

University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

---

Chemical & Biomolecular Engineering Theses,  
Dissertations, & Student Research

Chemical and Biomolecular Engineering,  
Department of

---

12-2017

# Sustainable Clean Coal Technology with Power and Methanol Production

Xiaomeng Wang

University of Nebraska-Lincoln, runewxm@gmail.com

Follow this and additional works at: <http://digitalcommons.unl.edu/chemengtheses>



Part of the [Chemical Engineering Commons](#)

---

Wang, Xiaomeng, "Sustainable Clean Coal Technology with Power and Methanol Production" (2017). *Chemical & Biomolecular Engineering Theses, Dissertations, & Student Research*. 30.

<http://digitalcommons.unl.edu/chemengtheses/30>

This Article is brought to you for free and open access by the Chemical and Biomolecular Engineering, Department of at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Chemical & Biomolecular Engineering Theses, Dissertations, & Student Research by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

SUSTAINABLE CLEAN COAL TECHNOLOGY with POWER and METHANOL  
PRODUCTION

by  
Xiaomeng Wang

A THESIS

Presented to the Faculty of  
The Graduate College at the University of Nebraska  
In Partial Fulfillment of Requirements  
For the Degree of Master of Science

Major: Chemical Engineering

Under the Supervision of Professor Yaşar Demirel

Lincoln, Nebraska

December, 2017

# SUSTAINABLE CLEAN COAL TECHNOLOGY with POWER and METHANOL PRODUCTION

Xiaomeng Wang M.S.

University of Nebraska, 2017

Advisor: Yaşar Demirel

The Coal-based chemical process is still indispensable in modern society due to the worldwide vast reserves and popular price of coal. Power generation and chemical production from coal still play an important role in the global chemical industrial market. Electricity generation and chemical production from coal is still the trend as long as the coal is plentiful and inexpensive. Modern chemical industry aims at sustainability and hence the development of clean coal technologies is critical.

Coal-based methanol economy, as an attractive liquid transportation fuel as well as an essential intermediate chemical feedstock, can fill a possible gap between declining fossil fuel supplies and movement toward the hydrogen economy. The integrated gasification combined cycle (IGCC) power plant with methanol production is simulated by Aspen Plus. Within the plant, firstly, the coal is fed to a pyrolysis reactor, and the volatile matter is fed into an oxy-combustion reactor, while the char is gasified in an entrained flow gasifier. The heat is used to produce electricity, while the syngas is converted to methanol. The integral plant consisting of an air separation unit, oxy-combustion of coal, gasification of char, electric power production, carbon capture and conversion to methanol has been designed and optimized by using the Aspen Plus package. The optimization includes the design specification, process heat integration using energy analyzer toward a more efficient clean-coal technology with methanol production. Multiple methods including life cycle assessment, sustainability metrics, and multi-criteria decision matrices are applied to analyze the sustainability of a certain clean-coal based IGCC power plant with methanol production.

The focus of this study is the kinetic study of a clean coal energy technology with power and methanol production. As an alternative method, chemical looping technology is discussed briefly. Chemical looping technology is a new method utilizing inherent CO<sub>2</sub> capture to address the concerns of growing levels of atmospheric CO<sub>2</sub>. The studied IGCC plant is compared with a conventional IGCC power plant to better understand the feasibility of the technology. A multi-criteria decision matrix consisting of economic indicators as well as the sustainability metrics shows that methanol and steam productions besides the power production may improve the overall feasibility of clean coal technology.

The goal of this work aims at developing the use of abundant resources of coal energy in the following aspects:

- Energy security
- Reduction of Greenhouse Gas emission
- Co-production and kinetics study in coal-based chemical processes
- Sustainability analysis

## **Dedication**

I would like to first thank the Chemical and Biomolecular Engineering Department at the University of Nebraska – Lincoln. The work and effort they have put in the last six and a half years towards my education has been invaluable. I would especially like to thank my advisor, Dr. Yaşar Demirel. Without him this work would not have been possible and his constant advice as a mentor for me in my graduate work is greatly appreciated.

## List of Figures

Figure 1 Cradle-to-Gate system boundary for the life cycle assessment of clean-coal technology with methanol production. ....	6
Figure 2 The hierarchy process flow diagram of the integrated clean-coal technology with methanol production. ....	7
Figure 3 Block flow diagram of the integrated clean-coal technology with methanol production (MT: metric tonne) .....	8
Figure 4 Gasification facilities classified by feedstock [27].....	10
Figure 5 Fluidized-bed coal gasifier [28].....	11
Figure 6 Moving-bed coal gasifier. [30] .....	12
Figure 7 Texaco entrained-flow coal gasifier [31]. ....	13
Figure 8 The block flow diagram of coal gasification. ....	13
Figure 9 Flow diagram of coal and char pyrolysis with quantified streams and reaction conditions. ....	15
Figure 10 Flow diagram of oxy-combustion with inputs and outputs. ....	17
Figure 11 Electricity generation in US by different energy sources [43]. ....	21
Figure 12 Block flow diagram of power production unit. ....	23
Figure 13 The pathway of element carbon (C) in the entire process. ....	25
Figure 14 The path of carbon dioxide in the entire process with unit of MT (metric tons)/day.....	25
Figure 15 Block flow diagram of carbon capture unit. ....	26
Figure 16 Methanol price and demand in recent history [55, 56, 61].....	27
Figure 17 Methanol use in 2016 [55].....	27

Figure 18 Life cycle assessment stages of integrated clean-coal technology power plant with methanol. production. ....	35
Figure 19 The path of CO <sub>2</sub> e emissions in integrated clean-coal technology power plant with methanol production. ....	37
Figure 20 Comparison of GHG emissions in this work and base case: Stage 1: Raw Material Acquisition, Stage 2: Raw Material Transportation, Stage 3: Chemical Process Facility [18,65,67].....	38
Figure 21 Water consumption in all the stages in two cases: Stage 1: Raw Material Acquisition, Stage 2: Raw Transportation, Stage 3: Chemical Process Facility [18,65,67]. ....	39
Figure 22 Energy consumption in integrated clean-coal technology power plant with methanol production and IGCC Plant (base case), MWh/MWh electricity. [18,65,67,69] .....	40
Figure 23 Greenhouse gas emission in the U.S. in 2015 [72].....	43
Figure 24 Basic flow diagram of chemical looping system.....	44
Figure 25 A basic chemical looping combustion scheme using metal oxide as OC. ....	45
Figure 26 Block flow diagram of the chemical-looping combustion system [76]. ....	46
Figure 27 Block flow diagram of chemical-looping combustion combined cycle [76]. .	47
Figure 28 Block flow diagram of the coal-based CLC plant. ....	47
Figure 29 Syngas chemical looping coal gasification with iron-based oxygen carrier [78]. ....	48
Figure 30 Flow diagram of iron-based coal-direct chemical looping gasification [79].	49

Figure 31 Block flow diagram of Fe-based chemical looping steam reforming and gasification systems for methanol, hydrogen and power production. ....	49
Figure 32 Conjunction of Chemical-looping and hydrothermal process using captured CO <sub>2</sub> for methanol production.....	59

## List of Tables

Table 1 Column specifications and results for low pressure (LP) and high pressure (HP) columns. ....	9
--	---



Table 2 Component attributes of Powder River Basin (PRB) coal and char1 in wt% [32]	15
Table 3 Estimated yields of coal pyrolysis products in reactors R201 and R202 used in the model.....	16
Table 4 Mass flow of inputs and outputs of gasifier.....	18
Table 5 Kinetic data of the heterogeneous reactions [34], where $T$ is the temperature, $P_t$ is the total pressure, and $d_p$ is the diameter of coal particle which is 500 $\mu\text{m}$ and $P_{O_2}$ , $P_{CO_2}$ , $P_{H_2}$ , $P_{H_2O}$ , $P_{CH_4}$ , $P_{CO}$ and $P_{H_2S}$ are the partial pressures, atm .....	19
Table 6 Equilibrium constants $K_{eq}$ of Reactions 8, 10 and 11 [35] .....	19
Table 7 Reaction rates of homogeneous reactions.....	20
Table 8 Heat streams for power production.....	23
Table 9 Column specifications and results for column in the methanol production [18].	29
Table 10 Sustainability indicators for integral clean-coal technology with methanol production. ....	30
Table 11 Sustainability metrics for the integral clean-coal technology with methanol production and IGCC power plant (base case) .....	32
Table 12 Unit energy cost for various utilities.....	33
Table 13 Economic data applied in CAPCOST]. The cost values are shown in million (MM)US\$ (2016) .....	34
Table 14 Air pollutant emissions from Stage 1, 2 and 3.....	36
Table 15 Multi-criteria decision matrix for feasibility analysis of integrated clean-coal technology plant with methanol production and the base case [20] .....	41
Table 16 Natural ores tested as oxygen carrier* [76, 80] .....	50

Table 17 Literature results of various tests of ilmenite as an oxygen carrier in chemical looping combustion (Solid fuels only).....	51
Table 18 Literature results using Mn-based ores as oxygen carriers in solid fuel based CLC.....	52
Table 19 A collection of results using copper-based ores as oxygen carriers in CLC. [76,80].....	53
Table 20 A collection of results using gypsum ( $\text{CaSO}_4$ ) as oxygen carriers in solid fuel - based CLC system.....	54
Table 21 Oxygen transport capability and theoretical oxygen transport capacities of conventional oxygen carrier and Natural ores. [80].....	55

# Contents

Dedication .....	iv
List of Figures .....	v
List of Tables .....	vii
Contents .....	x
CHAPTER 1 INTRODUCTION .....	1
CHAPTER 2 METHODOLOGY .....	1
2.1 Aspen Plus .....	4
2.2 Sustainability Analysis.....	4
2.3 Life Cycle Assessment.....	5
2.4 Techno-Economic Analysis (TEA).....	6
CHAPTER 3 IGCC-BASED COAL POWER PLANT.....	7
3.1 Air Separation Unit (ASU) .....	8
3.2 Coal Gasification .....	10
3.2.1 Coal Pyrolysis .....	14
3.2.2 Oxy-Combustion.....	16
3.2.3 Char Gasification .....	17
3.3 Steam Generation.....	20
3.4 Power Production.....	21

	xi
3.5 Water Gas Shift Unit.....	23
3.6 Carbon Capture and Sulfur Removal Unit.....	24
3.7 Methanol Production.....	26
3.8 Results.....	29
3.8.1 Optimization .....	29
3.8.2 Sustainability.....	29
3.8.3 Economic Analysis .....	32
3.8.4 Life Cycle Assessment.....	35
3.8.5 Feasibility Assessment by a Multi-Criteria Decision Matrix .....	40
3.9. Conclusions.....	41
CHAPTER 4 CHEMICAL LOOPING TECHNOLOGY .....	43
4.1 Introduction.....	43
4.2 Chemical looping combustion (CLC).....	44
4.3 Chemical looping gasification and reforming.....	48
4.4 Chemical looping technology using natural ores as oxygen carriers.....	50
4.4.1 Iron-based ores .....	51
4.4.2 Manganese-based ores .....	51
4.4.3 Copper-based ores.....	52
4.4.4 Natural gypsum ores .....	53
4.5.5 Comparison of Natural Ores with Conventional OC.....	54

	xii
4.6 Conclusion .....	55
CHAPTER 5. CONCLUSIONS, FUTURE REAERCH .....	57
APPENDIX.....	60
PUBLICATIONS LIST (RELEVANT TO THESIS).....	71
REFERENCES .....	72

## CHAPTER 1 INTRODUCTION

Coal plays an important part in worldwide energy markets due to its vast resources and affordable price. Currently, about 39% in the U.S. and 41% of global electricity generation come from coal-fired power plants [1]. As Roan et al. [2] suggested that a possible decline in recoverable fossil resources and movement toward a hydrogen economy could cause a time gap. Then the methanol production from coal may be one of the best options for filling the gap because of the steady and low cost of coal and its impact on the national energy security. Using coal as the feedstock will cause some issues such as environmental pollutant. While the traditional coal technique combined with methanol production which will fix carbon from coal and help to reduce the greenhouse gas. Such a clean-coal technology makes great efforts on overcoming the environmental issues.

As a result, coal-based methanol would be an ideal hydrocarbon fuel which can be used in different fields like transportation and manufacturing industry. [2]. Methanol can also be a valuable intermediate chemical feedstock for producing chemicals and biodiesel. Because coal is still an abundant and affordable energy source, the development of sustainable and efficient clean coal technologies with carbon capture are essential in producing coal-based power, steam, and chemicals [3]. Modern coal-based chemical industry efficiently converts coals into clean gaseous fuel which can be used for productions of power and chemicals. Currently, almost 97% of the world's coal-fired capacity is made up of pulverized coal (PC) power plants [3]. Integrated gasification combined cycle (IGCC) is a well-known coproduction technology developed capable of producing power and other feasible chemicals. It largely improves the energy efficiency and reduces the emissions compared with the traditional pulverized coal-fired system. The efficiency of the IGCC is about 36-39% while the conventional coal plants operate at 32-38% efficiency [4]. Gasification plant databases prepared by DOE-NETL compile information on the technologies and investments in major industrial coal gasification projects throughout the world [5].

## 1.1 Literature Research

Sustainability analysis assesses the nonrenewable material and energy depletions, as well as the Green House Gas (GHG) emissions with respect to the unit mass of primary product, and may provide a guideline on how to design sustainable processes. The strict standards for GHG emissions and high carbon fee are required for coal power plants. One efficient way to control GHG emissions is “oxy-combustion” which has been applied in the conventional pulverized coal power plants as well as in IGCC, from which CO<sub>2</sub> can be easily separated [6-9]. Siyu Yang et al [10] presented an integrated framework for modeling three coal-based energy and methanol synthesis processes as well as optimized these processes by calculating exergy efficiency and estimated sustainability.

Modern researches of coal technologies mostly concentrate on carbon capture, process optimization, and kinetics modeling to simulate the process. Govin et al. [11] proposed a one-dimensional model and found an optimized feedstock conditions by parametric studies. Consecutively, two-dimensional [12] and three-dimensional [13] models for entrained flow coal gasifier were developed to predict gas temperature profile and the compositions of the output and compare with measured values. After a macroscopic model was built, sensitivity analysis finds out how the specific operation conditions impact coal gasification; for example, Yang et al. [14] reported the impact of a single parameter such as pressure on the feasibility and possible improvements of the plant.

## 1.2 Objective

This work analyzes the feasibility of clean coal technologies by studying a well-designed IGCC power plant which mainly includes entrained flow gasification, power generation, carbon capture and methanol production. The objective of this study is to assess the feasibility of coproducing methanol in a commercial scale coal-based power plant with carbon capture unit and entrained-flow coal gasification using a kinetics-based model. This study also performs a cradle-to-gate life cycle assessment for GHG emission and energy consumption from raw material extraction,

transportation, gasification through power and methanol productions. The syngas produced by coal gasification is supplied to the methanol synthesis process. Capital cost, operating cost, and energy requirements are used to evaluate the techno- economic performance of this clean coal energy technology with methanol co-production. Another novel clean coal technology called Chemical Looping (CL) technology is discussed briefly as a possible near-future technology in power and chemical productions.

### **1.3 Motivation**

The goal of this work aims at developing the use of abundant resources of coal energy in the following aspects:

- Energy security
- Reduction of Greenhouse Gas emission
- Co-production and kinetics study in coal-based chemical processes
- Sustainability analysis



## CHAPTER 2 METHODOLOGY

### 2.1 Aspen Plus

The studied and based cases are all designed and simulated with Aspen Plus package, which consists of various optimization tools. The Soave-Redlich-Kwong (SRK) and IDEAL [18] thermodynamic property methods and related reaction kinetics data are used in the design. The coal-based IGCC power plant with methanol production has been analyzed by its sustainability, life cycle assessment, and techno-economic analysis.

### 2.2 Sustainability Analysis

As the modern society and chemical industry develop, the concept of sustainability is raised to guarantee the conservatively and wisely use of the finite resource with minimal negative effects on the environment, economic, energy and human health. Therefore, ways of measuring the degree of sustainability for a certain process known as sustainability indicators and metrics are proposed and employed in the analysis. The following sustainability metrics are estimated [15,16]: “

1. Material intensity (nonrenewable resources of materials depleted/unit mass of products)
2. Energy intensity (nonrenewable energy depleted/unit mass of products)
3. Potential environmental impact ( $\text{CO}_2\text{e}$  emissions/unit mass of products)
4. Potential chemical risk (toxic emissions/unit mass of products)”

Besides, the fresh water usage is also estimated as another sustainability indicator. For estimating these metrics material and energy balances as well as carbon dioxide equivalent ( $\text{CO}_2\text{e}$ ) emissions, which considers all the other greenhouse gasses are taken into account. The material, energy, and  $\text{CO}_2\text{e}$  emissions are then normalized per unit of mass/energy of the product, making them capacity independent for comparison with similar processes. Energy intensity and potential environmental impact are calculated by Aspen Plus [16,17]. The carbon equivalent emission and environment impacts are partially estimated by “Carbon Tracking” with the data coming from US-EPA-Rule-E9-5711, US-EPA’s ( $\text{CO}_2\text{E-US}$ ) and the fuel source of natural gas. Net carbon fee is estimated by

CO<sub>2</sub>e fee/tax of \$10/MT CO<sub>2</sub>e [18,19]. “Potential chemical risks” are estimated by the Life Cycle Assessment tool “GREET” [20,21].

## 2.3 Life Cycle Assessment

International standards for LCA are defined by ISO 14040 and 14044 which stipulate four steps: “(1) Goal and scope definition, (2) Life Cycle Inventory (LCI) [21,22] (3) Life Cycle Impact Assessment (LCIA) and (4) Interpretation [21,23-24].” These standards outline requirements and guidelines for all these steps [23].

The definition and scoping of goal determine the primary and secondary products, establish the boundaries for the process and declare the environmental effects that are to be reviewed. In the LCI analysis, the uses of energy, water, and raw materials are estimated accompanied by the environmental releases. The third step of LCA is the impact assessment. In this part, the data collected from inventory analyses are translated into visualized indicators including direct potential human and ecological effects. The last step is the interpretation of the inventory analysis results based on the environmental impacts of the products. At the same time, all the uncertainties in the LCA are addressed. Assumptions are made in the boundary, data, operations and criteria factors before the life cycle assessment starts [23,24].

This study evaluates the environmental impacts of clean-coal technology with power and methanol productions using the LCA with the system boundary of “cradle-to-gate” (Figure 1), which means that the assessment will begin with the extraction of raw material, transportation, and productions of power and methanol, and exclude the assessment of usage of the products. All needed data and methodologies come from Aspen Plus, GREET modeling, and published work in the literature. The core operations of the integral plant contain coal gasification, methanol production, and power generation.

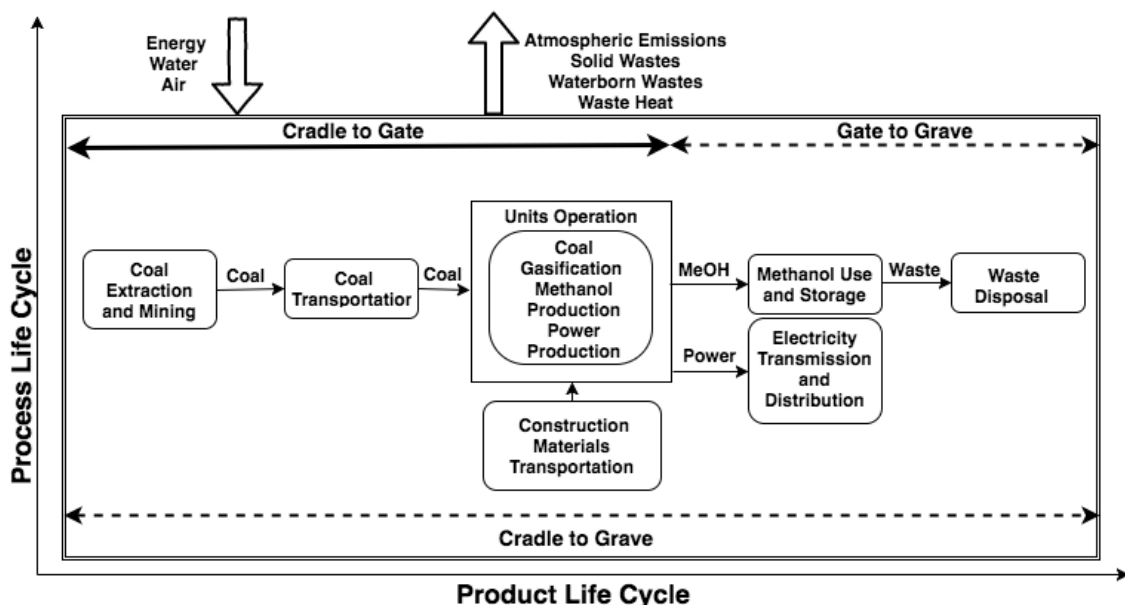


Figure 1 Cradle-to-Gate system boundary for the life cycle assessment of clean-coal technology with methanol production.

## 2.4 Techno-Economic Analysis (TEA)

Techno-economic analysis is based on the discounted cash flow diagrams for an assumed competitive operation of twenty years after the construction of the plant. Maximum Accelerated Cost Recovery System (MACRS) is used for estimating depreciation. Purchase costs of equipment are estimated by using the CAPCOST [25] program with the 2016 Chemical Engineering Plant Cost Index (CEPCI) [26]. Besides the deterministic analysis, stochastic evaluations are also performed by the Monte Carlo Simulations based on the possible deviations of the major economic data matrix.

## CHAPTER 3 IGCC-BASED COAL POWER PLANT

This plant includes seven sections represented by hierarchies (Fig. 2), which are Air Separation Unit (ASU), steam generation, coal gasification, Water Gas Shift (WGS) unit, power generation, methanol production and carbon capture unit. These seven sections are connected with material, heat and work streams to each other. The process hierarchy flow diagram and block flow diagram (BFD) of the integrated plant are shown in Figures 2 and 3, respectively.

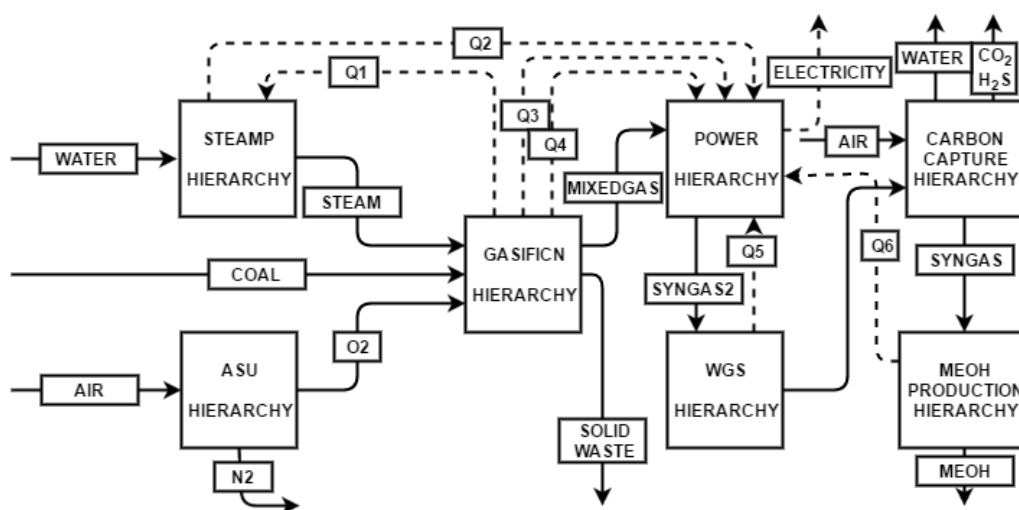


Figure 2 The hierarchy process flow diagram of the integrated clean-coal technology with methanol production.

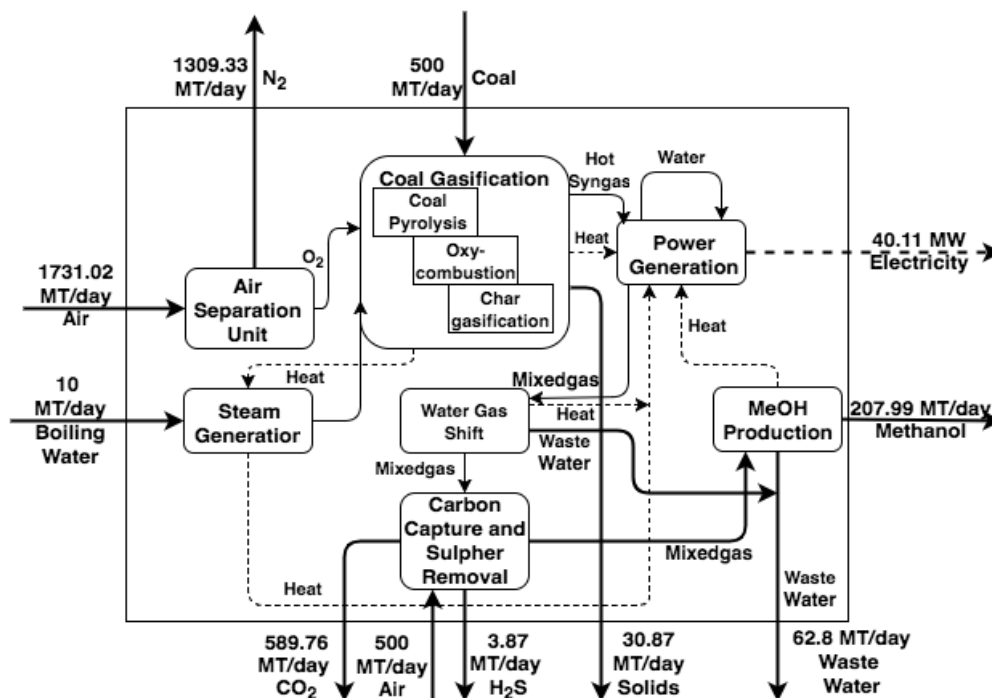


Figure 3 Block flow diagram of the integrated clean-coal technology with methanol production (MT: metric tonne)

Air, water and coal are the inputs of the integral process. The ASU produces 401.69 MT/day of O<sub>2</sub> and 1309.33 MT/day of N<sub>2</sub> by using 1731.02 MT/day of air. Steam generation unit produces 10 MT/day of steam by using the boiler feed water. 500 MT/day Powder River Basin (PRB) coal is fed into coal gasification by which 880.80 MT/day of syngas is produced together with 30.87 MT/day of wastes including solid waste and tail gas. Then the syngas is fed into the WGS unit. After the WGS reaction, 91.8% of CO<sub>2</sub> in the mixed gas is captured in carbon capture unit. The product gas containing mostly CO, H<sub>2</sub> and CO<sub>2</sub> is fed into methanol production unit and produce 207.99 MT/day of methanol. All the available heat streams are directed into the power generation unit where 40.11 MW of electricity is produced, as seen in Figure 2.

### 3.1 Air Separation Unit (ASU)

Air separation is a well-known technology which provides high-quality oxygen and nitrogen. ASU is integrated in the coal gasification process. Its function is controlling the amount of oxygen in gasifier for “partial oxidation” and participating in oxy-combustion. Oxy-combustion utilizes the

pure oxygen in fuel combustion to avoid the dilution of effluent by the nitrogen and facilitate easy capture of CO<sub>2</sub>. Oxygen and nitrogen from the ASU can be valuable products.

This plant utilizes 1731.02 MT/day of air with the assumed components of 21% oxygen and 79% of nitrogen by volume to provide oxygen in the oxy-fuel combustion. The cooled air is fed to a low-pressure separating column and a high-pressure separating column step by step. Both columns work interactively and separate oxygen and nitrogen respectively. With the higher boiling point (-183 °C), oxygen condenses out of gaseous streams. The ASU produces 401.69 MT/day of 95% O<sub>2</sub> and 1309.33 MT/day of 99.9% N<sub>2</sub>. The oxygen is delivered to the coal gasification unit as one of the main feedstock, while the nitrogen is sold as a byproduct.

The low-pressure column LPT101 has 60 stages with sieve trays. The column has a partial condenser and a reboiler. The mole purity of oxygen in the column is adjusted by varying the vapor side stream rate. The high-pressure column HPT102 has 60 stages. In a design specification block, by varying the ratio of liquid flow to feed flow rate, a mole purity of 99.9% of N<sub>2</sub> and a mole purity of 95% of O<sub>2</sub> are achieved. Table 1 shows the specifications and operating conditions for the columns. Process flow diagram and the stream table of the ASU are shown in Appendix A in Figure A1 and Table A1.

*Table 1 Column specifications and results for low pressure (LP) and high pressure (HP) columns.*

Configuration	LP T101	HP T102
Stages	60	60
Feed stage	15	16
Height (m)	37.6	37.6
Diameter (m)	1.83	1.61
Distillate rate (kmol/day)	28209.3	46786.1
Reflux ratio	1.27	0.31

### 3.2 Coal Gasification

Gasification is a method to convert carbon-based energy source into gaseous fuels such as syngas and flue gas. Due to the rich coal resources, coal will keep being the dominant feedstock in the worldwide gasification market. Gasification and Syngas Technology Council (GSTC) has reported that the existing gasification facilities are currently based on coal as the feedstock (Figure 4). In the forecast, it is seen that the number of coal gasification plants will stay growing.

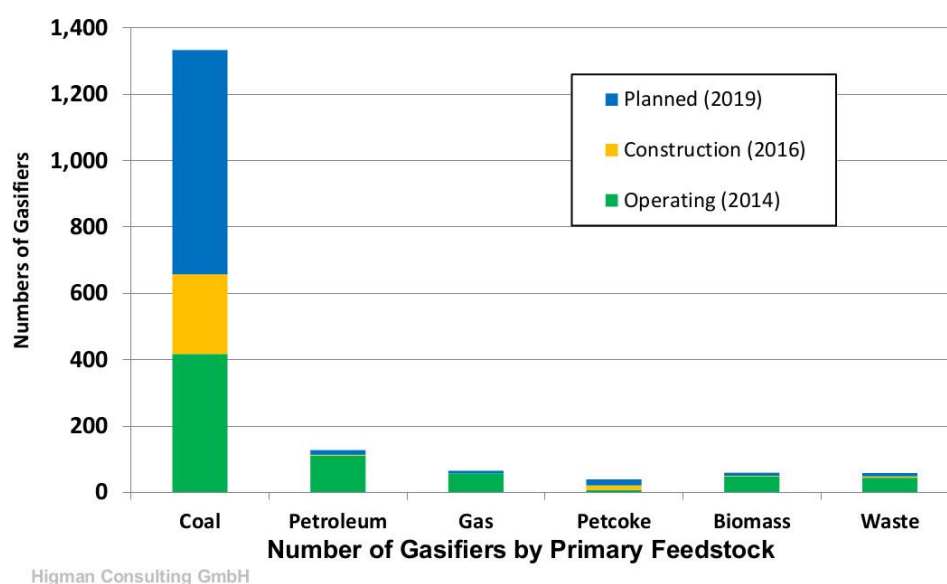
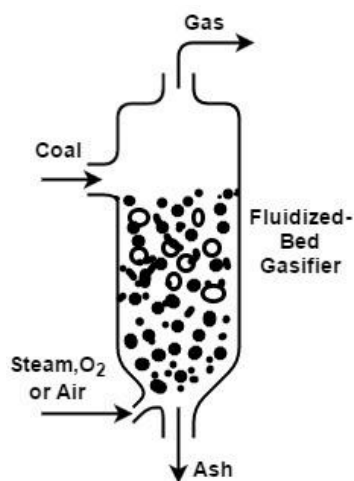


Figure 4 Gasification facilities classified by feedstock [27].

Coal gasification is also the core technique of clean coal technologies. It can convert coal into liquid transportation fuels, power and chemicals. Comparing with direct coal combustion, coal gasification releases less gas, which stands for the simplification of facilities and the reduction of capital cost. Basically, Coal gasification can be carried out by fluidized bed gasifier, fixed or moving bed coal gasifier and entrained flow coal gasifier based on the way that coal particles contact with gasification agents. Fluidized bed gasifiers keep the solid fuel particles suspending in upward-blowing jets of air and resulting in a turbulent mixing of solid and gas phase. This mixing makes the bed in the gasifier look like a bubbling fluid and helps increase the rate of heat transfer

and reactions. The sufficiently fluidized bed acts like liquid and since reflects some characteristics of the fluid.



*Figure 5 Fluidized-bed coal gasifier [28].*

The particle size of the feedstock of the fluidized-bed gasifier is normally between 0 to 6mm. Small particle size is beneficial to maintain the fluidization and increase the heat transfer surface. Coal is fed into the top of the gasifier while the steam or oxidant is fed at the bottom of the gasifier at an appropriate speed. The coal particles suspend at a uniform and moderately high temperature in the gasifier. The advantages of fluidized coal gasifiers are that they are capable of gasifying a wide range of feedstocks at a relatively stable condition. However, compared with entrained flow coal gasification, the carbon conversion is lower (90% - 95%). US Energy Government indicates that “The Clean Coal Technology Program led to the initial market entry of 1st generation pressurized fluidized bed technology, with the capacity of around 1000 megawatts installed” [29].

Another coal gasifier is fixed or moving-bed gasifier, shown in Figure 6. The coal is fed at the top of the reactor bed, and the oxidants or steam enters the gasifier at the bottom of the reactor. Coal particles and gasifying agents mixed counter-currently. The ash is disposed from the gasifier bottom. The input coal particles travel slowly down and contact with the oxygen-rich gas that going



upwards from the inlet of the gasifier. Typically, the reactor bed is separated into different parts with different functions

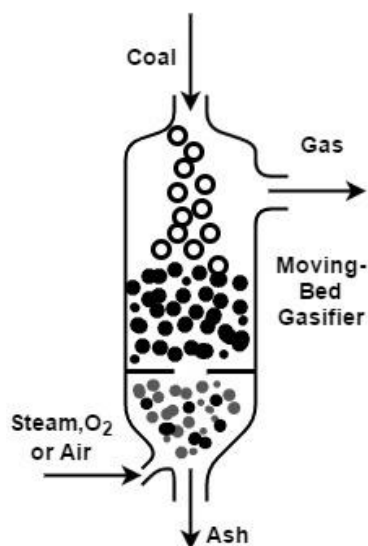


Figure 6 Moving-bed coal gasifier. [30]

Moving-bed coal gasification works at a relatively high equipment efficiency and requires a smaller amount of oxidant. This technique fits for the coal with high moisture and reactivity. The products usually contain high content of methane and hydrocarbon liquids. Products purification and coal fines treating will somehow increase the capital cost.

Another well-known coal gasification is entrained-flow coal gasification. Unlike other gasification, it allows the raw materials and the oxidant or steam entering the gasifier co-currently. Coal fines and gasification agents are fed at the top of the gasifier and mix with each other smoothly. The oxidant or steam entrain the coal particles and forms a dense cloud which helps the mixture moving through the entire gasifier. The entrained flow coal gasification requires a relatively high temperature and pressure to react. This results in a high reaction rate and carbon conversion (98 -99.5%). Figure 7 shows the scheme of Texaco gasifier equipped with a quench chamber with the coal water slurry (CWS) as the feedstock. In this work, the coal gasification hierarchy of IGCC power plant is demonstrated mainly based on entrained flow coal gasification model, mainly due to high reaction rates and carbon conversion.

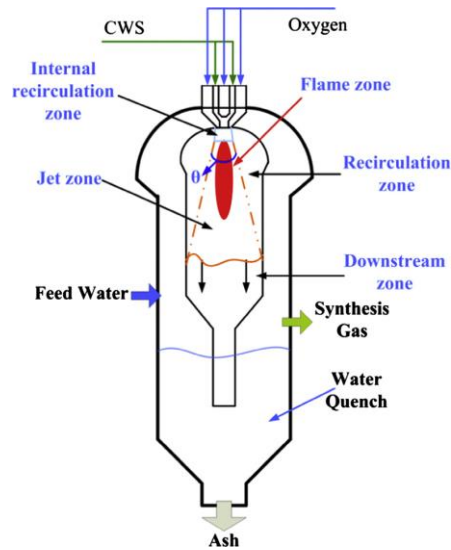


Figure 7 Texaco entrained-flow coal gasifier [31].

Coal gasification unit is the major part of the plant. The block flow diagram of coal gasification is shown in Figure 8. The entire coal gasification process can be split into three parts: coal and char pyrolysis, oxy-combustion, and char gasification. In this model, 500 MT/day of PRB coal [32] is utilized. The pressure of the coal is 1.1 bar and the temperature is 25°C. The diameter of pulverized coal is typically less than 500  $\mu\text{m}$  [33].

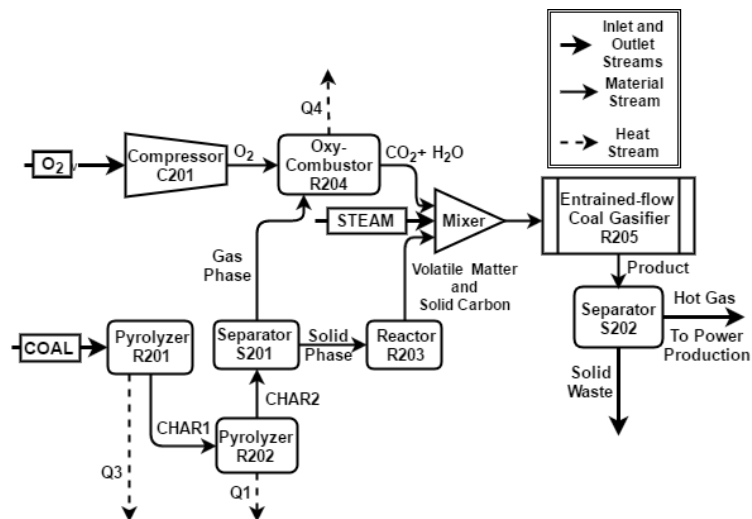


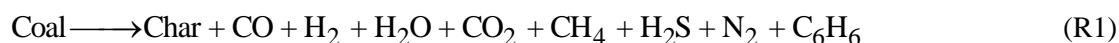
Figure 8 The block flow diagram of coal gasification.

Firstly, the coal is pyrolyzed in reactor R201 at 1.1 bar. The outputs are fed to the next pyrolytic reactor R202 at 24.3 bar. A separator S201 separates the gas phase and the solid (char) phase. The solid phase reacts further in an R-stoic reactor R203 where the char is converted to volatile substances, solid and ash (Figure 8). This part is called coal and char pyrolysis. Secondly, the separated gaseous constituents are introduced into the combustor R204 and burned with the oxygen coming from the ASU, which is known as oxy-combustion. The outputs of R203 and R204 combined with the steam enter the entrained flow gasifier R205 where the main gasification reactions occur. The gasifier operates at 24 bar with the diameter of 1.5 meters and length of 3.1 meters. This entrained flow gasifier contains two sections. The upper part is for coal gasification while the lower part is a quench chamber. Coal, steam and oxygen are the main feedstocks. Firstly, pulverulent coal is mixed with water to achieve coal-water slurry, which is fed along with the oxygen into the top section concurrently. In this part, there is a special refractory material lining to resist the severe operating environment and strong turbulence [11,18,31, 34-35]. The product of coal gasification is separated into 899.33 MT/day of syngas and 56.84 MT/day of solid waste consisting mainly ash, sulfur, and carbon by the separator 202.

### 3.2.1 Coal Pyrolysis

Coal processing is related to high-temperature reactions that are operated from 1000 °C to 1500 °C and produces a large amount of heat indicated by heat streams of Q1, Q3, and Q4 by the exothermic reactions taking place in reactors R201, R202 and R204, as shown in Fig. 8. Heat stream Q1 is utilized as the heat source of the boiler in steam generation unit, while heat streams Q3 and Q4 are used in power generation. The stream table of coal gasification is displayed in Figure A2 and Table A2 in the Appendix.

As Figure 9 displays, 500 MT/day of bituminous coal is fed into the first pyrolysis reactor R201 where the first pyrolysis reaction (R1) takes place



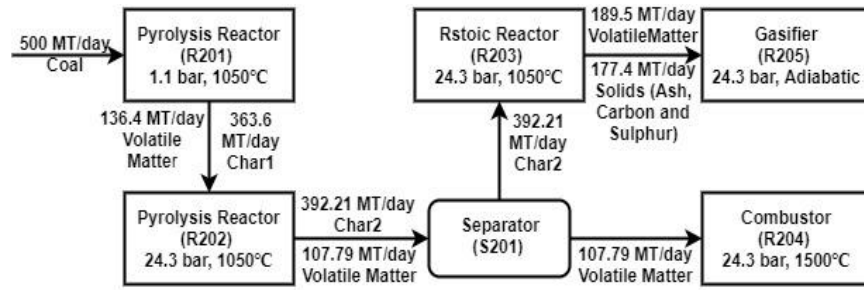


Figure 9 Flow diagram of coal and char pyrolysis with quantified streams and reaction conditions.

The first pyrolyzer R201 is operated at 1050°C and 1.1 bar and the coal is converted into 136.4 MT/day of volatile matter and 363.6 MT/day of char1. The second pyrolyzer R202 converts char1 into char2 at 24.3 bar. After the two-step coal pyrolysis, 500 MT/day of coal is converted to 107.79 MT/day of volatile matter and 392.21 MT/day of char2. The two-phase outputs from R202 are separated by a separator S201. The volatile matter goes to the combustor and the solid phase char2 enters an R-stoic reactor (R203) where the char2 pyrolysis takes place represented by reaction (R2).



The stoichiometric parameters of R2 are determined by the subroutine USRKIN. The Redlich Kwong Soave (RKS) thermodynamic model is applied. Table 2 displays the components' attributes of coal and char1. Components attribute of char2 is estimated by the element mass conservation by the subroutine USRKIN.

Table 2 Component attributes of Powder River Basin (PRB) coal and char1 in wt% [32]

Proximate Analysis, wt%			Ultimate Analysis, wt%			Sulfur Analysis, wt%		
Element	Coal	Char1	Element	Coal	Char1	Element	Coal	Char1
Moisture	29.2	0	C	49.65	41.8	Pyritic	0.06	0.07
Fixed carbon, db*	55.0	41.8	H	6.72	1.41	Sulfate	0.06	0.07
Volatile matter, db	40.0	51.48	N	0.73	0.52	Organic	0.06	0.07
Ash	4.88	6.72	O	37.7	48.1			
			S	0.32	1.21			
			Ash	4.88	6.72			

\*db: dry base

In the coal pyrolysis, two R-yield reactors are used. These reactors require the yields of the components of the product to simulate the pyrolysis reactions. The yields of char1 come from the experimental data. [35, 36] The adjusted yields are calculated by Eq. (1) in the user subroutine USRPRES. All the relative compositions of gas components are treated as constant.

$$Y_2 = Y_1(1 - a \ln P_t) \quad (1)$$

where  $Y_1$  is the total yield of gaseous products at 1.1 bar,  $Y_2$  is the total yield of gaseous products at the pressure of system  $P_t$ , and  $a$  is a constant which is 0.066 in this model. The yields of char1 and char2 are listed in Table 3.

*Table 3 Estimated yields of coal pyrolysis products in reactors R201 and R202 used in the model.*

Components	Yield %wt at 1.1 bar in R201, Char1	Yield %wt, at 24.3 bar in R202 using Eq. (1), Char2
Char	0.7272	0.7844
CO	0.0059	0.0047
H <sub>2</sub>	0.0084	0.0066
CO <sub>2</sub>	0.003	0.0024
H <sub>2</sub> O	0.0079	0.0062
H <sub>2</sub> S	0.0094	0.0075
N <sub>2</sub>	0.0035	0.0028
CH <sub>4</sub>	0.1637	0.1293
C <sub>6</sub> H <sub>6</sub>	0.071	0.0561
Total	1	1

### 3.2.2 Oxy-Combustion

After coal and char pyrolysis processes, the gaseous products from the pyrolysis reactor R202 are fed into the combustor R204 where oxy-combustion takes place (Figure 9). 107.79 MT/day of gaseous product burned completely in 383.99 MT/day of oxygen at 1200 °C and 24.3 bar. Reactions R3 to R6 show the major reactions in reactor R204.





The reactions are fast at the high temperature and the conversion of each reactant is regarded as 100%. The oxy-combustion converts the hydrocarbon to carbon dioxide and water and helps the char gasification to occur as shown in Figure 10.

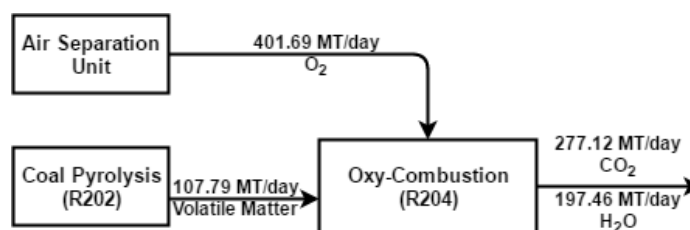


Figure 10 Flow diagram of oxy-combustion with inputs and outputs.

### 3.2.3 Char Gasification

Char gasification takes place in an R-Plug reactor R205 representing an entrained flow coal gasifier. The feed is at 1050 °C and 24.3 bar and contains 491.78 MT/day of mixed gas with mainly CO<sub>2</sub> and H<sub>2</sub>O produced by oxy-combustion, 10 MT/day of additional steam generated by Steam Generation Unit (SGU) and 392.20 MT/day of gas-solid mixture coming from char pyrolysis in reactor R203. The gasifier operates at 1500°C and 24.3 bar. At the outlet of the gasifier, 899.33 MT/day of syngas is produced which includes 47.75% CO, 1.46% H<sub>2</sub>, 22.03% H<sub>2</sub>O, 28.76% CO<sub>2</sub> and little of CH<sub>4</sub> and N<sub>2</sub>. Meanwhile, 5.57 MT/day of coal residue containing 5.28 MT/day of sulfur, 0.29 MT/day of carbon and 25.31 MT/day of ash are produced. Table 4 shows the inputs and outputs of the gasifier R205. According to Table 4, the input and output of solid carbon are 172.06 MT/day and 0.29 MT/day respectively. The carbon conversion is improved to 99.8% by using entrained flow coal gasifier.

Table 4 Mass flow of inputs and outputs of gasifier.

Char Gasification	Input	Output
Temperature, °C	1111.81	1500
Pressure, bar	24	24
Mass Flow, MT/day		
O <sub>2</sub>	205.99	0
CO	0	416.98
H <sub>2</sub>	11.05	12.72
CO <sub>2</sub>	277.12	251.23
H <sub>2</sub> O	207.46	192.43
H <sub>2</sub> S	3.71	3.78
N <sub>2</sub>	22.15	22.15
CH <sub>4</sub>	0	0.05
C	172.06	0.29
S	5.34	5.28
ASH	25.31	25.31

Ten reactions R4 to R13 are considered in the char gasification and displayed in Tables 5 to 7.

Reactions R7 to R11 are heterogeneous, while others are homogeneous. The heterogeneous reactions involve the solid carbon and sulfur reacted the with the gaseous phase at the surface. The accuracy of the predicted product distribution is highly dependent on the kinetic data used [18,34]..

All the heterogeneous reactions are assumed to be surface reactions. As a consequence, the unreacted-core shrinking model is utilized to be compatible with the kinetic data [40]. According to this model, ash layer diffusion, gas film diffusion effects, and chemical reaction effects are considered. The overall reaction rate of heterogeneous reactions is expressed by:

$$J_r = \frac{1}{\frac{1}{k_{\text{diff}}} + \frac{1}{k_s y^2} + \frac{1}{k_{\text{d,ash}} \left( \frac{1}{y} - 1 \right)}} (P_i - P_i^*) \quad (2)$$

where  $J_r$  is the reaction rate in g carbon/(cm<sup>2</sup> of coal particle surface  $s$ ),  $k_{\text{diff}}$  is the gas film diffusion constant.  $k_s$  is the surface reaction constant.  $k_{\text{d,ash}}$  is the ash film diffusion constant which depends on  $k_{\text{diff}}$  and ash layer voidage  $\epsilon$ :  $k_{\text{d,ash}} = k_{\text{diff}} \epsilon^n$ , where  $n$  is a constant between 2 and 3 [38]. In this

work,  $\mathcal{E}$  is equal to 0.75, and  $n$  is 2.5.  $y$  is expressed by  $y = r_c / r$  where  $r_c$  and  $r$  represent the radius of the unreacted core and the radius of the entire particle containing the ash layer.  $P_i - P_i^*$  is the partial pressure of  $i$ th-component considering the reverse reaction [35,37]. Table 5 lists the heterogeneous reactions and their kinetic data. Table 6 shows the values of  $K_{eq}$  of Reactions 8, 10 and 11 [35]. In this model, the chemical equilibrium is estimated in a single R-Gibbs reactor which will provide the data of components during the gasification. At the same time, homogeneous reactions take place in the gasifier. Table 7 displays the kinetic data for these reactions which are used in the user subroutine USRKIN. All the heterogeneous reaction rates are in the unit of kmole/(m s).

Table 5 Kinetic data of the heterogeneous reactions, [34, 35] where  $T$  is the temperature,  $P_t$  is the total pressure, and  $d_p$  is the diameter of coal particle which is 500  $\mu\text{m}$ ,  $P_i, P_i^*$  are the partial pressures, atm

No.	Reactions	$k_{\text{diff}}$	$k_s$	$P_i - P_i^*$
R7	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	$\frac{0.292 \left( \frac{4.26}{T} \right) \left( \frac{T}{1800} \right)^{1.75}}{P_t d_p}$	$8710 e^{\frac{17967}{T}}$	$P_{\text{O}_2}$
R8	$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	$\frac{1.0 \times 10^{-4} \left( \frac{T}{2000} \right)^{0.75}}{P_t d_p}$	$247 e^{\frac{-21060}{T}}$	$P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2} P_{\text{CO}}}{K_{eq}}$
R9	$\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$	$\frac{7.45 \times 10^{-4} \left( \frac{T}{2000} \right)^{0.75}}{P_t d_p}$	$247 e^{\frac{-21060}{T}}$	$P_{\text{CO}_2}$
R10	$\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$	$\frac{1.33 \times 10^{-3} \left( \frac{T}{2000} \right)^{0.75}}{P_t d_p}$	$0.12 e^{\frac{-18041}{T}}$	$P_{\text{H}_2} - \left( \frac{P_{\text{CH}_4}}{K_{eq}} \right)^{1/2}$
R11	$\text{S} + \text{H}_2 \rightarrow \text{H}_2\text{S}$	$\frac{1.33 \times 10^{-3} \left( \frac{T}{2000} \right)^{0.75}}{P_t d_p}$	$0.12 e^{\frac{-17921}{T}}$	$P_{\text{H}_2} - \frac{P_{\text{H}_2\text{S}}}{K_{eq}}$

Table 6 Equilibrium constants  $K_{eq}$  of Reactions 8, 10 and 11 [35]



Reactions	Reaction	$K_{eq}$
8	$C + H_2O \rightarrow CO + H_2$	$K_{eq} = e^{\frac{17.644T - 16811}{T}}$
R10	$C + 2H_2 \rightarrow CH_4$	$K_{eq} = 5.12 \times 10^{-6} e^{\frac{10222}{T}}$
R11	$S + H_2 \rightarrow H_2S$	$K_{eq} = e^{\frac{-5.0657T - 18557.73}{T}}$

### 3.3 Steam Generation

Steam is partially used as the gasifying agent in the entrained-flow gasifier. The entire process also requires steam as the utility which will be purchased from the utility department. Steam generation unit supplies the steam required in coal gasification. At 1.01 bar and 25°C, 10MT/day of boiler water is fed into a boiler to produce steam. The boiler consumes 14.58 MW of the heat and produces 10 MT/day of steam at 300°C and 1.01 bar. The steam is used as the intermediary in the entrained flow coal gasifier. As the heat streams Q1 and Q2 are utilized as a part of heat integration, this helps reduce the cost of operation and GHG emissions. The PFD and the stream table are displayed in Figure A3 and Table A3 in the Appendix.

Table 7 Reaction rates of homogeneous reactions.

Reaction	Reaction Rate: kmol/m <sup>3</sup> s	References
R3 $H_2 + 0.5O_2 \rightarrow H_2O$	$J_{r3} = 2.85 \times 10^{16} e^{\frac{-20130}{T}} [O_2]^{1.5} [H_2]^{0.25}$	[38]
R4 $CO + 0.5O_2 \rightarrow CO_2$	$J_{r4} = 1.0 \times 10^{17.6} e^{\frac{-20130}{T}} [CO][H_2O]^{0.5} [O_2]^{0.25}$	[39]
R5 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$J_{r5} = 5.44 \times 10^{12} e^{\frac{-24358}{T}} [CH_4]^{0.3} [O_2]^{1.3}$	[40]
R12 $H_2O + CO \leftrightarrow H_2 + CO_2$	$J_{r12} = 7.4 \times 10^8 e^{\frac{-36676}{T}} ([CO][H_2O] - [CO_2][H_2]/K_{15})$ $K_{12} = f \cdot 0.0265 e^{\frac{3968}{T}}, f = 1.11$	[41, 42]
R13 $CH_4 + H_2O \leftrightarrow CO + 3H_2$	$J_{r13} = 3.0 \times 10^8 e^{\frac{-15100}{T}} ([CH_4][H_2O] - K_{16}[CO][H_2])$ $K_{13} = 5.12 \times 10^{-14} e^{\frac{-27347}{T}}$	[38]

\* $f$  is a multiplier factor for the equilibrium constant of Reaction (R12).  $T$  is temperature, K;  $d_p$  is the diameter of coal particle,  $\mu m$ .

### 3.4 Power Production

Currently in the US, using coal to generate electricity is still a considerable option. Although the concern about the greenhouse gas emission and other environmental issues is growing, utilization of coal for power generation is still the trend in the foreseeable future due to its cheap price and vast reserves. US Energy Information Administration (EIA) [43] collects the preliminary data for electricity generation by different energy sources for 2016 (Figure 11). 30.4 % of US electricity power is produced by coal by 2016. As the conscious of environmentally friendly and green become strong, developing clean coal technologies to generates electricity is placed on the agenda.

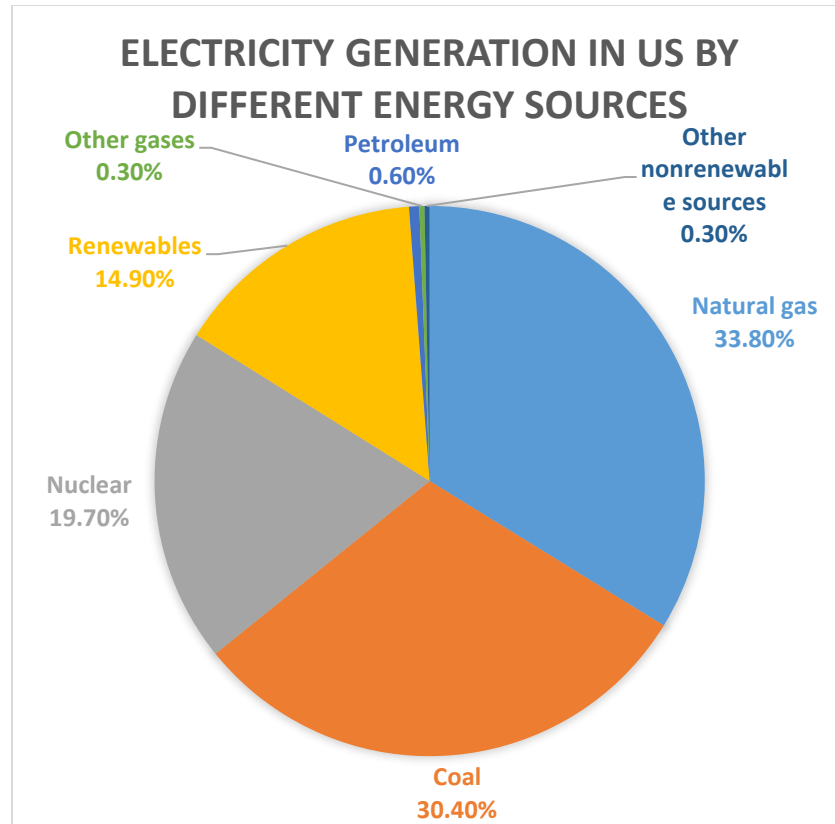


Figure 11 Electricity generation in US by different energy sources [43].

In traditional coal power plants, milled coal fines are burned in the pulverized coal combustion (PCC) system. A boiler utilizes the produced heat and hot gas convert water into steam, and the expand of steam drives the blades of turbine rotates at very high speed and generates electricity.

Things have changed since people have started to realize the economic value of co-production and multiple chemical processes coupled with electricity generation from coal. As a result, syngas and other chemical production are combined with conventional power production plants.

In this integral coal-based combined cycle power plant, part of the heat that comes from the combustor, pyrolysis, and methanol production is used in the power generation unit. The product of the coal gasification is mostly hot syngas which carries large amounts of heat, which can be used to produce electricity with a gas turbine. 2495 MT/day of recycling water is used as steam and cooling water. Two steam turbines and one gas turbine are utilized. Figure 12 shows the block flow diagram for the power production unit.

2270 MT/day of recycling water is pumped by P1 at 25°C and 1.01 bar to the boiler, which operates at 120 bar. 101.82 MW of heat gathered from coal gasification unit, steam generation, and methanol production unit is used in the boiler to convert the water to the steam used in the first steam turbine (T1) to generate 27.32 MW of electricity. At the same time, the hot gas produced by the coal gasification unit is injected into a gas turbine (T2) which generates 11.51 MW of electricity as the temperature of the hot syngas decreased from 1500 °C to 827 °C. The heat in the discharged gas is used to convert 225 MT/day of water to the steam by the heat exchanger H<sub>2</sub>. The hot steam that comes from heat exchanger H<sub>2</sub> drives another steam turbine T3 and generates 1.27 MW of electricity. The total outlet is 40.11 MW of electricity and 880.80 MT/day of syngas which is at 350 °C and 1 bar (Table 8). 7.2 MW of heat is carried by cooling water in the condensers and will be treated as a source for resident heating source instead of discharging directly into the environment. Considering all the utilities usage and consumed energy in power production, the efficiency of this power generation unit is calculated as 31.24%. According to the data from NETL [44], IGCC power plant with CO<sub>2</sub> capture has an efficiency of 32.6% and 31.0% for the GE radiant-only plus quench gasification-based IGCC with carbon capture and E-Gas<sup>TM</sup> two-stage gasification-based IGCC with carbon capture, respectively.

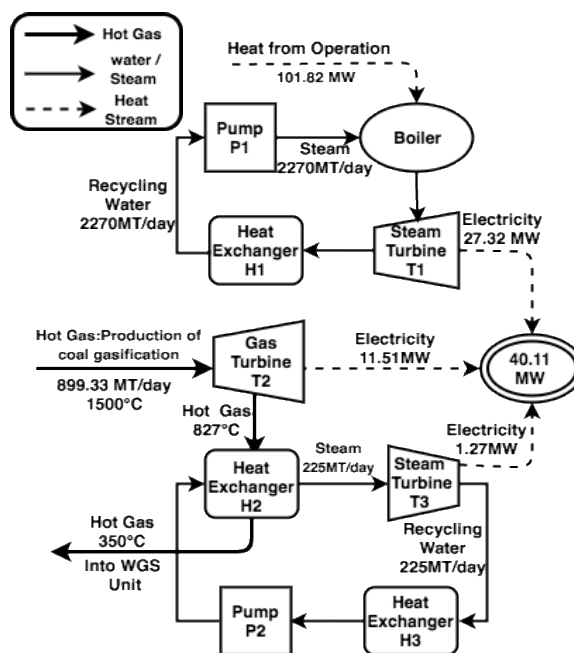


Figure 12 Block flow diagram of power production unit.

Table 8 Heat streams for power production.

Heat stream MW		
Input	Q2	40.55
	Q3	0.144
	Q4	51.74
	Q5	3.952
	Q6	5.427
Heat		101.82
Output	W1	27.32
	W2	11.51
	W3	1.27
Electricity		40.11

### 3.5 Water Gas Shift Unit

Using syngas to produce methanol is a traditional method in the chemical industry. However, methanol synthesis needs reactants with a high portion of  $H_2$  and a Water-Gas-Shift (WGS) unit can produce  $H_2$ -rich syngas for methanol production.

The gas mixture coming from coal gasification is injected into the WGS unit. The main components are  $CO$ ,  $H_2$ ,  $CO_2$ , and  $H_2O$ . Other impurities such as waste gas and solid residue are

removed in advance in the coal gasification unit. The inlet mixture consists of 416.67 MT/day of CO, 12.74 MT/day of H<sub>2</sub>, 251.72 MT/day of CO<sub>2</sub>, 192.20 MT/day of H<sub>2</sub>O. The process flow diagram and the stream table of WGS unit are shown in Figure A4 and Table A4 within the Appendix.

The hot gas coming from the power production goes to an equilibrium reactor where WGS reaction R14 occurs at 350 °C and 1 bar. [45]



R14 is an equilibrium and endothermic reaction. An R-equil reactor is utilized to simulate this process. Conversion of H<sub>2</sub> increases as temperature goes up. The utilization of the catalyst is essential for a proper selectivity. Both the high and low temperatures catalysts are available commercially. In this work, the reactions at the WGS occur at 350°C and 1.01 bar and uses Fe<sub>3</sub>O<sub>4</sub>/Cr<sub>2</sub>O<sub>3</sub> as the catalyst [45]. At the exit of WGS reactor, 168.45 MT/day of CO, 30.61 MT/day of H<sub>2</sub>, 641.72 MT/day of CO<sub>2</sub> and 32.55 MT/day of H<sub>2</sub>O are produced. 28.80 MT/day of water is separated by condensing from mixed gas at 5 °C and can be used or sold as cooling water. The rest of the mixture is fed to the carbon capture and sulfur removal unit where the selexol, which is hydrophilic solvent, is used as the solvent.

### 3.6 Carbon Capture and Sulfur Removal Unit

Carbon capture and sulfur removal in coal-based gasification are called acid gas removal. This operation removes redundant CO<sub>2</sub> in the syngas and adjusts the contents of reactants gas for methanol production. It also makes a great contribution to the remission of global warming. How to capture and store carbon from industry-scale fossil power plant is critical. Clarification of carbon path and especially the CO<sub>2</sub> path would help to control and therefore reduce the emission.

Figures 13 and 14 show the paths of the carbon and CO<sub>2</sub> in the entire process, respectively.

The main approaches are pre-combustion CO<sub>2</sub> capture, oxy-combustion CO<sub>2</sub> capture, and post-combustion CO<sub>2</sub> capture. [46] In this study, post-combustion CO<sub>2</sub> capture technology is applied and 589.76 MT/day of CO<sub>2</sub> is captured, compressed, and transported to a prepared storage site [47].

Selexol is used as a solvent, which is based on poly (ethylene glycol) dimethyl ether (PEGDME) and can efficiently capture  $\text{CO}_2$  and  $\text{H}_2\text{S}$  from lighter gases including  $\text{H}_2$  [48]. Using a hydrophobic solvent such as PEG-siloxane-1 has an only minimal effect on the cost of carbon capture [49]. Remaining gas mixture containing mainly  $\text{CO}$ ,  $\text{H}_2$  and  $\text{CO}_2$  is used as the feedstock for methanol production (see Figure 14).

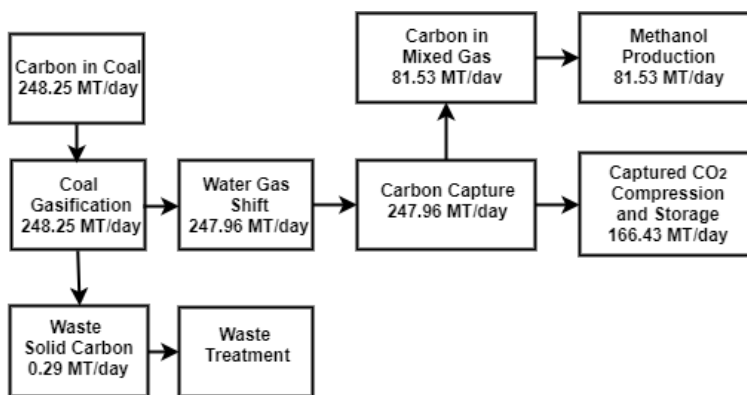


Figure 13 The pathway of element carbon (C) in the entire process.

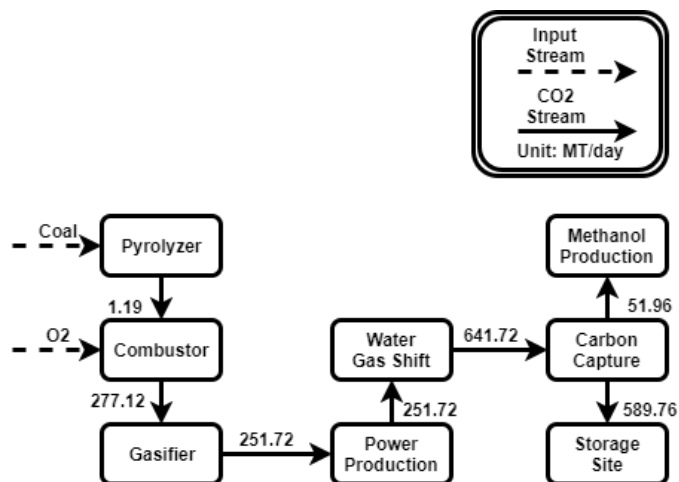


Figure 14 The path of carbon dioxide in the entire process with unit of MT (metric tons)/day.

The mixed gas in the inlet of carbon capture and sulfur removal unit consists of 168.45 MT/day of  $\text{CO}$ , 641.72 MT/day of  $\text{CO}_2$ , 30.61 MT/day of  $\text{H}_2$ , 3.78 MT/day of  $\text{H}_2\text{S}$  and 3.75 MT/day of water. This unit contains two absorbers, one stripper, a three-stage flash system and a condenser. One absorber absorbs  $\text{H}_2\text{S}$  by  $\text{CO}_2$ -rich Selexol solvent, while the absorber captures  $\text{CO}_2$  by lean and

semi-lean Selexol [48]. At the same time, a stripper regenerates and recycles Selexol. An  $H_2S$  condenser concentrates the  $H_2S$  from a  $CO_2$ -rich gas by purged air. The stage flash drums regenerate the  $CO_2$ -rich selexol [49]. 3.78 MT/day of  $H_2S$  and 589.76 MT/day of  $CO_2$  is removed from syngas by 4145.61 MT/day selexol. The ratio of  $H_2$  to  $CO$  of two is attained to produce methanol. Over 92% of  $CO_2$  is captured and most of the  $H_2S$  is removed to guarantee a clean reaction environment for methanol production. Captured  $CO_2$  is compressed by the multi-stage compressor to 120 bar, 46°C in the final stage in a liquid phase [50]. Figure 15 shows the block flow diagram of carbon capture and sulfur removal unit. The stream table and process flow diagram are shown in Table A5 and Figure A5, respectively in the Appendix.

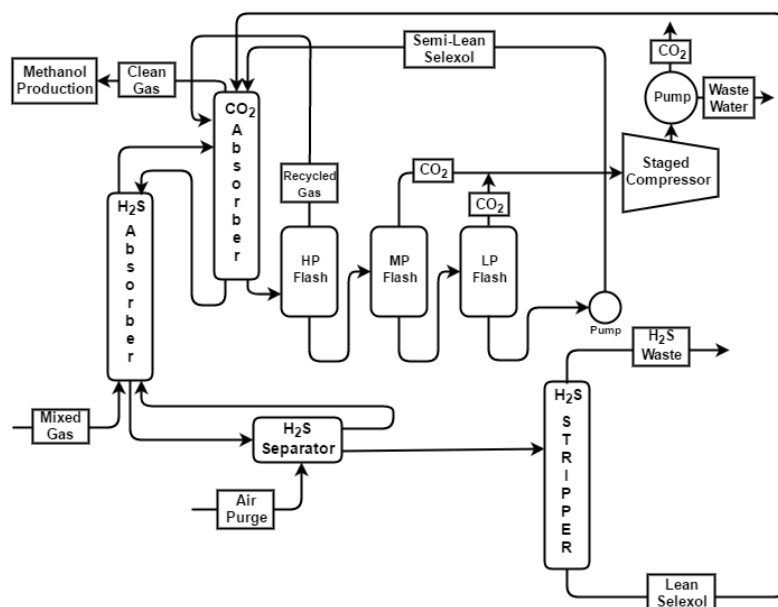


Figure 15 Block flow diagram of carbon capture unit. [49]

### 3.7 Methanol Production

Methanol is emerging as an alternative fuel due to its storage and transportation properties [51]. As the economy develops and industry progresses, the demand and price for global methanol may expand as shown in Figure 16. With over 90 plants worldwide the current production capacity is nearly 100 million metric tons [52-54].

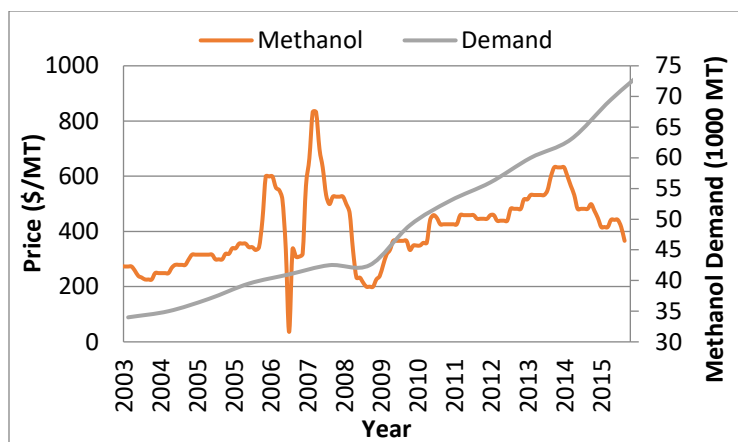


Figure 16 Methanol price and demand in recent history [55, 56, 61].

The demand for methanol is likely to increase by years. Methanol is a valuable chemical which is widely used in different areas. Figure 17 displays the distribution of the use of methanol in 2015. Methanol is a valuable feedstock of producing formaldehyde, acetic acid, biodiesel, and many other chemicals. Methanol is also a valuable solvent in different chemical operations.

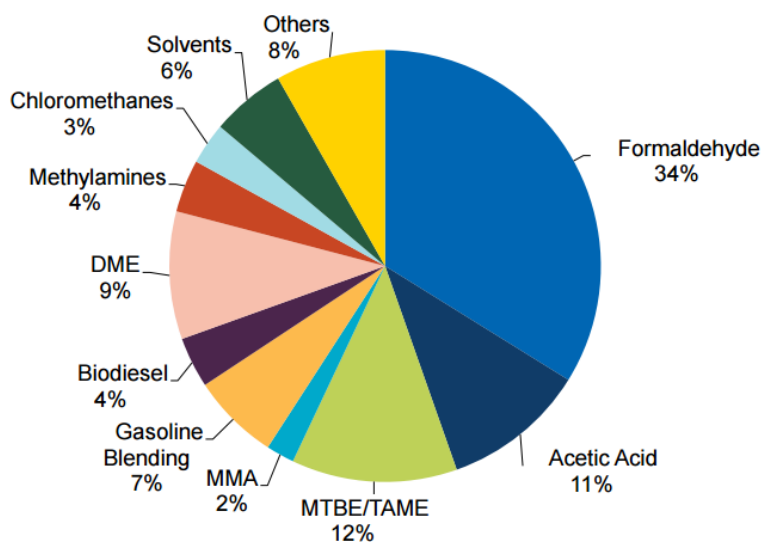
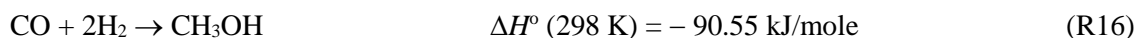
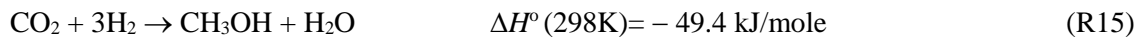


Figure 17 Methanol use in 2016 [55]

To produce methanol is becoming another way out for increasing profits and reduce CO<sub>2</sub> emission.



Typically, the entire process of methanol production from syngas can be described in four steps: syngas production, syngas reforming, methanol synthesis, and purification. In this work, pre-treated and cleaned syngas is used for methanol production based on the following reactions [56,57].



A stoichiometry factor  $S = \frac{\text{H}_2 - \text{CO}_2}{\text{CO}_2 + \text{CO}} \approx 2.0$  [58] was maintained for a high yield of methanol synthesis. The WGS unit is designed to produce enough hydrogen, while carbon capture and sulfur removal unit is built to remove a certain amount of  $\text{CO}_2$  and sulfur.

An R-stoic reactor representing the Lurgi reactor [56, 57, 59] is used to simulate the synthesis of methanol at 260 °C and 50 bar. Conversion is high for the overall process using reactions R15 and R16 and a Cu-based catalyst Cu/ZnO/ZrO<sub>2</sub> ZnO on an Al<sub>2</sub>O<sub>3</sub> support due to its high selectivity [45, 53, 60]. Based on the literature research, the conversion of  $\text{CO}_2$  of 98% can be achieved at 260°C and 50 bar, while the conversion of CO in reaction R16 approaches to a peak value of 52% [45]. Figure A6 and Table A6 within the Appendix show the process flow diagram and stream table, respectively for the methanol production. This plant uses 29.89 MT  $\text{H}_2$ /day, 157.17 MT CO/day and 51.96 MT  $\text{CO}_2$ /day, and produces 207.99 MT methanol/day at 99.8 wt% together with 30.59 MT/day of 99%  $\text{H}_2\text{O}$  waste water. The RSK thermodynamic model is used. The mixed gas at 134°C and 1 bar is cooled down to 25°C, and compressed into 50 bar. The mixed gas is injected into the main reactor R701. The outlet of the reactor goes into a flash separator after cooled down by another heat exchanger at 70°C. The amount of heat recovered is 5.427 MW and used in the boiler in power production unit to generate steam. The methanol is purified in a distillation column, while the rest of the unreacted mixture is compressed and recycled to the reactor. The column has 20 stages with sieve trays, the feed enters at stage 14. The column has a partial condenser operating at 61.7 °C. A recent publication has indicated that “Methanol production has the potential for the best possible technology deployment ranging from 16% to 35%.” [20, 45, 56] The methanol and

water are cooled by the heat exchangers to the storage temperatures. Column specifications and operating conditions are present in Table. 9.

*Table 9 Column specifications and results for column in the methanol production [18]*

Column configurations	Value
Stages	20
Feed stage	14
Height (m)	12.92
Diameter (m)	1.88
Reflux ratio (molar)	1.16
B:F* (molar)	0.48
Condenser temp (°C)	62.32

\*B:F Bottom flow to feed ratio

### 3.8 Results

Several optimization tools of the Aspen Plus package including ‘Energy Analysis’, sensitivity analysis, design specs, and optimization with constraints are applied.

#### 3.8.1 Optimization

Optimization block is based on the objective function for maximized power production (see Figure 12) by varying the recycling water amount under the constraint of the steam temperature. The optimized rate of electricity is eventually achieved as 40.11 MW.

#### 3.8.2 Sustainability

Sustainability analysis helped evaluate the feasibility of the plant. It presents three primary indicators, which are the material indicator, energy indicator, and environment impact indicator. In this analysis, the main sustainability indicators are the usage of nonrenewable material, nonrenewable energy, fresh water, and rate of GHG emissions. The environmental impact indicators are estimated by the Carbon Tracking method based on the CO<sub>2</sub>e emission factor data source of US-EPA-RULE-E9-57 and the ultimate fuel source of natural gas [18]. Sustainability metrics below are estimated by normalizing the sustainability indicators with respect to the unit amount of production

$$\text{Material intensity} = \frac{\text{Nonrenewable material depleted}}{\text{Unit amount of product}} \quad (3)$$

$$\text{Water intensity} = \frac{\text{Freshwater depleted}}{\text{Unit amount of product}} \quad (4)$$

$$\text{Energy Intensity} = \frac{\text{Nonrenewable energy utilized}}{\text{Unit amount of product}} \quad (5)$$

$$\text{Environmental Impact Intensity} = \frac{\text{Carbon dioxide equivalent emissions}}{\text{Unit amount of product}} \quad (6)$$

The coal gasification facility consists of an Air Separation Unit (ASU), steam generation unit, coal gasification unit, Water Gas Shift (WGS) unit, carbon capture unit, methanol production and power production unit. Table 10 shows the sustainability indicators of the entire process.

*Table 10 Sustainability indicators for integral clean-coal technology with methanol production.*

<b>Material usage</b>	ASU, Coal gasification, Steam prod, and WGS with Carbon capture	Methanol Prod.	Power Prod.
Water Input, MT/day	10		2495
Coal Input, MT/day	500		
Air Input, MT/day	2231.02		
O <sub>2</sub> input, MT/day	401.69		
Syngas input, MT/day		239.19	
Steam production, MT/day	10		
CO <sub>2</sub> production, MT/day	589.76		
Water production, MT/day	28.80	30.59	2495
Oxygen production, MT/day	401.69		
Nitrogen production, MT/day	1309.33		
Methanol production, MT/day		207.99	
Electricity production, MW			40.11
Syngas production, MT/day	880.80		
<b>Energy usage</b>			
Total heating utility, MW	111.06	0.98	0
Total cooling utility, MW	30.18	15.25	81.29
Electricity utility, MW	14.76	2.011	0.45
Total utility energy (heating+cooling+electricity), MW	156	18.24	81.74
Total heating cost, \$/h***	1679.41	10.14	0
Total cooling cost, \$/h	102.92	65.71	63.51
Electricity cost, \$/h	1094.62	155.91	31.78
Total cost (heating+cooling+electricity), \$/h	2876.59	231.76	95.29
<b>Carbon emissions</b>			

Net stream CO <sub>2</sub> e, MT/day	641.71	-51.95	0
Utility** CO <sub>2</sub> e, MT/day	637.65	22.33	2.43
Captured CO <sub>2</sub> e, MT/day	589.76		
Total Discharged CO <sub>2</sub> e, MT/day	637.65	-29.62	2.43
Net carbon fee, \$/day	6376.50	296.2	24.3

\*US-EPA-Rule-E9-5711; coal-bituminous; carbon fee: \$10/MT. ASU: Air separation unit

\*\* Fuel source: natural gas

\*\*\* All the costs are for US\$ 2016

CSS; carbon capture and storage

The net stream CO<sub>2</sub>e and total CO<sub>2</sub>e are high in this integrated clean-coal technology, mainly due to productions of CH<sub>4</sub> and N<sub>2</sub>O that are intensive GHGs. The total GHG emission is around 847.63 MT/day, of which 207.99 MT/day of CO<sub>2</sub>e is consumed by methanol production, 589.76 MT/day CO<sub>2</sub> is captured liquefied and stored which can be used, for example, in enhanced oil recovery. The integral facility requires 500 MT coal/day, 10 MT H<sub>2</sub>O/day and 2231.02 MT air/day in total and produces 207.99 MT methanol/day and 40.11 MW of electricity.

Table 11 presents the sustainability metrics in which the integral clean-coal technology power plant is compared with a conventional IGCC power plant of which the capacity is 339MW by utilizing 3020.17 of Powder River Basin as a feedstock [18,32]. Table 11 also compares the syngas-based methanol production in this study with the methanol production using renewable CO<sub>2</sub> and H<sub>2</sub>. [20].

The material intensity metrics show that the integrated clean-coal technology power plant with methanol production requires 0.52 MT coal to generate 1 MWh of electricity and the conventional IGCC power plant requires 0.37 MT coal to generate 1 MWh of electricity. One of the reasons for this difference is due to the different type of coals that the plants utilize. With the different ultimate analysis of the coals, the amounts of the coal and process water required are consequently different from each other. The energy intensities based on the use of natural gas for the utilities, as well as the energy of coal are 50% and 40% higher, respectively in the clean coal technology analyzed in this study. This may be due to the types of the coal used in the processes.

The environmental impact metrics show that the integral clean-coal technology power plant with methanol production produces 0.75 MT CO<sub>2</sub>e/MWh electricity that corresponds around 60% reduction. Considering the IGCC as the base case, the CO<sub>2</sub>e emission in the clean-coal plant is lower than the base cases. As expected, methanol production from renewable hydrogen and CO<sub>2</sub> can reduce the GHG emission.

*Table 11 Sustainability metrics for the integral clean-coal technology with methanol production and IGCC power plant (base case) [16, 18, 20, 65]*

	Clean-coal technology power plant (This Work)	IGCC power plant with ammonia production (Base Case) [18]	Methanol prod. by syngas (This Work)	Renewable Methanol prod. by CO <sub>2</sub> and H <sub>2</sub> (Base Case) [20]
<b>Material Intensity</b>				
Coal used/Unit electricity, MT/MWh	0.52	0.37		
Air used/Unit electricity, MT/MWh	1.79	1.41		
H <sub>2</sub> O used/Unit electricity, MT/MWh	0.01	0.60		
H <sub>2</sub> used/Unit methanol, MT/MT			0.14	0.19
CO <sub>2</sub> used/Unit methanol, MT/MT			0.25	1.43
CO used/Unit methanol, MT/MT			0.75	0
<b>Energy Intensity</b>				
Net utility duty/Unit product,	5.93 MW/MW	3.07 MW/MW	0.09 MW/MT	0.39 MW/MT
	electricity	electricity	MEOH	MEOH
Input coal energy /Unit product,	2.91 MW/MW	2.08 MW/MW	0.56 MW/MT	N/A
	electricity	electricity	MEOH	
<b>Environmental Impact Intensity</b>				
Total CO <sub>2</sub> e/Unit product,	0.75 MT/MWh	1.91 MT/MWh	-0.14 MT/MT	-0.97 MT/MT
			MEOH	MEOH
Net carbon fee*/Unit product	10.5 \$/MWh	20.9 MT/MWh	-1.40 \$/MT	-9.68 \$/MT
			MEOH	MEOH

\* US\$ 2016; Carbon fee: \$10/MT

### 3.8.3 Economic Analysis

The economic analysis of the integral clean-coal technology is accomplished by CAPCOST, and present the result by the discounted cash flow diagrams (DCFD). Conventional IGCC may operate

longer time, however, considering the catalyst life utilized in the methanol production, the useful life of the entire plant in this work is adjusted into 20 years.

Purchase costs are estimated by the CAPCOST programming [25]. Fixed capital investments (FCI), cost of land and working capital are estimated based on the FCI. Working capital is 20% of the FCI. Chemical Engineering Plant Cost Index (CEPCI-2017) (= 550.1) [26] is updated by 2017. CEPCI is utilized to estimate the costs and capacity by equation 8.

$$\text{Cost}_{\text{New}} = \text{Cost}_{\text{New}} \frac{\text{CEPCI}_{\text{New}}}{\text{CEPCI}_{\text{Old}}} \left( \frac{\text{Capacity}_{\text{New}}}{\text{Capacity}_{\text{Old}}} \right)^x \quad (8)$$

where  $x$  is the capacity factor, which is usually assumed to be 0.6 known as the six-tenths rule [25].

The economic analysis applied the Maximum Accelerated Cost Recovery System (MACRS) as the depreciation method with a 10-year of recovery period. According to the DCFD, Net Present Value (NPV), Payback Period (PBP), and Rate of Return (ROR) are calculated and included in the multi-criteria decision matrix as the economic indicators. Table 12 shows the unit costs of various utilities.

Table 12 Unit energy cost for various utilities [18]

Utility Name	Utility Type	T <sub>in</sub> °C	T <sub>out</sub> °C	CO <sub>2</sub> emission factor data source	Energy/Purchase price (US\$/Unit)
CW	Water	15	24	N/A	5×10 <sup>-3</sup> \$/MT
ELE	Electricity	N/A	N/A	Natural Gas	1.95×10 <sup>-2</sup> \$/MJ
FH1000	Coal	1000	400	Natural Gas	4.35×10 <sup>-3</sup> \$/MJ
FH2000	Coal	2000	400	Natural Gas	6.49×10 <sup>-3</sup> \$/MJ
RF	Refrigerator	-24	-25	Natural Gas	2.71×10 <sup>-3</sup> \$/MJ
AIR	Air	25	20	N/A	0
LPS	Steam	125	124	Natural Gas	2.19×10 <sup>-3</sup> \$/MJ
HPS	Steam	250	249	Natural Gas	19.65 \$/MJ

CW: Cooling water; ELE: Electricity; LPS: Low-pressure steam; HPS: High-pressure steam; FH1000: Fired heater 1000 °C inlet temperature; FH2000: Fired heater 2000 °C inlet temperature. RF: Refrigerator

At the current capacities, the total capital cost is estimated to US\$366.23 million (2016 US\$) for the entire integrated clean-coal technology power plant with methanol production. The FCI is US\$ 288.37 million, land cost is US\$5.76 million, and the working capital is US\$72.09 million. The

estimated annual revenue is around US\$ 156.75 million. The raw materials are the PRB coal, air, and water. The price of the PRB coal is \$11.5/MT [61]. The waste water, nitrogen, steam, surplus oxygen, and captured CO<sub>2</sub> are also considered as byproducts besides electricity and methanol. The value of revenue is based on the selling price of all the products [62,63]. Table 13 lists all the economic data.

The DCFD is based on the data given in Table 13. The values of NPV is around US\$ 83.37 million, the PBP is around 15.1 years, while ROR is 5.74 and indicate that all the economic criteria are favorable. Figure A7 and Table A7 in the Appendix display the DCFD based on the data with depreciation. Table A8 lists the probable variations of some major economic parameters, while Figure A8 shows the stochastic economic feasibility criteria of NPV, PBP, and ROR in probability densities estimated by the Monte-Carlo simulations. The stochastic economic analysis shows that the plant is also feasible.

*Table 13 Economic data applied in CAPCOST [25,64]. The cost values are shown in million (MM)US\$ (2016)*

Taxation Rate	25%
Annual Interest Rate	4%
Salvage Value	0
Cost of Land (CL), MM\$/year	5.00
Fixed Capital Investment (FCI), MM\$/year	288.37
Working Capital (WC), MM\$/year	72.09
Annual Revenue, MM\$/year	156.75
Raw Materials Costs, MM\$/year	2.08
Cost of Utilities, MM\$/year	26.15
Waste Treatment Costs, MM\$/year	7.42
Cost of Operating Labor, MM\$/year	1.8
Cost of Manufacturing, MM\$/year	119.65
Useful life of operation, years	20
Construction, years	3
Ney Present Value(NPV), MM\$	83.37
Discounted Cash Flow Rate of Return(ROR), MM\$	5.74%
Discounted Payback Period, years	15.1
Total Capital Cost*, MM\$/year	366.23

\* Total Capital Cost = FCI + WC +CL

### 3.8.4 Life Cycle Assessment

The Life Cycle Assessments (LCA) of integrated clean coal gasification power plant assesses the energy, water usage, and environmental impacts of the entire plant from cradle to gate. The assessment includes coal mining, transportation, and processing. For the boundary and scope, it is assumed that the lifetime of the entire plant is 20 years, and each year includes a week to allow maintenance. The coal extraction and mining both take place in North Wyoming and was treated to be large-scale underground long wall mining [65]. Transportation method is railroad. Coal travels in a series of trains with a 4400-horsepower diesel engine [66] from the extraction mine to the plant location in North Wyoming. The loss of coal is due to the transportation with fugitive dust emissions. There is no loss of coal during the loading and unloading. The transport distance will be 200 miles. During the entire life cycle, the content of mercury in the coal analysis is about 0.0703 ppm and 2.25 ppm in the fly ash. The impact of mercury in the air emissions is considered [67]. Greenhouse gas emission, water and energy consumptions are estimated and compared with a conventional IGCC plant (NETL IGCC plant) with carbon capture unit [67]. The NETL IGCC plant is a 543-MW facility using Illinois No.6 coal as a feedstock. Selexol is selected as the solvent in carbon capture and sulfur removal in both the base case and this work.

#### ● Definition of the Scope

The cradle-to-gate boundary used in this study includes the three stages that are the raw materials acquisition, raw material transportation, and chemical processes Facility as shown in Figure 18.

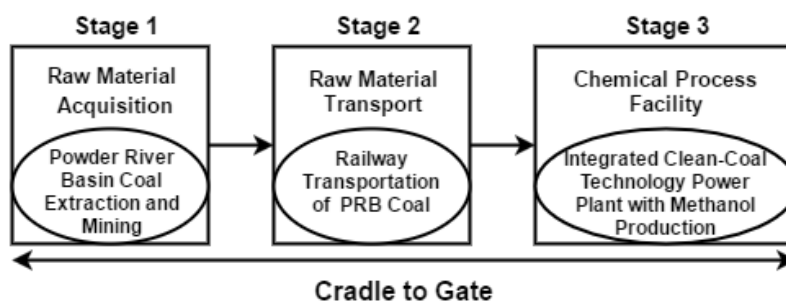


Figure 18 Life cycle assessment stages of integrated clean-coal technology power plant with methanol production.



## ● Inventory Analysis and Impact Assessment

The inventory analysis provides a list of inputs and outputs including material and energy consumed. Emissions and environmental impacts are also assessed.

## ● Air Pollutant Emission

Based on the elements that coal contains, the contents of the air pollutant emission discharged during the power plant life cycle are extremely different. Table 14 lists the criteria for air pollutants included in the LCA for integrated clean-coal technology plant with methanol production.

*Table 14 Air pollutant emissions from Stage 1, 2 and 3 [18, 65, 67]*

Air Pollutant Emissions		(Stage 1 and 2) MT emission /MT coal [67]	Stage 3, kg/kWh [18, 65]
Total Carbon Dioxide	CO <sub>2</sub>	0.033	25.23
Mercury	Hg	7.03E-14	2.25E-10
Volatile Organic Compounds	VOC	1.50E-05	6.50E-05
Carbon Monoxide	CO	5.73E-05	4.02E-05
Nitrogen Oxides	NO <sub>x</sub>	2.70E-04	2.20E-04
Particulate Matter 10	PM10	1.985E-4	1.77E-03
Particulate Matter 2.5	PM2.5	2.85E-05	5.10E-04
Sulfur Oxides	SO <sub>x</sub>	1.40E-04	9.48E-05
Methane	CH <sub>4</sub>	2.90E-03	1.28E-03
Nitrous Oxide	N <sub>2</sub> O	6.40E-07	1.38E-05
Sulfur Dioxide	SO <sub>2</sub>	1.06E-15	4.40E-08
Organic Chemicals	POC	5.35E-06	4.24E-05

Stage 1: Raw Material Acquisition, Stage 2: Raw Material Transportation, Stage 3: Chemical Process Facility

## ● Greenhouse Gas Emissions

The CO<sub>2</sub> emission caused by this power plant is stored, recycled and utilized. The CO<sub>2</sub> emission from the plant is partially used in methanol production and the rest is captured in carbon capture unit (Figure 19). The total CO<sub>2</sub>e emissions including the utility-based are 1281.79 MT/day. 589.76 MT/day of CO<sub>2</sub> was captured in carbon capture unit, while 51.96 MT/day of CO<sub>2</sub> is used as the feedstock in methanol production.

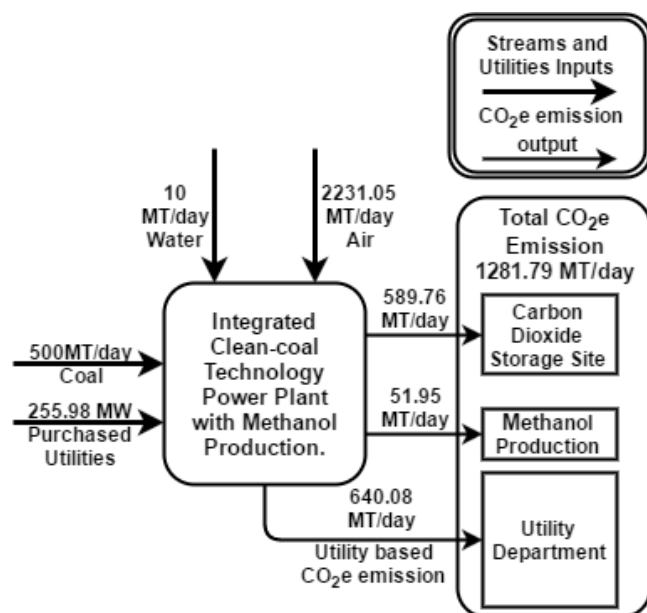


Figure 19 The path of CO<sub>2</sub>e emissions in integrated clean-coal technology power plant with methanol production.

This power plant needs 255.98 MW of utilities purchased from outside, which include cooling water, fired heat, high-pressure steam, low-pressure steam, refrigeration, and electricity. Figure 20 compares the GHG emissions for the integrated clean-coal plant with methanol production and the conventional IGCC per unit product of electricity [67]. Methanol production helps reduce the emissions slightly. Overall emissions in stage 3 are close to each other for both the cases with around 8% of reduction in the clean-coal technology. The improvements in stage 1 and 2 are around 100% in the clean-coal plant and show that the entire integrated clean-coal plant is an environmentally friendly process.

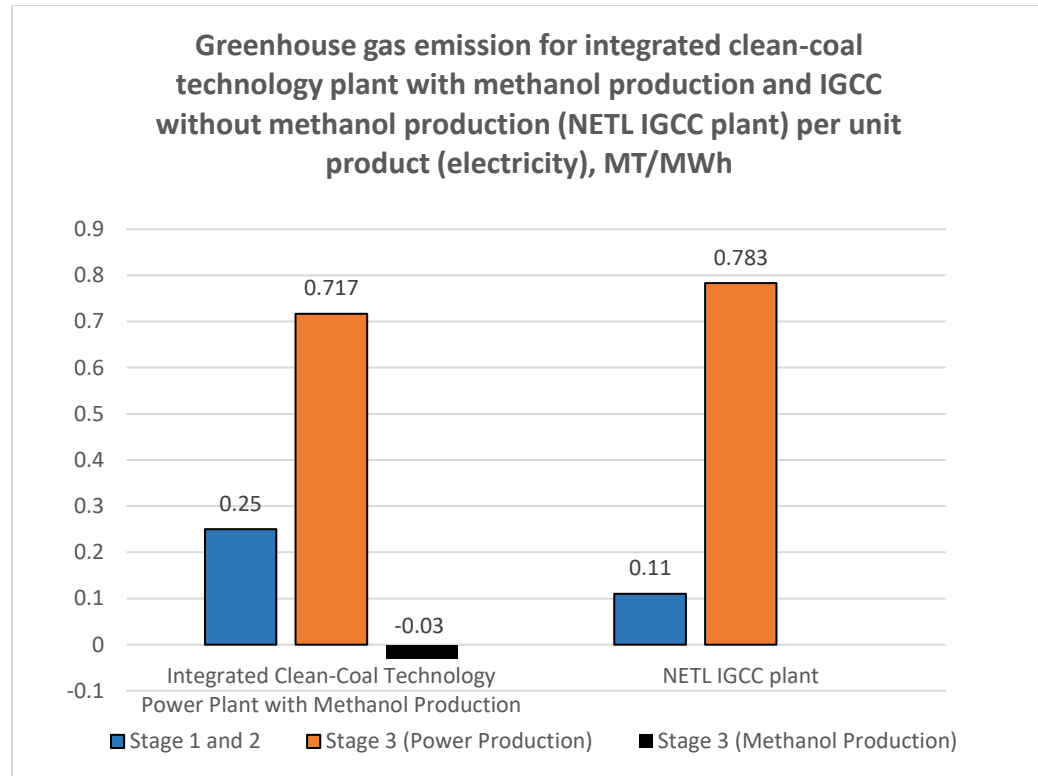


Figure 20 Comparison of GHG emissions in this work and NETL IGCC plant: Stage 1: Raw Material Acquisition, Stage 2: Raw Material Transportation, Stage 3: Chemical Process Facility. [18,65,67]

### ● Water Usage

In stage 1 and stage 2, only consider the water consumption in mining operations. Before the coal is prepared as a feedstock, it needs to be washed for dust suppression mainly using water, storm water, and sanitary water [63]. In stage 2, there is a little water evaporating from the coal and is neglected. Figure 21 shows the water consumption in all the stages in two cases [18, 65]. The total use of water is reduced from 1.91 to 1.41 MT water/MWh electricity representing around 40% decrease.

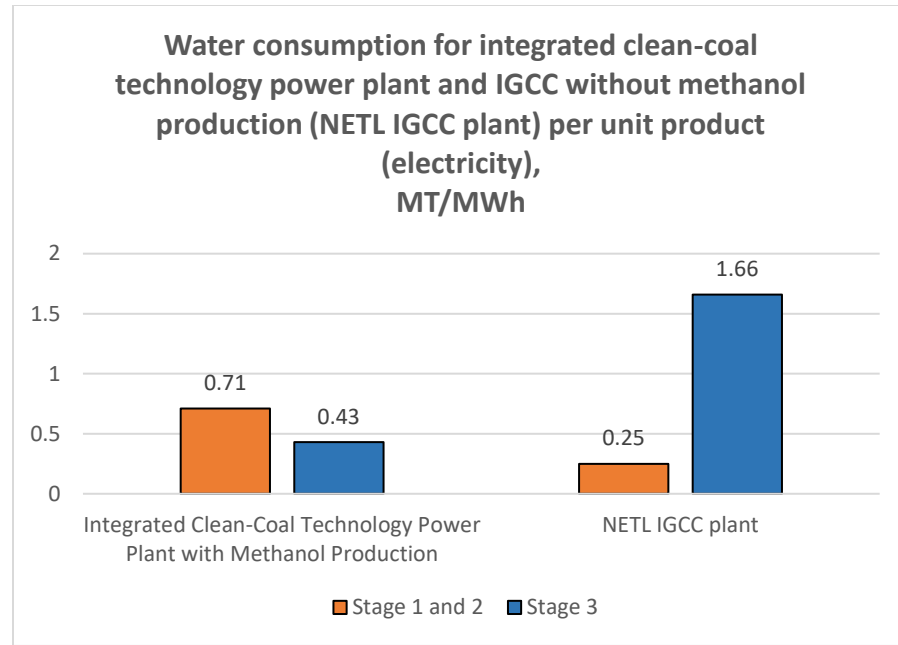


Figure 21 Water consumption in all the stages in two cases: Stage 1: Raw Material Acquisition, Stage 2: Raw Transportation, Stage 3: Chemical Process Facility [18,65,67].

### ● Energy Consumption

In the energy consumption analysis, several assumptions should be made [65].

1. The extraction and mining method for bituminous coal are assumed to be similar for both designs.
2. Coal transportation method is railroad, and the round-trip distance is 220 miles.
3. The construction of rail line and the train is pre-existing and will consume no additional energy.
4. Transportation only includes the main rail line between the coal mine to the plant location.
5. Transportation is diesel powered locomotive transports.
6. The energy loss in railway's catenary and electric power plant is not considered.
7. The utility properties are unified.

In coal mining and transportation (stage 1 and 2), the energy used to drive the equipment and trains are considered. On stages 3, energy consumption includes heating, cooling utilities and electricity used in the entire plant. The integrated clean-coal technology power plant with methanol production

is compared with an IGCC (NETL IGCC plant) in Figure 22 that shows the energy consumptions for both the cases [18,60,62,64]. The total energy use increased from 3.74 in the NETL IGCC plant to a total 6.21 in the clean-coal plant representing an increase of around 66%. The production of methanol has a marginal effect on this increase.

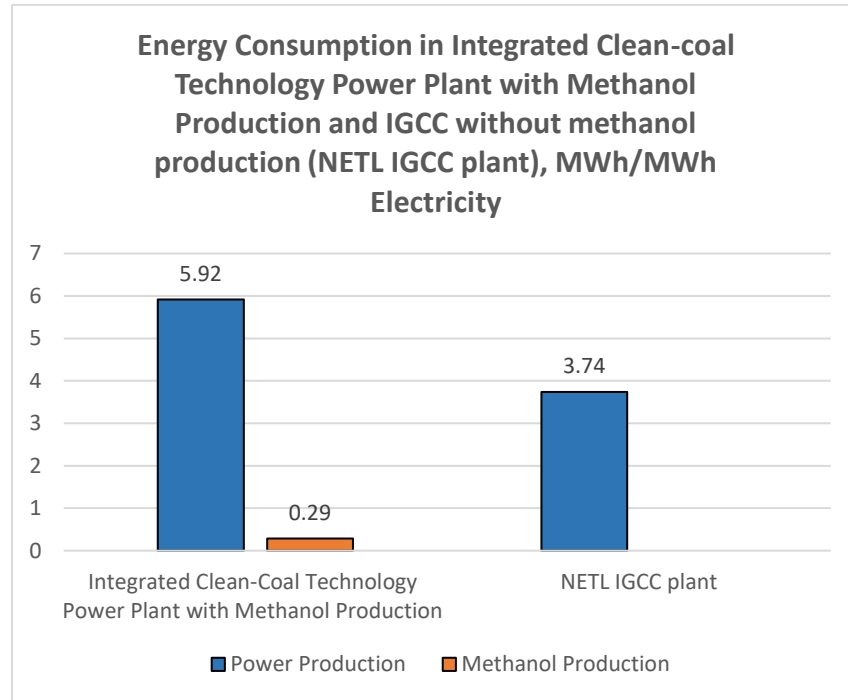


Figure 22 Energy consumption in integrated clean-coal technology power plant with methanol production and IGCC Plant (NETL IGCC plant), MWh/MWh electricity. [18,65,67,69]

### 3.8.5 Feasibility Assessment by a Multi-Criteria Decision Matrix

In the multi-criteria decision matrix, economics and sustainability indicators together are utilized in a qualitative manner for a comprehensive assessment of the feasibility of the cases considered [20, 70]. Table 15 shows the multi-criteria decision matrix, which utilizes '+' and '-' for the ratings and estimate the number of plus scores, minus scores, the overall total scores and the weighted total scores. The weight factors are decided by all the shareholders based on operation conditions, plant location, energy cost and security needs of a society. The weighted total scores are used to as guidance for comparing and decision making. Sometimes, the weight total scores could be very close to each other, then it will require to evaluate some more indicators to make an informed

decision [70]. As Table 15 shows the weighted total scores as +2.9 and -1.5 for the clean-coal plant and NETL IGCC plant, respectively. This implies that clean coal technology with methanol production seems more feasible.

*Table 15 Multi-criteria decision matrix for feasibility analysis of integrated clean-coal technology plant with methanol production and the base case [20]*

Economics and sustainability indicators	Weight factors:0-1	Integrated clean-coal technology plant with methanol production	Conventional IGCC Power Plant with Ammonia Production (base case) [60]
<b>Economic indicators</b>			
Net present value NPV	1	-	+
Payback period PBP	0.8	+	-
Rate of return ROR	0.8	-	+
Impact on employment	1	+	+
Impact on customers	1	+	+
Impact on economy	1	-	-
Impact on utility	0.7	+	-
<b>Sustainability indicators</b>			
Material intensity	0.7	+	+
Energy intensity	0.8	-	+
Environmental impact (GHG in production)	0.8	+	-
Environmental impact (GHG in utilization)	0.8	+	-
Toxic/waste material emissions, process safety and Public safety	1	+	-
Potential for technological improvements and cost reduction	0.8	+	+
Security/reliability	0.9	-	-
Political stability and legitimacy	0.8	-	-
Quality of life	0.8	+	-
Total positive score		8.4	6.1
Total minus score		-5.3	-7.6
<b>Weighted total net score</b>		<b>+3.1</b>	<b>-1.5</b>

### 3.9. Conclusions

The raw materials of this work are 10 MT/day of water, 2231.02 MT/day of air and 500 MT/day of coal and the productions are 207.99 MT/day of methanol, 1309.33 MT/day of nitrogen, 62.8 MT/day of water and 40.11MW of electricity. This clean coal technology power plant consists of air separation unit, steam production, coal gasification, water gas shift unit, power production,

carbon capture and methanol production process. The estimates show that the total capital cost is US\$366.23 million (2016 US\$) which includes US\$288.37 million of fixed capital investment, US\$5.76 million of land cost and US\$72.09 million of working capital cost. Based on the current economic data, price of the products, and raw materials, economic analysis estimates the discounted net present value around US\$83.37 million, the discounted payback period around 15 years, and the rate of return around 5.74% for a 20-year operation. All the economic indicators look favorable. Based cases are presented to compare the sustainability metrics of material intensity, energy intensity, and environmental impact intensity with this integral plant. Utilization of coal for power production and methanol production may lead to the decrease in GHG emission by combined cycle, heat integration, and using proper utilities. The use of oxy-combustion, steam production, and recycling of water and available heat streams contribute toward sustainability of the plant. A life cycle assessment of cradle-to-gate is applied to estimate the GHG emissions, water consumption, and energy consumption. The use of captured CO<sub>2</sub> in the methanol production decreases the carbon emissions directly and would have a positive impact on the environment and economics. Multi-criteria decision matrix, consisting of economic and sustainability indicators, assesses the feasibility of the entire plant and compares with the base case that is the traditional IGCC power plant. Multi-criteria decision matrix indicates that the integral clean coal plant with methanol production may be feasible. Further work may be needed to decrease the cost and increase the profit by converting CO<sub>2</sub> to more valuable chemicals and improve the efficiency of power production. Some solid waste treatments are required to reduce the environmental impacts.

## CHAPTER 4 CHEMICAL LOOPING TECHNOLOGY

### 4.1 Introduction

Chemical looping technology (CLT) is now attracting more and more attention in the research area of carbon capture and utilization. This novel technology is now developed especially for the reduction of the growing CO<sub>2</sub> emission. In 2015, carbon dioxide has accounted for 80% of the global greenhouse gas emission in the US (Figure23) [72]. Fossil fuel burning is the main source of the increasing of CO<sub>2</sub> emission.

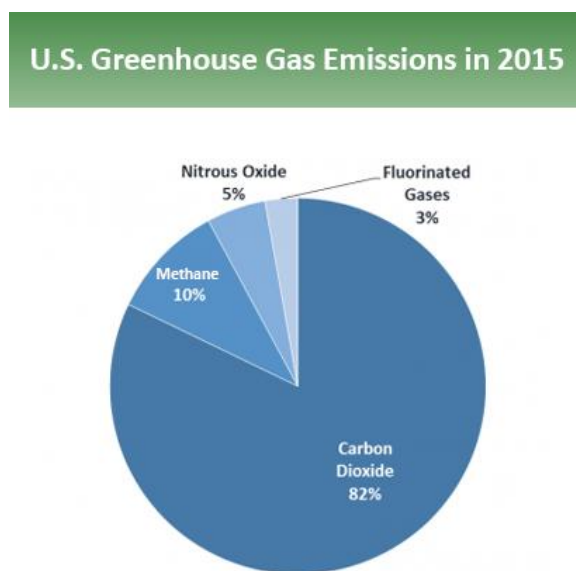


Figure 23 Greenhouse gas emission in the U.S. in 2015 [72]

Chemical looping technique is applied into chemical looping combustion (CLC), chemical looping gasification (CLG) and chemical looping reforming (CLR) with inherent carbon capture with low energy penalty of around \$10-50/ton CO<sub>2</sub>. The captured carbon dioxide is relatively pure and can be used for chemical production. Chemical looping system mainly constitutes three parts; fuel reactor (FR), air reactor (AR) and oxygen carrier (OC). Oxygen carrier (OC) will deliver the oxygen in the air to the fuel reactor (FR) where combustion, gasification, or reforming will occur by the reaction of fuel and transferred oxygen. The transportation between air and fuel using oxygen carrier ensures



the fuel only directly contacts with  $O_2$ , resulting in the nearly pure  $CO_2$  in the product gas. Oxygen carrier is a metal oxide ( $MeO$ ) which is reduced to carry the  $O_2$  in the air to the fuel reactor. After the reaction in FR, the reduced OC will be regenerated in the air reactor (AR) by reoxidization. (See Figure 24)

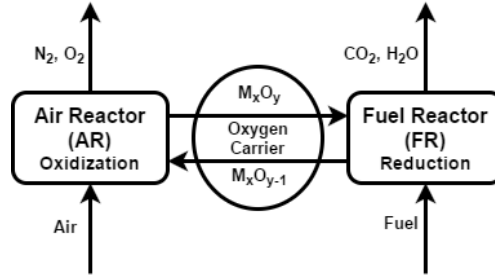
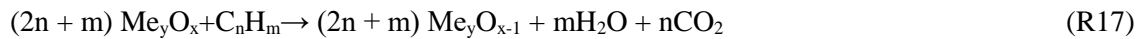


Figure 24 Basic flow diagram of chemical looping system.

This work introduces some backgrounds and basic information of chemical looping technologies and will mainly focus on the coal-based chemical looping systems and the relevant applications. The US holds the largest reserve of 22.1% of total coal by 2016 [73]. Although chemical looping system is not applied at commercial scale, this technique holds great potential in the clean coal technology development [74].

## 4.2 Chemical looping combustion (CLC)

Fossil fuels and renewable fuels are both suitable for CLC process. In gaseous fuel based combustion process, metal oxide is the ultimate source of oxygen which couples the combustion reaction to the reduction-oxidation loop by equation R17 and R18 [70].



The basic cycles of oxidation/reduction of CLC are shown in Figure 25.

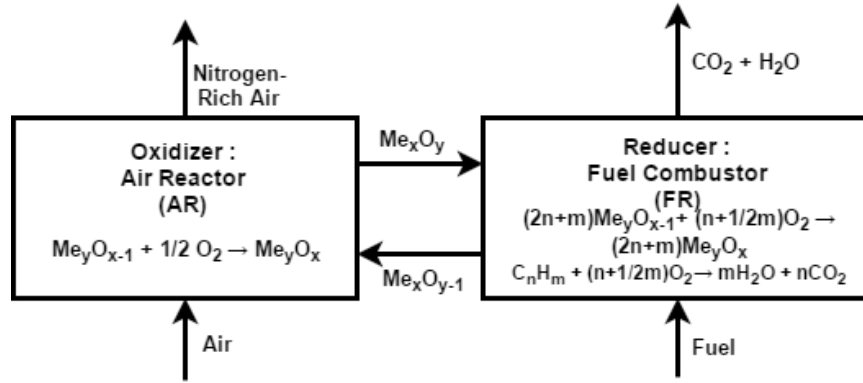
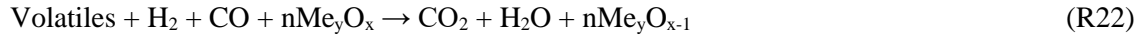
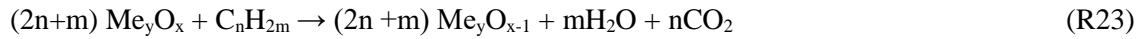


Figure 25 A basic chemical looping combustion scheme using metal oxide as OC.

Compared to gaseous fuel, coal requires additional treatment such as gasification which converts coal into the gas phase and reacts with carried oxygen. The entire process in the fuel reactor is derived by R19-R22 [70, 75, 76].



Overall reaction in the fuel reactor can be derived as R21.



Reactions R19 through R21 gasify the coal while R22 represents the reduction process. The oxygen carrier  $\text{Me}_y\text{O}_x$  is reduced into  $\text{Me}_y\text{O}_{x-1}$ . Then the reduced oxygen carrier is regenerated by the oxidization R24 in air reactor (AR).



According to R17 and R23, the combustion (reduction) in the fuel reactor both rely on the oxygen carried by oxygen carrier rather than air. This makes sure that the outlet streams of fuel reactor only contain  $\text{CO}_2$  and  $\text{H}_2\text{O}$  from which  $\text{CO}_2$  can be easily captured by condensing the water or steam.

Comparing solid fuels, gaseous fuel is easy to be dealt with in CLC system as it doesn't produce ash and Char or require additional gasification as the preparation for combustion. Nonetheless, the vast coal supply indicates that it is still considerable to study CLC with solid fuels. Generally, CLC with solid fuels is demonstrated by ex-situ gasification (eG-CLC), in-situ gasification (iG-CLC), and chemical looping with oxygen uncoupling (CLOU). Among these forms of chemical looping combustion, CLOU is a particular scheme of chemical looping as the gaseous  $O_2$  is spontaneously released from oxygen carrier in the fuel combustion reactor at a low oxygen partial pressure. Moreover, In CLOU, the reactions in the fuel and air reactor are exothermic in nature [77]. Figure 26 is the typical example of chemical looping combustion using a fluidized reactor [76].

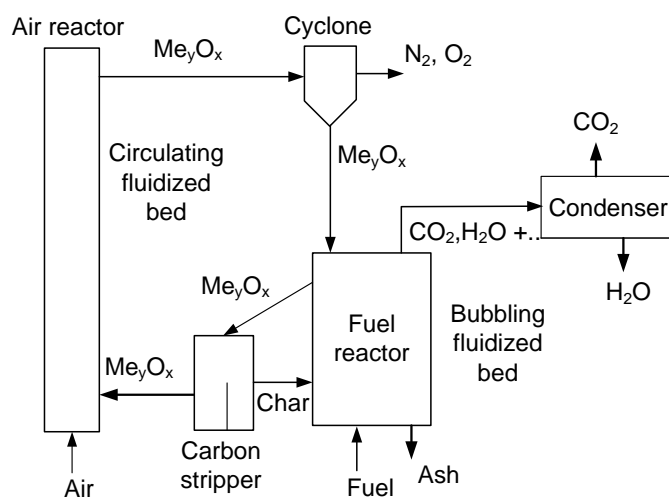


Figure 26 Block flow diagram of the chemical-looping combustion system. [76]

It is worthy to mention that chemical looping combustion is capable of combining with power production and other chemical production. Figure 27 shows utilizing CLC in power production with methanol production. The gaseous outlets from air reactor and fuel reactor are passed to air turbine and  $CO_2$  turbine respectively after gas cleaning. Although additional energy will be applied to the compressors and pumps, the utilization of exhaust gas of CLC is a great saving on the fuel energy.

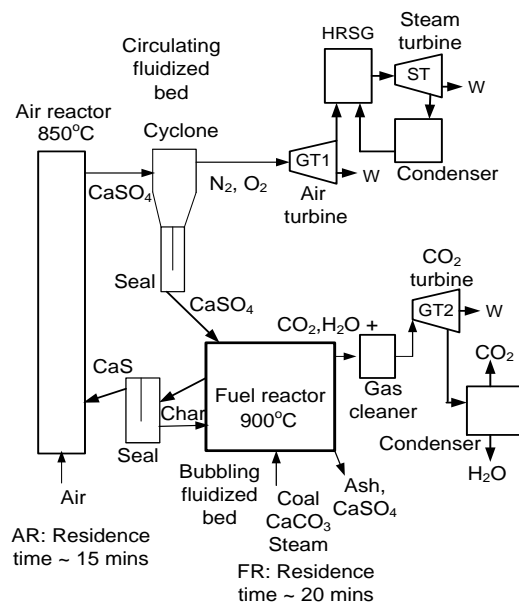


Figure 27 Block flow diagram of chemical-looping combustion combined cycle [76]

Carbon dioxide can be easily captured by a condenser and can be used as the raw material of another chemical production, for example, methanol production. The co-production in chemical looping combustion extremely increases the coefficient of fuel utilization and boosts the profits. A lab-scale coal-based CLC plant is simulated by Aspen Plus and the feasibility can be estimated by Aspen optimization tools and life cycle assessment method.

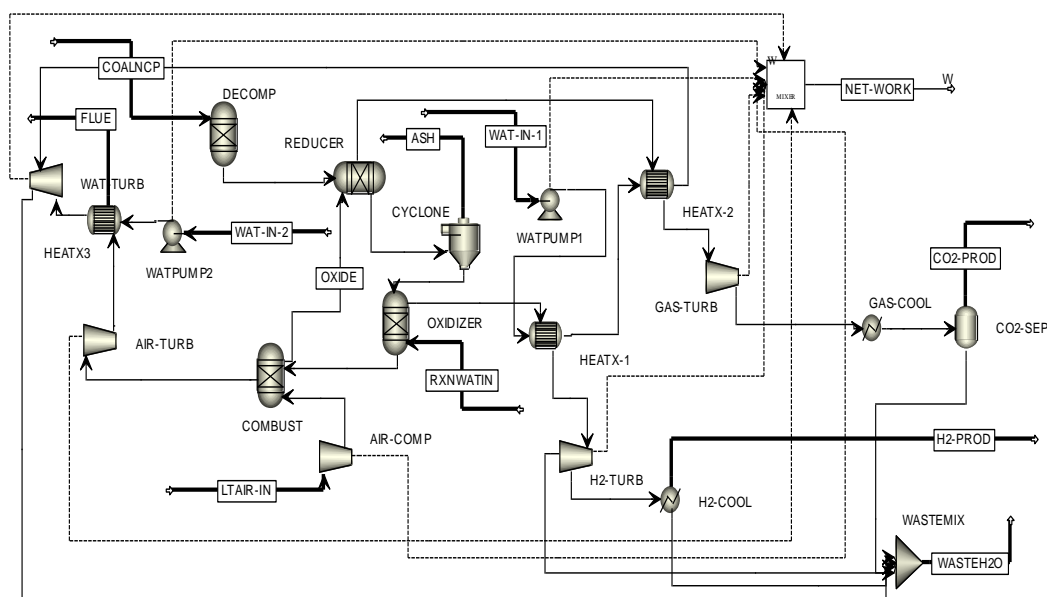
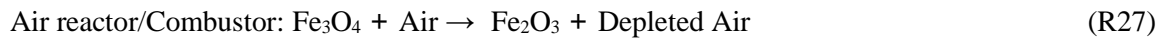


Figure 28 Block flow diagram of the coal-based CLC plant. [76]

### 4.3 Chemical looping gasification and reforming

Chemical looping gasification (CLG) and chemical looping reforming (CLR) system are both promising methods developed from chemical looping technique. Both systems convert fuel into available gaseous fuels and valuable chemicals with suitable oxygen carrier. Taking iron-based CLG/CLR system as an example, the reactions can be explained as R25 to R27 [78].



The suitable oxygen carriers for CLG are iron-based or Ca-based OCs. Taking CLG from coal using iron-based oxygen carrier for example (Figure 29), in syngas chemical looping system, coal is firstly gasified into syngas by the gasification agent which usually comes from the oxygen by ASU. The syngas will be passed into the fuel reactor and converted to  $\text{CO}_2$  and water. The mixture of  $\text{CO}_2$  and water carries a large amount of heat and can be used for power production. The oxygen carrier is oxidized and reacts with steam to produce hydrogen in the  $\text{H}_2$  reactor. The oxidized oxygen carrier is then reduced partially in the combustor; the hot depleted air is used for power production.

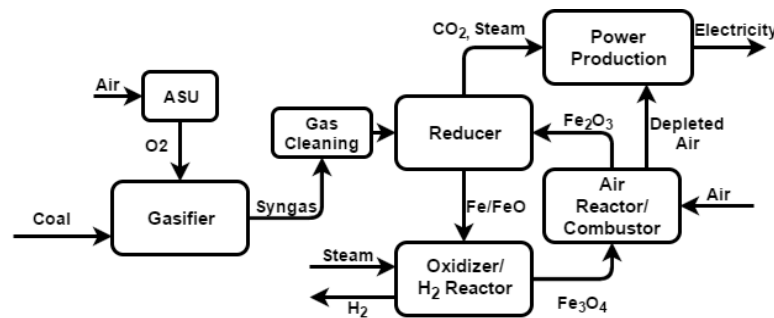


Figure 29 Syngas chemical looping coal gasification with iron-based oxygen carrier [78].

Coal-direct chemical looping is another developing method in CLG. As Figure 30 shown, this process feeds the coal directly into the fuel reactor rather than gasifying the coal with additional

gasifier or gasification agents. Typically, the coal reacts with iron-based oxygen carrier in the fuel reactor and is converted into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The reduced OC ( $\text{Fe}/\text{FeO}$ ) is fed into the oxidizer ( $\text{H}_2$  reactor) where steam from outside reacts with it and produces hydrogen.

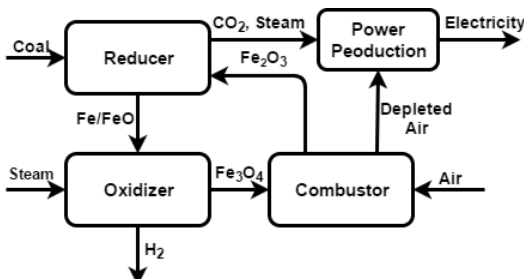


Figure 30 Flow diagram of iron-based coal-direct chemical looping gasification. [79]

Co-production is the highlight of chemical looping gasification technique as its direct products such as  $\text{CO}_2$ ,  $\text{H}_2$  or syngas can be used as the reactants in power and chemical production processes.

Chemical looping reforming is a main hydrogen production process. CLR utilizes steam from outside to increase the ratio of hydrogen to increase the yield of  $\text{H}_2$ . Figure 31 presents a combination of the application of CLG and CLR. In addition, this process applies capture carbon to generate methanol. The rational utilization of  $\text{CO}_2$  and hot gas into methanol and electricity production accomplishes the sustainable and energy-saving process.

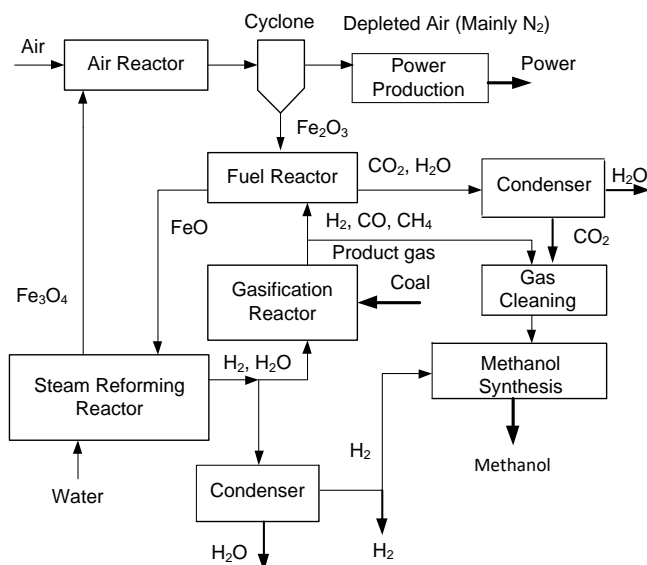


Figure 31 Block flow diagram of Fe-based chemical looping steam reforming and gasification systems for methanol, hydrogen and power production.

#### 4.4 Chemical looping technology using natural ores as oxygen carriers

Selection of OCs is important in a CLC process. Given a consideration of good oxygen transportation capacity and minor processing cost, natural ores are becoming great alternative raw materials to produce oxygen carrier in the chemical looping system. Conventional oxygen carrier contains support material and metal oxides as the active component. The support material enhances the stability of OCs and slows down the loss of OC. However, the synthesis of supporting material and metal oxide will increase the cost of chemical looping system. In the case of natural ores, the active and supporting materials are inherently combined. Some supporting materials such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$  are bound to the metal oxides in the natural ores to sustain natural ores with more stability. Consequently, the utilization of natural ores reduces the cost of CL processes.

Basically, some crucial characteristics must be considered when natural ores are selected as oxygen carriers: the high capacity of transporting oxygen in chemical looping system, be able to react with fuels, stable physical and thermal properties, safe, and be friendly to the environment. Among them, the most important characteristic is the oxygen transportation capacity. Natural ores are classified into different metal-based OCs (the active component) including the iron-based ores, manganese-based ores, copper-based ores and natural gypsum oxygen carriers. The compositions of some common natural ores are listed in Table 16.

Table 16 Natural ores tested as oxygen carrier\* [76, 80]

Oxygen carrier	Active component(s)	Composition (%)					
		CuO	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{TiO}_2$	$\text{CaSO}_4$
Chrysocolla	CuO	64.41	1.34	7.73	24.59	0.93	-
Cuprite	$\text{Cu}_2\text{O}$	15.7	2.66	18.18	61.04	2.09	-
Malachite	$\text{CuO}/\text{Fe}_2\text{O}_3$	15.08	12.12	12.82	52.64	7.08	-
Hematite	$\text{Fe}_2\text{O}_3$	0.76	94.23	2.55	1.39	1.01	-
Ilmenite	$\text{Fe}_2\text{O}_3/\text{TiO}_2$	0.76	46.01	6.26	10.84	36	-
Limonite	$\text{Fe}_2\text{O}_3$	2.184	66.97	8.78	18.11	3.79	-
Magnetite	$\text{Fe}_3\text{O}_4$	0.88	88.23	2.9	6.27	1.64	-
Taconite	$\text{Fe}_2\text{O}_3$	2.51	79.46	8.55	4.5	4.83	-
Anhydrite	$\text{CaSO}_4$	-	-	-	-	-	94.38

#### 4.4.1 Iron-based ores

Ilmenite is the most common iron-based ores used as OC. The idealized component of Ilmenite is  $\text{FeTiO}_3$  which can substitute to the titanium supported iron oxides. Minor cost and high crush strength improve the value of them acting as oxygen carriers [81-84]. It is found that Ilmenite performs better on the hydrogen conversion than CO conversion. [84] however,  $\text{CH}_4$  conversions of ilmenite are observed relatively low in most cases. Table 17 lists the researches for solid fuels using ilmenite in CLC process.

*Table 17 Literature results of various tests of ilmenite as an oxygen carrier in chemical looping combustion (Solid fuels only).*

Ores	Fuel Used	Testing Time	Conversion/Reformation	CCE**	O <sub>2</sub> Demand	Characteristics	Source
Ilmenite (Calcined)	Columbian bituminous coal		70% (870 °C), 95% (950 °C)		5-15%		[85]
Ilmenite (Calcined)	Columbian bituminous coal	26, 35 hr			5-15%	Decrease in $\text{R}_{\text{O}_2}$ from 4 to 3.9% observed after 26hr	[86]
Australian Ilmenite	German bituminous coal/syngas		Carbon conversion: 100% (syngas) 85% (Coal)			Reactivity increases over first cycles	[84]
Ilmenite	Mexican petcoke	18 hr	Solid fuel conversion: 55-75%	68-87%	*27-36%	1000 °C for 12 hr caused no problems	[87]
Norwegian Ilmenite	Colombian hard coal			80%	20%	Low solids circulation	[88]
Australian Ilmenite	Lignite dust	39 hr ( $\text{CH}_4$ ), 21 hr (Coal)		>95%	19.2%		[89]
Ilmenite	Mexican petcoke	11 hr	Solid fuel conversion: 66-78%	60-75%	25%	Very low attrition/fragmentation	[90]
Ilmenite	Bituminous coal/Mexican petcoke	4.75-13.5 hr	Fuel Conversion: 45-84%	51-95%	21.45%		[91]

\* Values are attributed to operating conditions or reactor setup not OC performance

\*\* CCE: Carbon conversion efficiency

#### 4.4.2 Manganese-based ores

Manganese-based ores are widely used as OC materials due to the low price and safe operating conditions. Comparing with iron-based oxygen carrier, they have a larger oxygen carrying capacity. The active component of manganese ores is the oxide form of manganese  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}$  with the



content of 30% to 60% [80]. In the solid fuel based CLC, the fuel conversions are relatively high. Arjamand et al. [92] concluded that the conversion of char can be improved by existing of alkali particles in the ore as a kind of catalyst. Alkali particles create cavities and channels in the fuel and hence increase the contact surface and reaction rate which is up to 4 times as fast as ilmenite. [93]. However, the catalysis impacts will disappear as the alkali is not regenerated and will be lost after multiple redox cycles [94]. On the other hand, Schmitz et al., [95] discovered that the Mn ores can work with low attrition rate, which helps to decrease the number of produced fines. Table 18 presents the cases of CLC using solid fuel with manganese-based ore OCs.

*Table 18 Literature results using Mn-based ores as oxygen carriers in solid fuel based CLC.*

Ores studied	Mn Content	Fuel Used	Cycles/ Testing Time	Fuel Conversion	Characteristics	Source
Brazilian Mn Ore	38%	Mexican petcoke	10.5 hr	91-97% Fuel conversion CCE: 89-98% O <sub>2</sub> demand: 13-17%	Fines production problems	[96]
6 ores: South Africa (x2), Norway, Brazil, Slovakia, Egypt	SA: 63.3, 57.2% NW: 63.3% BR: 68.8% SL: 62.3% EG: 48.8%	Mexican petcoke, wood char, CO:H <sub>2</sub> (50:50)		100% conversion of syngas, high char gasification	Some show stable conversion, some decrease	[92]
Brazilian Mn Ore	38%	Mexican petcoke	9.2 hr	90-94% Fuel conversion CCE: 68-76% O <sub>2</sub> demand: 15-16%	Fines production problems	[93]

#### 4.4.3 Copper-based ores

The idealized composition of copper-based ores is normally CuO. Treated CuO releases gaseous oxygen very fast in the fuel combustion reactor. Hence, it results in a high solid fuel conversion and greater fuel efficiencies. Using CuO as oxygen carriers performs well in the stability as the “low melting point agglomeration [80, 97] and sintering is a concern at high temperatures” [97-99]. One way to solve the problem of the agglomeration is to use Cu-based ores alternatively, however, with higher OC loadings [99]. Another issue needs to be dealt with is to reduce the sintering of the ores

to avoid the decrease of fuel conversions. Some results of Cu-based ores utilization for solid fuel CLC system from literature researches are displayed in Table 19.

*Table 19 A collection of results using copper-based ores as oxygen carriers in CLC. [76,80]*

Ores studied	Cu content (wt%)	Fuel Used	Conversion/Reformation	Characteristics	Cycles/ Testing Time	Source
Chrysocolla, Cuprite, Malachite	CuO: 64.41% CuO: 15.7% CuO: 15.08%	Coal and CH <sub>4</sub>	% combustion: 11.6-35%, % oxidation: 23.2-67.2%	Very stable conversion, no agglomeration, some loss of mechanical strength	30 cycles	[100]
Refined Chinese copper ore	CuO: 21% CuFe <sub>2</sub> O <sub>4</sub> : 70%	Chinese anthracite	Combustion efficiency: 96% CCE: 95%	Slight agglomeration and sintering, stable performance after 1 cycle	5 cycles (10 hr)	[101]
Refined Chinese copper ore	CuO: 21% CuFe <sub>2</sub> O <sub>4</sub> : 70%	Pine sawdust	Gasification efficiency: 26% CCE: 83.2%	Stable O <sub>2</sub> transport capacity, slight sintering, good fluidization	21 cycles	[102]
Refined Chinese copper ore	CuO: 21% CuFe <sub>2</sub> O <sub>4</sub> : 70%	Chinese anthracite, bituminous coal, lignite		Some agglomeration a 950 C, TOC 4.44%	5 cycles	[103]
Refined Chinese copper ore	CuO: 21% CuFe <sub>2</sub> O <sub>4</sub> : 70%	Syngas/Coal	CO <sub>2</sub> yield: 75-90% O <sub>2</sub> transport capacity: 12-14%	Sintering observed, O <sub>2</sub> transport/CO <sub>2</sub> yield decrease	20 cycles	[98]

#### 4.4.4 Natural gypsum ores

Natural gypsum ores are becoming more and more popular in the application of oxygen carrier.

Gypsum is mainly composed of CaSO<sub>4</sub>·2H<sub>2</sub>O and its active compound is mostly CaSO<sub>4</sub>. Compared with other oxygen carriers, gypsum oxygen carriers perform more environmental-friendly in the oxidized systems [104,105]. The outstanding merit of gypsum ores is the highly active component (CaSO<sub>4</sub>) content which can achieve 60–70% [80]. Some novel studies are presents by the latest researches. Xiao et al. [106] studied the “reduction kinetics of CaSO<sub>4</sub> with CO in a differential fixed bed”. Zheng [107] proposed a coal-based CLC system that used NiO and CaSO<sub>4</sub> as oxygen carriers in the interconnected fluidized beds. It has been proved that CaSO<sub>4</sub>/CaS is an available selection for the oxygen carrier in a CLC system [108,109]. Table 20 shows the literature results of CLC system

using gypsum ores.

Table 20 A collection of results using gypsum ( $\text{CaSO}_4$ ) as oxygen carriers in solid fuel -based CLC system.

Ores	CaO content (wt%)	Fuel Used	Conversion/Reformation	Characteristics	Source
Natural Anhydrite Ore	$\text{CaSO}_4$ : 94.38%	Bituminous Shenhua coal	$\text{CO}_2$ yield: 83.6-89.5%	Higher temperatures promote $\text{H}_2$ combustion, $\text{H}_2\text{S}$ and $\text{SO}_2$ emissions Steam gasification of coal char, Reactivity increases with temperature, $\text{CaSO}_4$ reactivity decreases with cycles	[109]
Natural Anhydrite Ore	$\text{CaSO}_4$ : 95.02%	Shenfu coal char	Low reactivity to $\text{CO}/\text{H}_2$		[110]

#### 4.4.5 Comparison of Natural Ores with Conventional OC

Natural ores are promising materials in the substitution of conventional oxygen carriers to meet the economic requirements in the chemical looping systems. The abundant resource and minor price increase the study value in the using natural ores as oxygen carriers.

Oxygen transport capacity is the most concerned property to estimate the ability of an oxygen carrier. The oxygen transport capacity ( $R_{O_2}$ ) can be defined by equation R26 [80, 111].

$$R_{O_2} = w_{OC} R_O \quad (\text{R26})$$

where,  $w_{OC}$  is the fraction of active material for oxygen carrier.  $R_O$  is called the oxygen transport capability which is defined as equation R27.[80,111]

$$R_O = \frac{m_o - m_r}{m_o} \quad (\text{R27})$$

where  $m_o$  and  $m_r$  are the mass of fully oxidized and reduced OC, respectively [72, 80]. Table 21 shows the oxygen transport capability and oxygen transport capacity of some conventional oxygen carriers and natural ores.

*Table 21 Oxygen transport capability and theoretical oxygen transport capacities of conventional oxygen carrier and Natural ores. [80]*

Active Components	R <sub>O</sub>	R <sub>O2</sub> of Conventional OCs	R <sub>O2</sub> of Natural Ores	Ref
CaSO <sub>4</sub> /CaS	0.47	0.4512	0.4435	[112], [113]
NiO/Ni	0.21	0.084	0.0725	[114]
CuO/Cu	0.20	0.1288	0.086	[114], [104]
Cu <sub>2</sub> O/Cu	0.11		0.0174	[104]
Mn <sub>2</sub> O <sub>3</sub> /MnO	0.10	0.047	0.0504	[114], [115]
Fe <sub>2</sub> O <sub>3</sub> /FeO	0.03	0.0096	0.0201	[114], [104]
Fe <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>	0.03	0.0096	0.0265	[114], [104]
CuO, Fe <sub>2</sub> O <sub>3</sub>	0.20, 0.03		0.0338	[104]
TiO <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub>	0.40, 0.03		0.1578	[104]

According to Table 21, most of the oxygen transport capacity of natural ores are not as high as the conventional oxygen carriers. The reduction of the oxygen transport capacity mostly dues to the existing of impurities contained in the natural ores. On the other hand, in view of the costs in the pre-treatment and synthesis of support material and metal oxides, natural ores are still preferential choices to replace the traditional oxygen carriers. It is mentionable that some natural ores usually contain multiple metal oxides. As a result, the total oxygen transport capacity may be increased to a degree. The utilization of mixed natural ores as OCs can be hence applied widely in various chemical looping systems.

## 4.5 Conclusion

Compared to the traditional electricity generation plants, Chemical Looping System is still a newly-developing industry. It is worth studying when associated with the application of natural ores. Some techniques such as chemical looping gasification(CLG) and chemical looping reforming (CLR) are the extends of chemical looping principle to concentrate on syngas and hydrogen production as well as electricity production. These methods are able to convert almost any solid and gas fuel into power and chemicals by using cheap and abundant raw materials.

However, some factors prevent chemical looping technologies becoming commercialized in hydrogen production or carbon capture. The stability and properties of oxygen carrier are very important in chemical looping systems. Therefore, the selection of oxygen carriers is a significant

consideration in developing of chemical looping system. The metal oxides with great performance have mostly high cost. As a result, using ores as OCs is becoming more and more attractive. The oxygen transport capacity of natural ores may not be as high as conventional OCs'; however, the low cost and abundant resources make them competitive oxygen carriers.

## CHAPTER 5 SUMMARY AND CONCLUSIONS

Modern chemical process engineering still pays attention to the development of coal-based energy technologies. Coal is a cheap and abundant energy resource that will not be abandoned in the upcoming decades. To meet the requirements of the concepts of “green chemicals” and improve the energy efficiency, more affordable and clean coal techniques and analysis methods need to be developed. Technologies such as coal gasification, carbon capture and chemical looping systems are proposed to prevent and fix those problems GHG emissions. This work studies the clean coal technologies with coproduction of power and methanol. Air Separation, steam generation, coal gasification, electricity production, water gas shift, carbon capture, methanol production and chemical looping system with natural ores are investigated. Besides the designed chemical processes, sustainability, economic performances and feasibility of the plant are analyzed. Indicators and metrics are also used to address the extent of sustainability of the entire plant. A cradle-to-gate Life Cycle Assessment is applied to estimate the environment impacts including greenhouse gas emission, water utilized and energy consumption. The combination of these novel technologies strengthens the feasibility of the integral operations.

Coal gasification would prevent the emissions caused by direct combustion. Combined with oxy-combustion, the gasification process ensures the tail gas only contains  $\text{CO}_2$  and water, which makes the capture of  $\text{CO}_2$  easy. This work utilizes an oxy-combustion before the coal entering into the gasifier. The goal of this oxy-combustion provides the  $\text{CO}_2$  required in the following char gasification. The carbon conversion can achieve as high as 99.8%.

The design of IGCC power plant with methanol production converts all the available energy from coal into heat and electricity. Disposed water and wastes are processed in the waste treatment department. The  $\text{CO}_2$  fixed in the coal is either captured and stored in a storage site or used to produce methanol. It is remarkable that the methanol production makes the entire plant valuable and sustainable as the methanol can be widely used as reactants, fuels, intermediate or solvent.

Operations of methanol will not produce new CO<sub>2e</sub> emission as it fixes CO<sub>2</sub> inherently. The co-production of IGCC power plant increases the revenue and the facility feasibility. Generally speaking, the entire design is sustainable and environmentally friendly.

Chemical looping combustion (CLC), chemical looping gasification (CLG) and chemical looping reforming (CLR) are well-developed techniques. Using ores as oxygen carriers in CLC decreases the cost with a comparable oxygen transfer capacity in the oxidation. CL technique is a promising method for capture carbon in the future.

## **CHAPTER 6 FUTURE RESEARCH**

Great efforts are needed in greenhouse gas control, especially when applying coal as the fuel source. Clean coal technologies are developed to better serve the requirements related to the environmental needs. Given the consideration to economic, environmental and energy saving issues, clean coal technology optimization and investigation are essential. Co-production is a reasonable method to better utilize coal. Future work can be focused on the related chemical production using coal gasification product. A techno-economic analysis coupled with a life cycle assessment of the entire ore production process and use in CLC would be an effective way to investigate the true feasibility of ore use as an OC.

To promote the development of coal energy technology, chemical looping system is brought forward. However, this technique is currently not commercialized due to the circulation of large amounts of oxygen carrier at a high temperatures and high cost of the entire process. Even so, chemical looping is still an ideal substitution for the conventional coal gasification and combustion in power generation and carbon capture. Chemical looping combustion, gasification and reforming processes are able to use to capture carbon dioxide. Using chemical looping technique in conventional coal gasification process and IGCC power plant to substitute carbon capture unit and

oxy-combustion is very encouraging. Optimization of the CL system and how to develop it into a commercial scale is the major forecast.

Future work also will keep an eye on the combination of chemical looping systems with other novel techniques. For example, the conjunction of chemical looping and hydrothermal processes is a possible extension of the chemical looping concept as it is capable of converting captured  $\text{CO}_2$  into formic acid and methanol. Hydrothermal processes are able to convert biomass and  $\text{CO}_2$  to organic acids, methanol, biocrude and some other valuable chemicals by aqueous chemical reactions under high temperature and pressure conditions [76]. Such a high temperature (around 200 - 350 °C) keeps the water under liquid phase and turns all the hydrogen from water into formic acid. This combined process [116] involves two chemical loops and can convert captured  $\text{CO}_2$  and glycerin to formic acid and lactic acid using a zero-valent metal as the oxygen carrier. The process scheme is displayed in Figure 32.

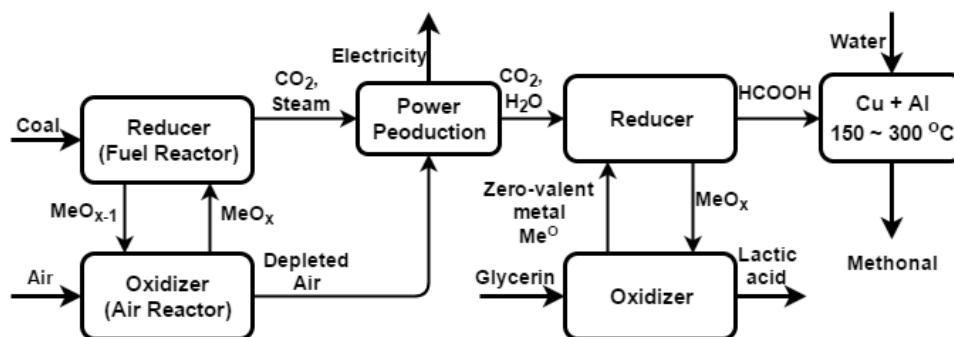
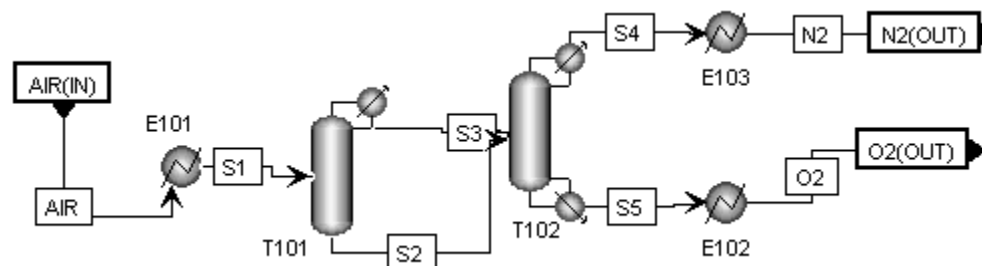


Figure 32 Conjunction of Chemical-looping and hydrothermal process using captured  $\text{CO}_2$  for methanol production.



## APPENDIX

### 3.1 Air Separation Unit (ASU).

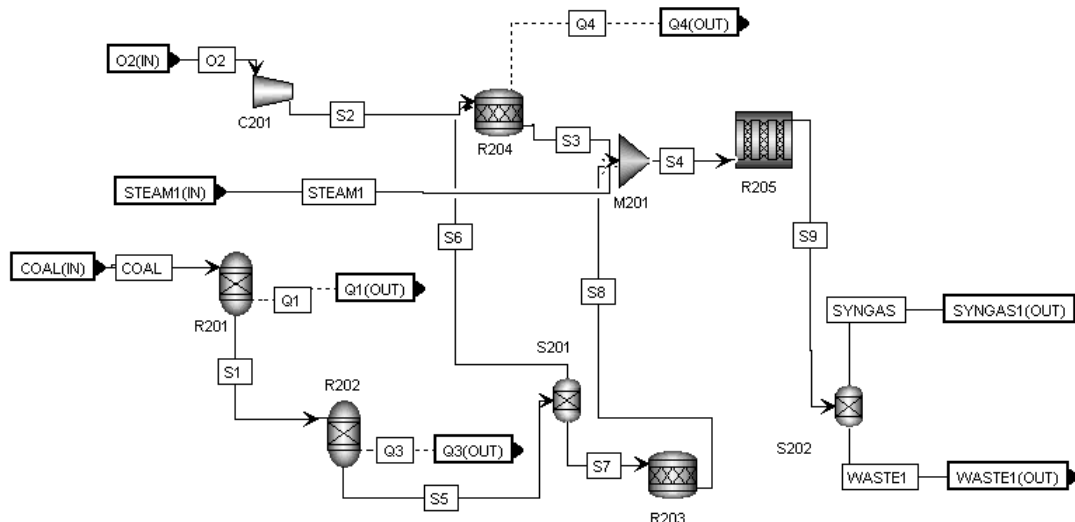


**Figure. A1.** Process flow diagram of Air Separation Unit (ASU).

**Table. A1.** Stream table of Air Separation Unit (ASU).

		Input Stream		Output Stream	
Stream Name		AIR	N2	O2	
Temperature	°C	25	25	25	
Pressure	bar	1.01	1.01	1.01	
Mass Flow	tonne/day	1731.02	1310.83	420.20	
Components	O2	403.18	1.50	401.69	
	N2	1327.84	1309.33	18.51	

### 3.2 Coal Gasification.

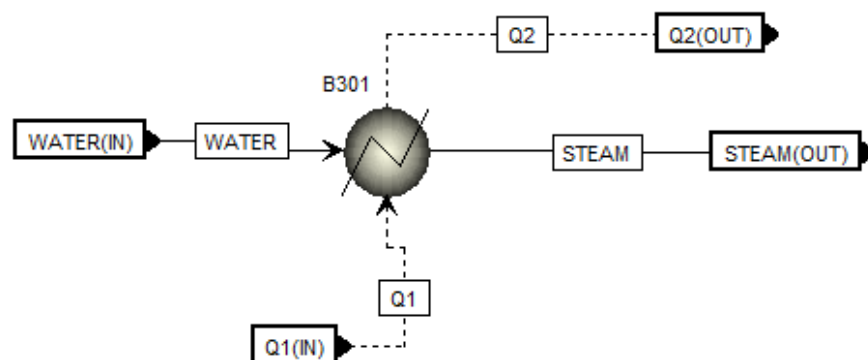


**Figure. A2.** Process flow diagram of coal gasification.

**Table. A2.** Stream table of coal gasification.

Stream Name		Input Stream				Output Stream	
		COAL	STEAM	O2		SYNGAS	SOLID
Temperature	°C	25	25	300		1500	1500
Pressure	bar	1.01	1.01	1.01		24.00	24.00
Mass Flow	tonne/day	500.00	10	10.00		880.80	30.87
Components	COAL	500.00	0	0		0	25.31
	ASH	0	0	0		0	25.31
	O2	0	0	401.69		0	0
	CO	0	0	0		416.67	0
	H2	0	0	0		12.74	0
	CO2	0	0	0		251.72	0
	H2O	0	10	0		192.20	0
	H2S	0	0	0		3.78	0
	N2	0	0	18.51		3.64	0
	CH4	0	0	0		0.0049	0
	C6H6	0	0	0		0	0
	C	0	0	0		0	0.29
	S	0	0	0		0	5.28

### 3.3 Steam Generation

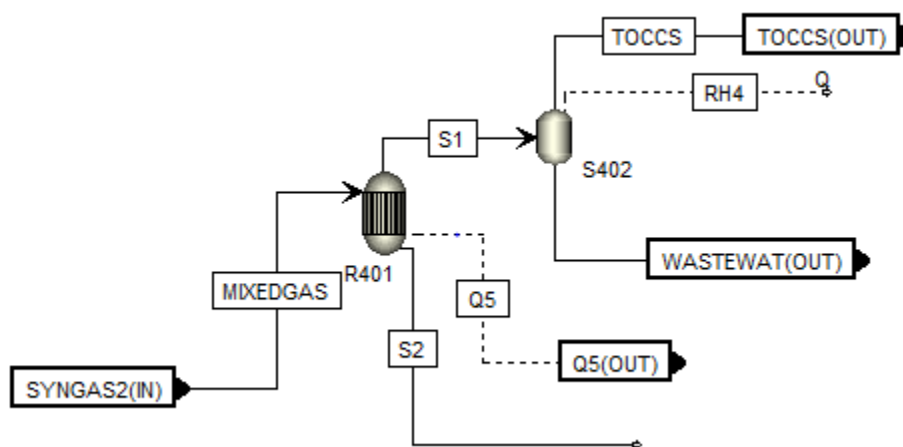


**Figure. A3.** Process flow diagram of steam generation.

**Table. A3.** Stream table of steam generation.

		Input Stream	Output Stream
Stream Name		WATER	STEAM
Temperature	°C	25	300
Pressure	bar	1.01	1.01
Mass Flow	mt/day	10.00	10.00
Components	H2O	10.00	10.00

### 3.5. Water Gas Shift (WGS) Unit

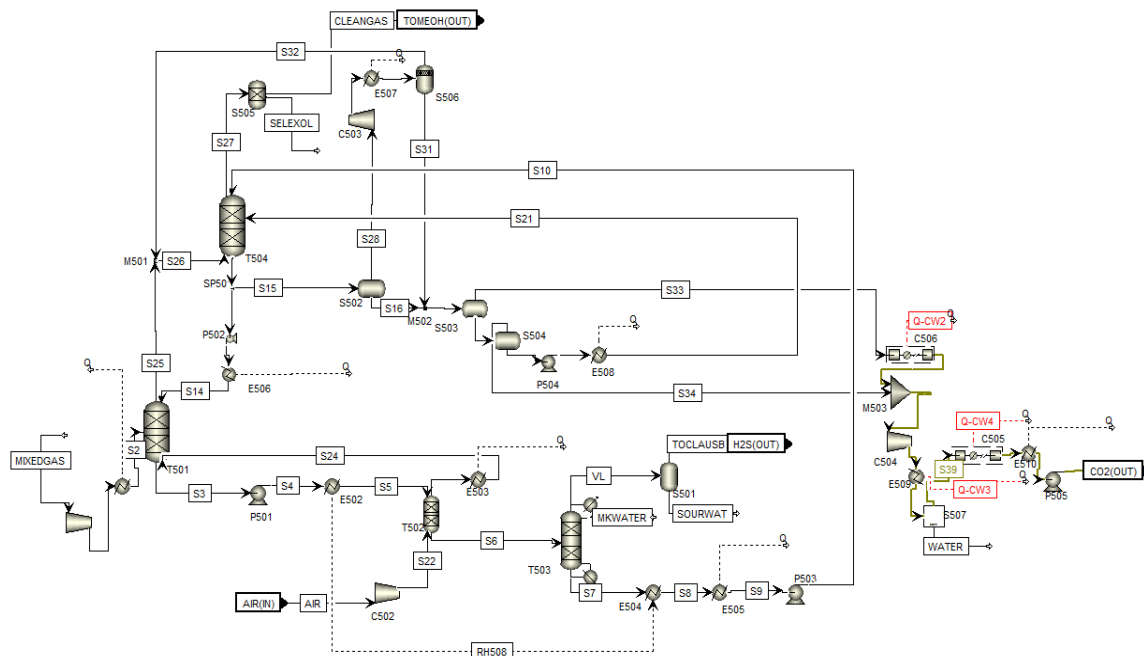


**Figure. A4.** Process flow diagram of Water Gas Shift (WGS) Unit.

**Table. A4.** Stream table of Water Gas Shift (WGS) Unit.

Stream Name		Input Stream	Output Stream	
		SINGAS2	WASTEWAT	TOCCS
Temperature	°C	350	5	5
Pressure	bar	1.00	1.00	1.00
Mass Flow	mt/day	880.80	28.80	852.00
Components	CO	416.67	0	168.45
	H2	12.72	0	30.61
	CO2	251.23	0	641.72
	H2O	192.42	28.80	3.75
	H2S	3.78	0	3.78
	N2	3.64	0	3.64
	CH4	0.0049	0	0.0049

### 3.6. Carbon Capture and Sulfur Removal

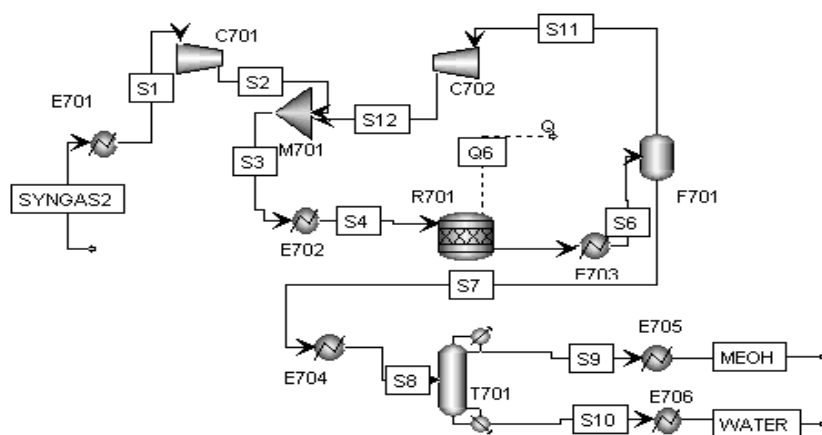


**Figure. A5.** Process flow diagram of carbon capture unit.

**Table. A5.** Stream table of carbon capture unit.

Stream Name		Input Stream		Output Stream			
		MIXEDGAS	AIR	CLEANGAS	CO2	WATER	H2S
Temperature	°C	350	25	134	46	18	25
Pressure	bar	1.00	1.00	1.00	120	15	1.00
Mass Flow	mt/day	852.00	500	239.15	621.98	0.77	5.95
Components	CO	168.45	0	157.17	11.28	0	0
	H2	30.61	0	51.96	0.71	0	0
	CO2	641.72	0	29.89	589.76	0	0
	H2O	3.75	0	0.1337	0.134	0.77	0.20
	H2S	3.78	0	0	0	0	3.78
	N2	3.64	390	0.04	20.09	0	1.99
	CH4	0.0049	0	0	0	0	0
	O2	0	110	0	0	0	0

### 3.7. Methanol Production

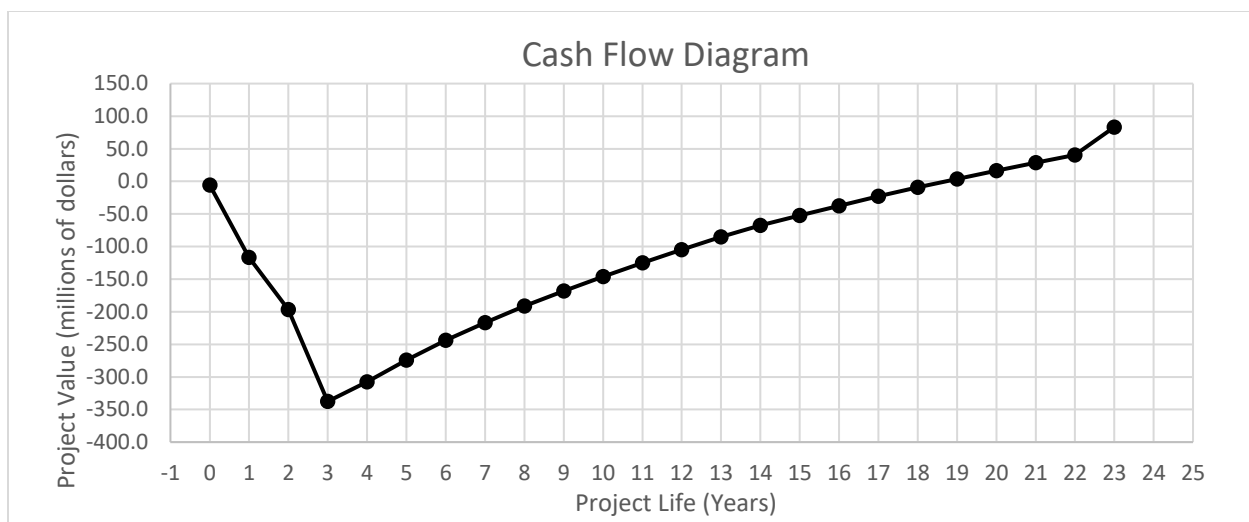


**Figure. A6.** Process flow diagram of methanol production unit.

**Table. A6.** Stream table of methanol production unit.

Stream Name		Input Stream MIXEDGAS	Output Stream MEOH	WATER
Temperature	°C	134	25	25
Pressure	bar	1	1.00	1.00
Mass Flow	mt/day	239.19	208.41	
Components	H2	29.89	0	0
	CO2	51.96	0	0
	MEOH	0	207.99	0.15
	H2O	0.1337	0.41	30.59
	CO	157.17	0	0
	N2	0.04	0	0

### 3.8.3 Economic Analysis

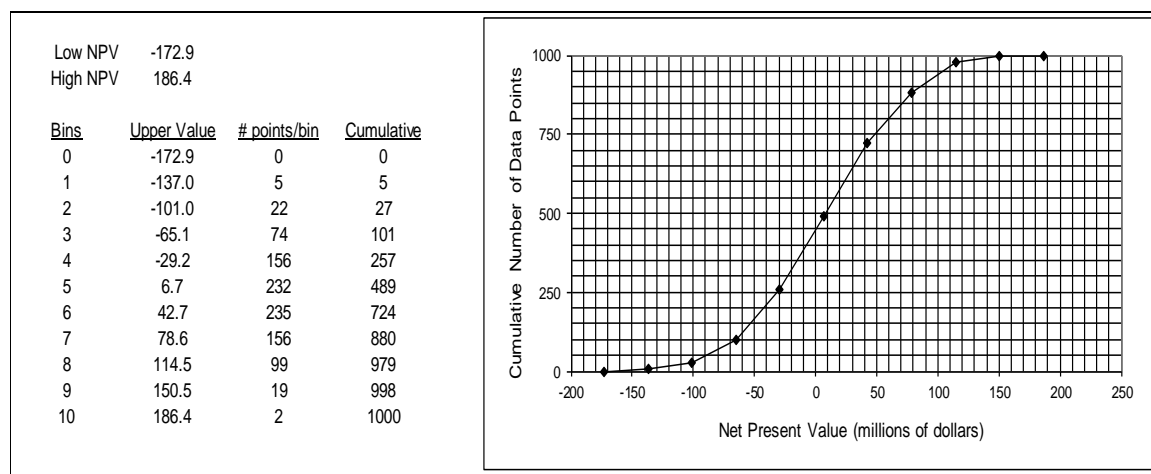


**Figure. A7.** Discounted cash flow diagram

**Table. A7.** Cash flow table with 3-year investment integrated clean-coal technology power plant.

Year	Investment	$d_k$	FCI <sub>L</sub> - Sd <sub>k</sub>	R	*COM <sub>d</sub>	(R-COM <sub>d</sub> - $d_k$ )*(1- t)+ $d_k$	Cash Flow (discounted)	Cumulative Cash Flow (discounted)
0	5.77		288.37				(5.77)	(5.77)
1	115.35		288.37				(110.91)	(116.68)
2	86.51		288.37				(79.98)	(196.66)
3	158.60		288.37				(141.00)	(337.66)
4		28.84	259.53	156.75	119.66	35.03	29.94	(307.72)
5		51.91	207.63	156.75	119.66	40.79	33.53	(274.19)
6		41.53	166.10	156.75	119.66	38.20	30.19	(244.00)
7		33.16	132.94	156.75	119.66	36.11	27.44	(216.56)
8		26.53	106.41	156.75	119.66	34.45	25.17	(191.39)
9		21.34	85.07	156.75	119.66	33.15	23.29	(168.09)
10		19.03	66.04	156.75	119.66	32.58	22.01	(146.09)
11		19.03	47.00	156.75	119.66	32.58	21.16	(124.93)
12		18.74	28.26	156.75	119.66	32.50	20.30	(104.62)
13		18.74	9.52	156.75	119.66	32.50	19.52	(85.10)
14		9.52	-	156.75	119.66	30.20	17.44	(67.66)
15		-	-	156.75	119.66	27.82	15.45	(52.22)
16		-	-	156.75	119.66	27.82	14.85	(37.37)
17		-	-	156.75	119.66	27.82	14.28	(23.08)
18		-	-	156.75	119.66	27.82	13.73	(9.35)
19		-	-	156.75	119.66	27.82	13.20	3.85
20		-	-	156.75	119.66	27.82	12.70	16.55
21		-	-	156.75	119.66	27.82	12.21	28.75
22		-	-	156.75	119.66	27.82	11.74	40.49
23		-	-	156.75	119.66	27.82	42.88	83.37

\*COM: Cost of Manufacturing

**Figure. A8.** Monte Carlo Simulation



**Table. A8.** Probable variation of key parameters over plant life

	<u>Lower Limit</u>	<u>Upper Limit</u>	<u>Base Value</u>
FCIL	-20%	30%	\$ 288,368,921
Price of Product	-10%	10%	\$ 156,747,000
Working Capital	-50%	10%	\$ 72,092,230
Income Tax Rate*	-20%	20%	25%
Interest Rate*	-10%	20%	4%
Raw Material Price	-10%	15%	\$ 208,000,0

**Table. A9.** Bare module cost of equipment.

Equipment ID	Equipment Description	Delivered Cost	Labor Effort	Installation Factor	Installed Cost
Gasification C20	Compressor	\$2,647,600	Complex	0.8	\$2,878,000
CCS C501	Compressor	\$1,309,100	Complex	0.8	\$1,496,500
CCS C502	Compressor	\$3,329,400	Complex	0.8	\$3,955,400
CCS C503	Compressor	\$670,700	Complex	0.8	\$783,700
CCS C504	Compressor	\$1,588,600	Complex	0.8	\$1,781,200
CCS C505	Compressor	\$1,227,600	Complex	0.8	\$1,373,500
CCS C506	Compressor	\$45,600	Complex	0.8	\$1,373,500
MEOH Prod C701	Compressor	\$929,400	Complex	0.8	\$1,672,920
MEOH Prod C702	Compressor	\$1,504,700	Complex	0.8	\$1,704,700
ASU E101	Heat exchanger	\$192,730	Complex	0.8	\$346,914
ASU E102	Heat exchanger	\$81,000	Complex	0.8	\$145,800
ASU E103	Heat exchanger	\$28,700	Complex	0.8	\$51,660
Power Prod E601	Heat exchanger	\$330,200	Complex	0.8	\$594,360
Power Prod E602	Heat exchanger	\$87,500	Complex	0.8	\$157,500
Power Prod E603	Heat exchanger	\$26,500	Complex	0.8	\$47,700
CCS E501	Heat exchanger	\$14,700	Complex	0.8	\$26,460
CCS E502	Heat exchanger	\$40,500	Complex	0.8	\$72,900
CCS E503	Heat exchanger	\$111,800	Complex	0.8	\$201,240
CCS E504	Heat exchanger	\$607,600	Complex	0.8	\$1,093,680
CCS E505	Heat exchanger	\$18,600	Complex	0.8	\$33,480
CCS E506	Heat exchanger	\$49,700	Complex	0.8	\$89,460
CCS E507	Heat exchanger	\$8,900	Complex	0.8	\$16,020
CCS E508	Heat exchanger	\$179,500	Complex	0.8	\$323,100
CCS E509	Heat exchanger	\$32,000	Complex	0.8	\$57,600
CCS E510	Heat exchanger	\$45,380	Complex	0.8	\$81,684
MEOH Prod E701	Heat exchanger	\$10,000	Complex	0.8	\$18,000
MEOH Prod E702	Heat exchanger	\$10,000	Complex	0.8	\$18,000
MEOH Prod E703	Heat exchanger	\$15,200	Complex	0.8	\$27,360

MEOH Prod E704	Heat exchanger	\$11,000	Complex	0.8	\$19,800
MEOH Prod E705	Heat exchanger	\$18,500	Complex	0.8	\$33,300
MEOH Prod E706	Heat exchanger	\$10,100	Complex	0.8	\$18,180
<hr/>					
Gasification R201	Fired Heater	\$5,423,000	Complex	0.8	\$9,761,400
Gasification R202	Fired Heater	\$501,600	Complex	0.8	\$902,880
Gasification R203	Fired Heater	\$1,287,000	Complex	0.8	\$2,316,600
Gasification R204	Fired Heater	\$8,382,000	Complex	0.8	\$15,087,600
Gasification R205	Fired Heater	\$1,254,000	Complex	0.8	\$2,257,200
WGS R401	Fired Heater	\$1,386,000	Complex	0.8	\$2,494,800
Steam Prod B301	Fired Heater	\$45,700	Complex	0.8	\$82,260
Power Prod B601	Fired Heater	\$294,000	Complex	0.8	\$529,200
MEOH Prod R701	Fired Heater	\$863,000	Complex	0.8	\$1,553,400
<hr/>					
Power Prod P601	Pump	\$194,346	Complex	0.8	\$349,823
Power Prod P602	Pump	\$52,400	Complex	0.8	\$94,320
CCS P501	Pump	\$12,800	Complex	0.8	\$23,040
CCS P502	Pump	\$54,100	Complex	0.8	\$97,380
CCS P503	Pump	\$100,100	Complex	0.8	\$180,180
CCS P504	Pump	\$527,000	Complex	0.8	\$948,600
CCS P505	Pump	\$156,500	Complex	0.8	\$281,700
<hr/>					
ASU T101	Tower	\$298,800	Complex	0.8	\$537,840
ASU T102	Tower	\$119,900	Complex	0.8	\$215,820
CCS T501	Tower	\$145,300	Complex	0.8	\$261,540
CCS T502	Tower	\$89,200	Complex	0.8	\$160,560
CCS T503	Tower	\$87,400	Complex	0.8	\$157,320
CCS T504	Tower	\$206,000	Complex	0.8	\$370,800
MEOH Prod T701	Tower	\$297,300	Complex	0.8	\$535,140
<hr/>					
Power Prod T601	Turbine	\$3,180,000	Complex	0.8	\$5,724,000
Power Prod T602	Turbine	\$2,480,000	Complex	0.8	\$4,464,000
Power Prod T603	Turbine	\$936,000	Complex	0.8	\$1,684,800
<hr/>					
Gasification M201	Vessel	\$10,100	Standard	0.6	\$16,160
Gasification S202	Vessel	\$2,860	Complex	0.8	\$5,148
Gasification S203	Vessel	\$13,300	Complex	0.8	\$23,940
WGS F401	Vessel	\$13,300	Complex	0.8	\$23,940
CCS S501	Vessel	\$15,600	Complex	0.8	\$28,080
CCS S502	Vessel	\$304,700	Complex	0.8	\$548,460
CCS S503	Vessel	\$222,900	Complex	0.8	\$401,220
CCS S504	Vessel	\$181,400	Complex	0.8	\$326,520

CCS S505	Vessel	\$20,600	Complex	0.8	\$37,080
CCS S506	Vessel	\$20,600	Complex	0.8	\$37,080
CCS S507	Vessel	\$18,500	Complex	0.8	\$33,300
CCS M501	Vessel	\$12,800	Minimal	0.5	\$19,200
CCS M502	Vessel	\$22,900	Minimal	0.5	\$34,350
CCS M503	Vessel	\$6,670	Minimal	0.5	\$10,005
CCS SP501	Vessel	\$24,800	Minimal	0.5	\$37,200
MEOH Prod M701	Vessel	\$8,830	Minimal	0.5	\$13,245
MEOH Prod F701	Vessel	\$192,000	Complex	0.8	\$126,700
Sub Total					\$73,082,299
Piping	Complex	0.5	of subtotal		\$36,541,149
Electrical	Complex	0.25	of subtotal		\$18,270,575
Instrumentation and Controls	Complex	0.2	of subtotal		\$14,616,460
	Square Footage	Cost per Sqft	Labor Effort	Installation Factor	Cost
Buildings	1000	\$100	Complex	0.2	\$120,000
	Acreage	Cost per Acre			Cost
Civil Impact	Complex	0.2	of subtotal		\$14,616,460
Environmental Operations				0.15	\$10,962,345
Utilities				0.18	\$13,154,814
DIRECT COST					\$181,364,101
Engineering Costs				0.24	\$43,527,384
Construction Costs				0.15	\$27,204,615
Contingency				0.2	\$36,272,820
Total Indirect Costs					\$107,004,820
Fixed Capital Investment (FCI)					\$288,368,921
LAND				2% FCI	\$5,767,378.41
WORKING CAPITAL				25% FCI	\$72,092,230.16
TOTAL CAPITAL COST: Fixed Capital Investment + Land + Working Capital					\$366,228,529.20

**PUBLICATIONS LIST (RELEVANT TO THESIS)**

1. Matzen M, Pinkerton J, Wang XM and Demirel Y. Use of natural ores as oxygen carriers in chemical looping combustion: A review. *IJGGC*. 2017;65:1-14.
2. Wang XM, Demirel Y. Feasibility of Power and Methanol Production by Entrained Flow Coal Gasification System. *Energy & fuels*. (Under review).

## REFERENCES

- [1] Energy Information Administration US, Electricity <https://www.eia.gov/electricity/monthly/>; [accessed 17.04.25]
- [2] Roan VP, Betts D, Twining A, Dinh K, Wassink P, Simmons T, An investigation of the feasibility of coal-based methanol for application in transportation fuel cell systems, Final Report, University of Florida, 2004.
- [3] World Coal Association, High Efficiency Low Emission Coal, <https://www.worldcoal.org/reducing-co2-emissions/high-efficiency-low-emission-coal/>; [Accessed 2016].
- [4] Energy Justice Network, FACT SHEET: ‘Clean Coal’ Power Plants, [file:///C:/Users/runew/Desktop/factsheet-IGCC-07%20\(1\).pdf](file:///C:/Users/runew/Desktop/factsheet-IGCC-07%20(1).pdf); [accessed 2007, 04]
- [dataset] [5] National Energy Technology Laboratory, Gasification Plant Databases, 2016. <https://www.netl.doe.gov/research/coal/energy-systems/gasification/gasification-plant-databases.>;
- [6] International Conference on Greenhouse Gas Control Technologies, Williams D, CSIRO & International Energy Agency. Greenhouse gas control technologies: proceedings of the Fifth International Conference on Greenhouse Gas Control Technologies. 2000; Cairns, Australia. CSIRO Publishing, Collingwood, Vic.
- [7] Chui EH, Douglas MA, Tan Y. Modeling of oxy-fuel combustion for a western Canadian sub-bituminous coal. *Fuel*. 2003;82(10):1201-1210.
- [8] Chui EH, Majeski AJ, Douglas MA, Tan Y, Thambimuthu KV. Numerical investigation of oxy-coal combustion to evaluate burner and combustor design concepts. *Energy*. 2004;29(9-10):1285-1296.
- [9] Chui EH, Gao H, Majeski AJ, Lee GK. International Conference on Climate Change. 2007; HongKong, China. Hong Kong Institution of Engineers; 2007.
- [10] Yang S, Yang Q, Li H, Jin X, Li X, Qian Y. An Integrated framework for modeling, synthesis, analysis, and optimization of coal gasification-based energy and chemical processes. *Ind Eng Chem Res*. 2012;51(48): 15763–15777.
- [11] Govind R, Shah J. Rakesh Govind, Modeling and simulation of an entrained flow coal gasifier. *AIChE J*. 1984 Jan 30(1):79-92.
- [12] Choi YC, Li XY, Park TJ, Kim JH, Lee JG. Numerical study on the coal gasification characteristics in an entrained flow coal gasifier. *Fuel*. 2001;80(15):2193-2201.
- [13] Chen C, Horio M, Kojima T. Numerical simulation of entrained flow coal gasifiers. Part I: modeling of coal gasification in an entrained flow gasifier. *Chem Eng Sci*. 2000;55: 3861-3874.

- [14] Yang H, Chen H, Ju F, Yan R, Zhang S. Influence of pressure on coal pyrolysis and char gasification. *Energy Fuels*. 2007;21(6):3165-3170.
- [15] Y. Demirel. Sustainable operations for distillation columns. *Chem Eng Pro Tech*. 2013;1005(1):1-15.
- [16] Martins AA, Mata TM, Costa CAV. Framework for sustainability metrics. *Ind Eng Chem Res*. 2007;46(10):2962-2973.
- [17] Sustainability Special Interest Group. Institution of Chemical Engineers, [http://nbis.org/nbisresources/metrics/triple\\_bottom\\_line\\_indicators\\_process\\_industries.pdf](http://nbis.org/nbisresources/metrics/triple_bottom_line_indicators_process_industries.pdf); 2002.[accessed 2014.10.8].
- [18] Aspen Technology. Version 9.0.1[software]. Burlington, MA, USA, 2016 [cited 2017 Mar 22].
- [19] Environmental Protection Agency. EPA Rule E9-5711:Federal Register. <https://www.gpo.gov/fdsys/pkg/FR-2009-04-10/pdf/E9-5711.pdf>; 2009. [accessed 2014.12.08]
- [20] Matzen M, Alhajji M, Demirel Y. Chemical storage of wind energy by renewable methanol production: Feasibility analysis using a multi-criteria decision matrix. *Energy*. 2015; 93(1-15): 343-353.
- [21] International Organization for Standardization, ISO 14040:2006, Environmental management - - Life cycle assessment -- Principles and framework. <https://www.iso.org/standard/37456.html>. 2006. [accessed 2006.07].
- [22] Vito. Energy. <https://vito.be/en/energy>; 2016.
- [23] Bo W. Avoiding co-Product allocation in Life-Cycle Assessment. *J Ind Ecol*. 2000; 4(3): 11-33.
- [24] Meyer L, Tsatsaronis G, Buchgeister J, Schebek L. Exergo environmental analysis for evaluation of the environmental impact of energy conversion system. *Energy*. 2009;34(1):75-89.
- [25] Turton R, Bailie RC, Whiting WB, Shaeiwitz JA, Bhattacharyya D. Analysis, Synthesis and design of chemical processes. 4th ed. Upper Saddle River: Prentice Hall, 2012.
- [26] Engineering, Chemical, The chemical engineering plant cost index. <http://www.chemengonline.com/pci-home>; 2016. [accessed 2017.02.12].
- [27] Gasification and Syngas Technologies Council(GSTC), “The Gasification Industry”, <http://www.gasification-syngas.org/resources/the-gasification-industry/;2016>.
- [28] National Energy Technology Laboratory(NETL), “Commercial Gasifiers”, <https://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/fluidizedbed>; 2016.

- [29] US Department of Energy. “Fluidized Bed Technology-Overview”, <https://energy.gov/fe/science-innovation/clean-coal-research/advanced-combustion-technologies/fluidized-bed-technology>; 2017.
- [30] National Energy Technology Laboratory(NETL), “Fixed (Moving) Bed Gasifiers”, <https://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/fmb>; 2017.
- [31] Kong X, Zhong W, Du W, Qian F. Compartment modeling of coal gasification in an entrained flow gasifier: A study on the influence of operating conditions. *Energy Convers. Manage.* 2014;82:202-211.
- [32] Jensen MD, Eylands KE, Heebink LV, Dockter BA. Final report. Grand Forks (ND): Nebraska Public Power District coal and fly ash analysis. Energy & Environmental Research Center; 2014.
- [33] Xu SS, Zhang DL, Ren YQ. Final report. Beijing: Large-scale coal gasification technology, Chemical Industry Press. 2006.
- [34] Aspen Technology. Model for entrained flow coal gasification. Aspen Technology, Inc, 2010-2012.
- [35] Wen CY, Chaung TZ. Entrainment coal gasification modeling. *Ind. Eng. Chem. Process Des. Dev.* 1979; 18(4): 684-695.
- [36] Wen CY, Chuang TZ. Entrained-Bed coal gasification modeling. [http://www.fischer-tropsch.org/DOE/DOE\\_reports/2274/Fe-2274-t1/Fe-2274-t1\\_toc.htm](http://www.fischer-tropsch.org/DOE/DOE_reports/2274/Fe-2274-t1/Fe-2274-t1_toc.htm); 1978.
- [37] Wen CY. Noncatalytic heterogeneous solid fluid reaction models. *Ind. Eng. Chem.* 1968; 60(9): 34-54.
- [38] Jones WP, Lindstedt RP. Global reaction schemes for hydrocarbon combustion, *Combustion and Flame.* 1988; 73(3): 233-249.
- [39] Dryer F, Glassman I. High-temperature oxidation of CO and CH<sub>4</sub>. In: 14th symposium (international) on combustion. Elsevier. 1973;987-1003.
- [40] Westbrook CK, Dryer FL. Chemical kinetic modeling of hydrocarbon combustion. *PECS.* 1984;10(1):1-57.
- [41] Qian F, Kong X, Cheng H, Du WL, Zhong WM. Development of a kinetic model for industrial entrained flow coal gasifiers. *Ind. Eng. Chem. Res.* 2013;52(5):1819-1828.
- [42] Bustamante F, Enick RM, Howard BH, Killmeyer RP, Rothenberger KS, Cugini AV, et al. Uncatalyzed and wall-catalyzed forward water–gas shift reaction kinetics. *AIChE J.* 2005;51(5):1440-1454.
- [43] US Energy Information Administration (EIA), “What is U.S. electricity generation by energy source?” <https://www.eia.gov/tools/faqs/faq.php?id=427&t=3>; 2016. [accessed 2.17.04.18]

- [44] National Energy Technology Laboratory (NETL), US. <https://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/igcc-efficiency>; 2016. [accessed 2016.10.20].
- [45] Anicic B, Trop P, Goricanec D. Comparison between two methods of methanol production from carbon dioxide. *Energy*. 2014;77(1):279-289.
- [46] Padurean A, Cormos CC, Agachi PS. Pre-combustion carbon dioxide capture by gas–liquid absorption for Integrated Gasification Combined Cycle power plants. *IJGGC*. 2012;7:1-11.
- [47] Illinois State Geological Survey. Illinois Continues Successful Injection of CO<sub>2</sub>: 500,000-Metric-Ton Mark Reached. <http://isgs.illinois.edu/illinois-continues-successful-injection-co2-500000-metric-ton-mark-reached>; 2017.
- [48] Field RP, Brasington R. Baseline flowsheet model for IGCC with carbon capture. *Ind. Eng. Chem. Res.* 2011;50(19): 11306–11312.
- [49] Siefert NS, Agarwal S, Shi F, Roth EA, Hopkinson D, Kusuma VA, Thompson RL, Luebke DR, Nulwala HB. Hydrophobic physical solvents for pre-combustion CO<sub>2</sub> capture: Experiments, computational simulations, and techno-economic analysis. *IJGGC*. 2016;49:364-371.
- [50] Moore JJ, Blieske M, Delgado H, Lerche A, Alsup C, Pacheco J, Bouhj M, Byard D. Research and development needs for advanced compression of large volumes of carbon dioxide, Workshop on Future Large CO<sub>2</sub> Compression Systems Sponsored by DOE Office of Clean Energy Systems, EPRI, and NIST March 30-31, 2009
- [51] Yang CJ, Jackson RB. China's growing methanol economy and its implications for energy and the environment. *Energy Policy*. 2012;41:878-884.
- [52] Toyir J, Miloua R, Elkadri NE, Nawdali M, Toufik H, Miloua F, Saito M. Sustainable process for the production of methanol from CO<sub>2</sub> and H<sub>2</sub> using Cu/ZnO-based multicomponent catalyst. *Physics Procedia*. 2009;2:1075-1079.
- [53] Machado CFR, Medeiros JL, Araújo QFQ, Alves RMB. A comparative analysis of methanol production routes: synthesis gas versus CO<sub>2</sub> hydrogenation. *Proceedings of the 2014 International Conference on Industrial Engineering and Operations Management*: 2014 Jan 7-9; Bali, Indonesia.
- [54] Graaf GH, Stamhuis EJ, Beenackers AACM. Kinetics of low-pressure methanol synthesis, *Chem. Eng. Sci.* 1988;43:3185-3195.
- [55] Marc Alvarado, HIS. <http://www.methanol.org/wp-content/uploads/2016/07/Marc-Alvarado-Global-Methanol-February-2016-IMPACA-for-upload-to-website.pdf>; 2016. [accessed 2016.01.05].



- [56] Chen L, Jiang Q, Song Z, Posarac D. Optimization of methanol yield from a Lurgi reactor. Chem. Eng. Technol, 2011;34:817-822.
- [57] Specht M, Bandi A. Final report. Stuttgart, Germany, 1999: "The Methanol-Cycle" - sustainable supply of liquid fuels. Solar Energy and Hydrogen Research.
- [58] Ren F, Li HS, Wang D, Wang J. Methanol synthesis from syngas in a slurry reactor. Prepr. Pap.- Am. Chem. Soc., Div. Fuel Chem. 2003;48(2):921-922.
- [59] Yusup S\* , Anh NP, Zabiri H. A simulation study of an industrial methanol reactor based on simplified steady-state model. IJRRAS. 2010;5(3):213-222.
- [60] Li C, Yuan X, Fujimoto K. Development of highly stable catalyst for methanol synthesis from carbon dioxide. Appl. Catal. 2014;469:306-311.
- [61] Energy Information Administration (EIA). Coal. <https://www.eia.gov/coal/>; 2017. [accessed 2017.04.07].
- [62] Methanex the power of agility. Methanex posts regional contract methanol prices for North America, Europe and Asia. <https://www.methanex.com/our-business/pricing>; 2017. [accessed 2017.05.03].
- [63] Energy Information Administration (EIA). Electricity Power Monthly. [https://www.eia.gov/electricity/monthly/epm\\_table\\_grapher.cfm?t=epMT\\_5\\_6\\_a](https://www.eia.gov/electricity/monthly/epm_table_grapher.cfm?t=epMT_5_6_a); 2017. [accessed 2017.04.25].
- [64] Energy Information Administration (EIA). Electricity. <https://www.eia.gov/electricity/>. 2017. [accessed 2016.12.12].
- [65] National Energy Technology Laboratory (NETL). Final report: Life Cycle Analysis: Integrated Gasification Combined Cycle (IGCC) Power Plant. U.S. Department of Energy, 2012.
- [66] General Electric. The Evolution Series Locomotives. [http://www.getransportation.com/na/en/docs/806527\\_20020%20-%20B%20Evo\[1\]\[1\].Series.lores.pdf](http://www.getransportation.com/na/en/docs/806527_20020%20-%20B%20Evo[1][1].Series.lores.pdf); [accessed 2008.08.14].
- [67] GREET Model, Version 2016. 2017 Jan 26. [cited 2017 Mar 5; downloaded 2017 Feb 23]. Available from: <https://greet.es.anl.gov/>.
- [68] Office of Waste Management NPDES. Galatia Mine NPDES Permit Reports. Springfield, Illinois: Renewed and modified NPDES permit to discharge into waters of the state. U.S Environmental Protection Agency. 2012 Feb. NPDES Permit No. IL0061727. Notice No. 5867c
- [69] U.S. Department of Energy. Report. Mining industry energy bandwidth study. BCS, Incorporated, United States. 2007 Jun.

- [70] Kowalski K, Sigrid S, Reinhard M, Ines O. Sustainable energy futures: Methodological challenges in combining scenarios and participatory multi-criteria analysis. *Eur J Oper Res.* 2009;197:1063-1074.
- [71] draw.io - Flowchart Maker & Online Diagram Software. <https://www.draw.io/>
- [72] Environmental Protection Agency. Overview of Greenhouse Gases. <https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2015>; <https://www.epa.gov/ghgemissions/overview-greenhouse-gases>; 2015. [accessed 2014.12.08]
- [73] BP Global, BP Statistical Review of World Energy <https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy/coal/coal-reserves.html>; 2016. [accessed 2017.06]
- [74] Kolbitsch P, Proll T, Bolhar-Nordenkamp J, Hofbauer H. Characterization of chemical looping pilot plant performance via experimental determination of solids conversion, *Energy and Fuels* 2009; 23:1450-1455.
- [75] Moghtaderi B. Review of the recent chemical looping process developments for novel energy and fuel applications. *Energy and Fuels*, 2012;26:15-40.
- [76] Demirel, Y., Matzen, M., Winters, C., Gao, X., Capturing and using CO<sub>2</sub> as feedstock with chemical looping and hydrothermal technologies. *Int. J. Energy Res.* 2015;39:1011–1047.
- [77] Adel F. Sarofim, JoAnn S. Lighty, Philip J. Smith, Kevin J. Whitty, Edward, Eyring, Asad Sahir et. Al., Chemical looping combustion reactions and systems, Reporting Period Start Date: October 2008.
- [78] Fan LS, Li FX. Chemical looping technology and its fossil energy conversion applications. *Industrial & Engineering Chemistry Research* 2010 49 (21), 10200-10211.
- [79] Zeng L, He F, Li FX, Fan L-S. Coal-direct chemical looping gasification for hydrogen production: reactor modeling and process simulation. *Energy & Fuels* 2012 26 (6), 3680-3690.
- [80] Matzen M, Pinkerton J, Wang XM and Demirel Y. Use of natural ores as oxygen carriers in chemical looping combustion: A review. *IJGGC.* 2017;65:1-14.
- [81] Azis MM., Jerndal E, Leion H, Mattisson T, Lyngfelt A. On the evaluation of synthetic and natural ilmenite using syngas as fuel in chemical-looping combustion (CLC). *Chem. Eng. Res. Des.* 2010;88:1505–1514.
- [82] Liu F, Zhang Y, Chen L, Qian D, Nearthery JK, Kozo S, Liu K. Investigation of a Canadian ilmenite as an oxygen carrier for chemical looping combustion. *Energy Fuels* 2013;27:5987–5995.

- [83] Leion H, Mattisson T, Lyngfelt A, Use of ores and industrial products as oxygen carriers in chemical-looping combustion. *Energy Fuels* 2009a;23(4):2307–2315.
- [84] Bidwe A, Mayer F, Hawthorne C, Charitos A, Schuster A, Scheffknecht G, Use of ilmenite as an oxygen carrier in chemical looping combustion-Batch and continuous dual fluidized bed investigation. *Energy Procedia*. 2011;4:433–440.
- [85] Cuadrat A, Abad A, Garcia-Labiano F, Gayan P, de Diego L, Adanez J, The use of ilmenite as oxygen-carrier in a 500 Wth chemical-looping coal combustion unit. *Int. J. Greenh. Gas Control*. 2011a;5:1630–1642.
- [86] Cuadrat A, Abad A, Garcia-Labiano F, Gayan P, de Diego LF, Adanez J, Ilmenite as oxygen carrier in a chemical looping combustion system with coal. *Energy Procedia*. 2011c;4:362–369.
- [87] Berguerand N, Lyngfelt A, Chemical-looping combustion of petroleum coke using ilmenite in a 10 kWth unite-high-temperature operation. *Energy Fuels*. 2009; 23:5257–5268.
- [88] Strohle J, Orth M, Eppler B. Chemical looping combustion of hard coal in a 1 MWth pilot plant using ilmenite as oxygen carrier. *Appl. Energy*. 2015;7:288–294.
- [89] Thon A, Kramp M, Hartge E-U, Heinrich S, Werther J, Operation experience with a system of coupled fluidized beds for chemical looping combustion of solid fuels using ilmenite as oxygen carrier. *Appl. Energy*. 2014;118:309–317.
- [90] Berguerand N, Lyngfelt A, The use of petroleum coke as fuel in a 10 kWth chemical-looping combustor. *Int. J. Greenh. Gas Control*. 2008;2:169–179.
- [91] Linderholm C, Lyngfelt A, Cuadrat A, Jerndal E. Chemical-looping combustion of solid fuels – operation in a 10 kW unit with two fuels, above-bed and in-bed fuel feed and two oxygen carriers, manganese ore and ilmenite. *Fuel*. 2012;102:808–822.
- [92] Arjmand M, Leion H, Mattisson T, Lyngfelt A, Investigation of different manganese ores as oxygen carriers in chemical-looping combustion (CLC) for solid fuels. *Appl. Energy*. 2014;113:1883–1894.
- [93] Linderholm C, Lyngfelt A, Dueso C, Chemical-looping combustion of solid fuels in a 10 kW reactor system using natural minerals as oxygen carrier. *Energy Procedia*. 2013;37:598–607.
- [94] Mei D, Mendiara T, Abad A, de Diego LF, Garcia-Labiano F, Gayan P, Adanez J, Zhao H, Manganese minerals as oxygen carriers for chemical looping combustion of coal. *Ind. Eng. Chem. Res*. 2016;55:6539–6546.
- [95] Schmitz M, Linderholm C, Hallberg P, Sundqvist S, Lyngfelt A, Chemical looping combustion of solid fuels using manganese ores as oxygen carriers. *Energy Fuels*. 2016;30(2): 1204–1216.

- [96] Linderholm C, Lyngfelt A, Cuadrat A and Jerndal E, Chemical-looping combustion of solid fuels - Operation in a 10 kW unit with two fuels, above-bed and in-bed fuel feed and two oxygen carriers, manganese ore and ilmenite, *Fuel*, 2012;102:808-822.
- [97] Zhao H, Wang K, Fang Y, Ma J, Mei D, Zheng C, Characterization of natural copper ore as oxygen carrier in chemical-looping with oxygen uncoupling of anthracite. *Int. J. Greenh. Gas Control*. 2014;22:154–164.
- [98] Tian X, Zhao H, Wang K, Ma J, Zheng C, Performance of cement decorated copper ore as oxygen carrier in chemical-looping with oxygen uncoupling. *Int. J. Greenh. Gas Control*. 2015;41:210–218.
- [99] Wen YY, Li ZS, Xu L, Cai NS, Experimental study of natural Cu ore particles as oxygen carriers in chemical looping with oxygen uncoupling (CLOU). *Energy Fuels*. 2012;26:3919–392.
- [100] Tian H, Siriwardane R, Simonyi T, Poston J, Natural ores as oxygen carriers in chemical looping combustion, *Energy Fuels*, 2013;2:4108-4118.
- [101] Zhao H, Wang K, Fang Y, Ma J, Mei D and Zheng C, Characterization of natural copper ore as oxygen carrier in chemical-looping with oxygen uncoupling of anthracite, *Int. J. Greenh. Gas Control*. 2014;22:154-164.
- [102] Guo L, Zhao H, Zheng C. Synthesis gas generation by chemical-looping reforming of biomass with natural copper ore as oxygen carrier, *Waste Biomass Valor*, 2015;6:81-89.
- [103] Wang K, Zhao H, Tian X, Fang Y, Ma J, Zheng C, Chemical-looping with oxygen uncoupling of different coals using copper ore as an oxygen carrier, *Energy Fuels*, 2015;29:6625-6635.
- [104] Song Q, Xiao R, Deng Z, Shen L, Xiao J, Zhang M. Effect of temperature on reduction of  $\text{CaSO}_4$  oxygen carrier in chemical-looping combustion of simulated coal gas in a fluidized bed reactor. *Ind. Eng. Chem. Res.* 2008a;47:8148–8159.
- [105] Wilder FA. Gypsum: its occurrence, origin, technology and uses. *Iowa Geol. Surv. Ann. Rep.* 28. 1918.
- [106] Xiao, R., Song, Q.L., Zheng, W.G., Deng, Z.Y., Shen, L.H., Zhang, M.Y., 2010b. Reduction kinetics of a  $\text{CaSO}_4$  based oxygen carrier for chemical-looping combustion. *Proceedings of the 20th International Conference on Fluidized Bed Combustion*.
- [107] Zheng M, Shen L, Feng X, Xiao J. Kinetic model for parallel reactions of  $\text{CaSO}_4$  with CO in chemical-looping combustion. *Ind. Eng. Chem. Res.* 2011;50:5414–5427.
- [108] Song Q, Xiao R, Deng Z, Shen L, Zhang M, Reactivity of a  $\text{CaSO}_4$  oxygen carrier in chemical-looping combustion of methane in a fixed bed reactor. *Korean J. Chem. Eng.* 2009;26(2):592–602.

- [109] Zheng M, Shen L, Feng X, In situ gasification chemical looping combustion of a coal using the binary oxygen carrier natural anhydrite ore and natural iron ore. *Energy Convers. Manage.* 2014;83:270–283.
- [110] Ding N, Zhang C, Luo C, Zheng Y, Liu Z, Effect of hematite addition to  $\text{CaSO}_4$  oxygen carrier in chemical looping combustion of coal char. *RSC Adv.* 2015;5:56362–56376.
- [111] Adanez J, Abad A, Garcia-Labiano F, Gayan P, de Diego LF, Progress in chemical-looping combustion and reforming technologies. A review. *Prog. Energy Combust. Sci.* 2012;38:215–282.
- [112] Geerts L, Rijns E, Witters H, Weltens R, Snijkers F, Health, safety and environmental impact study [Presentations Slides], Le Risque Chimique, 2015.
- [113] C. Linderholm, M. Schmitz, P. Knutsson and A. Lyngfelt, "Chemical-looping combustion in a 100-kW unit using a mixture of ilmenite and manganese ore as oxygen carrier," *Fuel*, vol. 166, pp. 533-542, 2016.
- [114] M. Matzen, M. Alhajji and Y. Demirel, "Chemical storage of wind energy by renewable methanol production: Feasibility analysis using a multi-criteria decision matrix," *Energy*, vol. 93, pp. 343-353, 2015
- [115] L. Xu, R. Edland, Z. Li, H. Leion, D. Zhao and N. Cai, "Cu-modified manganese ore as an oxygen carrier for chemical looping combustion," *Energy & Fuels*, vol. 28, pp. 7085-7092, 2014.
- [116] Jin F, Zeng X, Liu J, Jin Y, Wang L, Zhong H, Yao G, Huo Z. Highly efficient and autocatalytic  $\text{H}_2\text{O}$  dissociation for  $\text{CO}_2$  reduction into formic acid with zinc. *Nature Scientific reports* 2014; 4: 4503.