure 2.14: Hydroenergy Consumption By Region [6].

(Source: <https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf/>)

2.5 CO₂ Capture Methods

Previous sections showed that global energy supply will mostly be dependent on Coal and electricity demand is going to increase in the future, new ways need to be assessed in order to reduce the CO₂ emissions from the coal fired power plants. CO₂ can be captured basically by 3 different ways depending on the location where the capture took place.

1. Oxyfuel Combustion.
2. Pre Combustion CO₂ Capture.
3. Post Combustion CO₂ Capture.

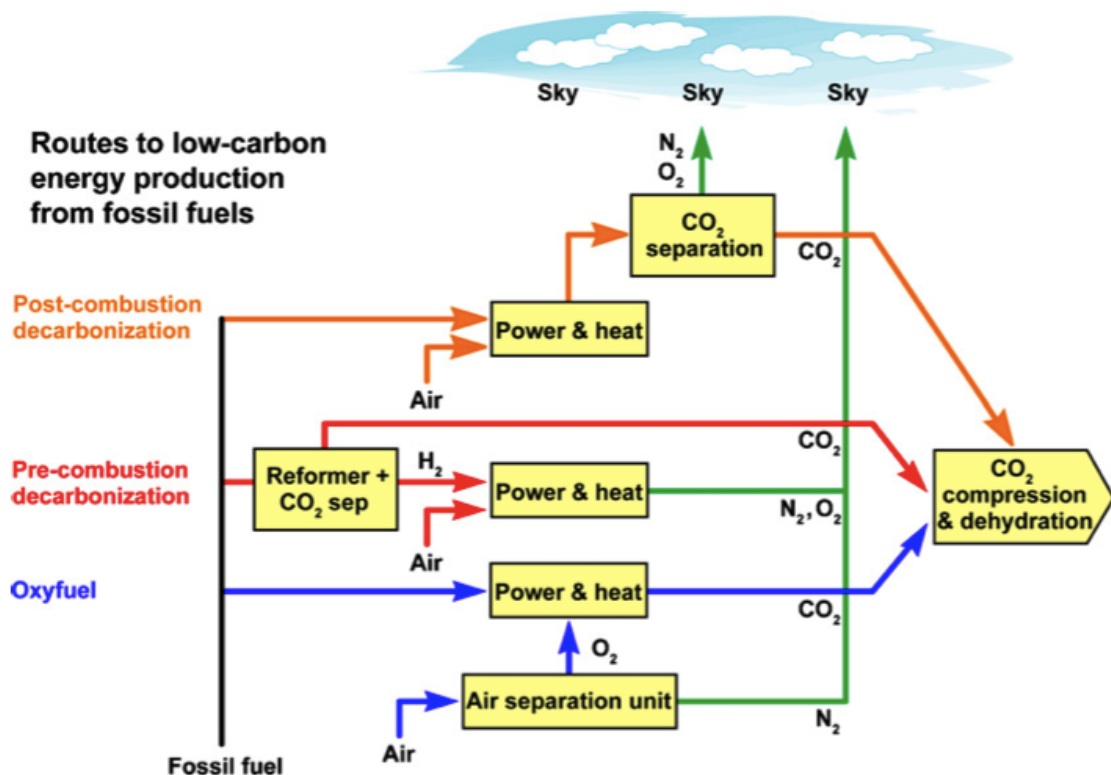


Figure 2.15: CO₂ Capture And Sequestration [7].

(Source: Power plant post-combustion CO₂ capture: An opportunity for membranes by Tim C. Merkel)

2.5.1 Oxy-Fuel Combustion

Pure oxygen is used instead of air in order to obtain fuel gas rich in CO₂ and H₂O. The oxygen is obtained by cryogenic separation of air components. In the Oxy-Fuel capture method the flame temperature is extremely high because fuel is burnt directly in pure oxygen but it is controlled by recycling the CO₂ and H₂O rich fuel gas to the combustion zone. Air Separation Unit (ASU) is used for separating Oxygen from air. High amount of energy is required for the separation to take place. Almost 15% of the electrical energy produced by power plant is consumed in the Air Separation Unit [18].

2.5.2 Pre-Combustion Capture

In this method carbon is captured before the fuel is combusted. Fuel is reacted with oxygen or air in order to produce synthesis gas which is a mixture of carbon monoxide and hydrogen. The carbon monoxide then undergoes the water gas shift reaction to give CO₂ and hydrogen. The CO₂ is then separated and H₂ is used as the fuel to produce electricity in the power plant. Integrated Gasification Combined Cycle works on this principle of carbon capture [18].

2.5.3 Post Combustion Capture

As the name suggests post combustion capture involves separating CO₂ from the flue gas after the combustion of fuels took place. The flue gas is not discharged into the atmosphere and instead pass through the separation unit which separates the CO₂. This does not disturb the design of the already running power plant and thats why its the most preferred capture method [18].

Various technologies for Post Combustion CO₂ capture are -:

1. Physical Absorption
2. Chemical Absorption
3. Membrane Separation
4. Adsorption
5. Cryogenic Separation

Physical Absorption

It is a well established technology. In physical absorption there is one gas-liquid contactor and then series of flash tanks for solvent regeneration. The contactor is at high pressure and CO₂ from the flue gas is captured in the solvent then the solvent passes through the low pressure flash drum where the solvent is regenerated and CO₂ is captured. It is a very simple process as there is no chemical reactions taking place between the solvent and the gas and hence the solvent can be easily regenerated by either reducing the pressure, passing the inert gas through the solvent or using thermal regeneration where temperature is increased to separate CO₂. Physical absorption prefers to takes place at high pressure and low temperature.[19]

Chemical Absorption

Chemical absorption is the most preferred method for separation of CO₂. It has been in use from 1930 for separation and capture of CO₂ from ammonia plant. Chemical absorption method involves passing the flue gas through the absorption and stripping column. In the absorber the CO₂ is absorbed into the aqueous alkaline solvent for example amine. And in the stripping unit also called desorber the absorbed CO₂ is released or stripped from the solution and a pure stream of CO₂ is recovered which can be sent for storage or further utilization. The regenerated solvent is sent to the absorption column and the cycle repeats.

High amount of thermal energy is required in the stripping column heat up the solvent and vaporize the water for stripping of CO₂, while electric energy is required to compress the flue gas before it enters the absorber and also compress the CO₂ in order to store it or transfer it by pumps and blowers [18].

Membrane Separation

In membrane separation method a membrane is used which allow only CO₂ to pass through it while blocking the other components. The membrane is made up of a composite polymer, one is thin selective layer which is bonded to thick non-selective layer. The thick non-selective layer provides the mechanical support needed by membrane. There can be different kind of membranes like Ceramic membranes, metallic membranes and polymeric membranes and hence it can get more efficient than liquid absorption process. The main issue with this technology is the flue gas composition like low CO₂ concentration.[20]

Adsorption

Adsorption process uses solid sorbent instead of the liquid absorbent as in chemical absorption process. The CO₂ is binded on the surface of the adsorbent. The regeneration process takes place either by TSA (Temperature Swing Adsorption) or PSA (Pressure Swing Adsorption). The PSA have an efficiency of about 85%. In PSA CO₂ is adsorbed on the surface of the sorbent at high pressure and then regeneration of the sorbent will take place at the low pressure which will release the CO₂. In TSA the sorbent is regenerated by increasing the temperature through hot air or steam. The regeneration time for sorbent is higher in TSA compare to PSA but the purity of CO₂ is higher than 95%. The main sorbents used are molecular sieves, activated carbon, zeolites, calcium oxides, hydro- talcites and lithium zirconate. The sorbents should have high surface area and high regeneration ability.[20]

Cryogenic Separation

Cryogenic gas separation process involves distillation at low temperature and high pressure. The flue gas is desublimed at -100 °C to -135 °C. The solidified CO₂ is separated from the other components and then it is compressed at a high pressure of 100-200 atmospheric pressure. The

Cryogenic separation method has an efficiency of 90-95% but the only drawback of this process is that it is an energy intensive process. As high amount of energy is require to reach such a low temperature and high pressure. [20]

2.6 CO₂ Storage and Usage

The main question that arises after separating CO₂ is what to do with it ?

There are two options either it can be stored or to utilise it in various industries, Health care units, and for environmental purposes.

First of all after separation of CO₂ it needs to be transported to storage site or the particular industries. There are many ways in which it can be done.

1. In the gaseous form-: It can be transported through pipelines at high pressure. These can be used for Enhanced Oil Recovery.
2. In the liquid form-: It can be transported in the ships as well as in road tankers and rails in tanks at low temperature and pressure.

1: Storage Of CO₂

Geological Storage

The storage sites for CO₂ must be generally located at depth of minimum 800m, so that due to the pressure CO₂ will remain in liquid or supercritical state.

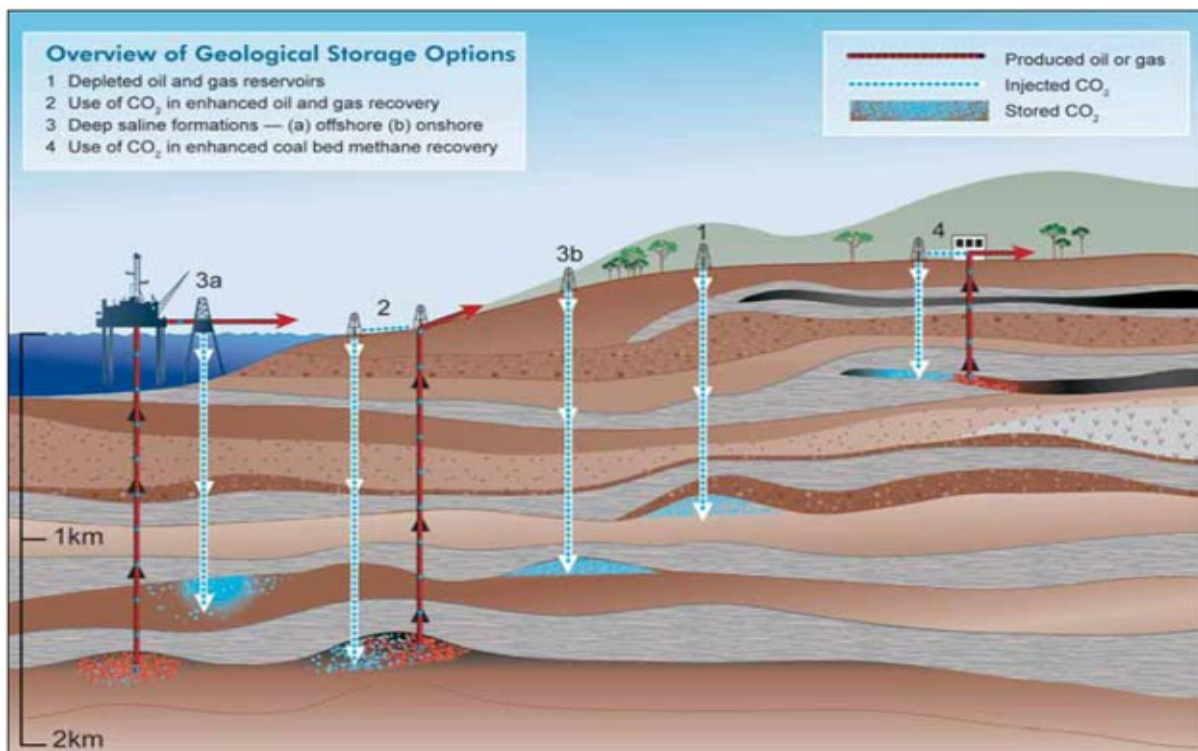


Figure 2.16: Geological Storage Of CO₂ [8].

(Source: IPCC CO₂ Capture and Storage: Technical Summary (2005))

It can be generally stored in depleted oil and gas reservoirs, deep saline formations, and

unminable coal seams. It is injected in dense form into a rock formation below earth surfaces. These rocks are porous which once hold the natural gas, oil or brine. In this way it is trapped there and won't move back to earth surface.[8]

Ocean storage

CO₂ is soluble in water. When the concentration of CO₂ increases in the atmosphere it gets absorbed on the surface of the ocean till equilibrium is reached. The captured CO₂ is injected into the deep ocean at depth of greater than 1000m. This is achieved by transporting CO₂ by using the pipelines or ships to storage site. The stored CO₂ will be isolated from the atmosphere for several hundred years [8].

For storing CO₂ for longer period of time the ideas include forming solid CO₂ hydrates or liquid CO₂ lakes on sea floor and by dissolving the alkaline minerals (limestone) to neutralise acidic CO₂. [8]

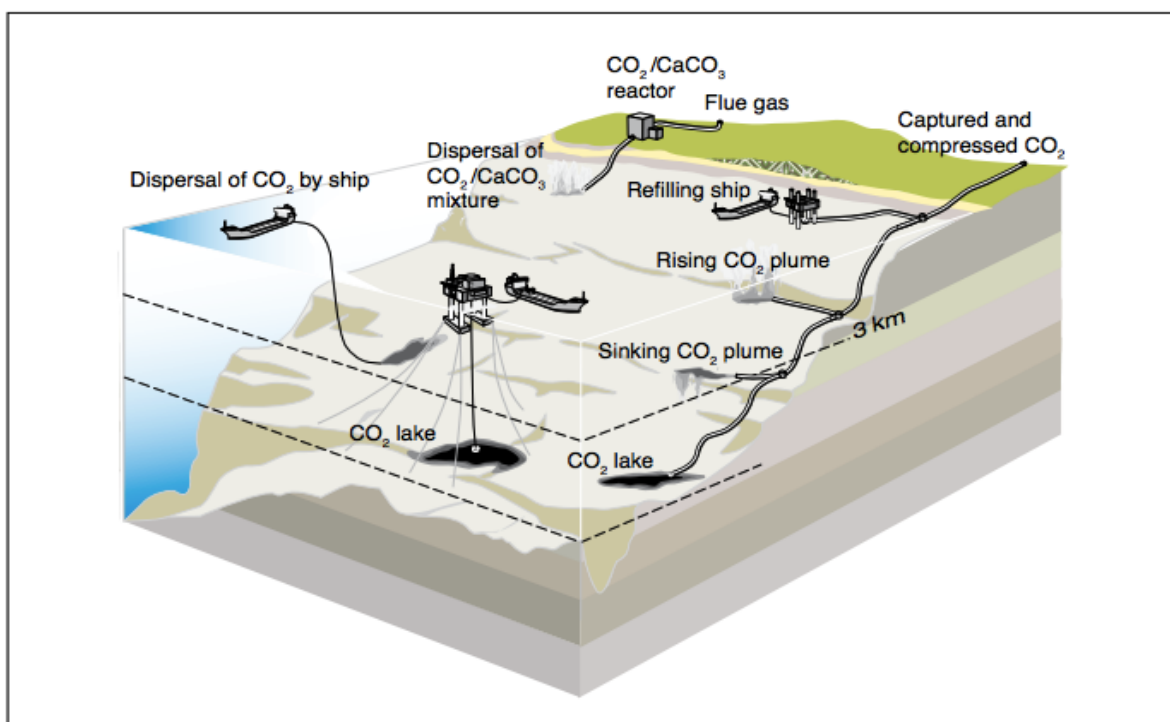


Figure 2.17: Ocean Storage Of CO₂ [8].

(Source: IPCC CO₂ Capture and Storage: Technical Summary (2005))

2: Usage of CO₂

1. In Industry

It is used for refrigeration and cooling in the liquid and solid form in the industries. For the manufacture of casting molds to enhance their hardness. In chemical plants it is used as an

inert gas for startups and testing of leakage in the process equipments [21][22].

2. Manufacturing and Construction

It is used as a shield gas in metal inert gas welding. It shields the metal which is welded from oxidation by surrounding air by forming a layer. In removing the paint from surfaces CO₂ is used in the form of dry Ice pellets [21][22].

3. Chemicals, Pharmaceuticals and Petroleum Industry

Used for the methanol and urea production in chemical industries. In petroleum field CO₂ is used for providing pressure and extracting the oil from the wells. It is used for supercritical fluid extraction in pharmaceutical industry [21][22].

4. Food and Beverages

Used for chilling and refrigeration of food and beverages during transport from one location to another. Liquid CO₂ is passed through nozzles with high pressure which convert it to mixture of gas and dry ice, which cover food surface. The dry ice then undergoes sublimation converting directly to the gas and in the process providing the refrigeration to the product. In beverage industry CO₂ is used for carbonating the soft drinks, sodas, bears etc[21][22].

5. Health Care

Used as a respiration stimulant in healthcare as an additive to Oxygen [22].

6. Environmental Use

Used for neutralising alkaline water and also used as a propellant in aerosol cans[21][22].

EDF CHP Plant, Krakow, Poland Description

3.1 EDF CHP Plant Overview

The coal fired power plant in EDF Krakow is a medium-size coal-fired power plant located in the eastern part of Krakow City. The construction process of power plant was started in 1963 and has been completed by 1986. The plant is divided into 4 units and each unit has its separate power cycle. Total capacity of plant is 460 MW electric and 1118 MW thermal. In the winter time EDF power plant acts as one of the major hot water distribution center of Krakow City. About 63% of the citizens in Krakow use hot water from municipal system of which 72% is delivered by EDF Krakow. In co-generation mode, total efficiency of power plant is about 85% but it only have 35% electricity generation efficiency.



Figure 3.1: EDF CHP plant, Poland, Krakow [9].

(Source:<http://www.gastopgroup.com/en/realizations/36-br3/249-krakow-heat-power-station>)

Power plant uses hard coal (bituminous coal) with Lower Heating Value: 19.5 – 22 MJ/kg, sulfur content below 0.8% and ash content between 22.0 – 28.0% and the chosen technology for sulfur reduction used here is the wet scrubbing FGD (Flue gas desulfurization).

EDF CHP plant is divided into following units :

1: CARBURIZING UNIT

Coal is being delivered here by trains and after unloading it is stored in the landfills. The coal landfill must be protected from auto-ignition and this is done by pressuring the coal. Coal is dosed to the coal bunkers using conveyors.

2: WATER TREATMENT UNIT

There are two water cycles operated in the power plant. First one called the boiler water requiring a high water purity which is achieved in water treatment station by using filtration and ions exchange. Second one is the cooling water, this one don't require that high purity.

3: COOLING FACILITY

There are two natural draft cooling towers in power plant which are used to remove the surplus of heat and obtain require water temperature which is returning to the river Vistula. They are mainly used for power units no. 3 and 4 which have no condenser, but in a smaller scale also for condensation units no. 1 and 2.

4: BOILERS AND MACHINERY BLOCK

The main part of the power plant. The machinery room is comprised of four power generation units. One unit contains a coal bunker, four coal mills, boiler with 16 burners (4 per each mill) plus over-fired air nozzles, a drum, turbine and 13.8 kV generator.

5: COAL COMBUSTION BYPRODUCTS

Coal combustion by-products treatment part of the plant is responsible for fly ash and slag treatment. Residues are being stored in the dedicated platform and then sold to the outside companies.

6: CONTROL SYSTEM

There are basically two main control rooms in power plant, one for units 1, 2 and another for units 3, 4. Nowadays, almost everything is operated by a dedicated software, thus the main management of the power plant is done in the control rooms. There are also another rooms to take care of power distribution and electrical issues and several smaller rooms besides more important departments like water treatment department.

7: POWER DISTRIBUTION

The 13.8 kV generators provide power to the transformers. There the voltage is transformed to 110 kV which allows the electricity to be transferred to the national grid. There is a significant consideration when a unit is being started because each generator must be first synchronized with the grid.

3.2 Functionality Of Units Of Power Plant

A pulverized coal fired boiler is an industrial or utility boiler that generates thermal energy by burning pulverized coal (also known as powdered coal or coal dust since it is as fine as face powder in cosmetic makeup) that is blown into the firebox. The basic functionality of a firing system using pulverized fuel is to utilize the whole volume of the furnace for the combustion of the solid fuels. Coal is ground into fine powder, mixed with air and then burned in the flue gas flow. Biomass can also be added to the mixture. Coal contains mineral matter which is converted to ash during combustion. The ash is removed as bottom ash and fly ash. The bottom ash is removed at the furnace bottom. This type of boiler dominates the electric power industry, providing steam to drive large turbines. Pulverized coal provides the thermal energy which produces about 50% of the world electric supply.

EDF CHP plant is comprised of four units. Two of them are equipped with 120MWe RAFAKO OP-380 pulverized coal boilers, connected with the condensing turbine containing steam split. Those splits are used in the winter time to heat up water for municipal heating network.

Another two units are equipped with 110MWe RAFAKO OP-430 pulverized coal boilers connected with the back pressure turbine. These two units do not contain condenser. When there isn't sufficient demand of hot water, then cooling towers are used to cool down steam from these units. There are two cooling tower in the power plant. All turbines are linked to the 13.8 kV, hydrogen-cooled generators.

There are also (HOBs) peak water boilers which are used only for producing hot water. These boilers are necessary as during the peak hours in winter time total heat produced by four units is not enough to satisfy the demand. These peak boilers are replaced by oil boilers.

There are 3 chimneys and two cooling towers in power plant. One of 3 chimneys is a part of FGD installation. A chimney is a structure which provides ventilation for hot flue gases or smoke from a boiler, stove, furnace or fireplace to the atmosphere. Chimneys are typically vertical, to ensure that the gases flow smoothly, drawing air into the combustion in what is known as the stack or chimney effect. The height of a chimney influences its ability to transfer flue gases to the external environment via stack effect. Additionally, the dispersion of the pollutants at higher altitude can reduce their impact on the immediate surroundings.

4.1 Aspen Plus description

Aspen Plus is a computer aided simulation and chemical process optimisation software used in petrochemical, polymer and other manufacturing industries for the design, operation, and optimization of safe, profitable manufacturing facilities.[23]

The simulation of a process is done in order to model and analyse the performance of that process without building the plant in the real world. This is done in order to optimise parameters, design specification, increasing efficiency and other cost related aspects. In simulation input parameters and flow diagram of the process are used to predict the outputs and results. Aspen plus utilises the physical relationships like material and energy balance, thermodynamic equilibrium and rate equations to give process performance like operating conditions, steam properties and equipment sizes.[10]

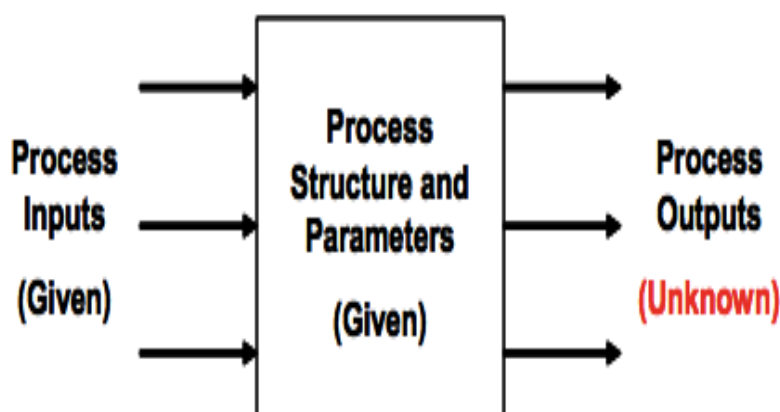


Figure 4.1: Process simulation model [10].

(Source:<http://wp.auburn.edu/eden/wp-content/uploads/2012/03/4460-Aspen-Notes-2012.pdf>)

Simulation softwares are used to predict the behaviour of the process and in order to do that a process model has to be defined. Process model is a complete layout and it consist of following : [24]

1. Flowsheet - flowsheet means mapping out the entire system. It consist of inlet stream entering into the first unit operation and then consisting of all the intermediate unit operations and interconnecting streams and also the product streams.
2. Chemical Components - chemical components are all the reactants that are used and all the products that are formed.
3. Operating Conditions - Process Models work under certain operating conditions like temperature, pressure, flow rate which needs to be provided to the simulation software.

4.2 Description of the practical work

Chemical absorption method was used among the available post combustion carbon capture methods for this work. The basic schematic of CO₂ capture is shown in figure 4.2. CO₂ from the flue gas is absorbed in solvent in the absorber section, cleaned gas is released from the top and solvent rich in CO₂ pass from the bottom of absorber to the stripper section. The solvent used for absorption of CO₂ is monoethanolamine (MEA). In the stripper section the CO₂ is stripped from the rich solvent and released from the top and the lean solvent is recycled back to the absorber column.

Process Description

Flue gas is compressed and cooled before entering into the absorber unit. The flue gas is cooled to a temperature of 40-45 °C since absorber operates at about 40 °C. Before the flue gas is passed through the absorption it is necessary to remove NO_x and SO_x because they forms heat stable salts with the amine solution. NO₂ levels in flue gas should be less than 20 ppm. And SO₂ levels should be generally less than 10 ppm. These impurities are removed in the desulphurisation section of the plant [25].

Flue gas after the desulphurisation section is cooled by passing though the direct contact cooling tower (DCC). In DCC cooling water comes from the top and flue gas enters from the bottom, there is a counter current flow. The temperature of flue gas is reduced by evaporation of water from it. Then the flue gas is passed through the blower/compressor in order to get compressed and increase its pressure. The pressure is increased as absorption works better in high pressure and low temperature environment [26].

The absorption column uses sieve trays in order to increase the surface area for CO₂ absorption and proper mass transfer. The lean amine solution enters from the top and flue gas enters from the bottom of absorber. They flow counter current in the packed absorber and absorption of CO₂ from flue gas to lean amine takes place. The flue gas free of CO₂ is released from the top of the column as exhaust and the rich amine leaves from the bottom. By lean amine it means the amine which is stripped of CO₂ and rich amine means the amine is loaded with CO₂. The first stage of the absorber is kept for water wash and lean amine enters through the second stage into the absorber. The water wash helps to remove any entrained amine present in the exhaust gases. Sometimes a separate water wash tower is used after the absorber [26].

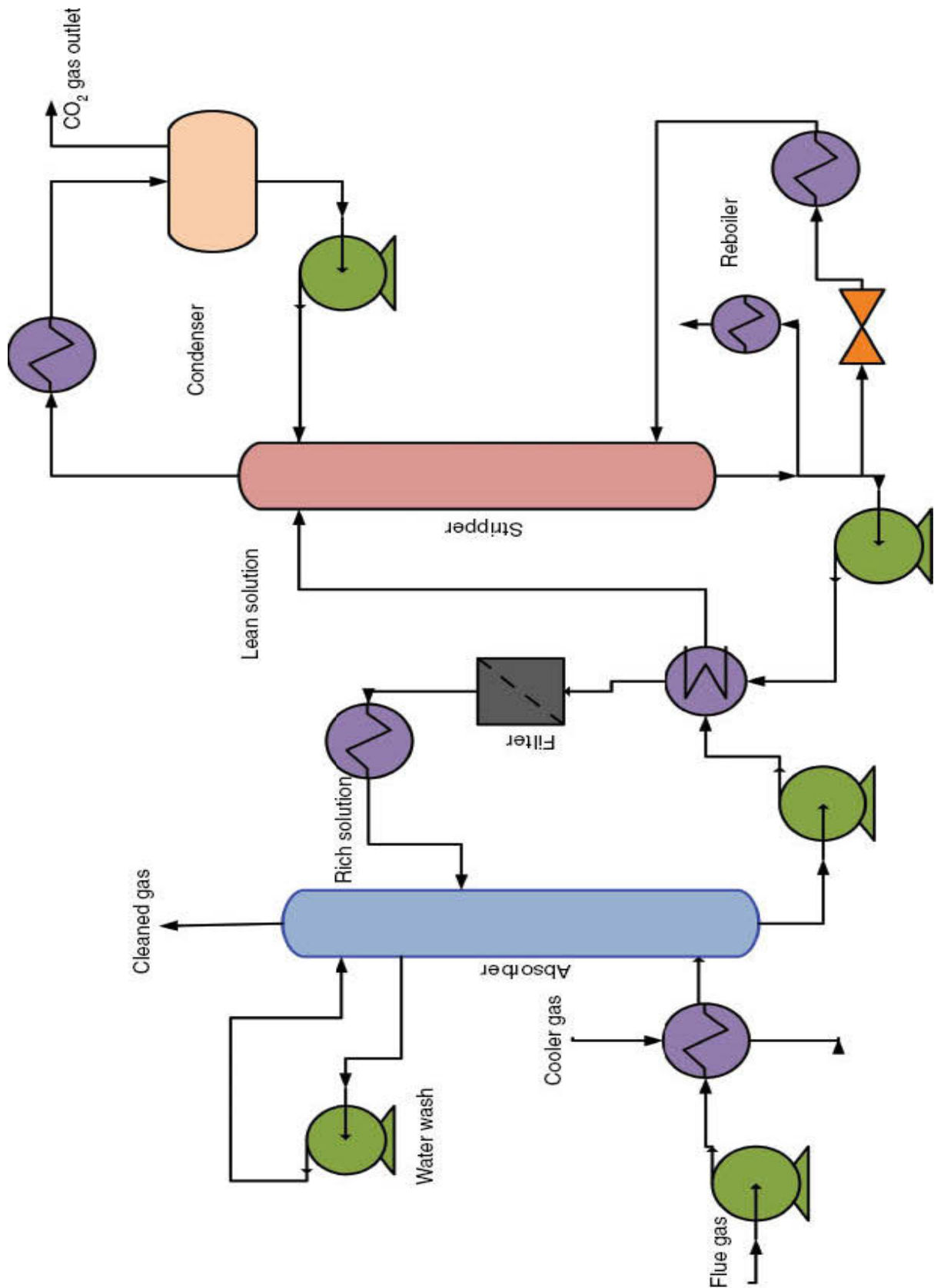


Figure 4.2: Basic Flowsheet Of Carbon Capture [11].

(Source: A review of CO₂ capture by absorption in ionic liquid-based solvents by S Babamohammadi, A Shamiri)

The rich amine passes through the pump which increases its pressure in order to go till the top of stripper column. Before the stripper column it passes through the cross-heat exchanger. In the heat exchanger the rich amine coming from absorber exchange the heat from the stripped amine coming from stripper. The rich amine then goes to the stripper column. Stripper is a packed column with kettle re-boiler. The rich amine enters into the second stage of the column and flows downwards and the vapors from the re-boiler flows upwards. The vapours strip the CO₂ from the rich amine and flows upwards and goes through the condenser which condenses the water present in the vapours. Then it passes through the flash drum where CO₂ and H₂O are separated, CO₂ gas is removed from the top and the water comes out from the bottom. Then a part of this water flows through the top stage of the stripper column and top stage acts as a water wash in order to remove any amine present in the Vapors. The reboiled in the stripper column requires heat duty in order to produce the vapors. The heat duty is provided by the power plant.

The CO₂ gas that is released from top of stripper is dried and then sent for storage or to particular industry for usage. The drying should be done in a proper way as if there is moisture present in the gas then it will corrode the piping used for transferring the CO₂. Generally a 4 stage compressor is used for drying with cooling between each stage [25].

The amine solvent that is recovered from the bottom of the stripper needs to be treated as it consist of heat stable salts formed by NO_x and SO_x. This is not desirable since it reduce the capacity of the amine solution to absorb CO₂, hence a makeup of amine is done and a part of the recovered amine solvent is purged. [26]

Chemistry

Different amines like MEA, MDEA, DEA can be used for absorbing CO₂. CO₂ is absorbed in the amines in different ways and it follows different mechanisms. These amines are bases and they react with the acid. The amines are soluble in water due to the presence of the alcohol group. The amines can be classified as primary, secondary or tertiary amines according to the different organic group that is attached to the Nitrogen. These different amines react differently, primary and secondary amines have higher heat of absorption and hence react faster compare to the tertiary amine but high amount of energy is required in order to regenerate the primary and secondary amine. CO₂ reacts with MEA amine solution to undergo Carbamate formation.[18]

Carbamate Formation

Carbamate formation takes place by 2 mechanisms :

1. Zwitterion Mechanism

Caplow proposed this mechanism in 1968. It is a 2 step mechanism. Firstly water reacts with amine and a hydrogen bond is formed between the Amine and water molecule. Then

the reaction with CO_2 takes place and a bond is formed between amine and CO_2 . This is an unstable intermediate which further undergo proton transfer to form the carbamate [12].

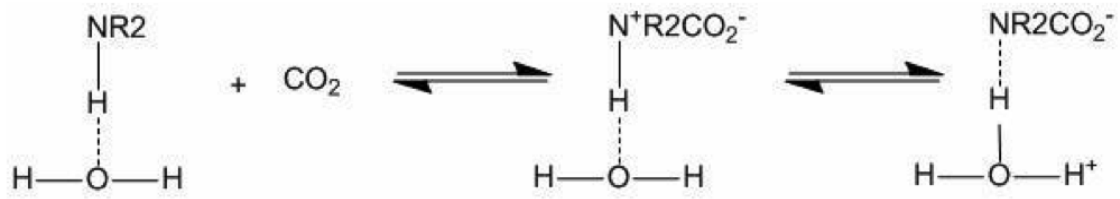


Figure 4.3: Zwitterion Mechanism [12].

(Source: CO_2 -fuel gas separation for a conventional coal-fired power plant (first approach) by A Syed Muzaffar)

2. Termolecular Mechanism

This is a single step mechanism. In it the bond formation and proton transfer take place simultaneously. B is the base molecule, the amine forms a bond with CO_2 and proton transfer take place in single step [12].

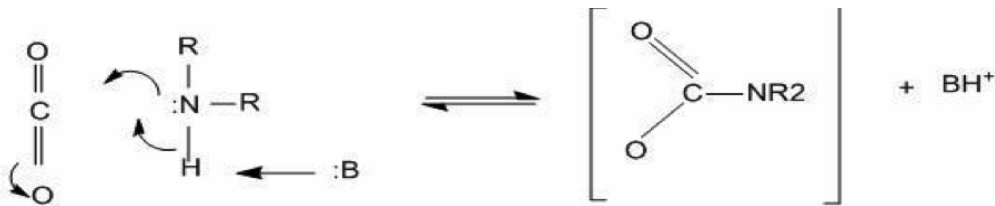


Figure 4.4: Termolecular Mechanism [12].

(Source: CO_2 -fuel gas separation for a conventional coal-fired power plant (first approach) by A Syed Muzaffar)

4.3 Model of power cycle

EDF CHP plant has 4 units, 2 with 120 MWe capacity and 2 with 110 MWe capacity. In this work one of the unit of power plant having 120 MWe capacity is modelled using the data of power plant as on 18th November 2011. The unit was operating at 84.853 MW load on that day. Coal was combusted at the mass flow rate of 32.5 ton/h, and the boiler produce about 212.4 MW of thermal energy. The model of steam cycle that simulates the performance of steam cycle of 84.8 MWe unit of EDF CHP plant was developed. The model predicts the power output from the turbine and conditions (temperature, pressure and flow rate) of steam in the steam cycle.

4.3.1 Overview

The steam cycle is divided basically into 3 sections

1. Turbines.
2. Condenser.
3. Preheaters or Regenerators.

Equipments

ODG is the vacuum drum which acts as a deaerator to remove dissolved gases from the water. LPSPLIT1, LPSPLIT2, LPOUTLET, MPOUTLET, MPSPLIT1, MPSPLIT2, HP are the turbines for generating the power from the steam. XA, XB are heat exchanger used for condensing the steam from LPSPLIT1 LPSPLIT2. XW1, XW2, XW3 are the regenerators/preheaters for preheating the condensate before it goes to blower section. XN1, XN2 are preheaters for heating the condensate before it enters the ODG.

Process Description

After the steam is produced in the boiler unit it flows to the HP turbine which have an efficiency of 69%. The steam is produced at the flow rate of 296.3 ton/h, 536.8 °C and 11182 kPa. Steam pressure is decreased to 2233 kPa and temperature to 394.8 °C. A part of steam is divided after the HP turbine and goes to XW3 (Preheater) and rest goes to the super-heater located in the boiler section. There the steam gain heat and its temperature rises to 537 °C and then flows to MP turbine. MP turbine is operating at an efficiency of 88% and is divided into 3 parts/splits and hence it is simulated as 3 different turbines in Aspen Plus MPSPLIT1, MPSPLIT2 and MPOUTLET.

The steam coming from the super-heater flows to the MPSPLIT1 at 1902 kPa and 537 °C. There the pressure of steam is reduced to 1149.9 kPa and temperature is reduced to 465.9 °C. A part of steam is then divided and goes to XW2 (Preheater) and rest goes to MPSPLIT2. In MPSPLIT2 the steam pressure is reduced to 607.3 kPa and temperature is reduced to 373.8 °C. After which a part of steam is divided and flows to XW1 (Preheater) and rest of it flows to the MPOUTLET. The outlet of MP turbine is divided into 3 streams, first flows to the ODG which is a vacuum drum or deaerator and other 2 flows to the LP turbine.

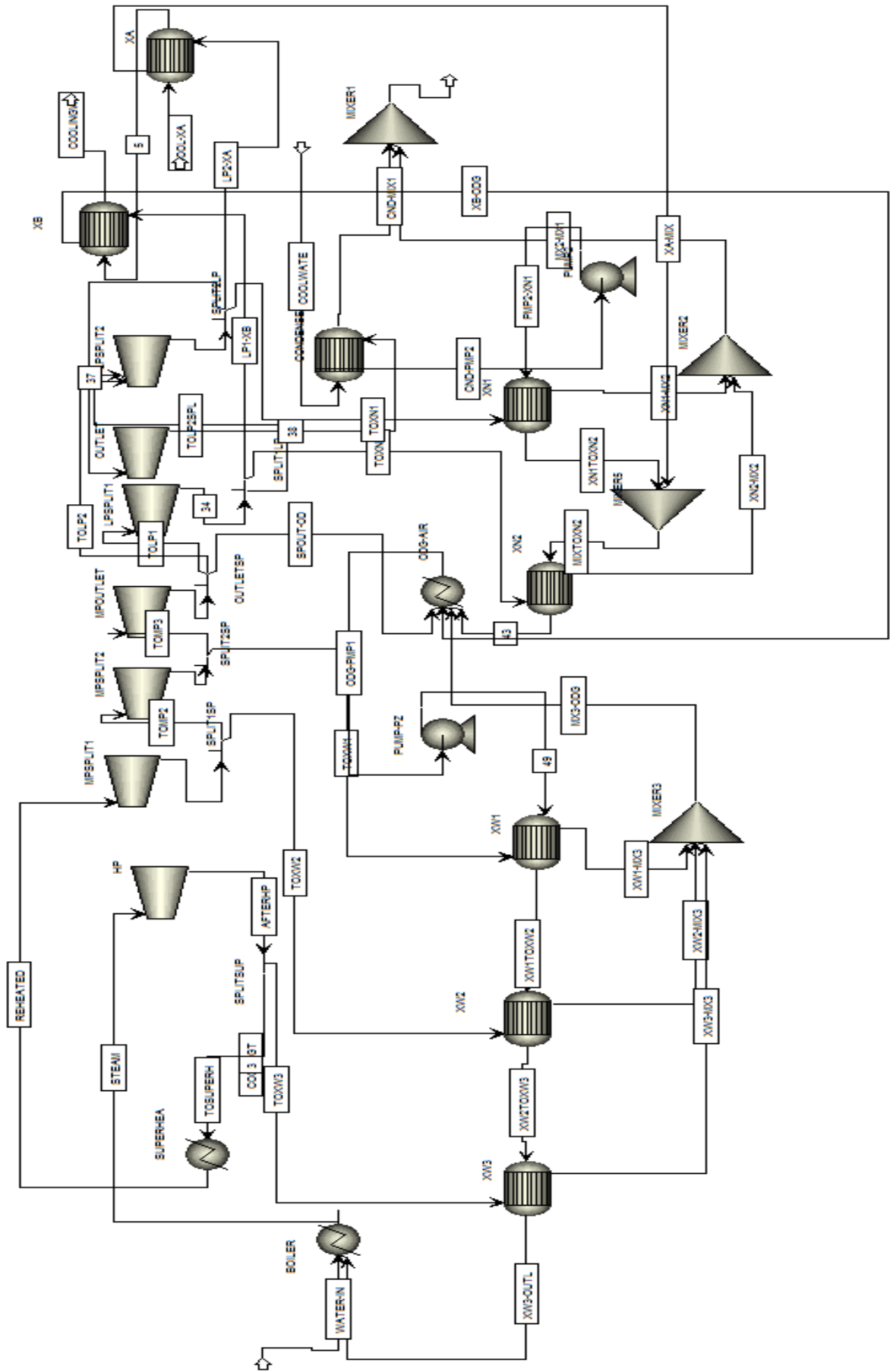


Figure 4.5: Aspen Plus steam cycle.

Since LP turbine is also divided into 3 parts hence 3 different turbines are used for simulating it that are LPSPLIT1, LPSPLIT2 and LPOUTLET. Lp turbine is operating at an efficiency of 66.3%. Steam at the Outlet of LPSPLIT1 is at 57.6 kPa and 137.2 °C and is further divided into 3 parts. One goes to the XN2 (Preheater), one to LPSPLIT2 and one goes to XB (Heat Exchanger). Steam at the Outlet of LPSPLIT2 is at 32.19 kPa and 98.8 °C and is divided into XN1, XA and LPOUTLET. From LPOUTLET steam goes to condenser where it condensate and the liquid flows to XN1 then XN2 and finally to ODG (Vacuum Drum). Vacuum Drum collects the condensate from XN2, XB, XW1 and steam from MPOUTLET.

The gases dissolved in the condensate are removed in the ODG (Vacuum Drum) and it is then pumped to the XW1 then XW2 and XW3 there it is preheated with the help of steam outlets from the turbine. After preheating a part of condensate goes to superheater and rest of it goes to the boiler unit for steam generation.

4.3.2 Components

Only water is used as the component in the steam cycle. Since the Boiler section is not simulated in the current work. So the inlet stream is steam.

4.3.3 Property Method

There are 2 property methods STEAM-TA and STEAMNBS within ASPEN PLUS for steam cycle simulation. STEAMNBS property method is used for the simulation of power cycle in Aspen Plus.

4.3.4 Stream Specification

Plant load controlled the flow rate of Steam-In. The feed data of 18th november 2011 was taken from EDF CHP plant, krakow, poland and feed specifications are as follows:-

Table 4.1: Steam Specification

	Units	Value
Temperature	°C	536.8
Pressure	kPa	11182
Mass Flow	ton/h	296.3

Block Specification

Table 4.1 shows the blocks used in Aspen plus and there respective UOM (Unit Operation Model).

Table 4.2: Aspen plus block specification for steam cycle.

Block	Unit Operation Model
SUPERHE	Heater
HP	COMPR
MPSPLIT1	COMPR
MPSPLIT2	COMPR
MPOUTLET	COMPR
LPSPLIT1	COMPR
LPSPLIT2	COMPR
LPOUTLET	COMPR
XA and XB	HeatX
CONDENSE	HeatX
XN1 and XN2	HeatX
XW1, XW2 and XW3	HeatX
CDG-AIR	Heater
PUMP-PZ	PUMP
MIXER1,2,3	Mixer

SUPERHE

Super heater is used for heating the steam after it passes through the HP turbine. The steam is heated to 537.5 °C. It is simulated by heater unit in Aspen Plus.

HP, MPSPLIT1, MPSPLIT2, MPOUTLET, LPSPLIT1, LPSPLIT2, LPOUTLET

There are 3 turbines used in the steam cycle. HP (High Pressure), MP (Medium Pressure) and LP (Low Pressure). The turbines are simulated by COMPR unit of Aspen Plus. The MP and LP turbine has 2 splits from where the steam is removed to preheat the condensate. The turbines HP, MP, LP are assumed to be isentropic and working at an efficiency of 69, 88 66.3 percentages respectively. The MP turbine is simulated as 3 separate turbines in aspen plus MPSPLIT1, MPSPLIT2, MPOUTLET and LP turbine is also simulated as 3 separate turbines i.e LPSPLIT1, LPSPLIT2 LPOUTLET.

XA, XB, XW1, XW2, XW3, XN1, XN2

The preheaters are used to increase the temperature of boiler feed water. The preheaters used are multipass shell and tube heat exchanger and ASPEN PLUS HeatX unit is used for the model.

CONDENSE

The condenser is used to condense the final steam outlet from the LP turbine which then goes to the XN1 for preheating. ASPEN PLUS HeatX unit is used for the model. Hot stream outlet temperature of 25.6 °C was input for the condenser unit.

4.4 Total Efficiency And Power Parameters

The unit modelled give the electric power of 84.453 MWe at 296 ton/h of steam flow rate. The plant is operating at 70% load. As the plant load is increased there is the increase in the steam flow rate. Table 4.2 describe the effect of Plant load on steam flow rate.

Tabular representation

Table 4.3: Effect of plant load on steam flow rate.

Plant Load(%)	Steam FlowRate (ton/h)
50	209
55	232
60	251
65	274
70	295
75	315
80	332
85	359
90	379
95	396

Graphical representation

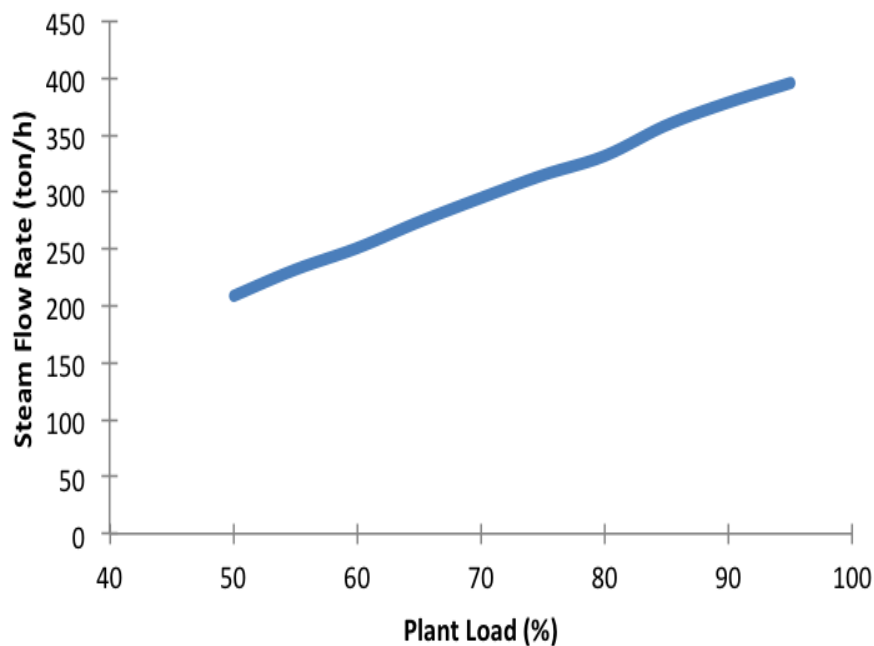


Figure 4.6: Effect of plant load on steam flow rate.

In the base model HP, MP and LP turbines were operating at different efficiency which was taken from the power plant data. Table 4.3 show the power produced by turbines at base model efficiency.

Table 4.4: Efficiency of turbines and power produced.

Turbine	Efficiency (%)	Power (MWe)
HP	69	28.8
MP	88	45.3
LP	66	10.66

Efficiency of the turbine is defined as the ratio of total input energy by total output energy. For maximum electric power generation the turbines should operate at 100% efficiency but that is not possible since there were many losses like the friction losses and heat loss in the turbine. Table 4.4 shows how the efficiency of the turbine effects the total power generated by each turbine.

Table 4.5: Efficiency Of HP turbine and power produced.

Efficiency (%)	Power (MWe)
50	20.8
60	25.0
70	29.2
80	33.3
90	37.5
100	41.7

Table 4.4 shows that as the efficiency of HP turbine is increasing the power generated by it also increasing. Base case was operating at 69% HP turbine efficiency and producing 28.8 MWe of electric power. If the losses in the the turbine can be minimized than more electric power can be generated while having the same plant load and CO₂ emissions.

4.5 Model of CO₂ Capture

CO₂ capture can be modelled in aspen plus in 2 ways, Thermodynamic Model and Rate Model. Thermodynamic model is used for simulation in this work. It is used in order to minimize the thermal energy required by the re-boiler and also for the easy convergence of the calculations compare to the complex rate based model. The thermodynamic model uses the E-NRTL theory which was developed by Chen and Evans (1979) and extended by Mock et al. (1986) for mixed solvent electrolyte systems. The CO₂ recovery of 85% is envisaged while modelling. The following sections describe the property method, stream specifications, block specifications used while simulating the plant in Aspen Plus [27].

Thermodynamic Model

Thermodynamic model assumes that the overall process occurs at equilibrium although CO₂ absorption is a non-equilibrium process. There is equilibrium at each stage of absorber between vapor and liquid phases. In this model number of moles of CO₂, H₂O and MEA is to be calculated in vapor and liquid phase at a particular temperature. Thermodynamic model involves the formation of Ions and polar molecules during reactions, ions are non-volatile and only soluble in the liquid phase and gas phase only consist of CO₂, H₂O and MEA [27].

Rate Model

CO₂ absorption is a non-equilibrium process. In rate based model rate of reaction is faster but they are not in equilibrium conditions. Reaction between CO₂ and MEA take place at finite rate and follow particular kinetics, which is temperature and composition dependent. Aspen Plus RATEFRAC mode is used for simulating absorber and stripper column in rate based model[27].

4.5.1 Components

First of all the components taking part in the CO₂ capture process were entered. The components entered were carbon dioxide(CO₂), Water(H₂O), Nitrogen(N₂), Sulphur Dioxide(SO₂), Monoethanol Amine (MEA), H₃O⁺, OH⁻, HCO₃⁻, MEA⁺, CO₃²⁻. Figure 4.7 shows all the components entered in simulation.

4.5.2 Property Method

Since ions and polar molecules are formed during the absorption of CO₂ in MEA hence ELECNRTL property method is used for the CO₂ capture simulation. This property method is an electrolyte property method and can handle very high and very low concentrations. This method is generally used when there are some sort of interactions between the species and the ions in the solution. [28]

Simulation 1.apwz - Aspen Plus V8.4 - aspenONE

Search aspenONE Exchange

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Clipboard Edit Paste Copy Unit Sets Setup Components Methods Draw Structure Clean Parameters Retrieve Parameters Methods Assistant DECHEMA NIST DECHEMA Analysis Assistant Estimation Regression Run Mode

Next Run Run Control Panel History Report Summary Input Pure Binary Mixture PT Envelope Ternary Diag Residue Curves

Properties Components - Specifications

Selection Petroleum Nonconventional Enterprise Database Information

Select components:

Component ID	Type	Component name	Alias
WATER	Conventional	WATER	H2O
CO2	Conventional	CARBON-DIOXIDE	CO2
N2	Conventional	NITROGEN	N2
O2	Conventional	OXYGEN	O2
MEA	Conventional	MONOETHANOLAMINE	C2H7NO
H2S	Conventional	HYDROGEN-SULFIDE	H2S
MEA+	Conventional	MEA+	C2H8NO+
H3O+	Conventional	H3O+	H3O+
MEACOO-	Conventional	MEACOO-	C3H6NO3-
HCO3-	Conventional	HCO3-	HCO3-
HS-	Conventional	HS-	HS-
OH-	Conventional	OH-	OH-
CO3--	Conventional	CO3--	CO3-2
S--	Conventional	S--	S-2

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Properties Simulation Energy Analysis

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Figure 4.7: Components used in Aspen Plus simulation.

4.5.3 Stream Specification

Two streams were specified for simulating the process, FLUE-IN and MAKE-UP.

FLUE-IN

Flue gas composition after desulphurisation unit is given in table 4.5. The data of 18th november 2011 was taken from EDF CHP plant, krakow, poland.

Table 4.6: Flue gas composition.

Components	Flue gas mass fraction (wt%)
CO ₂	18.66
N ₂	77.52
H ₂ O	3.82
O ₂	0
SO ₂	0

Flue gas is considered to be composed of only CO₂, H₂O and N₂ while other components like O₂ and SO₂ are neglected. The flue gas has a mass flow rate of 412.2 ton/h, temperature 150.1 °C, and pressure 98.8 kPa.

MAKE-UP

The gases from top of absorber and stripper consist a part of MEA. And a small percentage of MEA undergo degradation during the process. In order to compensate for these losses MEA make-up is added to the recycled stream before it enters into the absorber. Solvent is added at atmospheric pressure and temperature.

4.5.4 Blocks Specification

Table 4.6 shows the blocks used in Aspen plus and there respective Unit Operation Model.

Table 4.7: Aspen Plus block specification for CO₂ capture.

Block	Unit Operation Model
BLOWER	COMPR
ABSORBER	Radfrac
PUMP-RICH	PUMP
MAKE-UP	Mixer
COOLER	Heater
HEATER	HeatX
STRIPPER	Radfrac

BLOWER

Blower is provided in order to increase the pressure of flue gas in order to compensate for the pressure drop in the humidifier. Since the flue gas comes in contact with the water in humidifier there will be a pressure drop. And also better absorption take place at high pressure.

ABSORBER

Radfrac column is used to simulate the absorber unit in Aspen Plus. Absorber column does not have condenser or re-boiler. Absorber column is a packed tower with sieve trays which is used in order to increase the surface area between the flue gas and the Amine solution. The number of trays is directly proportional to the absorption quality. More the number of trays, better will be the absorption. But if there are too many trays then the trays might get dry. Feed enters from the middle of tower and the Amine solution enters from the top. Absorption is an exothermic process and therefore heat is released which raises the temperature inside the absorber column. The absorber operates at atmospheric pressure [27].

PUMP-RICH

Pump is used in order to increase the pressure of rich amine so that it can flow till the middle of the stripper column. Since stripper is generally a tall column so additional pressure is required in order to lift the rich amine. There is also a pressure drop in the HEATER block, so in order to compensate that losses rich amine need addition pressure.

MAKE-UP

A mixer is used to mix the recycle amine coming from the stripper with the make up of fresh amine solution.

COOLER

A Heater unit of Aspen Plus is used in order to cool the recycle amine stream before it enters into the absorber. Also FCOOLER1 and FCOOLER2 are used to cool the flue gas entering the absorber.

HEATER

A Shell and Tube heat exchanger is used in order to exchange the heat between rich amine coming from the absorber and the lean amine coming from the stripper column. The lean amine is at higher temperature and rich amine at lower temperature so heat transfer take place from lean to rich amine.

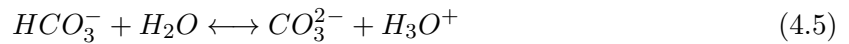
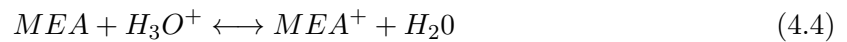
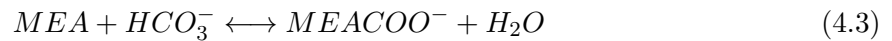
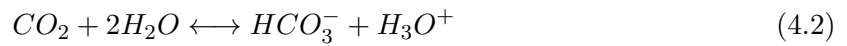
STRIPPER

In case of stripper a Radfrac column having condenser at the top and kettle re-boiler at the bottom is used. Stripper column is also fixed with sieve trays. The number of trays in the stripper is directly proportional to the holdup time in the stripper and hence the stripping

rate. Greater the holdup time higher will the stripping. The re-boiler is provided with heat duty from the plant. Heat duty is required in order to provide latent heat to the liquid flowing downwards in the stripper and convert it to vapors which will flow upwards and strip the CO₂ from the rich amine entering the column. Rich amine solution enter through the middle of the column.

4.5.5 Chemical Reactions

Reversible reactions 4.1 - 4.5 are involved in the CO₂ capture process. The equilibrium constants in the reactions were calculated on the basis of Gibbs energies [27].



4.5.6 Design Specification and Calculator Block

In order for optimizing the system and convergence to take place design specification and calculator block was utilized.

Stack

The amount of CO₂ captured in the absorber is maintained by varying the mass flow rate of the amine. This is done by defining the amount of CO₂ captured in the absorber which was envisaged to be 85% [12].

MakeUp

There will be Amine losses from the top of the absorber as well as the top of the stripper. It was assumed that there is no degradation of the amine taking place. So a calculator block was

used which calculate the sum of MEA in the Exhaust gases from top of Absorber and the MEA in the CO₂ from the top of stripper. The make up MEA was defined equal to this sum.

$$\text{MAKEUP} = \text{MEA-Exhaust} + \text{MEA-CO}_2$$

Heater

In order to model the heater as cross heat exchanger, initially 2 separate heat exchangers were used. And heat from one of the exchanger was transferred to the other exchanger. Outlet temperature of rich amine exchanger was defined as 105 °C and the heat duty required to heat the exchanger was provided from the Lean amine exchanger and its temperature was measured. Later instead of 2 exchangers 1 cross heat exchanger was used by inputting the temperatures and maintaining the approach temperature.

4.6 Integrating CO₂ Unit With Power Plant

The MEA based operating schematic diagram is shown in figure 4.8. The power plant schematic diagram is shown in figure 4.5. For capturing 85% of the CO₂ about 209 GJ/h of energy is required. The energy required is in the form of heat energy, which is required by the stripper re-boiler in order to vaporise the rich amine solution. The method used for the steam extraction is called Power Output Reduction Method(PORM). In this method total output power is reduced as the steam is being removed in between the turbines and provided to the Stripper re-boiler.[13]

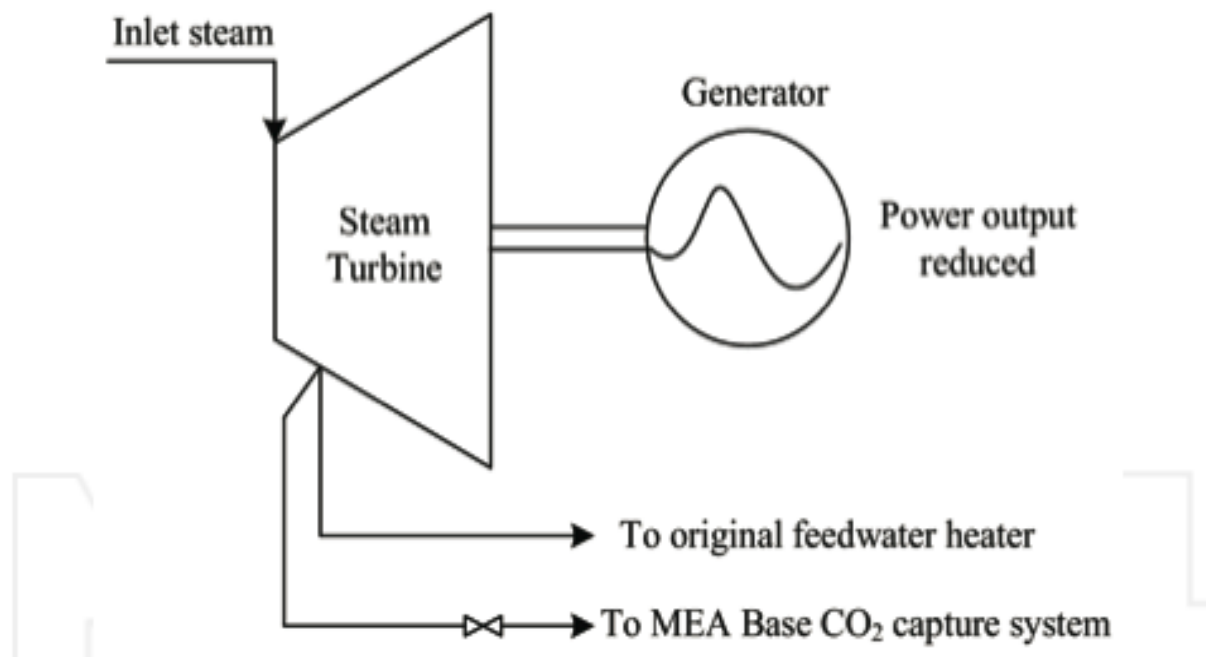


Figure 4.9: Schematic diagram of steam removal [13].

(Source: MEA-Based CO₂ Capture Technology and Its Application in Power Plants by Yongping Yang and Rongrong Zhai)

There are 9 possibilities to take the steam from the turbines outlet.

1. HP turbine Outlet to XW3
2. MP turbine Split 1 to XW2
3. MP turbine Split 2 to XW1
4. MP turbine Outlet to ODG
5. LP turbine Split 1 to XN2
6. LP turbine Split 1 to XB
7. LP turbine Split 2 to XN1
8. LP turbine Split 2 to XA

9. LP turbine Outlet to Condenser

Table shows the amount of steam in the each split and the heat duty of the steam at that split.

Table 4.8: Steam at each split.

Stage	Temperature(°C)	Enthalpy (kJ/kg)
HP Outlet-XW3	370	3124.5
MP Split1-XW2	463	3405.2
MP Split2-XW1	378	3215.7
MP Outlet-ODG	231	2912.4
LP Split1-XN2	137	2754.6
LP Split1-XB	137	2754.6
LP Split2-XN1	99	2682.3
LP Split2-XA	99	2682.3
LP Outlet-Condenser	29	2654.6

It is known that MEA solvent degrades at temperature above 122 °C, hence all the outlet point are not suitable for steam utilization. If the temperature approach of 15 °C is kept in the re-boiler then the temperature of steam should be about 137 °C. Hence steam from the outlet of LP turbine Split 1 was utilized for providing thermal energy to stripper re-boiler. The steam from this unit is going to XB heat exchanger which is used to heat cold water for supplying to the city.

5.1 CO₂ Capture Unit

The main problem with CO₂ capture is its high energy requirement. Different sensitivity analysis were carried out in order to optimize the energy requirement of the process. The analysis were done keeping the CO₂ capture rate of 85%. The carbon capture process needs energy mainly in 2 ways. First in the form of thermal energy in stripper re-boiler and second in the form of electric energy in the flue gas compressor. The energy requirement of the flue gas compressor is constant, since it depends mainly on the absorber pressure drop, absorber inlet pressure and the pressure at which flue gas is coming. Hence the process can be optimize only by varying the re-boiler duty requirement. So the optimal condition is one which require the minimum re-boiler duty.

Energy is required in the re-boiler for 3 purposes-:

1. Generate steam from the condensed water ($Q_{steamgeneration}$).
2. Strip the CO₂ from MEA+CO₂ solution(Q_{strip}).
3. Heat the incoming solvent to the re-boiler temperature($Q_{sensibleheat}$).

$$Q_T = Q_{strip} + Q_{steamgeneration} + Q_{sensibleheat} \quad (5.1)$$

$$Q_T = -nCO_2\Delta H_{abs,CO_2} + (V - nH_2O)\Delta H_{vap,H_2O} + LC_p(T_{bottom} - T_{top}) \quad (5.2)$$

where

nCO_2 = moles of CO₂ stripped in the stripper

$\Delta H_{abs,CO_2}$ = Heat of absorption of CO₂

V = Molar flow rate of vapour

nH_2O = moles of H₂O condensed in the column

$\Delta H_{vap,H_2O}$ = Heat of vaporization of H₂O

L = Molar flow rate of liquid

C_p = specific heat of liquid

T_{bottom} = Temperature at bottom of stripper

T_{top} = Temperature at top of stripper

The variables studied which are effecting the re-boiler duty are stripper pressure, solvent flow rate, and CO₂ capture rate.

Effect of stripper pressure

Figure 5.1 shows that as the stripper pressure is increasing the re-boiler temperature is also increasing. The main function of stripper is to strip the CO₂ from rich amine and re-boiler provide the require heat duty for vaporising the rich amine stream. Now at higher temperature the re-boiler duty is lower as less amount of energy is required. Hence stripper pressure should be kept higher so that minimum re-boiler duty is required. But since at the temperature above 122 °C MEA starts to degrade, re-boiler temperature has to be below 122 °C. In order to satisfy these conditions and minimize the re-boiler duty stripper pressure of 1.2 bar was used during the simulation.

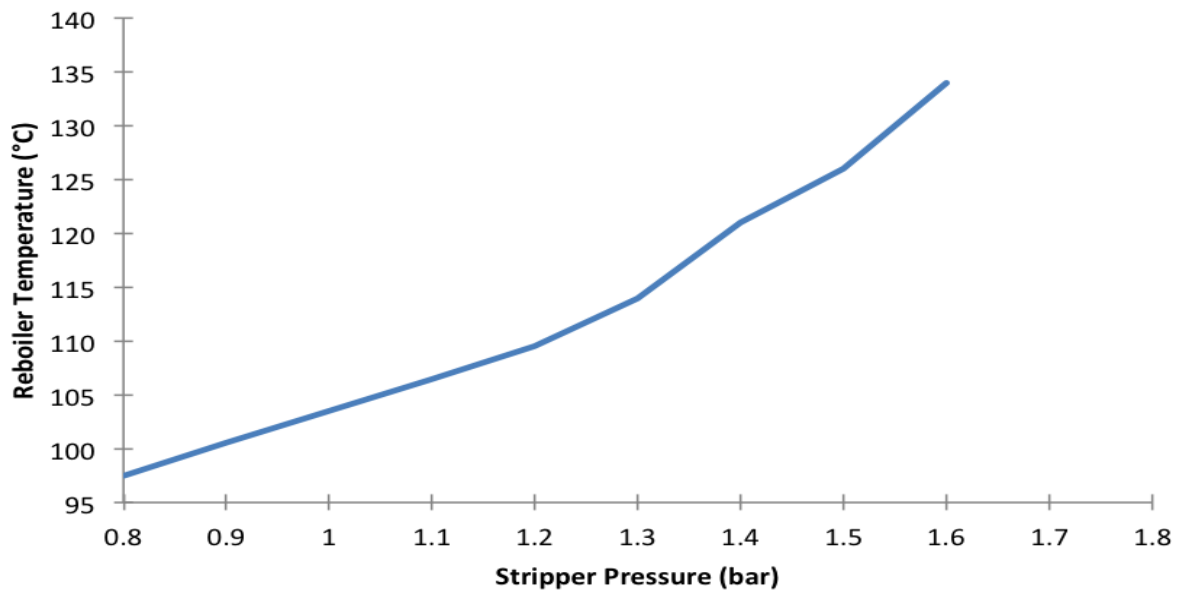


Figure 5.1: Effect of stripper pressure on re-boiler temperature.

Figure 5.3 shows how the stripper pressure affect the re-boiler duty. It can be seen that as the stripper pressure is increasing the re-boiler duty is decreasing. Since as the pressure increases there is increase in the temperature, and at higher temperature there is more H₂O and CO₂ in the gaseous phase so less amount of steam is required for stripping the CO₂ from the rich amine solvent.

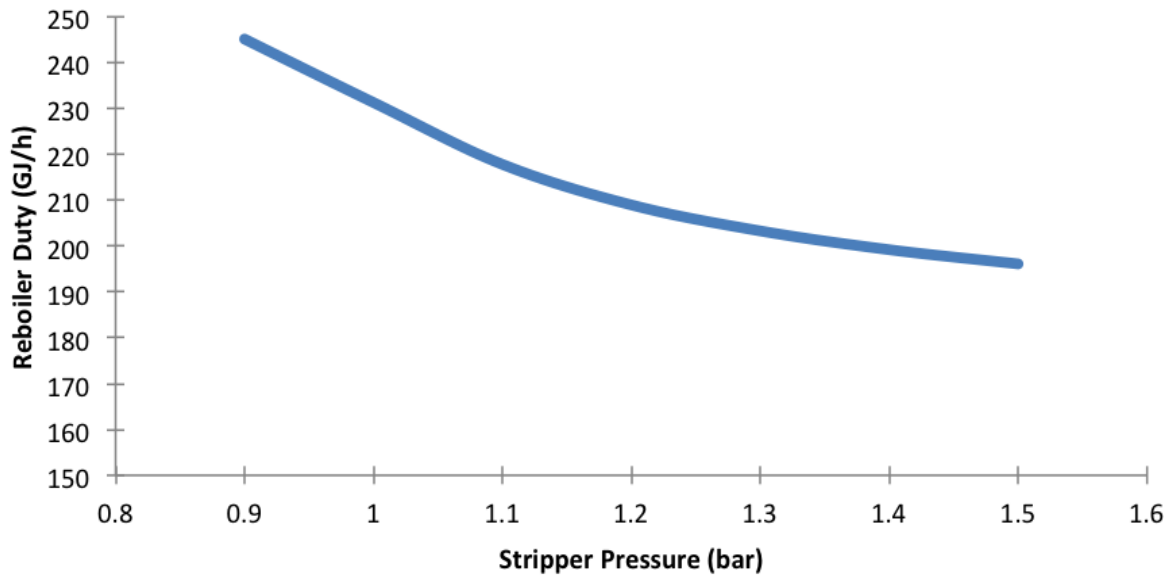


Figure 5.2: Effect of stripper pressure on re-boiler duty.

Figure 5.3 shows how the stripper temperature changes at different stages. It is lowest at stage 1 since the condensed liquid is flowing back to the stripper on stage 1. The temperature suddenly rises at stage 4 as the feed enters the stripper and the temperature is highest at stage 8, where the vapors enters from the re-boiler.

Effect of solvent flow rate and lean loading

As the solvent flow rate in the absorber is reduced the absorption rate also reduced since lean loading is increased in the absorber. Lean loading is the ratio of moles of CO_2 to moles of MEA present in the lean amine solvent. Due to the increased lean loading there is less absorption of CO_2 in the absorber so in order to keep the high absorption rate lean loading has to be kept low. But at low lean loading the re-boiler duty was much higher since more energy was required in order to heat the solvent and vaporize the water. For the optimal condition lean loading of 0.08 was kept. Due to the convergence problem, initially an open flow sheet was simulated with 30% MEA concentration in solvent and the flow rate of 624.1 ton/h.



Figure 5.3: Stripper temperature at different stages.

Effect of absorber temperature and number of stages

The flue gas enters the absorber from bottom and lean amine from the top. As the flue gas temperature is increased the amount of CO₂ absorption decreased and thus it was necessary to reduce the flue gas temperature before it enters the absorber. Heat-exchangers are used in order to decrease the flue gas temperature. The no of stages was having direct effect on the % of CO₂ capture. As the number of stages were increased the capture % also increased since there was more surface area for the transfer to take place between lean amine and flue gases. So the number of stages were fixed such that there was no drying of trays. The number of trays used were 15.

Effect of CO₂ capture rate on re-boiler heat duty

As told in the previous section 85% CO₂ capture was envisaged in the base model. The capture rate is defined as the ratio of mass flow rate of CO₂ from top of stripper to mass flow rate of CO₂ in flue gases.

Mass flow of CO₂ in flue gas = 76.9 ton/h

Mass flow of CO₂ from top of stripper = 65.3 ton/h

Table 5.1 depicts the effect of CO₂ capture % on the re-boiler duty. Re-boiler duty is increasing as the capture rate is increasing, since more solvent is required to capture the increased amount of CO₂ and thus more energy is required for sensible heat in the re-boiler.

Table 5.1: Effect of carbon capture % on re-boiler heat duty.

Capture Rate (%)	Re-boiler Duty (GJ/h)
90 %	242
85 %	209
80 %	184
70 %	146
60 %	108

5.2 Power Plant Efficiency After Capture Process

As discussed earlier there are 2 major energy requirement in the CO₂ capture process, first the energy required by the compressor to pressurize the flue gas and second the energy required by the stripper re-boiler in order to strip the CO₂ from the rich amine solvent.

In the base case of 85% CO₂ capture compressor utilizes 8.10 MW of energy to compress the flue gas from 98 kPa to 157 kPa. Also a small amount of energy is required by rich amine pump which is 42.47 kW, so a total of 8.142 MW of energy is required in CO₂ capture unit. This energy requirement is satisfied by the electric power produced by the steam turbine which is about 84.4 MW. This leads to the electric power efficiency reduction of about 9.64% .

Table 5.2: Electric energy required.

Equipment	Value
Flue Gas Compressor	8.1 MWe
Rich Amine Pump	42.47 kWe

In the power plant unit about 467.5 GJ/h of heat energy is used for providing heat to district heating and 419.8 GJ/h is used for the electric energy production in turbines. Heat duty required by the re-boiler for the stripping process is 209 GJ/h, which is about 3.2 GJ/ton of CO₂ captured, this value is bit lower than the published literature value of 3.65 GJ/ton of CO₂ [29]. A part of this energy requirement is satisfied by the heat duty from the heat exchanger used to cool the flue gas. About 35.8 GJ/h is produced in flue gas cooler 1 and 44 GJ/h is produced in flue gas cooler 2 so a total of 79.8 GJ/h of heat duty is obtained.

Hence total amount of heat duty required by the re-boiler is 209 - 79.8 GJ/h i.e 129 GJ/h. Steam from LP split 1 is utilized for providing this heat duty, this steam is going to XB heat exchanger, and flowing at the rate of 94 tonnes/h , temperature 137 °C and having an enthalpy of 2754.6 kJ/kg. The amount of steam required for providing 129 GJ/h of heat duty is calculated to be 47 tonnes/h.

Thermal efficiency of the power plant is reduced by 30.8 % in providing the steam to stripper re-boiler while assuming there is no heat loss taking place in heat exchangers during transfer of thermal energy.

Table 5.3: Efficiency reduction after CO₂ capture process.

Energy	Efficiency Reduction (%)
Electric Energy	9.64
Thermal Energy	30.8

6.0.1 Summary

In the first part of thesis emissions in the world is discussed i.e global emission of CO₂ is rising at such a high rate and global energy demand in the world is increased about 1/3rd from 2000-2014 which is further going to increase. Then the study of usage and reserves of fossil fuel were discussed which shows that still Coal is the major source of energy production and has more reserves than oil or natural gas. After that a brief introduction to the methods available for CO₂ capture was discussed. Post combustion is the best fit technology for the currently operating coal power plants since it can be easily retrofitted into the old plants. And hence post combustion capture methods were discussed in detail using Monoethanolamine (MEA) as the solvent.

CO₂ capture simulation is complex in nature and when the closed loop system was modelled initially it didn't converge due to calculation errors in the mass and energy balance. So an open loop system was simulated and then that data form it was used for the closed loop system. In the Aspen plus thermodynamic equilibrium model was used for simulation since it assumes the equilibrium between gaseous and liquid phase at each tray in the absorber column. And also in order to reduce the complex calculations and convergence problems in simulation.

MEA was used as the solvent in the process since it is highly reactive with CO₂. MEA is a primary amine and highly alkaline in nature. It gives high separation rate of CO₂. Since its highly reactive it is also difficult to regenerate the solvent after absorption and hence high amount of steam is required in stripping tower.

After simulating and optimizing CO₂ capture process ways by which it can be integrated in the currently operating EDF CHP plant was discussed. It was observed that only the LP steam can be used for since HP and MP steam was having high temperature which can lead to degradation of the MEA solvent in the stripper.

6.0.2 Conclusion

The model was designed as an example of CHP plant with CO₂ capture unit in order to capture 85% of the CO₂. From the results obtained it can be seen that a large amount of thermal energy is required by the re-boiler which leads to thermal efficiency reduction of 30.8%. Hence it can be concluded that the energy penalty by capture process is too high and it is not feasible to place a capture unit in power plant. Although in the future work different solvents or different

post combustion capture methods like physical adsorption method can be used to study the effect on electric and thermal efficiency of the power plant.

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