Coal Conversion and utilization for reducing CO2 emissions from a power plant

Final Report

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Executive summary

In order to reduce the CO₂ emission, an IGCC power plant using oxygen-co-gasification is planned in this project.

For the feedstock, biomass/coal co-gasification is used for this power plant. Biomass has a lower price compare to coal. The higher violate matter content in biomass can also improve the coal conversion ratio. The lower carbon and ash content can improve the gasification efficiency as well as reduce the carbon dioxide emission. Biomass need transportation, this may also limit the size of the power plant.

Different gasifiers are examined in this system. Usually fluidized-bed gasifier and entrained-bed gasifier are used for IGCC power plants. The price for fluidized-bed gasifier is much lower than that of the entrained-bed gasifier. In addition, fluidized-bed gasifier can accept feedstocks in different size and densities, which is fit for the biomass co-gasification.

A simulation program is used to find the impact of different conditions in the gasifier affect the product gas. The pressure has little effect for the gasifier. After 800°C, temperature does not change the composition of the product gas. Higher temperature is used to improve the coal conversion ratio in the gasifier. Steam and CO_2 are used to keep the temperature of the gasifier while higher CO_2 concentration will cost more for the CO_2 capture part. CO_2 in the oxidant gas can also improve the coal conversion ratio.

The goal of air separation unit is to provide large tonnage of high purity oxygen for gasifier. In this project, the separation technique we used is Ion transport membrane (ITM) based on mixed conducting ceramic membrane because of its low production cost and high purity of oxygen output. After oxygen amount needed to react with the feedstock is calculated, we can design and estimate total membrane area for the separation unit. The details of designing parameters are given in the Ion Transport Membrane Design section. The ITM unit is thermally activated, thus it can be integrated to IGCC power plant by setting next to the combustion turbine (provide not air to the ITM unit). The cost of ITM depends on the separation membrane itself and gas compression unit. For the 122 MW plant size, the total cost of ITM unit is approximately 127 USD/kW which is very low compare to the conventional air separation unit. Moreover, it was found that integration of ITM unit to IGCC power plant can also increase plant efficiency by 1.2 percent.

The IGCC power plant is designed to cooperate with H_2S/CO_2 co-capture technology using Selexol solvent to reduce CO_2 emission from the power plant. The CO_2 mitigation cost is added to the total cost around 6.35 \$/ton CO_2 avoided or 142\$/kW_e. Cost for storage, monitoring and verification is around 4 \$/ton CO_2 .

The capital cost for this IGCC power plant is about \$1,393/KW. With a LCOE at 6.9 cents/KW and the price for electricity 7 cents/year, the NPV turns positive after 26 years when interest rate is 5% per year.

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Problem Statement

This project will examine the Oxy-co-gasification method and Ion Transport Membrane for an Integrated Gasification Combined Cycle power plant which incorporates the highest potential technology for carbon capture.

Objectives

- 1. Enhance power generation and reduce CO_2 emissions from an IGCC power plant using cogasification of coal and biomass.
- 2. Reduce production cost by introducing new gas separation technology (Ion Transport Membrane).
- 3. Reduce pollutant emissions using H_2S and CO_2 co-capture.

1 Introduction

Atmospheric levels of carbon dioxide have increased steadily since the beginning of the industrial revolution and these levels are projected to increase even more rapidly as the global economy grows. Global temperature increased about 0.74° C during the 20th century. This has been caused by increasing concentrations of greenhouse gases such as CO₂. The issue of CO₂ emission is drawing much more concern because of the increasing strict legislation. The annual coal consumption in the United States is about 1,100 million tons/year.

The emission of greenhouse gas is caused mainly by human activities such as burning of the fossil fuels and deforestation. The combustion of hydrocarbon fuel emits some pollutant such as SO_x and CO_2 which cause environmental problems.^[1] The CO_2 emission is mainly contributed by electricity generation, transportation, industrial and residential use, as shown in Fig. 1-1.



Fig. 1-1 CO₂ emission for the United States.^[2]

Coal is mainly used for electricity generation. In Pennsylvania, about 50% of electricity is generated by coal. The other sources came from natural gas and nuclear energy. Reducing the CO_2 emission from coal-fired power plants can be effective to reduce the total CO_2 emission within the United States.

In this project, we aim to examine different methods of coal conversion/utilization for an Integrated Gasification Combined Cycle power plant that incorporates the highest potential technology for carbon capture and storage.

2 Integrated Gasification Combined-cycle (IGCC)

IGCC is a newly developed technology for a power plant that turns carbon-containing material into synthesis gas (syngas). The system is designed to be able to remove impurities from the gas before it is combusted. This results in lower emissions of SOx, particulate matters and mercury. Excess heat from the primary combustion is passed to a steam cycle which results in improved efficiency compared to a conventional pulverized – coal plant. However, IGCC plants are still not completely commercial. The aim of IGCC plants development is to improve the environmental performance and decrease the production cost.

2.1 Why IGCC is Needed

The following are reasons why IGCC plants may be needed: ^[3]

- Emit lowest NOx, SOx, particulate matter and hazardous air pollutants
- CO₂ can be captured using available technologies such as water gas shift reaction by transforming CO into CO₂
- Less water consumption and less waste
- Low- cost electricity for economic growth

2.2 Market Barrier

The barriers to market penetration follow:

- Currently higher capital and operating costs relative to supercritical boilers or pulverized- coal plants.
- Standard designs and guarantee packages are not yet fully developed, and there are long construction periods and few real experiences/applications.

2.3 IGCC Elements

The IGCC system combines a gasification system with a combined- cycle power system (gas turbine/ steam turbine). The system consists of the following components:

- 1. Gas separation unit (Air Separation Unit)
- 2. Gasifier
- 3. Gas Cleanup unit
- 4. Water- Gas- Shifter
- 5. Gas turbine
- 6. Steam turbine



Fig. 2-1 IGCC power plant.^[4]

2.4 How IGCC Works

In an IGCC power plant, carbon-containing material such as coal, biomass, coke, and waste are fed to gasifer. These feedstocks react with oxygen steam from a gas separation unit forming synthesis gas (CO + H₂). The synthesis gas is cleaned up before being combusted in a gas turbine. The combustion gases expand in a gas turbine and are ready for electricity generation. The waste heat is used in a combined cycle to turn a steam turbine to generate additional electricity. In some cases, a

water-gas-shifter unit is added to convert CO molecules in the synthesis gas into CO_2 through water-gas-shift reaction.^[5]

2.5 Plant Location

In order to decide for a suitable plant location, there are various factors needed to be concern such as transportation of coal and biomass resource, transmission of energy and the demand of electricity in each area. The distribution of Pennsylvania coal and biomass resources in USA shows a rich in coal and biomass resource both in Pennsylvania and nearby area. Thus, it is possible to locate coal power plant here.

Since bituminous coal is required as our feedstock, we will focus on the Pittsburgh field which is rich in this type of coal. There are many coal mines under the city of Pittsburgh, the South Hills of Pittsburgh, the Burgettstown District, the lower Monongahela valley, the Pigeon Creek District of Washington County, and the lower Youghiogheny River valley.

Moreover, Pittsburgh is a very big city, so the demand of electricity will be very high. Thus, to reduce the cost of feedstock transportation and to supply great demand of electricity, the coal power plant will be located on the Washington County, Pittsburgh field.



Fig 2.2 Pittsburgh Field^[64]

3 Gasifier

In direct gasification, there are mainly three kinds of gasifiers: fixed-bed gasifier which is also called moving-bed gasifier, fluidized-bed gasifier and entrained-bed gasifier, as shown in Fig. 3-1.Every kind of gasifier also has several species.



Fig. 3-1 Types of gasifier.

3.1 Fixed-bed Gasifier

A fixed-bed gasifier is the first kind of gasifier which is used for industrial power generation. The three kind of fixed-bed gasifier includes updraft fixed-bed gasifier, downdraft fixed-bed gasifier and cross draft fixed-bed gasifier, as shown in Fig. 3-2.



Fig 3-2 a) downdraft fixed-bed gasifier, b) updraft fixed-bed gasifier, and c) cross draft fixed-bed gasifier.^[6]

In an updraft gasifier, the reaction gas goes from the bottom to the top. The gas flow is counter current with the feed stock, and this gasifier is also called a counter current gasifier. In a downdraft gasifier, the reaction gas goes from the top to the bottom, concurrent with the feedstock, so this gasifier is called a concurrent gasifier. The third gasifier in Fig 3-2 (c) is cross-draft gasifier, in which the reaction gas goes across the gasifier.^[7]

As shown in Fig. 3-2, there are several zones in a fixed-bed gasifier: drying zone, pyrolysis zone, combustion zone and reduction zone. In the drying zone, the moisture contained in the biomass and coal goes out and the coal/biomass becomes dry. In the pyrolysis zone, the coal/biomass goes through a process also called devolatilization. The volatile of the coal is devolatilized and char is left. In the combustion part, coal char is completely oxidized into CO_2 and H_2O . After that, in the reduction part, some of the combustion gas is further reduced by char into CO and H_2 . These stages in the gasification process make the coal conversion ratio and gasification efficiency very low.

The cost for the fixed-bed gasifier is low but no fixed-bed gasifier is used for a IGCC power plant. The fixed-bed gasifier produces a large amount of tar and oil, which requests the gasifier to be cleaned up from time to time. The coal conversion ratio is also low in this kind of gasifier, and the temperature changes dramatically for different zones in this gasifier (shown in Fig 3-3), which in addition makes it not fit to run a steam turbine for an IGCC power plant.



Fig. 3-3 Working principle and temperature zone in a fixed-bed gasifier.^[8]

3.2 Entrained-bed Gasifier

The second type of gasifier is the entrained-bed gasifier. The throughput rate is very high due to the high reaction rate in this gasifier. The complete coal conversion ratio and the elimination of tar and oil is another advantage of this gasifier. This kind of gasifier is good for oxygen gasification, and the temperature is equivalent inside this gasifier. The bottom combustion zone can reach a temperature as high as 2000°C. The feedstock, steam and gas flow all go from the top of the gasifier, shown in Fig. 3-4. In spite of the many advantages of an entrained bed gasifier, which is used in many of the IGCC power plants, the feedstock needs to be pulverized which is unsuitable for biomass. In addition, the cost for the entrained-bed gasifier is very high.



Fig. 3-4 Working principle and temperature zone in a entrained-bed gasifier.

3.3 Fluidized-bed Gasifier

The fluidized-bed gasifier seems to be the best gasifier for biomass co-gasification

, which is shown in Fig. 3-5. The fluidized-bed gasifier is able to accept feeds of different sizes and densities, which makes this kind of gasifier a good solution for low-rank coals and biomass. Since it costs less than the entrained-bed gasifier, this kind of gasifier also has low-tar/oil output, good solid mixing and a similar temperature throughout the gasifier.



Fig. 3-5 Working principle and temperature zone in fluidized-bed gasifier.

In the circulating fluidized-bed gasifier (shown in Fig. 3-6), the fluidized-bed gasifier is improved by adding a recycle cyclone to the area where gas comes out. The soot particles go back to the gasifier while the clean gas goes out from the top of the recycle cyclone. This gasifier is acceptable for a wide range of feeds, such as wood, straw, nutshells and sludge. The investment cost is highly suitable for small and medium-sized power plants. So the circulating fluidized-bed gasifier is chosen for the power plant to be built in PA.



Fig 3-6. circulating fluidized-bed gasifier.^[9]

4 Biomass co-gasification

4.1 Coal and Biomass in Pennsylvania

Pennsylvania is a state with an abundance of coal and biomass. Fig. 4-1 is the coal map in Pennsylvania and table 4-1 shows the coal production in Pennsylvania in the recent years. It produces about 65 million tons of coal each year, which is more than 11 percent of the total US coal production. This figure is very stable during the recent years. Pennsylvania produces bituminous coal in the east part of the state. Bituminous coal is a high-rank coal and has a lower heating value (LHV) about 30kJ/kg. PA also produces a little anthracite coal. In addition, the biomass production is also abundant in Pennsylvania, as shown in Table 4-2. Pennsylvania produces 36,733 tons of sawdust and 106,028 tons of wood waste per year. This amount of biomass is enough for a small or medium-sized biomass power plant.



Fig. 4-1 coal map in Pennsylvania.^[10]

Table 4-1 Coal production in Pennsylvania. (million tons/year).^[10]

| ¢. | 2004 🤟 | 2005 🤟 | 2006 @ | 2007 🤟 | 2008 🤟 |
|----------------------|--------|--------|--------|---------------|---------------|
| Pennsylvania Total+? | 66.0 @ | 67.5 @ | 66.0 @ | 65.0 <i>e</i> | 65.3 <i>e</i> |
| Anthracite 🤟 | 1.7 @ | 1.6 @ | 1.5 @ | 1.6 @ | 1.7 @ |
| Bituminous 🤟 | 64.3 @ | 65.8 @ | 64.5 @ | 63.5 e | 63.6 @ |

| Timberland-Total | 16,346,062 Acers | Mill residual-Total | 108,659,271 cubic feet | |
|---------------------|---------------------|---------------------|---------------------------|--|
| -Timberland- | 492,465 Acers | -Mill residual- | 23,405,078 | |
| National Forests | | fiber byproduct | cubic feet | |
| -Timberland- | 3,731,353 Acers | -Mill residual- | 27,968,398 | |
| State owned | | fuel byproduct | cubic feet | |
| -Timberland- | 11,653,917 | -Millresidual- | 11,519,587 | |
| Private land | Acers | unused | cubic feet | |
| Timberland | 29,704,198,000 | -Mill residual- | 95,988,977 | |
| growing stock-Total | cubic feet | hardwood | cubic feet | |
| -Hardwood | 26,935,487,000 | -Mill residual- | 12,670,294 | |
| growing stock | cubic feet | Softwood | cubic feet | |
| -Softwood | 2,768,711,000 | -Mill residual- | 56,633,169 | |
| growing stock | cubic feet | course wood | cubic feet | |
| Logging residual- | 124,622,578 | -Mill residual- | 33,125,129 | |
| hardwood | cubic feet | fine wood | cubic feet | |
| Logging residual- | 9,502,427 | -Mill residual- | 18,900,976 | |
| softwood | cubic feet | bark | cubic feet | |
| Residual- | 36,733 | Residual- | 106,028 | |
| Sawdust waste | tons/year | wood waste | tons/year | |

 Table 4-2 Biomass in Pennsylvania.
 [11]

4.2 Feedstock analysis for the oxygen co-gasification IGCC Power Plant

Table 4-3 shows the feedstock analysis for this IGCC power plant. Coal and biomass are used for feedstock. Pitts 8# coal is chosen for this power plant. Normally, bituminous coal has a lower heating value at about 30MJ/kg, carbon content at around 80% and ash content at about 10%. For biomass, the pine tree provides a typical example for most woods. Biomass contains a lot of violate matter, which can increase the coal conversion ratio and gasification efficiency. Usually, Biomass has a lower heating value about half of that of bituminous coal. Biomass also has a higher oxygen content which can reduce the CO_2 emission of the whole power plant.

Table 4-3 Proximate and ultimate analysis for coal and biomass

| | Coal (Pitt 8#) | Biomass (Pine Tree) |
|-----------------------------|----------------|---------------------|
| Proximate Analysis (wt%) | | |
| Fixed Carbon | 0.524 | 0.16652 |
| Volatile Matter | 0.352 | 0.70196 |
| Moisture | 0.024 | 0.08 |
| Ash | 0.1 | 0.05152 |
| Ultimate analysis (wt%) | | 1 |
| Carbon | 0.833 | 0.528 |
| Oxygen | 0.083 | 0.392 |
| Hydrogen | 0.057 | 0.057 |
| Nitrogen | 0.014 | 0.022 |
| Sulphur | 0.013 | 0.0009 |
| Ash | 0 | 0.056 |
| Lower Heating value (KJ/Kg) | | |
| LHV | 30410 | 16365 |

4.3 Why Use Biomass Co-gasification

First, biomass is a renewable resource, and the combustion of biomass does not add to the total emission of carbon dioxide as long as the burned biomass does not exceed the renewed production. If carbon capture is included, the total carbon footprint can be zero or even negative. Second, biomass contains more oxygen and less carbon than coal(as shown in Table 4-4). For the same energy content, using biomass instead of coal can reduce the CO_2 emission effectively. Third, biomass has low ash, nitrogen and sulfur content which makes the product gas much cleaner than coal gas. The higher volatile content makes the reactivity very high for biomass and the gasification process is improved.

However, biomass is highly dispersed over a wide area, which requires a cost for collection and transportation. In addition, biomass is a seasonal product, so the price and supply for biomass may

not be stable during the year. The energy content in biomass is low compared to bituminous coal. The lower heating value for biomass is about 15 MJ/Kg, while the lower heating value for bituminous coal is between 20-30 MJ/Kg. The density for biomass is also low, which leads to a much high volume of feedstock for biomass gasification.^[12]

| | Coal | Coke | Wheat straw | Barley straw | Pine wood | Olive tree | Wine tree | Cynara |
|-------------------|-----------------|--------|-------------|--------------|-----------|------------|-----------|--------|
| Moisture (wt%) | 2 | 2 | 12.1 | 13.8 | 8 | 15 | 15 | 8 |
| Proximate analys | sis (wt%, d.b.) | | | | | | | |
| Volatile | 22.1 | 12.4 | 73.6 | 75 | 76.3 | 78.1 | 76.6 | 76.5 |
| matter | | | | | | | | |
| Fixed carbon | 31.4 | 87.0 | 18.5 | 19.3 | 18.1 | 18.9 | 20.7 | 17.7 |
| Ash | 46.5 | 0.58 | 7.9 | 5.7 | 5.6 | 3.0 | 2.7 | 5.8 |
| Ultimate analysis | s (wt%, d.b.) | | | | | | | |
| С | 40.6 | 87.7 | 45.6 | 45.6 | 47.2 | 49.8 | 49 | 46.8 |
| н | 2.8 | 3.8 | 5.7 | 5.6 | 5.7 | 6.0 | 5.7 | 5.8 |
| 0 | 8.4 | 0.19 | 40 | 42.5 | 39.2 | 40.4 | 41.8 | 40.7 |
| N | 0.82 | 1.5 | 0.7 | 0.5 | 2.2 | 0.7 | 0.7 | 0.7 |
| S | 0.88 | 6.2 | 0.09 | 0.09 | 0.09 | 0.06 | 0.05 | 0.13 |
| Ash | 46.5 | 0.58 | 7.9 | 5.7 | 5.6 | 3.0 | 2.7 | 5.9 |
| LHV (kJ/kg, w.b. | .) | | | | | | | |
| LHV | 15,109 | 33,228 | 14,472 | 14,403 | 16,365 | 15,784 | 15,189 | 16,041 |

Table 4-4 Proximate and ultimate analysis for coal, coke and different biomass.^[13]

4.4 Gasifier Modeling

Van der Burgt uses a simple model based on a constant fuel conversion ratio. Volatilisation is the decomposition of coal into volatiles and a carbon residue called char. This process can be represented by the following equation:

 $CH_{hf}O_{of}N_{nf}S_{sf}(H_2O)_wZ{\rightarrow}CH_hO_oN_nS_sZ{+}V{+}wH_2O$

In the combustion and gasification stages, char particles react with O_2 (combustion), CO_2 (bondouard reaction) and H_2O steam gasification), which had passed through the as layer from the gas to the core surface. The chemical reaction follows:

 $\begin{array}{l} Char + aO_2 \rightarrow bCO + cCO_2 + dH_2O + eH_2S + fN_2 \\ Char + CO_2 \rightarrow 2CO + (o/2)H_2O + (h/2 - s - o)H_2 + sH_2S + (n/2)N_2 \\ Char + (1 + o)H_2O \rightarrow CO + (1 - o + h/2 - s)H_2 + sH_2S + (n/2)N_2 \\ Char + (2 + o + s - h/2)H_2 \rightarrow CH_4 + oH_2O + sH_2S + (n/2)N_2 \end{array}$

In the gas phase, a water-gas shift reaction and a methane reforming reaction take place and reach equilibriums, as follows:

 $\begin{array}{c} \text{CO+H}_2\text{O} \longleftrightarrow \text{CO}_2 + \text{H}_2 \\ \text{H}_2\text{S} + \text{CO}_2 \longleftrightarrow \text{--} \text{COS} + \text{H}_2\text{O} \\ \text{CO+3H}_2 \longleftrightarrow \text{--} \text{CH}_4 + \text{H}_2\text{O} \end{array}$

4.5 Biomass Co-gasification Reduce the Carbon Footprint and Improved the Gasification Efficiency

For the high oxygen and low carbon content of biomass, CO_2 can be reduced if using biomass instead of coal/coke. In Antonio Valero's paper, he discussed using biomass to take the place of a mixture of coal/coke. The result is shown in Fig. 4-2, coal and coke are 30/70 in weight and 50/50 in energy content. The CO content can drop by 3-4 percent if 10% biomass is added into the feedstock, which is likely to be the largest amount of biomass that can be contained in the feedstock for an industrial power plant. The CO content reduces more for the replacement of coke than for coal.



Fig. 4-2 CO output versus wheat percentage (coal/coke mixture:30/70 in energy, 50/50 in weight).^[13]

Biomass can improve the gasification process. In the research of Juan J. Hernandez, the team used an entrained-bed gasifier on a lab scale to gasify biomass/coal. ^[14-16] They tested biomass content from zero up to 80 percent at different equivalence ratios. The result is shown in Fig. 4-3, CO content, H_2 content and gasification efficiency are all increased with the increasing of biomass content. These parameters are very important for the gasification process.



Fig. 4-3 Effect of the addition of biomass on the producer gas CO and H_2 content, gasification efficiency and H_2 /CO ratio.^[14]

4.6 Oxygen and O₂/CO₂ Co-gasification

Oxygen gasification means using oxygen as the primary oxidant instead of air. The final product gas for oxygen gasification contains no nitrogen, which is ready for sequestration. NOx is highly reduced when there is no nitrogen in the gasification gas, which can make the gas-cleanup process much easier. In addition, the Cp of CO_2 is higher than that of N_2 , so the gasification temperature can be reduced when using pure oxygen for the gasification process.

In order to improve the gasification efficiency and coal conversion ratio, CO_2 can be added into the combustion gas. CO_2 can react with char through the Boudouard reaction to improve the coal conversion ratio. When the portion of CO_2 is increased, less carbon from coal will form CO_2 and more CO can be produced from the Boudouard reaction. The gasification efficiency can be also improved for the CO_2 produced from coal and biomass can be highly reduced when the CO_2 concentration is low and some of the initial CO_2 can be reduced into CO for further combustion.

Lian Zhang ^[17]did research about how the gasification process is improved when using O_2/CO_2 as the oxidation gas. As shown in Fig. 4-4, the coal conversion ratio when O_2/CO_2 ratio= 21/79 is lower than that of air. But when the ratio of O_2 is increased to 27%, the coal conversion ratio will be increased especially when the temperature and reaction distance is low. Although this result is not compared with gasification in the pure gas, but in the gasifier of a power plant, the increase in the gasification efficiency is more important than just the increase of the coal conversion ratio. Adding CO_2 to the oxidation gas can increase the gasification efficiency beyond only using oxygen.



Fig. 4-4 Coal conversion rate as a function of reaction distance for the temperature of 800°C (a) and 1000°C (b).^[17]

4.7 Water-gas Shift Reaction

For pre-combustion CO_2 capture, a water-gas shift reactor needs to be added after the gasifier and the gas-cleanup process. The syngas contains CO, H_2 and a little part of CO₂, H_2O and CH₄. In the water-gas shift reactor, the syngas and steam are mixed together and the reaction goes as follow:

$$CO+H_2O\rightarrow CO_2+H_2$$
, $\Delta H \circ 298 = -41.1 \text{ kJmol}^{-1}$

Due to the exothermic nature of the WGS reaction, higher CO conversions are favored at lower temperatures. The WGS equilibrium Through this water-gas reaction, CO is turned into CO_2 and the H_2 is the final product. More than 95% percent of the CO can be converted into CO_2 by the water-gas shift reaction. The CO_2 is captured before combustion using a membrane. After the reactor, only H_2 is left for combustion and steam is the final product which can be released to the environment directly. constant is nearly 80 times greater when the temperature is decreased from 600 to 200 °C.

Unsupported metallic copper catalysts or copper supported on Al2O3, SiO2, MgO, pumice or Cr2O3 were characterized by relatively short life (6–9 months) and low space velocity operation. Important progress was made by the addition of ZnO or ZnO/Al2O3; not only did the lifetime of these catalysts increase considerably, but also due to a strong support effect an increase of the turnover numbers in the order of magnitudes were observed.

In our IGCC power plant, Fe/Cr oxide catalyst was chosen for the water-gas shift reactor. Fe/Cr oxide was the first catalyst used for water gas shift reaction, which has a working temperature at about 330°C. The cost of Fe/Cr/Cu and Cu/Zn catalysts are \$10.6 l^{-1} and \$17.3 l^{-1} , respectively. Table 4-5 shows the parameters for the water-gas shift reactor in this IGCC power plant.

In the first step, promoted Fe/Cr oxide catalysts are applied at a reactor inlet temperature of 300–360 °C and a total pressure between 10 and 60 bar. Industrial HTS converters exclusively apply Febased catalysts because of their excellent thermal stability, poison resistance and good selectivity especially in the case when low steam to CO ratios are applied where the formation of hydrocarbons is favored.

Table 4-5 parameters for water-gas shift reactor.

| Flux rate | 100 to 200 scfh/sq foot |
|--|-------------------------------------|
| Working Temperature | 300-360℃ |
| WGS reactor pressure | 10-20 bar |
| Membrane Material and All Module Costs | \$60-80/ft ² of membrane |
| Durability | 1,100 hours |
| Operating Capability | 500 psi |
| Hydrogen Recovery | 80% of total gas |
| Hydrogen Quality | 95% of total dry gas |
| CO2 conversion ratio | >99% |

5. Gas Separation Unit

In an IGCC power plant, the gas separation unit in which oxygen is separated from air is a key component for an effective gasification system. Oxygen-blown gasification produces synthesis gas with a high energy value because it is not diluted by nitrogen in the air. A conventional Air Separation Unit (ASU) has been successfully applied to support a gasification unit worldwide with high purity of oxygen. In addition, it is able to supply tonnage quantities of oxygen to the system. However, after a century of development, this technology has reached maturity with few possibilities to provide significant step-change cost reduction. Among various gas- separation techniques, longer term development is focusing on Ion Transport Membrane technology (ITM) to support cost improvement for effective production of oxygen steam.^[20,21]

5.1 Classification of Gas Separation

There are two fundamental approachs for gas/air separations

- Cryogenic distillation or so called Air Separation Unit (ASU) is a technique that applies to a system which requires tonnage quantity of oxygen at very low temperature (approximately -185 °C). The separation consists of four main steps: air compression, air purification, cooling, and distillation.^[22]
- 2. **Non-cryogenic distillation** is a technique that can be applied on a small to large scale of an oxygen separation system at ambient or high temperature. Important non-cryogenic distillation in industrial use are^[23,24,28,29]:

Molecular sieve adsorbents are suitable for a small-to medium-scale plant (20-150 tons/day). The processes are based on the ability of material to adsorb the particles. For example, in air separation, a bed of zeolite material is used to adsorb nitrogen molecules, which are more polarizable, resulting in oxygen-rich steam exiting the bed. However, in the adsorption process, the bed size is the controlling factor in capital cost because production is proportional to bed volume. Thus, capital cost will increase rapidly as the production rate increases.

Polymeric membrane is usually limited to the production of oxygen up to 20 tons/day. Membrane processes are based on the difference of the diffusion rate of particles through a membrane. In this case, flux and selectivity are the properties that determine the economics of a membrane system, and they are specific for each material. The advantages of a membrane system are the simple, continuous nature of the process and operation at near-ambient conditions.

Ion Transport Membrane (ITM) uses: solid inorganic oxide ceramic materials that conduct oxygen ions at elevated temperatures. It produces oxygen by the passage of oxygen

ions through the ceramic crystal structure. An ITM system operates at high temperature (approximately 800-900 °C) and since it is in the development stage, it is easy to scale up to supply a large amount of oxygen steam to the system.

Table 5-1 below shows a comparison between different non-cryogenic distillation techniques. In this case, Ion Transport Membrane (ITM) seems to be the most appropriate alternative to supply high-purity and high-tonnage oxygen to our system.

| | Ion transport Membrane | Molecular sieve adsorbents | Polymeric Membrane |
|------------------|--|---|---|
| Production range | large | Less than 150 Tons per day (small plant) | Less than 20 Tons per day |
| Purity (vol. %) | 99+ - 100% | 93-95% | approx. 40% |
| Status | developing | semi-mature | Semi-mature |
| Others | operate at high temperature i.e. 800- 900 °c | bed volume control capital cost | poor chemical resistance, limited temperature |

Table 5-1 Non- cryogenic distillation comparison.^[24,28]

5.2 Ion Transport Membrane (ITM)

P.N. Dyer et al. reported a wide variety of applications of Ion Transport Membrane technology that will have significant future potential for gas separation industries, for example, the separation of oxygen from air and the conversion of natural gas to syngas. Materials and processes for the ITM technique are now being developed; we can divide ITM into three categories by the driving-force mechanism.^[29]

1.) Electrical Driven - SEOS[™] Oxygen Generator: a membrane is fabricated from material that has low electron conductivity, so we need to apply voltage across the membrane to separate oxygen from a low-pressure source. SEOS[™] is developed by Air Products Company and purposed to use for medical oxygen generation and high-purity oxygen for cutting and welding.

2.) Pressure Driven – ITM Oxygen: a membrane is fabricated from mixed-ionic and electronic conductors, at high temperature oxygen ions will move from the high-pressure to the low- pressure side. There is no need to apply any voltage to the system since the membrane material itself can conduct both oxygen ions and electrons. ITM oxygen is useful for tonnage-level oxygen production and co-generation of high-purity oxygen and steam.

3.) Chemical Potential Driven – ITM Syngas: a membrane is also fabricated from a mixedconducting ceramic membrane but the driving force for oxygen movement is due to reduction of the oxygen pressure on one side of the membrane through chemical reaction. Oxygen ions will then move from low-pressure air to higher-pressure reaction steam. ITM syngas is aimed at applications for syngas production and gas conversion to liquid.



Fig. 5-1 a.) electrical driven b.) pressure driven c.) chemical driven.^[29]

5.3 Advantages of Ion Transport Membrane

Conventional Air Separation (ASU) is known as an effective oxygen separation technique that produces a tonnage of oxygen with high purity. The only drawback is ASU consumes a large fraction of the plant internal energy ie.15% of IGCC capital cost. Since a conventional Air Separation Unit has reached its maturity level^[20,21], it is so difficult to develop and reduce the production cost. Ion Transport Membrane (ITM) can reduce the cost while producing large amounts of higher- purity oxygen. The economic case studies revealed that using the ITM technique results in 25-30% reduction in *capital requirements* over conventional ASU oxygen plants, e.g., cooling cost, and 35-60% reduction in *power consumption*. Moreover the *operational cost* for oxygen is reduced by 30%.

In the technical aspect, ITM can be integrated with high-temperature processes to produce electrical power and/or steam from air. It has a compact design and involves no moving parts, which makes it easy to operate and maintain.

5.4 Oxygen Separation by Ion Transport Membrane (ITM Oxygen)

ITM oxygen uses mixed-conducting ceramic membranes, which have both electronic and oxygen-ionic conductivity when operated at high temperature (800-900 °C). The mixed conductors such as $[(La,Sr)(Fe,Co,Cu)_{O3-\delta}]$ are a stoichiometric lack of oxygen which creates oxygen vacancies in the lattice structure^[21]. These vacancies play an important role during ion transport. Oxygen ion transport can be explained by the following steps^[22]:

- 1. Imposing an oxygen partial pressure difference across the membrane which provides a driving force for oxygen transfer.
- 2. O_2 from air feed adsorbs onto the surface, where it dissociates and ionizes by electron transfer from membrane (thermally activated).
- 3. O^{2-} fill vacancies in the lattice structure and then diffuse through the membrane under a O_2 chemical-potential gradient which is applied by maintaining a difference in O_2 partial pressure on opposite sides.
- 4. O^2 releases electrons, recombines, and desorbs from the surface as O_2 molecules.



Fig. 5-2 Ion transport through membrane.^[19]

Since the ion transport does not allow other ions rather than oxygen ions to pass through the membrane, the separation is 100% pure oxygen. The solid-state diffusion of oxygen anions is following Wagner's law. Assuming a constant ionic conductivity that is much less than electronic conductivity, the ionic/oxygen flux can be expressed as^[29]:

$$j_{o2} = \frac{\sigma_i RT}{4Ln^2 F^2} \ln\left(\frac{P'_{o2}}{P''_{o2}}\right)$$
[Eq.5-1]

Where j_{o2} is the oxygen flux

F is Faraday's constant L is the membrane thickness n is the charge of charge carrier (n = 2) R is gas constant T is absolute temperature σ_i is the ionic conductivity P'₀₂ is the oxygen pressure at the feed surface of the membrane P'₀₂ is the oxygen pressure at the permeate surface of the membrane

An important note about this equation is the inverse relationship between O_2 flux and membrane thickness. In order to obtain high flux, the membrane layer should be designed as a thin film. However, the thin film needs to be able to support the pressure difference necessary to develop the driving force.^[20,22]



Fig. 5-3 Membrane with supported structure (wafer).^[23,29]

The porous sub-layer support structure is developed by Air Products Company to help support the thin film layer. It is also made from an ITM oxygen material but with larger pore dimensions. The mechanical load due to applied pressure is distributed over the supporting layer. In order to minimize this mechanical load, a medium-pressure air feed steam (100- 300 psia) is applied^[25].

There are two models for ITM that will be scaled up for commercialization.^[23]

- The planar model consists of individual wafers joined together, each fitted with a ceramic spacer ring to maintain a consistent gap between adjacent wafers as shown in Fig. 5-4 a.). In this example, each wafer joined together forms a 12-wafer submodule; such submodules produce on the order of 0.1 tons/day of oxygen in pilot scale.
- The tubular model consists of an array of multi-wafer modules in a common flow duct which are connected through a series of manifolds to an oxygen header as shown in Fig.5-4 b. Each module can produce approximately 1 tons/day of oxygen.



Fig. 5-4 a.) planar model b.) tubular model.^[23]

5.5 ITM Oxygen/ IGCC Integration

From the previous section, we can conclude that ITM oxygen technology is suitable for integration with IGCC power generation as an oxygen-supply unit for a gasifier. The ITM oxygen unit could become an alternative for lower cost oxygen supply instead of using a conventional Air Separation Unit. Fig. 5-5 shows how to integrate an ITM oxygen unit with an IGCC plant. Because ITM itself is thermally activated (i.e. by hot air), so it should be connected to the process cycle that includes a heating air feed to high operating temperature.^[22,28] To achieve an effective cycle, an ITM oxygen unit is connected to a gas turbine power generation system. Air is extracted from the compressor section of a gas turbine, and then heated to the ITM oxygen operating temperature using direct combustion with a synthesis gas. Hot air passes through the membrane resulting in high-purity oxygen that permeates and exits the membrane and is cooled before compression for use in the gasifier. The non-permeated steam from the ITM oxygen vessel is further heated by direct combustion before being transported into the turbine unit.^[29]



Fig. 5-5 ITM integrated to IGCC system.^[29]

5.6 Advantages of ITM Oxygen for IGCC Application

As ITM oxygen requires neither an electrode nor an external circuit to operate and the cooling cost is reduced.

An ITM oxygen unit can help lower the production cost at compared to a conventional Air Separation Unit. Table 5-2 shows the cost and performance comparison between a conventional ASU/ Cryogenic and ITM. The Cryogenic case consumes 3,180 tons/day of coal and 2,565 tons/day of oxygen (95% pure), while the ITM oxygen case consumes 3,176 tons/day of coal and 2,420 tons/day of oxygen (99+ % pure). An ITM oxygen unit also saves 31% of the installed cost. The economic benefits are also shown in table 5-2.

Table 5-2 Comparison between ASU and ITM integrated in IGCC.^[29]

| | Cryogenic | ITM | Delta | % Change |
|--|---------------------|------------|-------|----------|
| | O ₂ Case | O_2 Case | | |
| IGCC Facility Capital Investment (\$Million) | 641 | 610 | (31) | (4.8) |
| IGCC Facility Capital Investment (\$/kW) | 1567 | 1453 | (114) | (7.3) |
| Power Production (MW) | 409 | 420 | 11 | 2.7 |
| Thermal Efficiency (%HHV) | 45.2 | 46.5 | 1.3 | 2.9 |
| Cost of Electricity (mills/kWh) | 55.5 | 51.9 | (3.6) | (6.5) |

5.7 Ion Transport membrane (ITM) design

5.7.1 Membrane Type

Mixed conducting ceramic membranes are exclusive type of material which exhibits a mix conducting properties of both ions and electrons in the same time, resulting in a unique separation mechanism (high selectivity). The performance of mixed conducting ceramic membranes is strongly dependent on the properties of materials, which are mainly governed by the material compositions and structures ^[33]. Mixed conducting materials are perovskites which are calcium titanium oxide (CaTiO₃) mineral species. Their orthorhombic structure makes perovskites materials very stable at high temperature. However, the perovskite itself does not show the capability to conduct oxide ions; there must be a certain amount of imperfections or defects produced due to the nonstoichiometry for the conduction or diffusion to take place ^[34].

Doping is the method to modify material properties of mixed conducting membrane through a formation of nonintegral stoichiometry phase by homogeneous doping with proper elements. For example, the oxide ZrO_2 doped with Y_2O_3 to create mobile oxygen vacancies and it can be described in terms of defect chemical notation by Kroger and Vink as Y2O3 (ZrO2) $\rightarrow 2Y_{zr} + V_0 + 3O_0$. A total conductivity of material is expressed by combining conductivity of both ions and electrons.

A permeation of oxygen through dense membrane with high ionic and electronic was first reported by Teraoka et al. Recently, various ionic and electronic oxygen conducting materials have been developed and studied for their transport properties, chemical stabilities, and performance in oxygen permeation by a number of researchers. There are two major concerns in developing conducting membrane materials which are increasing ion and electron conductivity and improving the stability of the materials ^[33,35].

Since, different materials result in different ionic and electronic conductivity. Perovskite- type material can be classified into three main groups ^[36]

1.) $Sr(Co,Fe)O_{3-\delta}(SCFO)$

Most of perovskite oxides are based on SrCoO₃ and SrFeO₃ materials because they exhibit highest oxygen permeability ^[37]. It was found that the properties of these materials are dependent on the chemical compositions and are able to be changed when Sr or Co/Fe is partially substituted with other metal ions. However, they show some drawbacks such as a structurally unstable when temperature and pressure changed.

2.) La(Co,Fe)O3-δ (LCFO)

LCFO based materials exhibit much higher electronic conductivity than ionic conductivity. Thus, the ionic conduction is the rate-limiting factor for oxygen permeation ^[35]. Moreover, comparing to SCFO, oxygen permeability of LCFO is much less than that of SCFO type. However, the advantage of LCFO is an ability to minimize some problems in SCFO.

3.) LaGaO₃ (LGO)

In contrast to LCFO, Kharton et al. reported that LGO based oxides show a lower electronic conductivity, but a much higher in ionic conductivity.

In this project, mixed conducting ceramic membrane of SCFO perovskite type is used to separate oxygen from air due to its high oxygen permeability. However, due to the unstable structure, these perovskites must be stabilized by substituting $SrCoO3-\delta$ oxides with proper cations ^[35]. From a study reported by Meng et al., it was found that $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$ oxide exhibit high oxygen permeability, high structural stability and good mechanical strength at high temperature. So we will use $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$ ceramic membranes in Ion Transport Membrane unit design.

5.7.2 Ion Transport Membrane Structure

As mention earlier in previous section, Different membrane pattern such as flat disc sheet, tubular or hollow fiber membrane, plays important role in the overall systems for air separation. In most research, the disc shape membranes are normally used since it is easy to fabricate using conventional static-pressing methods ^[36]. However, there are many drawbacks of disc shape membrane which make them unfavorable in practical application such as high temperature sealing, limited membrane area (< 5 cm²), and high electrochemical transport resistance due to symmetric structure.

Tubular membrane pattern were developed to reduce these problems. Even though many problems are improved, the tubular pattern appears to have a small surface to volume ratio and high membrane thickness which resulting in lower oxygen permeation rates.

Recently, hollow fiber membranes are developed using spinning/sintering process. The hollow fiber membrane have attracted considerable interests due to the large membrane area per unit volume and their asymmetric structure exhibit less resistance to oxygen permeation^[37].



Fig. 5.7 SEM image of a hollow fiber membrane and sample of a fiber membrane unit ^[39]

Due to the high surface area and the low in oxygen permeation resistance $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$ hollow fiber ceramic membranes are chosen for our Ion Transport Membrane design. Hollow fiber membranes are cylindrical tube with hole in the middle and membrane thickness must be very small. An outer side of the cylindrical is called shell side where pressurized air is fed through this side of membrane; an inner side is called lumen side which allows permeated oxygen to flow out of the membrane tube.

5.7.3 Membrane Performance Analysis

Before choosing a parameter in the design, it is important to investigate a performance of membrane at different conditions and parameters for the best result. In this case, we will consider three important parameters which are a flow pattern, operating temperature and pressure.

1.) Flow pattern

There are two different flow patterns, first one is co-current flow in which pressurized air and permeated oxygen, flow through the fiber tube in the same direction. Another is called counter-current flow in which pressurized air and permeated oxygen flow in opposite direction.

Tan et al. reported a superior oxygen productivity of co-current flow over counter- current flow when the vacuum pressure (pressure at the lumen side) is less than 0.05 atm. However, when the vacuum pressure is higher than 0.05 atm, the difference between two flow patterns becomes small as shown in fig. Thus we will design the ITM system using co- current flow. A schematic diagram of the co-current flow is shown in Fig. 5.8 as follows;



Fig .5.8 Effect of Co-current and Counter-current flow pattern^[35]

2.) Operating temperature

As mentioned in the literature review part, a proper range of operating temperature is around 800-900 °C. However, different material requires different operating temperature due to their physical properties and stabilities.

Meng et al. reported an experimental/ modeling comparison of oxygen permeation rate on SCFO membrane at different temperature, ranging from 500 - 900 °C as shown in Fig.5.9 The result shows that the oxygen permeation rate increases with increasing temperature. At 900 °C, the highest oxygen permeation rate is obtained.



Fig. 5.9. Effect of temperature on the oxygen permeation ^[37]

3.) Operating pressure and membrane area

An effect of membrane area on the oxygen productivity at different lumen pressure when operating pressure at shell side is fixed to 1 atm, was investigated by Li et al. as shown in Fig.5.10. The result shows an increasing of oxygen productivity as the membrane area is increasing up to one maximum value and remains stable no matter how much the area is increased. Form this finding; we will set the lumen pressure to 0.01 atm and the range of membrane area should be in the range of $0.001 - 0.05 \text{ m}^2$.



Fig 5.10 Effect of lumen pressure and membrane area on oxygen productivity ^[35]

5.7.4 Oxygen Flux and Flow Equation

An analysis of oxygen permeation through a mixed conducting fiber membrane can be done either by set up an experiment or using mathematical model. In this project, we will investigate the oxygen permeation by using the model based on the following assumption [38].

- 1. The ceramic membrane reactor is operated at steady state under isothermal and isobaric conditions
- 2. Plug flow for both the air and the sweep gas
- 3. The internal mass transfer resistance between the gas and the membrane surface is neglected.
- 4. Ideal gas law is used to describe the gas behavior



Fig. 5.11 Diagram of Co-current flow

The mass conservation equation for the shell and lumen gas stream can be written, respectively, as follows ^[37,38];

Shell side for oxygen

$$\frac{d}{dl}\left(\frac{P'o_2V_s}{RT}\right) = -2\pi R_m Jo_2$$

Lumen side for oxygen

$$\frac{d}{dl}\left(\frac{P''o_2V_l}{RT}\right) = 2\pi R_m J o_2$$

Boundary condition $p'o_2 = 0.21p_a, p''o_2 = 0$, and l = 0

The local oxygen permeation flux through the hollow fiber membranes, Jo_2 can be calculated by ^[37];

$$Jo_{2} = \frac{k_{r}[(p'o_{2})^{0.5} - (p''o_{2})^{0.5}]}{R_{0}(p''o_{2})^{0.5} + \frac{(2k_{f}(R_{0} - R_{in})(P'o_{2}P''o_{2})^{0.5}}{D_{v}} + \frac{R_{m}}{R_{in}(P'o_{2})^{0.5}}}$$

Where

$$R_m = (R_o - R_m) / \ln \left(\frac{R_o}{R_{in}} \right)$$

And p'o₂ and p''o₂ are oxygen partial pressure in the lumen and shell side, respectively.

The model equation can be solved using numerical Runge- Kutta method with the parameter listed in Table 5-3, we obtained;

$$Jo_2 = 4.41 \ \frac{ml}{cm^2 * min}$$

Let: density (D) = 1.429 g/L and molecular weight (MW) = 32 g.

$$Jo_2 = 3.28 \ x \ 10^{-6} \ \frac{mol}{cm^2 * s}$$
Table 5-3^[35,36,37] Design parameters

| Design Parameters | |
|---|---|
| Temperature (°C) | T = 900 (exhibit high stability) |
| Thickness (mm) | h = 0.62 (thin, high flux) |
| Outer radius (mm) | R _{out} =2.35 |
| Inner radius (mm) | $R_{in} = 1.73$ |
| Length (cm) | L = 30 |
| Air feed flow rate (mL/min) | F = 200 |
| Pressure at shell side (atm) | $\mathbf{P}_{s} = 1$ |
| Pressure at lumen side (atm) | $P_1 = 0.01$ |
| Diffusivity of oxygen vacancy (cm ² /s) | $D_v = 1.58 \times 10^{-2} \exp(-8852.5/T)$ |
| Forward reaction rate constant (cm/atm ^{0.5} *s) | $k_{\rm f} = 5.9 \times 10^6 \text{*exp}(-27291/\text{T})$ |
| Reverse reaction rate constant (mol/cm ² *s) | $K_r = 2.07 \times 10^4 * \exp(-29023/T)$ |
| Oxygen flux (ml/cm ² *min) | $\mathbf{Jo}_2 = 4.41$ |

Thus, we can calculate oxygen amount per day

$$O_2 = (3.28 x \, 10^{-6}) x \, 32 x \, 10^4 x \, 24 x \, 60 \, x60 = 90685.44 \, \frac{g}{m^2 * day}$$

In order to produce **700 TPD of oxygen** (approximately 19.971 mol O_2/kg feedstock) for 764 TPD coal and 191 TPD biomass, total membrane area ($A_{m, Total}$) is equal to

 $A_{m, Total} = 700 \text{ TPD/ oxygen amount per day} = 7718.9 \text{ m}^2$

From the report of Media Process Technology Inc., ceramic membrane cost is 1000 USD/m^2 [40]. We can calculate total membrane cost,

Total membrane cost = 7,718,900 USD

And number of fiber tube N = Total membrane area/ 1 unit tube area, where 1 unit tube area A_m = 0.00427 m^2/unit tube,

Numbers of fiber tubes are 1,807,704.92.

The above calculation can be summarized by the following table;

| Calculation result | |
|--|-------------------------|
| Oxygen flux (mol/cm ² *s) | 3.28 x 10 ⁻⁶ |
| Oxygen amount per m ² (g/m ² *day) | 90685.44 |
| Total membrane area (m ²) | 7718.9 |
| Total membrane cost (USD) | 7,718,900 |

5.8 Others

Apart from an ability to produce a high purity oxygen stream for gasifier, ITM unit integrated to IGCC is found to increase an efficiency of the whole power plant by 1.2 percent ^[41]. This might results from lower energy consumption, since ITM unit itself is thermally activated.

6 CO₂ Capture Technologies

The emission of CO_2 by the power generation industry can be reduced by combining the Integrated Gasification Combined Cycle (IGCC) power plants with CO_2 capture technologies. Nowadays, no commercial IGCC plant with CO_2 capture has been built yet.^[47]

6.1 Technical options for CO₂-emissions control

The CO₂ emission control by selecting an energy input with low CO₂ output, converting CO₂ to chemical products, using CO₂ capture.^[48]

6.1.1 Energy choice

Energy choice is a general method to reduce CO_2 emission by selecting the energy input with less CO_2 -intensive form.^[48] In general, it can be considered by hydrogen-to-carbon ration; the energy source with higher H/C ration emits lower CO_2 . Natural gas is an energy choice for electricity generation instead of coal. However, natural gas is more expensive than coal and impact to electricity price. The combination of biomass with fossil fuel energy, such as coal, is one way is being explore. The major concern of using biomass is the availability of the biomass in seasons and regions.^[48]

6.1.2 CO₂ utilization

In case of CO₂ utilization, there are many applications carbon dioxide such as chemicals, drinks and foods, solvent, pharmaceuticals, synthetic fuel, and oils and gas recovery.^[48-49] The current status of CO₂ uses in industries was summarized by C. Song (2006) as shown in Table 1.

| Table 6-1 Current status of CO ₂ uses in various industrial applications. | | | | |
|---|--|--|--|--|
| Sectors | Industrial applications | | | |
| Chemicals | CO₂ is used in chemical synthesis and for controlling reactor temperatures. CO₂ is employed to neutralize alkaline effluents. CO₂ is used as a blowing agent for polyurethane and polystyrene foam production and for blow molding manufacturing of plastic bottles, and containers. CO₂ is used under supercritical conditions for purifying or dying polymer, animal or vegetable fibers. | | | |
| Pharmaceuticals | • CO ₂ is used for making chemicals such as salicylic acid and Aspirin; for use as an inert | | | |

| | gas, and for supercritical fluid extraction. |
|----------------|--|
| | • CO ₂ is used for product transportation at low |
| | temperature (-78 °C or -108 °F) and also |
| | acidification (pH) of wastewater. |
| Foodstuffs | • Liquid CO ₂ can be used as cryogenic fluid in |
| | chilling or freezing operations or as dry ice |
| | for temperature control during the storage |
| | and distribution of foodstuffs. |
| | • Packaging of foodstuffs to increase the shelf |
| | life of many food products due to its inerting |
| | properties and its growth inhibiting effect of |
| | CO_2 on micro-organisms |
| | • Stunning of pigs and poultry in |
| | slaughterhouses instead of using electrical |
| | stunning |
| Deverage | Stummig. |
| Develage | • Carbonation of beverages such as soft |
| | CO is used to remove soffeing from soffe |
| | CO ₂ is used to remove caneme from conee |
| | |
| | • CO_2 is used as shielding gas for preserving |
| | drink quality, and propellant gas for |
| | emptying tanks of drinks |
| | • CO ₂ is also used in drinking water treatment |
| | in modern water works together with lime or |
| | chalk. |
| Healthcare | • CO ₂ produces close-to-physiologic |
| | atmospheres for the operation of artificial |
| | organs. |
| | • CO ₂ is used as a component in a mixture of |
| | oxygen or air as respiratory stimulant to |
| | promote deep breathing. |
| | It is also used for the surgical dilation by |
| | intra-abdominal insufflations. |
| Environment | • Small amount of liquid CO ₂ can be used in |
| | recycling of waters from Acid Mine |
| | Drainage. |
| | • Waste water treatment and waste liquid |
| | treatment by injection of CO ₂ for the pH of |
| | liquid effluents. CO ₂ is an excellent |
| | alternative to sulfuric acid for pH balance |
| | control. |
| Pulp and paper | • CO_2 enables sharp tuning of the pH of |
| - mb muc habor | recycled mechanical or chemical nulps after |
| | an alkaline bleaching |
| | • CO_{1} and CO_{2} and C |
| | \bullet CO_2 can be used in the rall OII |

| | neutralization and for increasing the performance of paper machines. Precipitated calcium carbonate obtained from CO₂ and CaO is used as a whitener for the paper industry. |
|-------------------------|---|
| Electronics | CO₂ is usually used as a cooling medium in environmental testing of electronic devices. CO₂ can be used to add conductivity to ultrapure water. CO₂ can also be used as an environmentally friendly supercritical fluid for removing photoresist from wafers |
| Metals industry | CO₂ is typically used as an inert gas or for environment protection. CO₂ is used for red fume suppression during scrap and carbon charging, for nitrogen pick-up reduction during tapping and for bottom stirring. CO₂ is used for fume suppression during ladle transfer of matte (Cu/Ni production) or bullion (Zn/Pb production) in the nonferrous metallurgy. Special grades of CO₂ are used in CO₂ lasers. |
| Laboratories & analysis | • Supercritical CO ₂ is the mobile phase in both supercritical chromatography and supercritical fluid extraction applications. |
| Safety and others | CO₂ is used as carbon dioxide snow for fire extinguishers; pH control and regulation of waste waters, swimming pools, etc. |

6.2 CO₂ capture technology

The most common CO_2 capture technologies are classified at three types: postcombustion capture (Fig. 6-1), oxyfuel combustion (Fig. 6-2), and pre-combustion capture (Fig. 6-3).[50] Each system is described below.

6.2.1 Post-combustion

The principle concept of post-combustion CO_2 capture technology is the carbondioxide is captured from the exhaust gas, after energy conversion process (combustion) as illustrated in Fig. 6-1.^[51] The post-combustion technology is considered as a widely considered for existing power plants. The most widely considered technology for post-combustion capture involves the use of chemical solvents - typically an amine such as a *monoethanolamine or MEA*. The mechanism for carbonioxide capture using MEA is showed later in MEA topic.^[52] To achieve a significant footprint, the scrubbing plant required for capturing CO_2 is typically two scrubbers and one stripper associated with a 500MW power plant.^[52] The drawback of using MEA is the heat requirement of the solvent regeneration is high and has a major impact on the overall efficiency of the power plant.^[52]



Fig. 6-1 CO₂ post-combustion diagram.

6.2.2 Oxyfuel-combustion

In oxy-fuel combustion technology, oxygen gas is used as an oxidant instead of air for fuel combustion leading to the generation of high H₂O and CO₂ (CO₂ content varies from 70% to above 95% depending on the fuel, the process used, the air in-leakage, the O₂ purity and the excess O₂) in a flue gas, which is readily to be captured. ^[53] The oxyfuel-combustion diagram is illustrated in Fig. 6-2. Comparing to using air as an oxidant, oxy-combustion offers several benefits a 60-70% reduction in NO_x emissions and increasing of mercury removal. ^[53] Industrial scale applications such as in glass melting and the steel and aluminium industry have been applied the oxyfuel-combustion into the processes. It shows that the potential of this technology

is the requirements in less plant area, less volume, less weight and less cost than normal circulated fluidized bed (CFB) plants. Moreover, it is potential for 100% CO_2 capture and potential to be operated at high pressure, which means less CO_2 compression energy is required. [53]

Nonetheless, high energy-penalty cost is subjected to air separation unit which has a major impact on the overall efficiency of the power plant.^[53]



Fig. 6-2 CO₂ oxyfuel-combustion diagram.

6.2.3 Pre-combustion

In this system, a primary fuel is reacted with either steam or oxygen and produce synthesis gas (mainly H_2 and CO) which is then converts the CO to CO₂ in a water-gas-shift (WGS) reactor. The CO₂ and H_2 molar concentrations are increased to approximately 40% and 55%, respectively. The CO₂ is now readily to be removed and the H_2 -rich gas can be then converted to electrical or thermal power. The current state-of-the-art technology for pre-combustion is physical/chemical absorption technology is a physical glycol-based solvent such as Selexol or methanol-based Rectisol.^[52]

The advantage of pre-combustion technology is that it is a proven technology for industrial scale such as in refineries. Under this system, CO_2 can be capture under pressure and the CO_2 is present at much higher concentrations in syngas than in post-combustion flue gas, thus CO_2 capture for pre-combustion process should be less expensive than for post-combustion capture.^[52-53] In addition, pre-combustion technology is very relevant for IGCC power plant which is much suitable for this project.

However, there are few gasification plants in full-scale is being operated and the capital costs are higher than for PC plants. ^[52] According to this problem, the H_2S/CO_2 co-capture technology is considered to be used in our project. The information about this system is provided in detailed later.



Fig. 6-3 CO₂ pre-combustion diagram.

There is a study of additional costs comparison using those three systems from MIT as shown in Table 6-2. The studied showed that using pre-combustion technology in IGCC causing the lowest additional cost for new construction. According to the comparison of those three CO_2 -capture technologies, pre-combustion is selected to be applied into IGCC power plant in this project.

| Table 6-2 | MIT | estimates | of | additional | costs | of | selected | carbon | capture | technology | (percent |
|-------------|--------|--------------|-----|--------------|---------|------|------------------------|--------|---------|------------|----------|
| increase in | electr | ric generati | ing | costs on lev | velized | l ba | usis). ^[54] | | - | | - |

| | New construction | Retrofit* | | |
|--------------------------|------------------|----------------|--|--|
| | | | | |
| Post-combustion (MEA) | 60-70% | 220-250% | | |
| | | | | |
| Pre-combustion (IGCC) | 22-25% | Not applicable | | |
| Oxy-fuel combustion | 46% | 170-206% | | |

* Assumes capital costs have been fully amortized.

6.3 Solvents used in CO₂-capture technologies

Several solvents used in CO₂-capture technology such as monoethanolamine, selexol (glycol), and ionic liquid are considered in this project.

6.3.1 Chemical absorption: monoethanolamine (MEA)

Aqueous amine processes are currently used to remove CO_2 in more than 95% of U.S. natural gas sweetening operations. However, amine processes often suffer from issues with high energy consumption, corrosion, amine degradation, and solvent losses. The increasing energy

consumption might cut the plant output and efficiency. Further, the solvent regeneration process causes an increase of total plant capital cost from \$571M (without CO_2 capture) to \$705M (27% of gross plant capacity).^[55]

The monoethanolamine (MEA) technology is commercially applied to produce high-purity CO_2 (>99 vol%) from the exhaust of coal and gas-fired boilers, furnaces and turbines. ^[50] The high-purity CO_2 is mainly used in enhanced oil application. This solvent can applicable to low- CO_2 partial pressures and can be recovered up to 98%. Due to its low production cost, the MEA is the state of the art solvent being considered for carbon dioxide capture via chemical absorption process. ^[56] The MEA is suitable for low CO_2 partial pressures as present in flue gas for post-combustion CO_2 capture. Using MEA system amine scrubbing for post-combustion capture is applicable for retrofitted to existing power plants. Moreover, it has been commercially proven on a small scale. ^[52]



However, there are drawbacks using this solvent such as solvent degradation by carbamate polymerization as illustrated below.^[56]



MEA associates with CO_2 to form MEA carbamate.



The MEA carbamate reacts with a free MEA molecule and irreversibly dehydrolize to form N,N'-di(2-hydroxyethyl)urea.



The 2-Oxazolidone can also react with another molecule of MEA to form 1-(2-

hydroxyethyl)-2-imidazolidone which is sometimes referred to as HEIA.



Then the HEIA is hydrolyzed to form N-(2-hydroxyethyl)-ethylenediamine or HEEDA.

The 2-oxazolidone, dihydroxyethylurea, HEIA and HEEDA compounds plus further polymerization products are believed to be the main products of thermal degradation. The rate of formation of these products is faster at higher temperature. Moreover, in the present of higher CO_2 loading and MEA concentration leads to the higher carbamate-amount present. ^[56] The MEA make-up costs from degradation in the stripper are low at temperatures below 110 °C, but can become significant if the pressure in the stripper is increased in order to take advantage of thermal compression. ^[56]

In addition, concentrations of SO_x and NO_x in the gas stream combine with the MEA to form non-regenerable, heat-stable salts. The MEA, therefore, is consumed as long as the process is run. Thus, the flue gas needs to be pre-treated to reduce acid gas (NO₂ and SO₂) concentrations to extremely low levels to prevent these reacting irreversibly with the solvents.^[51]

6.3.2 Physical absorption: Selexol (glycol)

The solvent used in Selexol technology is a mixture of dimethyl ethers polyethylene glycol with the formulation of $CH_3(CH_2CH_2O)_nCH_3$, where n is between 3 and 9.^[58] The selexol has a higher capacity to absorb gases than amines. Fig 6-5 shows the capacities of chemical and physical absorption solvents. By increasing pressure in the system, physical-absorption solvent can be improved the absorption capacity but chemical-absorption solvent has a limitation by doing that. In other word, the Selexol solvent can be regenerated by reducing pressure in the system.

Due to no need in heat for regeneration process, the net power loss associated with the Selexol-based CO_2 capture is much less than amine CO_2 -recovery systems.



Fig. 6-5 Comparison of physical solvent vs. chemical solvent.

6.3.3 Physical absorption: Ionic liquid (IL)

Ionic liquids (ILs) are a promising materials considered to be used in CO_2 -capture technology and natural gas sweetening.^[59] ILs present a highly versatile and tunable platform for the development of new processes and materials aimed at the capture of CO_2 from power plant flue gas and in natural gas sweetening.

RTILs-amine (RTILs: Room temperature Ionic liquids) is (largely) organic salts that are molten at ambient conditions; they have different properties from common organic solvents such as non-volatility, thermal stability, and tunable chemistry.^[55] The poly(RTIL)-RTIL composite membranes showed stronger interaction between the polymer and RTILs. The strong interaction occurred due to the poly(RTIL)-RTIL composites having been tailored for maximum compatibility with the RTIL component. Thus, the large degree of ionic interactions between the poly(RTIL) and RTILs is much stronger than any interactions between conventional polymers and RTILs. The amount of "free" RTIL within the composite was increased so as to further increase gas permeability. By the stronger interaction, liquid phase loss into the gas steam is improved.

Table 6-3 shows the impact of using IL and MEA was compared to for post-combustion technology. Using IL can lower cost for CO_2 capture down to 63 \$/metric ton CO_2 which is more that 50% lower than using of MEA as a solvent. However, there is no proven evidence in large scale for IL in CO_2 capture. It still need more study on the technology in term of economic and engineering. As a result, we selected Selexol technology for our IGCC system.

| Post-combustion | MEA | IL |
|--|--------|--|
| CO ₂ capacity (metric tons/yr) | 47,100 | 46,900 |
| CO ₂ recovery (%) | 91.4 | 91.3 |
| CO ₂ purity (%) | 95.3 | 98.7 |
| Equipment cost (\$1,000) | 1,623 | 1,192 |
| Total investment (\$1,000) | 18,133 | 16,200 |
| Cost for CO ₂ capture (\$/metric ton CO ₂) | 147 | 63 * Not optimized yet (Next goal is 33) |

Table 6-3 The comparison of using MEA and ionic liquid in post-combustion technology.^[60]

6.3 H₂S/CO₂ co-capture technology vs. separated H₂S and CO₂ captures

Due to the much increasing of capital cost of IGCC power plant in the present of CO_2 - capture technology, the studies of H_2S/CO_2 co-capture have been considered.¹ The comparison of IGCC systems cooperated with separated H_2S and CO_2 capture units, and co-capture are discussed below.

6.4.1 IGCC with 80% CO₂ Capture

This plant also has two full-size GE Energy (formerly Texaco) gasifiers, two gas turbines, each one with its respective HRSG, and one steam turbine. However, the syngas produced in the gasifiers, which consists mostly of CO (39%) and H₂ (29%), is steam shifted in two stages to convert most of the CO in the fuel gas to CO_2 and H₂. The shifted gas is scrubbed by a glycol plant, yielding a hydrogen-rich fuel and an acid-gas stream that is processed in a Claus/SCOT section for sulfur recovery. In the glycol plant, 80% of the carbon dioxide contained in the syngas is captured and compressed to 110 bar (1,595 psi). The clean, hydrogen-rich fuel gas is diluted with nitrogen and moisturized with water before entering the gas turbines. The plant's net power output is 488 MW. The CO₂-capture glycol plant diagram is shown in Fig. 6-6.

6.4.2 IGCC without CO₂ Capture

The IGCC plant studied included two full-size Texaco (now GE Energy) quench gasifiers, each one feeding a syngas combustor equipped gas turbine. The combined cycle power plant employs two 7FA gas turbines, each one exhausting to an unfired, free-circulation heat recovery steam generator (HRSG). Steam at three pressure levels is produced in the HRSGs, and fed to a single, two-flow, reheat, condensing GE D-11 steam turbine. The gasification plant includes a cold gas cleanup section, glycol-based sulphur removal and a Claus/SCOT sulphur-recovery section. An external cryogenic air separation unit (ASU) supplies 95%-purity oxygen, for gasification, and high-pressure nitrogen that is injected in the gas turbines for NOx abatement. No air integration exists between the gas turbines and the ASU. The plant's net power output is 577 MW.



Fig. 6-6 CO₂ capture glycol plant diagram. H₂S and CO₂ captured separately.

6.4.3 IGCC with CO₂ and H₂S Co-capture

This plant is also based on the plant described in the case of IGCC with 80% CO₂ capture. The difference is that the CO₂ and H₂S are removed from the fuel gas simultaneously in a single step, thereby eliminating the need for a sulphur-recovery section. The absorption plant design is simpler than that in the previous cases, consisting solely of one acid-gas absorber, a two stage glycol flash and an acid-gas stripper for concurrent CO₂ and H₂S recovery. These gases are removed in the absorber and recovered downstream in the flash drums and acid-gas stripper. The CO₂ capture level remains at 80%, while the H₂S removal is virtually complete. The acid gas, consisting mainly of CO₂ with traces of H₂S (2 ppm), is compressed to an export pressure of 110 bar as in the previous cases. This plant's net power output is 552 MW. The CO₂–H₂S co-capture glycol plant diagram is shown in Fig. 6-7.



Fig. 6-7 CO₂–H₂S co-capture glycol plant diagram.

Fig. 6-8 shows the carbon dioxide emissions of the studied power plants as compared to a conventional coal-fired plant. The IGCC plant without CO_2 capture has the highest carbon dioxide emissions (744 g/kW h), which is in close concordance with the one reported by Riemer and smaller than the value provided by Texaco in the previous reports. The evidence confirms that IGCC plants without CO_2 capture emit 24% less carbon dioxide than a conventional coal-fired power plant. IGCC with 80% CO_2 capture has the lowest average CO_2 emissions of all the plants (193 g/kW h), followed by IGCC with CO_2 and H_2S co-capture (358 g/kW h).



Fig. 6-8 CO₂ emissions comparison.

The IGCC with 80% CO_2 capture presents the highest capture penalty and the lowest power output of the three plants, as shown in Fig. 6-9. The IGCC with H₂S and CO₂ co-capture has only 4% less power output than the IGCC without capture. The power output decreases by 11% at 60% capture and by 16% at 80% capture as compared to the IGCC without capture.



Penalty due to CO₂ capture

Net Power Output

Fig. 6-9 Power output comparison.

Table 6-4 summarizes the internal plant electricity consumption of all the studied plants. In IGCC with 80% CO₂ capture, the average ancillary power requirements double (173 MW) those of IGCC without CO₂ capture. The glycol plant power consumption increases eight fold and six fold, with respect to IGCC without CO₂ capture, and for IGCC with 80% CO₂ capture, respectively.

The energy required for CO_2 compression increases when CO_2 capture is increased. The energy for CO_2 compression is significant, representing 23% of the total auxiliary load for the case of IGCC with 80% CO_2 capture.

The average power required for capture and compression in IGCC with 80% CO₂ capture is 245 kWh per tons of CO₂ captured. In contrast to the case of IGCC with 80% CO₂ capture, the increase in ancillary power for the IGCC with co-capture is much less dramatic. The IGCC with co-capture has the same CO₂ emissions as those of the IGCC with 80% capture, yet its power output is only 4% less than that of an IGCC without capture. The IGCC with co-capture reduces the power needed for the recycle compressors to less than half of that required in the IGCC with 80% capture. It is also needs less process units. The net effect on the IGCC with co-capture plant performance is a 29% net increase in auxiliary power demands, compared to an IGCC without capture, while at the same time cutting CO₂ emissions by 80%.

| Auxiliary load (MW) | IGCC without | IGCC with | IGCC with |
|-----------------------------|--------------|-------------|------------|
| | capture | 80% capture | co-capture |
| Plant auxiliaries | 11.2 | 11.3 | 11.6 |
| Air separation unit | 69.5 | 71.9 | 76.2 |
| Selexol plant | 5.9 | 50.4 | 8.4 |
| CO ₂ compression | n.a. | 39.3 | 15.3 |
| Total | 86.5 | 172.9 | 111.5 |

 Table 6-4 Plant consuption camparision.

The efficiency comparisons are illustrated in Fig. 6-10. The IGCC showed a higher efficiency

with respect to a conventional coal-fired plant; as observed, it is 6% more efficient than the conventional one. Once CO_2 capture is implemented, the efficiency drops by 7% with 80% CO_2 capture. The efficiency of the IGCC with co-capture is similar to those of the 80% co-capture with the lowest CO_2 emissions. Despite the efficiency penalty for CO_2 capture, IGCC plants are still more efficient than IGCC with co-capture or equally efficient (IGCC with 80% CO_2 capture) as a conventional coal-fired power plant while emitting significantly less carbon dioxide.



Fig. 6-10 Efficiency comparison.

The cost of electricity production is mainly affected by fuel costs and capital costs, as seen in Fig. 6-11. The effect of operating labor, maintenance and chemicals on the final electricity cost is less significant. The electricity cost for IGCC without capture is 5.09 US¢/kWh, followed by the IGCC with 80% co-capture (5.48 US¢/kWh). The IGCC with 80% capture has the highest electricity cost of all the plants around 6.67 US¢/kWh. For the IGCC plants, the largest changes in the final cost of electricity are linked to capital costs. The capital costs represent around 65% of the cost of electricity in all cases.



Fig. 6-11 Power production cost comparison.

6.5 CO₂ Mitigation Cost Comparison

CO₂ mitigation costs of different plants can be calculated as shown in the following equation:

$$MC = \frac{COE_{cap} - COE_{ref}}{E_{ref} - E_{cap}}$$
[Eq. 6-1]

where COE is the cost of electricity (US¢/kWh), E is the CO₂ emissions (kg/kWh) and the indices *ref* and *cap* represent the reference and capture plants, respectively.

The CO₂ mitigation cost comparison is presented in Table 6-5. The IGCC without CO₂ capture is used as the reference plant. The IGCC with co-capture has the lowest CO₂ mitigation cost, \$7/tons CO₂ avoided. The IGCC with 80% capture showed \$28/tonne CO₂ avoided. IGCC with co-capture has the lowest CO₂ mitigation cost due to the lower capital costs and minimal CO₂ emissions. It has over four times CO₂ mitigation costs lower than those of the IGCC plant that captures CO₂ and H₂S separately.

| Plant | CO ₂ emissions | COE | Mitigation cos | ts |
|---|---------------------------|------------|----------------|-----------------------------|
| | (kg/kW h) | (US¢/kW h) | (US¢/tonne CO | O_2 avoided) ^a |
| IGCC without capture | 0.744 | 5.09 | - | - |
| IGCC with 80% capture | 0.191 | 6.67 | 28 | 28 ^a |
| IGCC with co-capture | 0.193 | 5.48 | - | - |
| ^a with PC as reference plant | | | | |

Table 6-5 CO₂ mitigation cost comparison.^{1b}

In conclusion, current technologies for CO_2 removal from other gases, such as those used in natural gas sweetening, are also capable of capturing CO_2 from power plant emissions.^[59] Aqueous amine processes are found in the vast majority of natural gas sweetening operations in the United States. However, conventional aqueous amine processes are highly energy intensive; their implementation for post-combustion CO_2 capture from power plant emissions would drastically cut plant output and efficiency. Membranes, another technology used in natural gas sweetening, have been proposed as an alternative mechanism for CO_2 capture from flue gas. Although liquid ionic materials offer a potentially selectivity and capacity with less energy-intensive approach, but their development and industrial implementation are far behind those of amine and Selexol processes. In order to apply into industrial scale, more research studies are still required to make a right decision on a real project. Thus, IGCC power plant in this project is designed to cooperate with H₂S and CO₂ co-capture using Selexol technology, which is a proven technology in large scale.

Summary key parameters of CO_2 capture unit used in the IGCC power plant in this project is showed in Table 6-6.

| Technology | H ₂ S/CO ₂ co-capture |
|--|---|
| Solvent | Selexol |
| CO ₂ capture efficiency (%) | 90 |
| CO ₂ mitigation cost (US\$/ton CO ₂ avoided) ^{1b} | 6.35 (or 142\$/kW _e) |
| Storage (US\$/ton CO ₂) ² | 3 |
| Monitoring and verification (US\$/ton CO ₂) ² | 0.2-1.0 |
| | |

Table 6-6 Key parameters of CO_2 capture unit used in the IGCC power plant in this project.

7 Gasifier Simulations

A simulation program "gasify" is applied here to find the most appropriate temperature, pressure, amount of oxygen, the portion for biomass in total feedstock, portion of CO2 in total oxidant and the steam/feedstock ratio.

There are several problems about this simulation program. 1) It cannot take the reaction time into consideration. 2) It always considers the reaction to be complete and equivalent. So this program cannot take coal conversion ratio and the several stages of coal gasification into consideration. The gasification process is always considered to happen in equivalent environment and enough time is given for the whole gasifier to became equivalent.

Although this is not the case happen in gasifier, this simulation can also provide many valuable information to improve the conditions in a fluidized-bed gasifier.

7.1 Feedstock simulation

Table 7-1 shows the analysis for pure coal, 10% biomass, 20% biomass in weight percentage. The lower heating value and the need for oxygen decrease when biomass is added into the feedstock. The gasification temperature will also decrease when higher percentage of biomass is used. The gasification efficiency also increases a little when biomass is added in the feedstock.

For a 122MWe power plant, when 20% biomass in weight percentage is added into the feedstock and the energy efficiency is about 40%. The power plant needs 764 ton of coal and 191 ton of biomass per day.

| | Coal | 10%Biomass (wt%) | 20%Biomass (wt%) |
|--------------------------------|------------------|---------------------|---------------------|
| Combustion | | | |
| LHV (KJ/Kg) | 30410 | 29005 | 27601 |
| Oxygen (mole/100kg) | 6.4208 | 5.9983 | 5.5942 |
| Gasification | | | |
| Oxygen (mole/Kg) | 24.737 | 22.3 | 19.971 |
| Equivalence Ratio | 2.5956 | 2.6898 | 2.8011 |
| Gasification Efficiency | 0 6968 | 0 6968 | 0 6982 |
| Temperature $(^{\circ}C)$ | 1100.27 | 885 12 | 652 72 |
| | | | |
| Need For Feedstock for a 122MW | e Power Plant (H | Energy efficience | cy 40%) |
| Coal/Biomass (TPD) | 874 | 818/91 | 764/191 |

Table 7-1 Equivalence ratio for gasification, oxygen needed for per 100kg feedstock, gasification efficiency and temperature.

7.2 Amount oxygen in gasifier

The desired condition for a gasifier is that the product gas contains only H_2 and CO, as well as a little SO₂. But there is no enough time for the gasification process to reach this equilibrium condition. More oxidant gas than needed is provided the gasification process. Fig. 7-1 to Fig. 7-3 shows how oxygen affects the product gas when temperature is at 1000°C, the percentage of hydrogen and steam keep the same while the concentration of CO decrease and CO2 concentration increase sharply.



Fig.7-1 Mole ratio of product gas when different amount of oxidant gas is in the gasifier for 100g feedstock (different equivalence ratio). Temperature is 1000° C, oxidant gas is pure oxygen and feedstock is pure coal.



Fig.7-2 Mole ratio of product gas when different amount of oxidant gas is in the gasifier for 100g feedstock (different equivalence ratio). Temperature is 1000° C, oxidant gas is pure oxygen and 10% of biomass contains in the feedstock.



Fig.7-3 Mole ratio of product gas when different amount of oxidant gas is in the gasifier for 100g feedstock (different equivalence ratio). Temperature is 1000° C, oxidant gas is pure oxygen and 20% of biomass contains in the feedstock.

7.3 CO₂ concentration in oxidant gas

Adding CO_2 into the oxidant gas can improve coal conversion ratio effectively, and also control the gasifier temperature. As have talked about before, this program cannot deal with coal conversion ratio. It always assumes that the reaction is complete. But this simulation still can show us how the product gas and the need for oxidant gas change while the CO_2 concentration changes. Fig. 7-4, Fig. 7-5 and Fig. 7-6 show that as when the concentration of CO_2 is increased, the need for oxidant gas increases sharply. The concentration of CO_2 in product gas also increases dramatically when the percentage of CO_2 increase in the input gas. This would put a lot of pressure for the CO_2 capture unit. So only about 10-20% percent of CO_2 is added in the oxidant gas.



Fig.7-4 Mole of input/output gas and the mole ratio in product gas for CO_2 concentration in oxidant gas is from 0 to 50%. When temperature is 1000°C biomass percentage is 0% in feedstock.



Fig. 7-5 Mole of input/output gas and the mole ratio in product gas for CO_2 concentration in oxidant gas is from 0 to 50%. When temperature is 1000°C biomass percentage is 10% in feedstock.



Fig. 7-6 Mole of input/output gas and the mole ratio in product gas for CO_2 concentration in oxidant gas is from 0 to 50%. When temperature is 1000°C biomass percentage is 20% in feedstock.

7.4 Gasifier Temperature

Fig. 7-7 and Fig. 7-8 is the how temperature affects the amount of input/output gas for a gasifier and the percentage of the product gas. In these two simulations, the need for oxidant gas increase when temperature is going up, especially when higher CO_2 percentage is in the oxidant gas. The percentage of each portion in the product gas stays similar when the temperature is higher than 900°C. The percentage of H₂ increases when temperature first began to increase and then stays the same. But the portion of CO will decrease and CO_2 percentage increase with the reaction temperature increasing. From the result, high temperature is not good for the gasification process. In our project, 1000°C is chosen for the temperature of the gasifier. Reaction time is not taken into consideration in this software, but fluidized-bed gasifier has a relative longer reaction time, for this reason it can be assumed that the gasifier has an equivalent environment.



Fig. 7-7 Mole of input/output gas and the mole ratio in product gas when gasifier temperature is from 750-1300°C when biomass percentage is 20% in feedstock and

 CO_2 percentage is 10% in the oxidant gas.



Fig. 7-8 Mole of input/output gas and the mole ratio in product gas when gasifier temperature is from 750-1300 °C when biomass percentage is 20% in feedstock and CO₂ percentage is 20% in the oxidant gas.

7.5 Gasifier pressure

Fig. 7-9 and Fig. 7-10 are the effect of pressure for a gasifier. In this simulation, the pressure goes from 1 to 30 bar. In these two simulations, it seems pressure does not affect the amount of input and output gas, and also has little effect for the portions of product gas. When pressure increase from 1 to 30 bar, we only observe a decrease of H2 and an increase of CO less than 5%. However, pressure does have effect for the kinetics of the reaction in the gasifier. In the literatures, normally an average pressure of 20 bar is used for most gasifiers.



Fig.7-9 Mole of input/output gas and the mole ratio in product gas when gasifier pressure is from 1-30bar when temperature is 1000° C biomass percentage is 20% in feedstock and CO₂ concentration is 10% in the oxidant gas.



Fig.7-10 Mole of input/output gas and the mole ratio in product gas when gasifier pressure is from 1-30bar when temperature is 1000° C biomass percentage is 20% in feedstock and CO₂ concentration is 20% in the oxidant gas.

7.6 Steam/Feedstock ratio

Steam in gasifier provides an important way to reduce the temperature in the gasifier. Gasification in pure oxygen can make the temperature in the gasifier very high. Although CO_2 has a high Cp value and can reduce the temperature, the amount of CO_2 can put a lot of pressure in the CO_2 capture part. Water-gas reaction can take place when steam is added into the gasifier.

Fig. 7-11 to Fig. 7-14 shows the amount of input/output gas and the percentage of each component in the output gas. From the graphs, the amount of CO_2 in the oxidant gas does not affect the content for the final product a lot. The concentration of H_2 and CO_2 will increase with the increasing amount of steam. Compare to 10% of biomass in feedstock, 20% of biomass can result in a little more hydrogen and less CO.

For there is a water-gas shift reactor following the gasifier, it's does not affect a lot if more steam in added into the gasifier. In order to keep the temperature at around 1000°C, about 20-30% of steam in weight percentage of the feedstock is added into the gasifier for the gasification process.



Fig. 7-11 Mole of input/output gas and the mole ratio in product gas when steam/feedstock ratio is from 0 to 1 mol/100 g, when temperature is 1000°C biomass percentage is 10% in feedstock and CO₂ percentage is 10% in the oxidant gas.



Fig. 7-12 Mole of input/output gas and the mole ratio in product gas when steam/feedstock ratio is from 0 to 1mol/100g, when temperature is 1000 °C biomass percentage is 10% in feedstock and CO₂ percentage is 20% in the oxidant gas.



Fig.7-13 Mole of input/output gas and the mole ratio in product gas when steam/feedstock ratio is from 0 to 1 mol/100g, when temperature is 1000°C biomass percentage is 20% in feedstock and CO₂ percentage is 10% in the oxidant gas.



Fig.7-14 Mole of input/output gas and the mole ratio in product gas when steam/feedstock ratio is from 0 to 1 mol/100g, when temperature is 1000°C biomass percentage is 20% in feedstock and CO₂ percentage is 20% in the oxidant gas.

7.7 Gasifier parameters

The following table (Table 7-2) is the parameters for the gasifier in the IGCC power plant. These parameters are selected from the graphs of the simulation as well as from the literatures.

| Temperature | 1000℃ |
|----------------------------------|---------|
| Pressure | 20 bar |
| Steam/Feedstock Ratio (Weight) | 0.2 |
| Coal Feed per Day | 764 ton |
| Biomass Feed per Day | 191 ton |
| Oxygen per Day | 611 ton |
| Mole ratio of CO2 in oxidant gas | 10% |

Table 7-2 Working conditions for the gasifier in oxygen co-gasification IGCC power plant.

8 Economic analyses for IGCC power plant.

8.1 IGCC power plant parameters

Table8-1 shows the parameters for the power plant. This power plant use low pressure indirectly heated gasification. The IGCC power plants usually have a life cycle about 30 years and capacity factor about 30 years. General electric and other turbine manufactures are incorporating air extraction provisions into some utility turbine designs including the MS-6101FA. This is a smaller advanced utility gas turbine. The increased mass flow and temperature of the turbine exhaust also allows the use of more sophisticated steam cycles in this size range. The pressure ratio of utility machines was also more compatible with demonstrated biomass gasifier operation^[62].

| Construction period | 2 years |
|-----------------------|--------------|
| Life cycle | 30 years |
| Capacity factor | 80% |
| Energy efficiency | 40% |
| Coal conversion ratio | 99.8% |
| Gas turbine | GE MS 6101FA |
| Gas turbine output | 82.1 MW |
| Steam turbine output | 55.1 MW |
| Internal consumption | 15.2 MW |
| Net system output | 122 MW |

 Table 8-1 IGCC power plant parameters

8.2 Biomass/Coal as Feedstock

Table 8-2 is the price for coal, biomass, transportation and the water-gas shift catalyst. The price for biomass is about \$30/ton, which is very competitive compare to coal. The price of bituminous coal is about \$42/tom. The policy price for CO_2 capture is \$30 per ton, which can still save the investment for the power plant. The energy efficiency for an IGCC power plant is around 40%, which is about 10% more than the general electricity power plants. Using biomass co-gasification can still increase this figure by about 3%. ^[18,19]

Biomass is a seasonal product; the supply and price may not be stable during the whole year. Biomass needs collection and transportation, so a power plant based on biomass should be a small or mid-sized power plant.

The price for the water-gas shift catalyst is calculated from the price showed in table 4-5. When the pressure is at about 20 bar, the membrane has a flux rate of 200 scfh/sq foot per hour. The membrane has a life cycle at about 1,100 hours and a price at $60-80/\text{ft}^2$. The cost for membrane per ton of feedstock is about \$2.4.

| | \$/ton |
|---------------------------------|--------|
| Coal | 42 |
| Biomass | 30 |
| Transportation | 12 |
| WGS catalyst (ton of feedstock) | 2.4 |

Table 8-2 Feedstock, transportation and catalyst cost

8.3 ITM and Economical Consideration

A main consideration for ITM -IGCC integrated facility design includes air compression unit, separation unit (fiber membranes), and product compression unit [42]. The previous reported by PN. Dyer et al shows that ITM-IGCC integrated systems are able to decrease 31 percent of gas separation investment with 3 percent increasing in thermal efficiency. A case study on 420 MW IGCC power plants reveals the cost of gas separation capital investment as 100 USD/kW. In our project the total cost of the ITM unit is calculated based on the percentages shown in table, which equals to 15,437,800 USD or approximately **127 USD/kW** for 122 MW power plants.

This result is comparable to the case study; any variation might result from different size of power plant and the type of ceramic membrane used in the separation part. Table 8-3 summarizes the cost for ITM gas separation unit.

| Cost, O ₂ (700 TPD) | Percentage | USD |
|--------------------------------|------------|------------|
| Air compression | 17% | 2,624,426 |
| Separation part | 50% | 7,718,900 |
| Product compression | 33% | 5,094,474 |
| Total ITM cost | 100% | 15,437,800 |

Table 8-3 ITM cost analysis

8.4 CO₂ Capture and Storage

Table 8-4 Summary key parameters of CO_2 capture unit used in the IGCC power plant in this project is showed in Table 6-6.

| Tuble 0 + Rey purameters of CO ₂ cupture unit used in the 1000 power plant in this project. |
|---|
|---|

| Technology | H_2S/CO_2 co-capture |
|--|----------------------------------|
| Solvent | Selexol |
| CO_2 capture efficiency (%) | 90 |
| CO_2 mitigation cost (US\$/ton CO_2 avoided) ¹ | 6.35 (or 142\$/kW _e) |
| Storage $(US\/ton CO_2)^8$ | 3 |
| Monitoring and verification (US\$/ton CO ₂) ⁸ | 0.2-1.0 |

8.5 Power Plant Capital Cost and LCOE

Table 8-5 summarizes the capital cost for the IGCC power plant. Fluidized-bed gasifier and ITM can reduce the cost for the whole system. Normally an entrained-bed gasifier would have a price more than \$300/KWe and the price for ITM is about 60% of the price for ASU unit. Fluidized-bed gasifier can accept a variety of feed stock, so we do not need an additional feedstock milling unit. The capital cost for this IGCC power plant is about \$1,393/KWe. The cost of fuel is calculated from its lower heating value and the energy efficiency of the power plant. Table 8-6 shows the LCOE calculation for this IGCC power plant. The levelized cost of electricity is about 6.9 cents/KWh.

| | Capital Cost (\$/KWe) | Cost W/O Cont (\$1000) |
|---------------|-----------------------|------------------------|
| Wood Handling | 36 | 4,400 |
| Wood Drying | 45 | 5,448 |
| Gasifier | 150 | 19,585 |
| HRGS | 63 | 7,686 |
| Gas Turbine | 217 | 17,850 |
| Steam Turbine | 230 | 12,668 |
| ITM | 128 | |
| CO2 Capture | 142 | |
| Construction | 382 | |
| Total | 1,393 | |

Table 8-5 Capital Cost for IGCC power plant

Table 8-6 Levelized cost of electricity.

| | - |
|--------------------|------------------------|
| Total Capital Cost | \$1.303/KW not |
| Total Capital Cost | |
| | |
| | |
| O&M Cost | \$ 120 Million/KW_vear |
| Octivi Cost | |
| | |
| | |
| Fuel Cost | 1.96 cents/KW |
| 1 401 0051 | |
| | |
| | |
| LCOE | 6.9 cents/KW |
| 2002 | |
| | |

8.6 Net Percent Value and Cash Flow

The price for electricity is about 7 cents in Pennsylvania. The interest is about 5%. The Credits for CO2 capture is about \$30/ton. Table 8-7 shows the economics parameters for this IGCC power plant.

Table 8-7 Economics parameters for the IGCC power plant.

| Interest rate | 0.05 |
|-------------------|--------------------|
| overnight cost | \$169,946,000/year |
| maintain cost | \$14,640,000/year |
| generation cost | \$73,741,680/year |
| generation income | \$74,810,400/year |
| income from CO2 | \$26,619,450/year |
| net income | \$13,048,170/year |

Table 8-8 shows the cash flow and NPV for the power plant. Fig.8-1 and Fig.8-2 shows that the cash flow equals 0 at the 16th year. While the Net Present Value (NPV) turns positive on the 26th year. The net present value for the generator would be 15.19 million dollars, if the power plant can successfully run 30 years.



Fig.8-1 Cash flow for the IGCC power plant



Fig.8-2 NVP in years for the IGCC power plant
| year | net income (\$/year) | Present | Cash Flow | NPV(million |
|------|----------------------|----------------|--------------|-------------|
| | | Value(\$/year) | (million \$) | \$) |
| 1 | -169.946 | -169.946 | -169.946 | -169.946 |
| 2 | 0 | 0 | -169.946 | -169.946 |
| 3 | 13.04817 | 11.83507483 | -156.89783 | -158.111 |
| 4 | 13.04817 | 11.27149984 | -143.84966 | -146.839 |
| 5 | 13.04817 | 10.73476175 | -130.80149 | -136.105 |
| 6 | 13.04817 | 10.22358262 | -117.75332 | -125.881 |
| 7 | 13.04817 | 9.736745352 | -104.70515 | -116.144 |
| 8 | 13.04817 | 9.273090811 | -91.65698 | -106.871 |
| 9 | 13.04817 | 8.831515058 | -78.60881 | -98.0397 |
| 10 | 13.04817 | 8.410966722 | -65.56064 | -89.6288 |
| 11 | 13.04817 | 8.010444497 | -52.51247 | -81.6183 |
| 12 | 13.04817 | 7.628994759 | -39.4643 | -73.9893 |
| 13 | 13.04817 | 7.265709295 | -26.41613 | -66.7236 |
| 14 | 13.04817 | 6.919723138 | -13.36796 | -59.8039 |
| 15 | 13.04817 | 6.590212512 | -0.31979 | -53.2137 |
| 16 | 13.04817 | 6.276392869 | 12.72838 | -46.9373 |
| 17 | 13.04817 | 5.977517018 | 25.77655 | -40.9598 |
| 18 | 13.04817 | 5.69287335 | 38.82472 | -35.2669 |
| 19 | 13.04817 | 5.421784143 | 51.87289 | -29.8451 |
| 20 | 13.04817 | 5.163603946 | 64.92106 | -24.6815 |
| 21 | 13.04817 | 4.917718044 | 77.96923 | -19.7638 |
| 22 | 13.04817 | 4.683540994 | 91.0174 | -15.0802 |
| 23 | 13.04817 | 4.460515232 | 104.06557 | -10.6197 |
| 24 | 13.04817 | 4.248109745 | 117.11374 | -6.37162 |
| 25 | 13.04817 | 4.045818805 | 130.16191 | -2.3258 |
| 26 | 13.04817 | 3.853160767 | 143.21008 | 1.527356 |
| 27 | 13.04817 | 3.669676921 | 156.25825 | 5.197033 |
| 28 | 13.04817 | 3.494930401 | 169.30642 | 8.691963 |
| 29 | 13.04817 | 3.328505143 | 182.35459 | 12.02047 |
| 30 | 13.04817 | 3.170004898 | 195.40276 | 15.19047 |
| NPV | | 15.19047346 | | |

Table 8-8 Net present value and cash flow for the IGCC power plant

Conclusions

Coal is mainly used for electricity generation in the United States. Reducing the CO_2 emission in coal-fired power plants can contribute a lot to environment protection. To do this, fluidized-bed gasifier and entrained-bed gasifier can be used in IGCC power plants. In our project, a circulating fluidized-bed gasifier is chosen because it can accept feeds at different dimensions, which is especially a good fit for a biomass co-gasification power plant. The fluidized-bed gasifier also have a price at about half of the price for entrained-bed gasifier, it can also increase the coal conversion ratio for the gasifier also have a additional circulating unit.

Pennsylvania is a state with sufficient coal and biomass supply, which makes this state a good fit to build biomass co-fire power plant. As a renewable energy source, biomass co-gasification provides an effective way to reduce CO_2 emissions to the environment. Use of O_2/CO_2 as the oxidant can improve the coal conversion ratio and gasification efficiency. But increase the percentage of CO_2 in the oxidant gas will increase the concentration of CO_2 in the product gas, which can put a lot of pressure for the CO_2 capture union.

Steam is also used for the gasification process to keep the temperature of the gasifier. Steam will cause more CO_2 and hydrogen in the product gas. But this conversion will also take place in the water-gas shift reactor followed by the gasifier. So only about 10-20% of CO_2 is added in the oxidant gas while more steam is used to keep the temperature. Pressure does little affect the product gas in the gasifier. And when the temperature is over 800°C, the content in the product gas also does not change a lot. A temperature of 1000°C is used for the gasifier to keep the coal conversion ratio above 99%.

Recent research shows that the Ion Transport Membrane technique (ITM) has provided new approach for tonnage, high-purity (99+ %) oxygen separation. Even though an ITM unit is still in the development phase, there is a high possibility to scale it up to supply the great demand of oxygen in the near future.

Ion transport membranes technique, based on mixed- conducting ceramic membranes type have a great success providing high purity oxygen to gasification systems. The unique separation mechanism due to a movement of ions and electron make this technique superior to others such as cryogenic distillation and polymeric membranes. Moreover, due to a compact design and less complex operation unit, an ITM unit can be properly integrated with an IGCC system. The ITM unit requires neither an electrode nor an external circuit to operate, which result in lower cost of operation. However, different types of ceramic materials result in different gas permeation or separation efficiency. SCFO types is the most suitable material for oxygen separation since it exhibits the highest oxygen permeability, only some concerns on its unstable structural properties in which can be overcome by substitute SrCoO₃ with proper cations. In ITM design, the first three parameters that need to be concern are flow pattern, operating temperature, and pressure. In this project, co-current flow pattern is used at the temperature of 900° C with lumen pressure 0.01 atm. As a result, the oxygen flux is found to be equal to 4.41 ml/cm²min. Since, 700 TPD of oxygen are needed to supply for gasifier, we can simply calculate the total membrane area. Cost of membrane per square meter is 1000 USD, so we can calculate cost of membrane used in separation process and ITM unit cost which is 127 USD/kW.

The CO₂/H₂S co-capture technology using Selexol solvent is added into IGCC power plant in order to reduce CO₂ emission. By using this designed system, the CO₂ mitigation cost is impact to the total cost around 6.35 \$/ton CO₂ avoided or 142\$/kW_e. Also, the combination of cost for storage, monitoring and verification is around 4 \$/ton CO₂ which is much less than cost of CO₂ mitigation.

With a price of electricity at about 7 cents/KW in Pennsylvania, the NPV turns positive at the 26^{th} year and cash flow equals zero at 16^{th} year.

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