



DISSERTATION REPORT TK186801

OPTIMIZATION OF CARBON DIOXIDE CAPTURE, STORAGE, AND CONVERSION SYSTEM IN ORDER TO MITIGATE GREENHOUSE GAS EMISSION

ADITYA ANUGERAH PUTRA
02211360010005

ADVISORS

Prof. Ir. Renanto, M.Sc., Ph.D
Juwari, S.T., M.Eng., Ph.D
Prof. Rafiqul Gani

DOCTORAL PROGRAM
CHEMICAL ENGINEERING DEPARTMENT
FACULTY OF INDUSTRIAL TECHNOLOGY & SYSTEM ENGINEERING
INSTITUT TEKNOLOGI SEPULUH NOPEMBER
SURABAYA
2020



DISSERTATION REPORT TK186801

OPTIMIZATION OF CARBON DIOXIDE CAPTURE, STORAGE, AND CONVERSION SYSTEM IN ORDER TO MITIGATE GREENHOUSE GAS EMISSION

**ADITYA ANUGERAH PUTRA
02211360010005**

ADVISORS

**Prof. Ir. Renanto, M.Sc., Ph.D
Juwari, S.T., M.Eng., Ph.D
Prof. Rafiqul Gani**

**DOCTORAL PROGRAM
CHEMICAL ENGINEERING DEPARTMENT
FACULTY OF INDUSTRIAL TECHNOLOGY & SYSTEM ENGINEERING
INSTITUT TEKNOLOGI SEPULUH NOPEMBER
SURABAYA
2020**

APPROVAL SHEET

The dissertation is written to fulfill one of requirements to obtain title
Doctor of Chemical Engineering

At

Institut Teknologi Sepuluh Nopember

By:

Aditya Anugerah Putra

NRP: 02211360010005

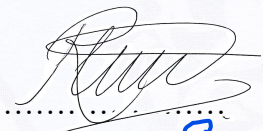
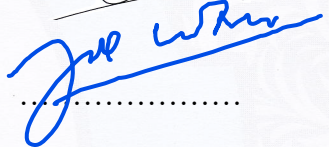
Examination Date: August 25th, 2020

Graduation Period: September 2020

Approved by:

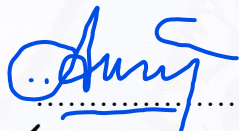
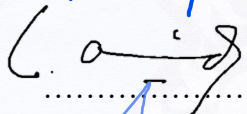
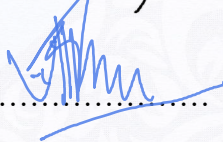
Advisors:

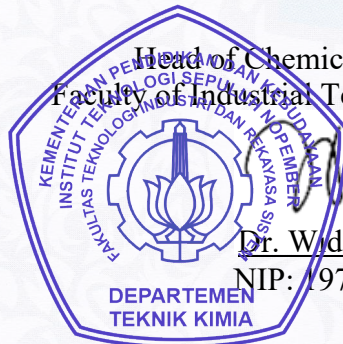
1. Prof. Ir. Renanto, M.Sc., Ph.D.
NIP. 19530719 197803 1 001
2. Juwari, S.T., M.Eng., Ph.D.
NIP. 19730615 199903 1 003
3. Prof. Rafiqul Gani
Technical University of Denmark


.....

.....
.....

Examiners:

1. Prof. Dr. Ir. Ali Altway, MS.
NIP. 19510804 197412 1 001
2. Prof. Dr. Ir. Kuswandi, DEA.
NIP. 19580612 198403 1 003
3. Prof. Dr.Eng. Ir. Arief Budiman, MS.
NIP. 19600628 198601 1 001


.....

.....

.....



Head of Chemical Engineering Department
Faculty of Industrial Technology & System Engineering


Dr. Widiyastuti, S.T., M.T.
NIP: 197503062002122002

This page is intentionally left blank

OPTIMIZATION OF CARBON DIOXIDE CAPTURE, STORAGE, AND CONVERSION SYSTEM IN ORDER TO MITIGATE GREENHOUSE GAS EMISSION

By : Aditya Anugerah Putra
Student Identity Number : 02211360010005
Supervisor : Prof. Ir. Renanto, M.Sc. Ph.D.
Co-Supervisor : Juwari, S.T., M.Eng., Ph.D.
Prof. Rafiqul Gani

ABSTRACT

Global warming is a phenomenon which is suspected by temperature rising on the earth surface. One of the causes of global warming is the high level of greenhouse gas in the atmosphere, and carbon dioxide is the biggest amount of greenhouse gas in the atmosphere. A solution is needed to mitigate the amount of those gases, which is using carbon capture technology. After carbon dioxide has been captured, carbon dioxide will be injected and stored into sink. In practice, there is a possibility that the availability of sources and sinks is not matched and sources and sinks are not in the same region and the capacity of the sinks is not enough to store all the carbon dioxide emission from the same region. Because of those differences, there will be unstored carbon dioxide and need an alternative storage. This research will simulate a carbon dioxide capture, storage, and conversion. Flue gas from sources will be captured using monoethanolamine. Product from carbon capture is then injected into sink using carbon storage network. Unstored carbon will be used as a reactant in methanol production process. Optimization is done to find the optimum minimum time difference for carbon storage network and minimum total annual cost for carbon capture and conversion to methanol. From the research, simulation of carbon capture gives satisfying result with 87.92 kg/s product flow with 98.1 % carbon dioxide purity. Carbon storage network can store 93.86 % of carbon dioxide using sequential method and 83.94 % of carbon dioxide using simultaneous method. For the total annual cost of carbon storage network, the most efficient cost is obtained in simultaneous method with optimum minimum time difference 6 years, which needs \$ 67,857,256, compared to sequential method with optimum minimum time difference 4.5 years, which needs \$ 78,233,875. From carbon dioxide capture and conversion process, it is found that carbon dioxide capture and conversion to methanol process is technically and economically feasible with 99.6 % purity and 52.96 kg/s of product stream. Later optimization gives a reduction of total annual cost from \$ 316,010,158 to \$ 291,550,576.

Keywords: Capture, carbon dioxide, conversion, optimization, storage

This page is intentionally left blank

OPTIMISASI PROSES PENANGKAPAN, PENYIMPANAN, DAN KONVERSI KARBON DIOKSIDA DALAM RANGKA MENGURANGI EMISI GAS RUMAH KACA

Nama Mahasiswa : Aditya Anugerah Putra
NRP : 02211360010005
Pembimbing : Prof. Ir. Renanto, M.Sc. Ph.D.
Ko-pembimbing : Juwari, S.T., M.Eng., Ph.D.
Prof. Rafiqul Gani

ABSTRAK

Pemanasan global adalah fenomena yang ditandai dengan kenaikan suhu di permukaan bumi. Salah satu penyebab pemanasan global adalah tingginya kandungan gas rumah kaca di atmosfer, dan karbon dioksida merupakan komponen terbesar penyusun gas rumah kaca di atmosfer. Solusi untuk mengurangi jumlah gas rumah kaca sangat dibutuhkan, dan salah satu yang paling menjanjikan adalah teknologi penangkapan karbon dioksida. Setelah karbon dioksida ditangkap, karbon dioksida akan dimasukkan dan disimpan di dalam media penyimpanan. Pada praktiknya, terdapat kemungkinan sumber emisi dan media penyimpanan tidak tersedia dalam waktu dan wilayah yang sama, dan jumlah karbon dioksida yang dikeluarkan lebih banyak daripada kapasitas maksimum media penyimpanan. Karena perbedaan tersebut, akan terdapat karbon dioksida yang tidak tersimpan dan membutuhkan media penyimpanan alternatif. Penelitian ini akan mensimulasikan penangkapan, penyimpanan, dan konversi karbon dioksida. Sumber emisi akan ditangkap menggunakan media *monoethanolamine*. Produk dari penangkapan karbon dioksida kemudian disimpan di media penyimpanan yang tersedia menggunakan metode jaringan penyimpanan karbon dioksida. Karbon dioksida yang tidak bisa disimpan akan dikonversi menjadi metanol. Optimisasi dilakukan untuk menemukan selisih tahun minimum optimal untuk jaringan penyimpanan karbon dioksida dan biaya tahunan total untuk penangkapan dan konversi karbon dioksida. Dari penelitian yang dilakukan didapatkan proses penangkapan karbon dioksida memberikan hasil yang baik dengan laju alir 87,92 kg/detik dengan kemurnian 98,1 %. Penyimpanan karbon dioksida dapat menyimpan 93,86 % karbon dioksida yang dihasilkan dengan menggunakan metode sekuensial dan 83,94 % pada metode simultan. Untuk selisih tahun minimum optimal didapatkan pada 6 tahun dengan biaya tahunan total sebesar \$ 67.857.256 pada metode simultan dibandingkan 4,5 tahun dengan biaya tahunan total sebesar \$ 78.233.875 pada metode sekuensial. Dari proses penangkapan dan konversi karbon dioksida, didapatkan laju alir produk sebesar 52,96 kg/detik dengan kemurnian metanol 99,6 %. Optimisasi yang dilakukan dapat menurunkan biaya tahunan total dari \$ 316.010.158 menjadi \$ 291.550.576.

Kata kunci: Karbon dioksida, konversi, optimisasi, penangkapan, penyimpanan

This page is intentionally left blank

PREFACE

The author thank God almighty for giving me strength and opportunity, so the author can complete the dissertation entitled “OPTIMIZATION OF CARBON DIOXIDE CAPTURE, STORAGE, AND CONVERSION SYSTEM IN ORDER TO MITIGATE GREENHOUSE GAS EMISSION”. This dissertation is written as a requirement for doctoral program in Chemical Engineering Department, Institut Teknologi Sepuluh Nopember.

The author want to say thank you to everyone, who has helped the author to finish this dissertation. Without them, this dissertation could not be done in time. Specifically, the author want to thank to his parents and Kreydita Handini Fitri for all of their support. The author also want to thank to DIKTI – PMDSU research program for the financial support on a contract of 015657/IT2.11/PN.08/2016. The author is deeply indebted to his advisor, Prof. Ir. Renanto, MS., Ph.D and his co-advisors Juwari, ST., M.Eng., Ph.D and Prof. Rafiqul Gani for their intellectual support and guidance during process of progress writing. Last but not least, the author would like to say thank you to Dr. Tantular Nurtono, S.T., M.Eng. as Head of Process System Engineering Laboratory for the opportunity to use the laboratory to complete this research, Head of Chemical Engineering Department, and Head of Post Graduate Program of Chemical Engineering Department.

However, this dissertation is not perfect yet. Therefore, the author will be very grateful if there is any recommendation in this dissertation.

Surabaya, August 31st, 2020

Author

This page is intentionally left blank

TABLE OF CONTENTS

APPROVAL SHEET	i
ABSTRACT	iii
ABSTRAK	v
PREFACE	vii
TABLE OF CONTENTS	ix
TABLES	xi
ILLUSTRATIONS	xiii
NOTATIONS	xv
CHAPTER 1 INTRODUCTION	
1.1. Background	1
1.2. Problem Statement	3
1.3. Purpose	3
1.4. Scope of Work	3
1.5. Benefit	5
1.6. Novelty	5
CHAPTER 2 LITERATURE STUDY	
2.1. Global Warming	7
2.2. Carbon Capture	9
2.3. Post-Combustion Carbon Capture using Absorption Process	12
2.3.1. Absorption using Monoethanolamine (MEA) Solvent	14
2.3.2. Reaction Mechanism of Carbon Dioxide Absorption	16
2.3.2.1. Reaction Mechanism	16
2.3.2.2. Vapor-Liquid Equilibrium Model	18
2.3.2.3. Absorption-Rate / Kinetics Model	20
2.4. Pinch Technology	22
2.5. Methanol Production Process	24
2.6. Former Research	27
CHAPTER 3 RESEARCH METHODS	
3.1. Literature Study and Data Collection	29

3.2. Making of Carbon Capture Simulation.....	31
3.3. Validation of Carbon Capture Simulation	34
3.4. Generating Cascade Table for Carbon Capture and Storage Network	34
3.5. Generating Grid Diagram for Carbon Capture and Storage Network	35
3.6. Optimizing Carbon Capture and Storage Network.....	36
3.7. Making of Carbon Conversion to Methanol Simulation	39
3.8. Validation of Carbon Conversion to Methanol Simulation.....	42
3.9. Optimizing Carbon Capture and Conversion to Methanol Simulation.....	42
CHAPTER 4 RESULT AND DISCUSSION	
4.1. Simulation of Carbon Dioxide Capture	45
4.1.1. Overview of Carbon Capture Simulation	45
4.1.2. Making of Carbon Capture Simulation	45
4.1.3. Result of Carbon Capture Simulation.....	46
4.2. Simulation of Carbon Dioxide Storage Network.....	47
4.2.1. Carbon Capture and Storage Network using Simultaneous Method.....	48
4.2.2. Carbon Capture and Storage Network using Sequential Method	53
4.2.3. Optimization of Carbon Capture and Storage Network	59
4.3. Simulation of Carbon Dioxide Conversion to Methanol.....	62
4.3.1. Overview of Methanol Synthesis Simulation.....	62
4.3.2. Making of Methanol Synthesis Simulation	63
4.3.3. Result of Methanol Synthesis Simulation	65
4.3.4. Optimization of Carbon Capture and Conversion to Methanol Process	66
CHAPTER 5 CONCLUSION	75
REFERENCES	77
ATTACHMENTS	83
AUTHOR BIOGRAPHY	87

TABLES

Table 2.1. Comparison of Solvents to Absorb CO ₂	13
Table 2.2. Equilibrium Constants Used in VLE Model	19
Table 3.1. Source Data	30
Table 3.2. Sink Data	30
Table 3.3. Flue Gas Stream Specification	31
Table 3.4. MEA Solvent Stream Specification	32
Table 3.5. Values of Equilibrium Constant Equations	32
Table 3.6. Equipment Specification for Carbon Capture Simulation	33
Table 3.7. Carbon Dioxide Feed Specification	40
Table 3.8. Hydrogen Feed Specification	40
Table 3.9. Equipment Specification for Carbon Conversion Simulation	41
Table 3.10. Basic Calculation of Equipment	43
Table 3.11. Utility Price	43
Table 3.12. Design Variable and Constraints for Optimization	44
Table 4.1. Carbon Capture Simulation Result	47
Table 4.2. Summary of Carbon Capture and Storage Result	59
Table 4.3. Total Annual Cost Calculation	60
Table 4.4. Result of Simulation	65
Table 4.5. Total Annual Cost of Base Case	66
Table 4.6. Total Annual Cost for Changing Number of Absorber Stages	68
Table 4.7. Total Annual Cost for Changing Stripper Feed Inlet Stage	69
Table 4.8. Total Annual Cost for Changing Number of Stripper Stages	70
Table 4.9. Total Annual Cost for Changing Inlet Reactor Temperature	71
Table 4.10. Total Annual Cost for Changing Reactor Pressure	72
Table 4.11. Summary of Optimization	73
Table A.1. Detailed Stream Specification in Carbon Capture Simulation	83
Table A.2. Detailed Stream Specification in Carbon Conversion Simulation	84
Table A.3. Detailed Stream Specification in Carbon Conversion Simulation (cont.)	85

This page is intentionally left blank

ILLUSTRATIONS

Figure 2.1. Block Diagram of Post-Combustion Carbon Capture	10
Figure 2.2. Block Diagram of Pre-Combustion Carbon Capture.....	11
Figure 2.3. Block Diagram of Oxy-Fuel Combustion Carbon Capture	11
Figure 2.4. Scheme of Carbon Dioxide Absorption Process using MEA	15
Figure 2.5. Single Step Termolecular Reaction Mechanism.....	18
Figure 2.5. Composite Curve in Pinch Technology	23
Figure 2.6. Scheme of Entrained Flow Process	25
Figure 2.7. Comparison Usage of Methanol Conversion Process	25
Figure 2.8. Methanol Production Process	26
Figure 4.1. Cascade Table for Δt 0 Years Using Simultaneous Method	48
Figure 4.2. Grid Diagram for Δt 0 Years Using Simultaneous Method.....	49
Figure 4.3. Cascade Table for Δt 5 Years Using Simultaneous Method	50
Figure 4.4. Grid Diagram for Δt 5 Years Using Simultaneous Method.....	50
Figure 4.5. Cascade Table for Δt 10 Years Using Simultaneous Method	51
Figure 4.6. Grid Diagram for Δt 10 Years Using Simultaneous Method.....	52
Figure 4.7. Single Region Cascade Table for Δt 0 Years	54
Figure 4.8. Grid Diagram for Δt 0 Years Using Sequential Method	55
Figure 4.9. Single Region Cascade Table for Δt 5 Years	56
Figure 4.10. Grid Diagram for Δt 5 Years Using Sequential Method	56
Figure 4.11. Single Region Cascade Table for Δt 10 Years	57
Figure 4.12. Grid Diagram for Δt 10 Years Using Sequential Method	58
Figure 4.13. Optimum Total Annual Cost Calculation Using Simultaneous Method	61
Figure 4.14. Optimum Total Annual Cost Calculation Using Sequential Method	62
Figure 4.15. Number of Absorber Stages Effect to Total Annual Cost	68
Figure 4.16. Stripper Feed Inlet Stage Effect to Total Annual Cost	69
Figure 4.17. Number of Stripper Stages Effect to Total Annual Cost	70
Figure 4.18. Inlet Reactor Temperature Effect to Total Annual Cost.....	71

Figure 4.19. Reactor Pressure Effect to Total Annual Cost	72
Figure A.1. Carbon Capture Simulation Flowsheet	83
Figure A.2. Carbon Conversion Simulation Flowsheet.....	84

NOTATIONS

Symbol	Description
C_j	concentration of component j in the liquid, mol/dm ³
d	diameter, cm
D_j or D	diffusivity of component j, cm ² /s
E	enhancement factor, dimensionless
h	jet length, cm
He	Henry's law constant, kPa dm ³ /mol
k	second order reaction rate constant, dm ³ /mol s
k_b	second order reaction rate constant for base B, dm ³ /mol s
k_{H_2O}	third order reaction rate constant for H ₂ O, dm ⁶ /mol ² s
K_i	equilibrium constant of reaction number i
k_i	first or second order reaction-rate constant of reaction i, 1/s or dm ³ /mol s
K_j	equilibrium constant of component j
k_j	first or second order reaction rate constant of component j, 1/s or dm ³ /mol s
k_L^0	physical mass transfer coefficient, cm/s
k_{RNH_2}	third order reaction rate constant for MEA, dm ⁶ /mol ² s
k^T	temperature dependence reaction rate, mol/dm ³ s
L	liquid flow rate, cm ³ /s
\dot{m}	flow rate, kg/s
N_{ave}	mass transfer flux in average condition, mol/s cm ² interfacial area
N_j	mass transfer flux of j, mol/s cm ² interfacial area
P	pressure, bar
P_j	partial pressure of j, bar
Re	Reynold number
r_i or r	reaction rate of reaction i, mol/dm ³ s

R_M	rate of methanol production per unit mass of catalyst, mol/h
R_R	rate of CO production per unit mass of catalyst, mol/h
T	temperature, K
t	time, s
x	spatial variables measured from the interface into the liquid bulk, cm
ε	surface roughness, m
μ	viscosity, Ns/m ²
ρ	density, kg/m ³
τ	contact time, s

CHAPTER 1

INTRODUCTION

1.1. Background

Global warming is an issue that is being discussed in the international community recently. Global warming is suspected by temperature rising on the earth's surface. The temperature rise varies between 0.74 ± 0.18 K over the last hundred years.

One of the causes of global warming is the high level of greenhouse gas in the atmosphere. Carbon dioxide is one of the components in the greenhouse gas with the biggest amount in the atmosphere.

The high content of carbon dioxide in the atmosphere is caused by the increasing population significantly years by years. The increasing population in the earth will lead to increasing energy requirements. Energy needs are mostly supplied by fossil fuel sources, such as petroleum, natural gas, and coal. Usage of fossil fuel, especially petroleum and coal will produce gaseous emissions, such as carbon dioxide (CO₂), carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen monoxide (NO), and other gases. Those gas, along with some other gases, such as methane and water vapor will form the greenhouse gas that leads to global warming (Maroto-Valer, 2010).

With the increasing of greenhouse gas in the atmosphere, especially carbon dioxide, a solution is needed to mitigate the amount of those gases. The solution needs to be applied in a short time and large scale, thus the effect of global warming can be minimized. One of the solutions is using carbon capture technology. Carbon capture technology consists of three main technologies, which are widely applied in industry, those are:

1. Post-combustion carbon capture
2. Pre-combustion carbon capture
3. Oxy-fuel combustion carbon capture

From those three technologies, post-combustion carbon capture using chemical absorption process is the most common used technology in the industry

(Bailey & Feron, 2005). Besides its simple application, its ability to absorb carbon dioxide are some reasons why post-combustion carbon capture is widely used.

After carbon dioxide has been captured, carbon dioxide will be injected and stored into sink, which most of them are depleted oil and gas reservoirs. Therefore, in practice, there is a possibility that the availability of sources and sinks is not matched, which means sinks are not ready while sources are already operated, or vice versa, so that it can be a problem in the planning of carbon dioxide capture and storage network. Besides the time availability problem, another problem that can arise is a location problem. There is a possibility that sources and sinks are not in the same region and the capacity of sinks is not enough to store all the carbon dioxide emissions from the same region. Because of those problems, it is possible that carbon dioxide capture and storage network can be done in a multi-region, where the location of sources and sinks is far apart. This research will simulate a carbon dioxide capture and storage network using a simultaneous and sequential method to find the amount of carbon dioxide that can be stored using each method and calculate the optimum minimum time difference between sources and sinks availability using total annual cost calculation.

Because of the difference in sources and sinks availability, there will be carbon dioxide that has been captured but can not be stored in a sink. That unstored carbon dioxide will need alternative storage, and in this case, it will be used as a reactant for methanol production process. For now, carbon dioxide used for the reactant comes from a specified designed process. As for methanol, required carbon dioxide is obtained from coal gasification process (Higman & van der Burgt, 2003). Since coal is a non-renewable resource, it will be depleted in the coming years, and with the increasing usage of methanol, a new source for carbon dioxide needs to be found. This research will simulate carbon dioxide capture and conversion process to methanol and check whether the process is technically and economically feasible or not. After that, those processes will be optimized by changing its operating conditions to find the minimum total annual cost.

1.2. Problem Statement

The problem that will be solved in this research is how much carbon dioxide can be stored using a simultaneous and sequential method and find the optimum minimum time difference between sources and sinks availability to get minimum total annual cost using each method of carbon dioxide capture and storage network. Another thing that will be solved is how to optimize carbon dioxide capture and conversion to methanol process using absorption process with monoethanolamine (MEA) as a solvent through changing operating conditions of the process so that the total annual cost will be minimized.

1.3. Purpose

This research aims to find the amount of captured carbon dioxide using a simultaneous and sequential method and find the optimum minimum time difference of the carbon capture and storage network so that minimum total annual cost can be obtained in each method, and find the minimum total annual cost of carbon dioxide capture and conversion to methanol process by changing its operating conditions.

1.4. Scope of Work

The scope of this work is bound to:

1. Carbon dioxide capture
 - The composition of flue gas feed from sources is assumed to be the same.
 - The amount of flue gas feed is total flue gas produced divided by the longest duration of source.
 - Carbon dioxide is captured using post-combustion carbon capture technology. Process of capturing carbon dioxide is using absorption process with monoethanolamine solvent.
2. Carbon dioxide storage network
 - The simulation simulates five sources and six sinks in two regions.

- The amount of carbon dioxide injected into sink comes from the product stream of carbon dioxide capture process and is defined by a fixed carbon dioxide flow rate from each emission source. Time availability for each source, which is the time that the industry starts its first carbon dioxide capturing process, is defined based on the consideration that every source can not start its capture process together.
- Each carbon dioxide sink is defined by the maximum carbon dioxide injected into each sink. Time availability for each sink, which is the time while carbon dioxide is injected to sink for the first time, is defined. Operation lifetime is based on the assumption that the duration of every CCS process can not be done at the same time.
- Matching of sources and sinks will be done either in simultaneous method and sequential method with 0, 5, and 10 years of minimum time difference.
- The total annual cost calculated for carbon dioxide network consists of the total annual capital cost for piping and shipping and total annual operating cost for piping, shipping, and penalty fee.

3. Carbon dioxide conversion to methanol

- The capacity of methanol conversion process is the smallest amount of alternative storage needed from carbon dioxide storage network.
- Making fresh hydrogen feed is not simulated in this work, fresh hydrogen feed is bought from elsewhere.
- Total annual cost calculated consists of total annual capital cost and total annual operating cost for each equipment in carbon dioxide capture process and carbon dioxide conversion to methanol process.
- Optimization of simulation is done by changing operating conditions to find minimum total annual cost.

1.5. Benefit

This research is expected to have considerable benefits in the future. One of its benefits is this research can decrease the amount of carbon dioxide in the atmosphere significantly, which leads to a reduction of global warming issues. This research will help to find the amount of carbon dioxide that can be stored using two widely known methods, which are simultaneous and sequential method, and determine the optimum minimum time difference between sources and sinks availability so that total annual cost will be minimized. Another benefit from this research is carbon dioxide, which needs alternative storage before sinks are available, can be used as a reactant for a useful chemical product so that this research can be used as a reference for industry in development of carbon dioxide processing.

1.6. Novelty

The novelty of this research is how to find the amount of stored carbon dioxide using a simultaneous and sequential method and find the optimum minimum time difference between sources and sinks availability to get minimum total annual cost in multi-region sources and sinks carbon dioxide capture and network. Another novelty is the integration between carbon capture process and carbon conversion to methanol process. There are already some researches that study about how to capture carbon from flue gas, and there are already some researches that study about how to produces some chemical products that need carbon dioxide as their reactant, but not much talking about integration of the two processes above, and consider about the total annual cost.

This page is intentionally left blank

CHAPTER 2

LITERATURE STUDY

2.1. Global Warming

Global warming is a phenomenon that is characterized by increasing average temperature on the Earth's surface. It increases approximately 0.74 ± 0.18 K over last hundred years. There are some impacts that will result from increasing earth's surface temperature, those are:

1. Unstable climate

During global warming, northern hemisphere will suffer greater warming than any other hemisphere. As a result of this warming, the icebergs will melt and ice land will be smaller than ever. Areas that previously experienced light snowfall, will not experience it again. Mountains in subtropical areas will have smaller snow-capped on its peak.

2. Increasing Sea Level

When the temperature of atmosphere is increasing, the temperature of sea surface will be warmer, so that the volume of seawater will become greater and sea level will be higher. Global warming will melt the polar ice caps, which will raise the volume of seawater. Sea level has risen 10-25 centimeters during 20th century and is predicted to increase 9-88 centimeters during 21st century.

3. Ecological Disturbance

In global warming, some animals tend to migrate toward the poles and up the mountains. However, human development will block their migration. Species that migrate to north or south will be impeded by cities and farms. Some types of species that are not able to migrate to north or South Pole could be extinct.

The most important cause of global warming is high level of greenhouse gas in the atmosphere. Greenhouse gas is needed to ensure the life of creatures on the earth, because without greenhouse gas, average temperature of the earth's surface will only 255.15 K. Carbon dioxide is one of the greenhouse gas that has

greatest amount in the atmosphere. Carbon dioxide gas comes from fossil fuel combustion reaches 56.6 %, from forest destruction reaches 17.3 %, whereas methane reaches 14.3 %, and nitrogen oxide reaches 7.9 % (IPCC, 2007).

Power plants are the largest contributor of carbon dioxide emission, with emission is about 0.17 GtCO₂ in 2008 in the UK (BERR, 2009). Based on a report from the International Energy Outlook in 2008, total carbon dioxide emission from the whole world is estimated at 28.1 GtCO₂ and will increase by about 1.7 % per year from 2005 to 2030 (EIA, 2008).

Several methods are used to cope with increase of carbon dioxide emission, but generally consist of three main strategies, those are:

1. Changing fuel into low-carbon fuel.
2. Improving energy efficiency and conservation of industrial machines that require fossil fuel.
3. Applying carbon capture and storage technology to reduce carbon dioxide emission, while the use of fossil fuels continues.

Changes of fuel into low-carbon fuel is quite difficult to do. Fossil fuels (especially coal) have a percentage of 86 % of world energy use (Orr, Jr., 2009), and are expected to remain dominant energy source (McKinsey & Company, 2008). Although there is considerable concern over increasing carbon dioxide emission (Bachu, 2008), alternative energy sources or renewable energy are still experiencing fundamental obstacles to be applied.

For example, there are some security and environmental issues against usage of nuclear power as energy source. And for other energy sources, such as wind, sunlight, water, ocean wave, and geothermal energy, those sources could not provide energy in sufficient quantity as fossil fuel provides.

Reduction of carbon dioxide emission can also be done by applying efficient energy. Innovative power generation technology, such as Integrated Gasification Combined Cycle (IGCC), can increase the efficiency of chemical energy conversion of fuel from 28-32 % up to 52 %. Fuel flexibility can also affect the reduction of emission. For example, a change from coal to petroleum than to natural gas can reduce carbon dioxide emission per kWh from 1 kg to 0.75 kg then 0.5 kg. However, even with increased efficiency and reduced emission, rapid

expansion of world's energy needs will constantly increase carbon dioxide emission.

2.2. Carbon Capture

Carbon capture and storage (CCS) is one of the method that technically able to reduce carbon dioxide emission from large source emission, such as power plant, up to 90 % (IPCC, 2005). Its major advantage is fossil fuels, including coal, can still be used as fuel for power plant, while releasing of carbon dioxide into the atmosphere can be reduced (IRGC, 2008). Overall, CCS consists of three main steps, namely:

1. Separate and capture carbon dioxide from emission source
2. Compress carbon dioxide to a super critical state to be carried to sink location
3. Injection into sink location, as well as last isolation from the atmosphere

Although some components of CCS technology have been used in industry for a long time, but until now there is no commercial application of integrated CCS system. Several CCS pilot-scale projects have been conducted in several countries and showed positive result. China, which took over USA in terms of carbon dioxide emission from consumption and flaring of fossil fuel, with emission 6 GtCO₂ compared to USA with 5.9 GtCO₂ (EIA, 2008), show significant progress in CCS project

A major difficulty in applying CCS technology is the reluctance of some companies to invest in CCS technology, considering that some companies do not have cost allocation to reduce carbon dioxide emission. In addition, uncertainty over the future regulation about usage of coal power plant and carbon dioxide storage, and the need for further research and development will make CCS technology hard to be applied (Gibbins & Chalmers, 2008). Public perception and support are also important aspect for application of CCS technology. The main concerns of public are related to safety issues and whether CCS technology can provide a solution to climate change (Gough & Shackley, 2005; van Alphen et al., 2007).

Cost estimation for CCS technology involves high uncertainty. This uncertainty comes because CCS technology costs may develop over times, and potential variation in the technical requirements and application of projects. According to report in 2008, commercial project of CCS in 2020 is estimated to cost €30-50 per ton carbon dioxide (McKinsey & Company, 2008).

There are three main CCS technologies that already known widely, those are:

1. Post-combustion carbon capture
2. Pre-combustion carbon capture
3. Oxy-fuel combustion carbon capture

Those three main CCS technologies will be explained below and represented by Figure 2.1, Figure 2.2, and Figure 2.3.

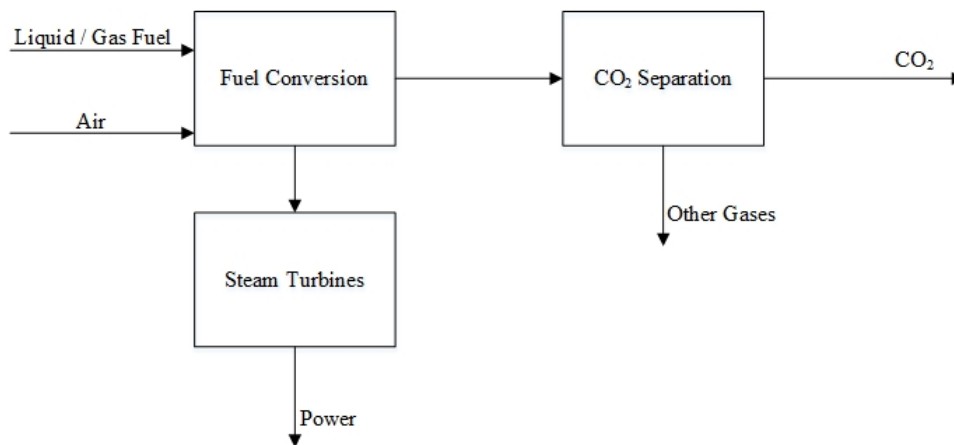


Figure 2.1. Block Diagram of Post-Combustion Carbon Capture

Figure 2.1 shows block diagram for post-combustion carbon capture, where carbon dioxide is separated from other gases, such as NO_x and SO_x, which are produced during combustion. The common technique for post-combustion capture is chemical absorption, for example using monoethanolamine (MEA). This technique is used in the natural gas industry for over 60 years.

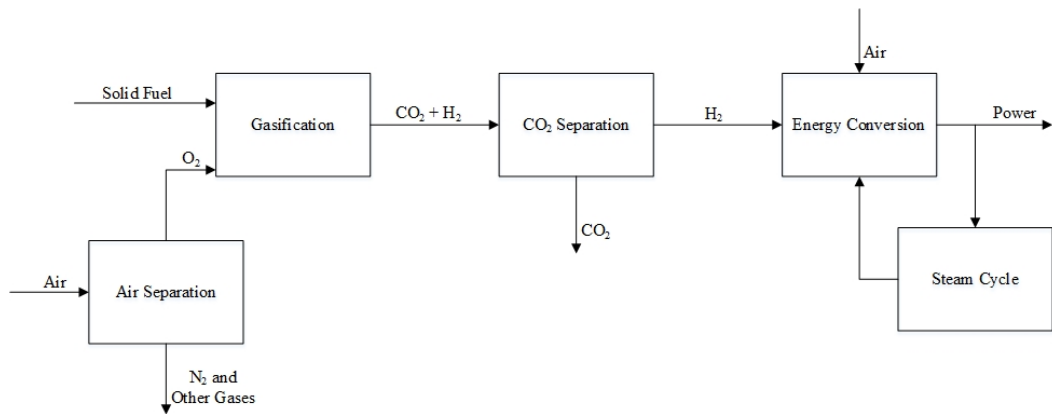


Figure 2.2. Block Diagram of Pre-Combustion Carbon Capture

Block diagram for pre-combustion carbon capture is shown in Figure 2.2, where carbon dioxide is removed from the fuel before combustion. The fuel is converted into a mixture of carbon dioxide and hydrogen using a reforming process, or to a mixture of carbon monoxide and hydrogen via coal gasification process. Basically, same as post-combustion carbon capture, chemical or physical processes, such as MEA absorption or pressure swing absorption, is used to capture carbon dioxide.

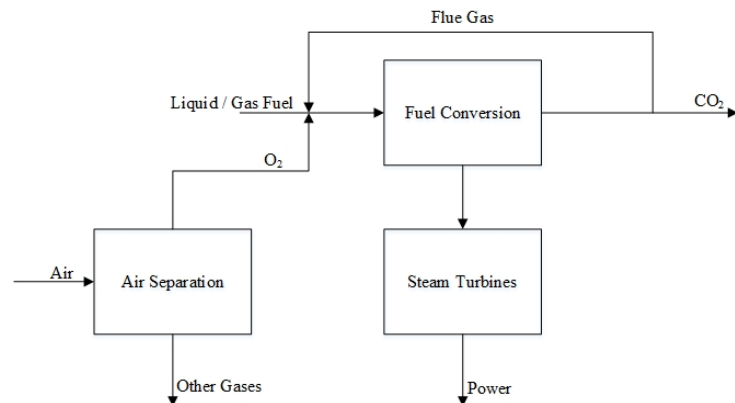


Figure 2.3. Block Diagram of Oxy-Fuel Combustion Carbon Capture

Figure 2.3 shows how oxy-fuel combustion carbon capture works. Fuel is burned in a pure oxygen stream. Oxygen is used as a fuel oxidizing agent instead of air. The main separation step in these plants is separating oxygen from other

gases. The resulting flue gas is a high-purity carbon dioxide stream, so it does not need any further separation processes (Maroto-Valer, 2010).

2.3. Post-combustion Carbon Capture using Absorption Process

Every combustion process of fossil fuel will produce flue gas, which consists of carbon dioxide, water vapor, and other gases. In order to avoid carbon dioxide emission from that source into the atmosphere, carbon dioxide needs to be separated from water vapor and other gases. One of the separation method is using post-combustion carbon capture. In post-combustion carbon capture, capture and separation process are done after combustion. The most common process of post-combustion carbon capture is using absorption process.

Absorption process with chemical solvents are currently the most used technology for post-combustion carbon capture (Wilson et al., 2004). The state-of-the-art process to separate CO₂ from a flue gas is a solvent process in which CO₂ reacts with an absorption liquid. These chemical absorption process are in general applicable to gas streams at both high and low overall process pressure, but which have a low CO₂-partial pressure. They make use of the reversible nature of the chemical reaction, effected by a temperature different (Bailey & Feron, 2005).

Absorption process with chemical solvent is highly used because this technology is the most efficient process and have the lowest operating cost compared to other processes. Another reason is because absorption process has reached its commercial scale for carbon dioxide separation from natural gas and carbon dioxide production as technical gas from coal combustion and gasification (Romeo et al., 2008). Although absorption has reached commercial scale for some processes, this technology has not reached commercial scale for power plant with 400-500 MW capacity.

The heat of carbon dioxide absorption is approximately 50-80 kJ/mole CO₂, and in order to reuse the solvent, this system needs regeneration process, where carbon dioxide is desorbed from the solvent at high temperature (373.15 – 413.15 K) and at moderate pressure (1 bar) (Bailey & Feron, 2005).

Since power plant flue gases are generally at atmospheric pressure, CO₂ partial pressure is very low. Also flue gas contains oxygen and other impurities,

therefore an important aspect of an absorption process is in the proper choice of solvent for the given process duty. High CO₂ loading and low heat of recovery energy are essential for atmospheric flue gas CO₂ recovery. The solvents must also have low by-product formation and low decomposition rates, to maintain solvent performance and to limit the amount of waste materials produced. Some types of solvents are used to capture carbon dioxide from flue gas. Comparison of some solvents that are widely used can be looked at Table 2.1 (Bailey & Feron, 2005):

Table 2.1. Comparison of Solvents to Absorb CO₂

Solvent	MEA	DGA	DEA	DIPA	MDEA
Concentration in water solution (% mass)	<30	<60	<40	<40	<50
Solvent loading (mole/mole)	0.3	0.35	0.3-0.7	0.45	0.45
Heat regeneration (MJ/kg CO ₂)	2.0	2.0	1.5	1.5	1.3
Chemical formula	C ₂ H ₇ NO	C ₄ H ₁₁ NO ₂	C ₄ H ₁₁ NO ₂	C ₆ H ₁₅ NO ₂	C ₅ H ₁₃ NO ₂

Remarks:

MEA : *Monoethanolamine*

DGA : *Diglycolamine*

DEA : *Diethanolamine*

DIPA : *Diisopropanolamine*

MDEA: *Methyldiethanolamine*

Besides its advantage, absorption process still have some disadvantages. The main disadvantages of this process is flue gas needs to be cleaned to avoid scaling, plugging, and foaming in the absorber. Furthermore, because carbon dioxide is a flue gas that is not used anymore, this process requires high operating cost without any profit.

The following requirements are importance in the development of chemical absorption for power plants:

1. Regeneration energy should be as low as possible to reduce energy consumption
2. Chemical stability at the operating temperature and pressure and low degradation level
3. Low volatility to minimize evaporation losses
4. Oxygen can be tolerated to enable use of carbon steel
5. SO_x should be eliminated, because can form corrosive salt
6. Fly ash should be eliminated to avoid foaming and plugging in the absorber
7. Flue gas temperature should be reduced to 323.15 K

2.3.1. Absorption using Monoethanolamine (MEA) Solvent

MEA has been the most commonly used solvent in chemical plants producing carbon dioxide from power plant, boiler, and furnace up to 1200 tons per day. Most plants that use MEA are based on the three commercially available processes (Bailey & Feron, 2005), namely:

1. Kerr-McGee/ABB Lummus Crest
This process can operate from natural gas boiler to high-sulphur coal boiler, and uses a 15 to 20 weight% aqueous MEA solution. The first process unit is started in 1978 in California with capacity 800 ton CO₂/day. Carbon dioxide came from natural gas, coal, and coke boiler (Arnold et al., 1982).
2. Fluor Daniel/Dow Chemical
This process uses 30 weight% aqueous MEA solution, and can process flue gas with oxygen, NO_x, and SO_x. This process uses an inhibitor to avoid corrosion due to high amine concentration. The process can generate pure carbon dioxide with purity up to 99.95 % that is used for urea and food industries.
3. Kansai Electric Power Company/Mitsubishi Heavy Industries
The process is based upon sterically hindered amines and already three solvents (KS-1, KS-2 and KS-3) have been developed. KS-1 was

commercialized in a urea production application in Malaysia in 1999. The major benefits in this process are low heat requirements for regeneration, low amine losses and low solvent degradation without the use of inhibitors or additives.

Chemical process to capture and separate carbon dioxide from other gases is done in two steps, carbon dioxide absorption by lean solvent in absorber, and carbon dioxide separation from enriched solvent in stripper. As stated before, since power plant flue gases are generally at atmospheric pressure, CO₂ partial pressure is very low. Due to low CO₂ partial pressure, the operation process of the whole system can be done in slightly higher than atmospheric pressure. The inlet temperature of absorber is generally in the ranges of 313.15 – 323.15 K and the inlet temperature of stripper is generally in the ranges of 373.15 – 413.15 K (Wu et al. 2014). Scheme of the process is shown in the Figure 2.4.

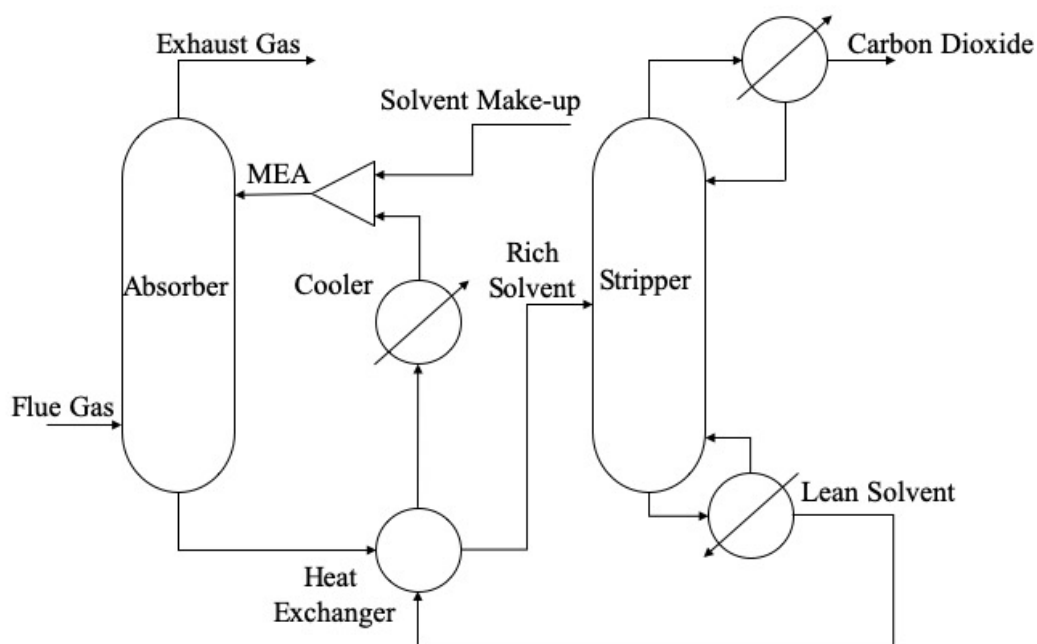


Figure 2.4. Scheme of Carbon Dioxide Absorption Process using MEA

Flue gas enters absorber column after being cooled to temperature approximately 323.15 K and slightly higher than ambient pressure, 1.57 bar. In the absorber, flue gas is contacted with aqueous amine and produce CO₂-lean gas and carbon-rich amine solution that exits from bottom absorber. Carbon-rich amine

solution is pumped to heat exchanger to increase its temperature before entering stripper. Heating medium for the heat exchanger is lean solvent that exits from the bottom of the stripper. The integration of rich solvent that needs to be heated and lean solvent that needs to be cooled aims to reduce operating cost from utilities.

Carbon-rich amine solution then enters to the stripper. The regeneration of the chemical solvent is carried out in the stripper at elevated temperatures (373.15 – 413.15 K) and pressure not very much higher than atmospheric pressure. Heat is supplied to the kettle reboiler to maintain the regeneration condition, which leads to a thermal energy penalty as a result of heating up the solvent, providing the required desorption heat for removing the chemically bound CO₂ and for steam production which act as a stripping gas. Steam is then recovered in the condenser and fed back to the stripper. CO₂ product gas leaves at the top of the column, while regenerated solvent exits from the bottom of the stripper column and will recirculate to the absorber.

2.3.2. Reaction Mechanism of Carbon Dioxide Absorption

2.3.2.1. Reaction Mechanism

The reaction between carbon dioxide and monoethanolamine (MEA) solution have been described in the literature by two mechanism, namely the zwitterion mechanism introduced by Danckwerts in 1979 and the termolecular mechanism introduced by Crooks and Donnellan in 1989. The zwitterion mechanism consists of the formation of a complex called a zwitterion, followed by the deprotonation of the zwitterion by a base (Danckwerts, 1979).

Reaction 2.1 – 2.10 may occur when carbon dioxide absorbs into and reacts with aqueous MEA. All the species represented are in aqueous solution.

Ionization of water:



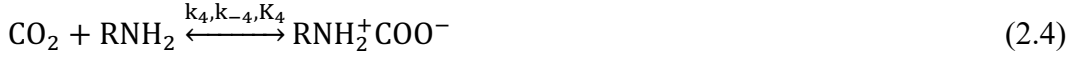
Dissociation of dissolved carbon dioxide through carbonic acid:



Dissociation of bicarbonate:



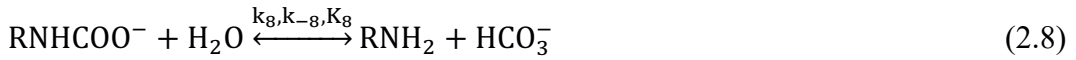
Zwitterion formation from MEA and carbon dioxide reaction:



Carbamate formation by deprotonation of the zwitterion:



Carbamate reversion to bicarbonate:



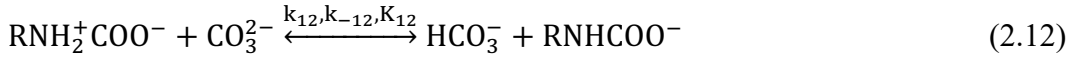
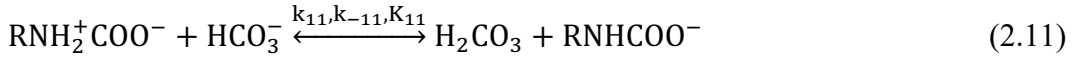
Dissociation of protonated MEA:



Bicarbonate formation:



Since carbon dioxide-loaded aqueous MEA solutions were used in the experimental work, the concentration of bicarbonates and carbonates in the aqueous solutions were considered significant. As a result, additional reactions 2.11 and 2.12 became essential in describing the mechanism.



Based on this reaction scheme, the general rate of reaction of carbon dioxide with MEA via the zwitterion mechanism could be described in Equation 2.13 (Versteeg et al., 1996).

$$r_{\text{CO}_2-\text{MEA}} = \frac{[\text{CO}_2][\text{RNH}_2] - k_{-4}/k_4 [\text{RNHCOO}^-](\sum k_{-b}[\text{BH}^+]/\sum k_b[\text{B}])}{\frac{1}{k_4} + (k_{-4}/k_4 \sum k_b[\text{B}])} \quad (2.13)$$

Where B designates any species in the solution that can act as a base to abstract the proton from the zwitterion. In this case, the expected species for a loaded MEA solution are $[\text{RNH}_2]$, $[\text{H}_2\text{O}]$, $[\text{OH}^-]$, $[\text{HCO}_3^-]$, and $[\text{CO}_3^{2-}]$.

The termolecular mechanism assumes that the reaction as a single-step between carbon dioxide and MEA where the initial product is not a zwitterion but

a loosely bound encounter complex with a mechanism of the type shown in Figure 2.5.

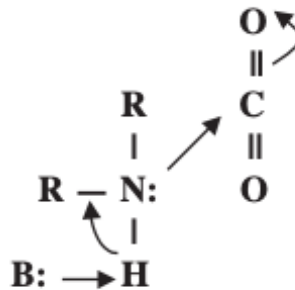


Figure 2.5. Single Step Termolecular Reaction Mechanism

Most of these complexes are intermediates, which break up to give reagent molecules again, a few react with a second molecule of amine, or a water molecule, to give ionic products. Bond-formation and charge-separation occur only in the second step. The forward reaction rate for this mechanism is presented in Equation 2.14.

$$r_{CO_2-MEA} = -(k_{RNH_2}[RNH_2] + k_{H_2O}[H_2O])[RNH_2][CO_2] \quad (2.14)$$

2.3.2.2. Vapor-Liquid Equilibrium Model

Liquid bulk concentrations of all chemical species are required for kinetic analysis. It has been assumed that all of the chemical reactions are at equilibrium. The concentration of water is assumed to remain constant because its concentration is much larger than the concentration of all other chemical species and also because of the short contact time in the laminar jet absorber. The concentrations for the remaining eight chemical species shown in the chemical reactions were calculated by solving the mass balance equations and the Henry's law correlation in Equation 2.15 – 2.23.

MEA balance:

$$[RNH_2] + [RNH_3^+] + [RNHCOO^-] = [MEA]_0 \quad (2.15)$$

Carbon balance:

$$[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [RNHCOO^-] = \alpha[MEA]_0 \quad (2.16)$$

Charge balance:

$$[\text{RNH}_3^+] + [\text{H}_3\text{O}^+] = [\text{HCO}_3^-] + [\text{OH}^-] + 2[\text{CO}_3^{2-}] + [\text{RNHCOO}^-] \quad (2.17)$$

Independent equilibrium constants:

$$K_1 = [\text{OH}^-][\text{H}_3\text{O}^+] \quad (2.18)$$

$$K_2 = [\text{HCO}_3^-][\text{H}_3\text{O}^+]/[\text{CO}_2] \quad (2.19)$$

$$K_3 = [\text{CO}_3^{2-}][\text{H}_3\text{O}^+]/[\text{HCO}_3^-] \quad (2.20)$$

$$K_8 = [\text{RNH}_2][\text{HCO}_3^-]/[\text{RNHCOO}^-] \quad (2.21)$$

$$K_9 = [\text{RNH}_2][\text{H}_3\text{O}^+]/[\text{RNH}_3^+] \quad (2.22)$$

In addition to these mass balance equations, the Henry's law relationship between the equilibrium partial pressure and the free concentration of carbon dioxide is required.

$$P_{\text{CO}_2} = \text{He} \times [\text{CO}_2] \quad (2.23)$$

In order to solve these nonlinear algebraic equations for the bulk concentrations and the equilibrium partial pressure, the values of the solubility (in terms of Henry's law constant, He) and the equilibrium constants are required. The solubility of carbon dioxide in amine was calculated using the N₂O analogy (Tsai et al., 1992).

The equilibrium constants K₁, K₂, K₃ were calculated by the correlations developed by Edwards et al. in 1978. These correlations are well established and have been utilized in many VLE models such as Austgen et al. in 1989. The equilibrium constants K₈ and K₉ can be calculated from simple correlations developed by Kent & Eisenberg in 1976. The equilibrium constants are shown in Table 2.2.

Table 2.2. Equilibrium Constants Used in VLE Model

	a₁	a₂	a₃	T range (K)
K ₁ , (mol/dm ³)	-13445.9	-22.4773	140.932	273-498
K ₂ , (mol/dm ³)	-12092.1	-36.7816	235.482	273-498
K ₃ , (mol/dm ³)	-12431.7	-35.4819	220.067	273-498
K ₈ , (mol/dm ³)	-3090.83	0.0	6.69425	298-413
K ₉ , (mol/dm ³)	-5851.11	0.0	-3.3636	298-413

$$\ln K = \frac{a_1}{T} + a_2 \ln T + a_3 \quad (2.24)$$

2.3.2.3. Absorption-Rate / Kinetics Model

A comprehensive absorption-rate/kinetics model was developed for interpreting the absorption data of carbon dioxide into MEA solutions, from which the kinetics data were extracted. The model takes into account the coupling between chemical equilibrium, mass transfer, and chemical kinetics of all possible chemical reactions. The mathematical model is capable of predicting gas absorption rates and enhancement factors from the system hydrodynamics and the physico-chemical properties, as well as predicting the kinetics of reaction from experimental absorption data. A rigorous numerical method to solve the system of unsteady state partial differential equations was developed. The numerical scheme employed utilizes the Barakat–Clark method (Barakat & Clark, 1966) for solving diffusive differential equations. In brief, the diffusion equation in Equation 2.24 is the one most frequently used to represent the absorption of gas into liquid jets. This equation governs the variation in time and space of the concentration of the reactants and the products in the liquid phase (one equation for each component or material balance).

$$D_j \frac{\partial^2 C_j}{\partial x^2} = \frac{\partial C_j}{\partial t} + r_i \quad (2.24)$$

The chemical species in reaction 2.1 – 2.12 have been renamed for convenience in the numerical treatment as follows: $C_1=[CO_2]$, $C_2=[RNH_2]$, $C_3=[RNH_3^+]$, $C_4=[HCO_3^-]$, $C_5=[OH^-]$, $C_6=[CO_3^{2-}]$, $C_7=[H_3O^+]$, $C_8=[RNHCOO^-]$, and $C_9=[H_2O]$.

Equation 2.25 – 2.29 which are based on Equation 2.24 represent the diffusion of the gas accompanied with reaction into the liquid near the interface
Carbon dioxide reaction balance:

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} + r_2 + r_{CO_2-MEA} + r_{10} \quad (2.25)$$

The total carbon dioxide balance:

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_4}{\partial t} + \frac{\partial C_6}{\partial t} + \frac{\partial C_8}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} + D_4 \frac{\partial^2 C_4}{\partial x^2} + D_6 \frac{\partial^2 C_6}{\partial x^2} + D_8 \frac{\partial^2 C_8}{\partial x^2} \quad (2.26)$$

Total MEA balance:

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_3}{\partial t} + \frac{\partial C_8}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2} + D_3 \frac{\partial^2 C_3}{\partial x^2} + D_8 \frac{\partial^2 C_8}{\partial x^2} \quad (2.27)$$

Charge balance:

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_7}{\partial t} - \frac{\partial C_4}{\partial t} - \frac{\partial C_5}{\partial t} - 2 \frac{\partial C_6}{\partial t} - \frac{\partial C_8}{\partial t} = D_3 \frac{\partial^2 C_3}{\partial x^2} + D_7 \frac{\partial^2 C_7}{\partial x^2} - D_4 \frac{\partial^2 C_4}{\partial x^2} - D_5 \frac{\partial^2 C_5}{\partial x^2} - 2D_6 \frac{\partial^2 C_6}{\partial x^2} - D_8 \frac{\partial^2 C_8}{\partial x^2} \quad (2.28)$$

Carbamate balance

$$\frac{\partial C_8}{\partial t} = D_8 \frac{\partial^2 C_8}{\partial x^2} + r_8 - r_{\text{CO}_2\text{-MEA}} \quad (2.29)$$

Equilibrium instantaneous reactions:

In order to eliminate the likelihood of using very large reaction rates for the instantaneous reactions (reactions 2.1, 2.3, and 2.9) from the model equations, their equilibrium constant expressions were used to complete the model equations for concentration profile calculations. These equilibrium constant expressions are given in Equation 2.30 – 2.32.

$$K_1 = C_5 C_7 \quad (2.30)$$

$$K_3 = \frac{C_6 C_7}{C_4} \quad (2.31)$$

$$K_9 = \frac{C_2 C_7}{C_3} \quad (2.32)$$

The above eight equations (Equation 2.25 – 2.32) were solved for the concentration profiles of the eight chemical species, C_1, C_2, \dots, C_8 , subject to the initial and boundary conditions given in Equation 2.33 – 2.36.

Initial conditions:

For all chemical species, $j=1, 2, \dots, 8$.

$$C_j(x, 0) = C_j^0 \text{ at } t=0 \text{ and } 0 \leq x \leq \infty \quad (2.33)$$

Boundary conditions:

For all chemical species, $j=1, 2, \dots, 8$.

$$C_j(\infty, t) = C_j^0 \text{ at } x=\infty \text{ and } 0 \leq t \leq \tau \quad (2.34)$$

For all volatile chemical species, $j=1$

$$C_j(0, t) = C_j^* = \frac{P_j}{H_{e_j}} \text{ at } x=0 \text{ and } 0 \leq t \leq \tau \quad (2.35)$$

For all non-volatile chemical species, $j=2, 3, \dots, 8$.

$$\frac{dC_j}{dx}(0, t) = 0 \text{ at } x=0 \text{ and } 0 \leq t \leq \tau \quad (2.36)$$

Using the obtained concentration profile data of the absorbed gas, C_1 , the local absorption rate per unit area was calculated using Equation 2.37.

$$N = -D_1 \left(\frac{\partial C_1}{\partial x} \right)_{x=0} \quad (2.37)$$

The term $(\partial C_1 / \partial x)_{x=0}$ is the concentration gradient at the surface and it is a function of time. The average absorption rate per unit area of solute gas by the liquid jet of length h is obtained by integrating Equation 2.37 over the contact time as shown in Equation 2.38 (Danckwerts, 1970).

$$N_{ave} = -\frac{D_1}{\tau} \int_0^\tau \frac{\partial C_1}{\partial x} (0, t) dt \quad (2.38)$$

When the dissolved gas reacts with the liquid, it is often convenient to present the effect of a chemical reaction in terms of the enhancement factor, E , defined as the ratio of absorption rate of a gas into a reacting liquid to that if there was no reaction, as given in Equation 2.39.

$$E = \frac{N_{ave}}{k_L^0 (C^* - C^0)} \quad (2.39)$$

N_{ave} was obtained from Equation 2.38 whereas k_L^0 was evaluated from $k_L^0 = 4 / d\pi \sqrt{(DL/h)}$, an expression that is valid in the case of laminar jet absorber Aboudheir et al. (2003).

2.4. Pinch Technology

Pinch technology is build based on heat transfer in thermodynamic laws. This technology is dominated by heat exchanger network method, which will lead to minimum energy cost. The ease and good performance of this technology makes it widely used as a standard method for designing and analyzing process system.

Term of “pinch technology” has been introduced by Linnhoff and Hindmarch in 1983 to present a thermodynamic based method that can guarantee minimum energy in the design of heat exchanger network. Pinch technology is often used to present applications and algorithms for learning industrial processes. Pinch technology introduces a simple method for systematic analysis in a chemical process and utility system.

By using pinch method, it can be shown which one is the hot stream that needs to be cooled and the cold stream that needs to be heated as shown in Figure

2.6. In pinch method, there is a value called pinch point which is the optimum point of process design, where the stream above pinch point is a source of heat and the stream below pinch point requires heat. Heat sources can be used to heat cold stream and vice versa, cold stream can be used to cool hot stream by installing heat exchanger in both streams. Pinch method can determine which stream can be connected using heat exchanger and how much heat transfer is transferred in heat exchanger to obtain the most optimum heat exchanger network.

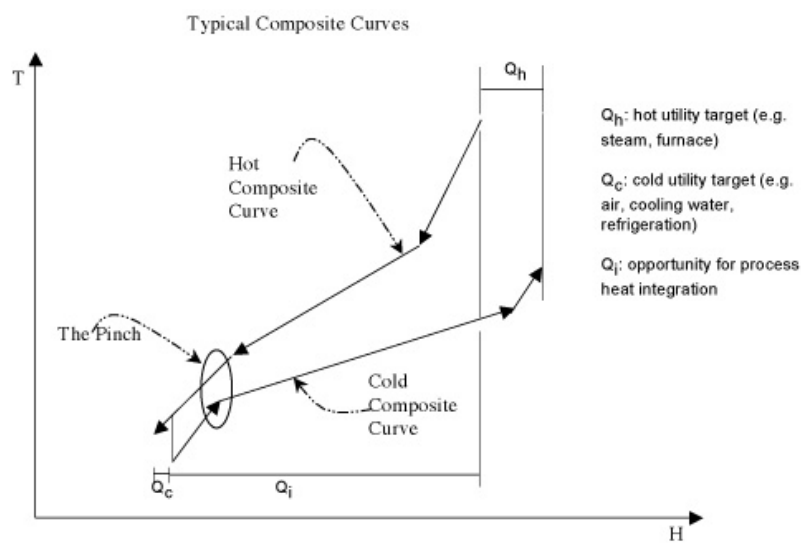


Figure 2.6. Composite Curve in Pinch Technology

In the carbon dioxide capture and storage network concept, pinch point is the time when there is no mass transfer. Mass transfer occurs before and after pinch point, so that mass transfer can not exceed the pinch point.

In terms of heat exchanger network, there are two main ways to solve the problems, sequential method and simultaneous method. Sequential method use the strategy of dividing heat exchanger network problem into a series of subproblem in order to reduce the computational requirements for obtaining a network design. This method typically involves partitioning of heat exchanger network problem into a number of intervals, which is usually accomplished by dividing the temperature range of the problem into temperature intervals. These intervals are important for modelling heat exchange while obeying the laws of thermodynamics. The problem is decomposed into a series of target subproblems which are solved successively in

order of decreasing significance with respect to the total annual cost of the heat exchanger network based on heuristic rules.

For simultaneous method, the goal of simultaneous heat exchanger network is to find the optimal network without decomposition of the problem. Simultaneous method is primarily mixed integer nonlinear programming (MINLP) formulations of the heat exchanger network problem subject to various simplifying assumptions used to facilitate the solution of these complex models (Furman & Sahinidis, 2002).

In making carbon dioxide capture and storage network, same analogy is used. Carbon dioxide capture and storage network will be made in two methods, simultaneous and sequential method. In simultaneous method, there is no consideration about which region do source and sink belong, every source and sink can be paired without any region limitation. In sequential method, region limitation of source and sink is considered. Source and sink which belong to the same region is paired first. The alternative storage that arises from single region pairing is then transferred to another region, so that some amount of carbon dioxide that needs alternative storage can be paired with sink from another region.

2.5. Methanol Production Process

Methyl alcohol, or methanol, is an organic chemical with chemical formula CH_3OH . Methanol has a very important use, both in daily life and in industry. Recently, methanol is used for alternative fuel to reduce usage of fossil fuel and reduce carbon dioxide emission. Basically, methanol production process consists of two steps, namely:

1. Gasification process of coal to syngas
2. Conversion process of syngas to methanol

Coal gasification process is the conversion of coal into product gases, which in this case are carbon dioxide, carbon monoxide, hydrogen, and other gases. There are some coal gasification process into gas, those are moving bed, fluidized bed, and entrained flow. Entrained flow is the most commonly used process in large scale industry. In this process, contact between coal powder and mixture of steam and air is made very quickly. Coal feed that is used can be a slurry feed or dry feed

with coal size $<100\ \mu\text{m}$. This process has advantages that the contact time is very short, so the occurrence of agglomerate can be minimized. Another advantage is this process can be used for any type of coal (Higman & van der Burgt, 2003). Scheme of entrained flow process is shown in Figure 2.7.

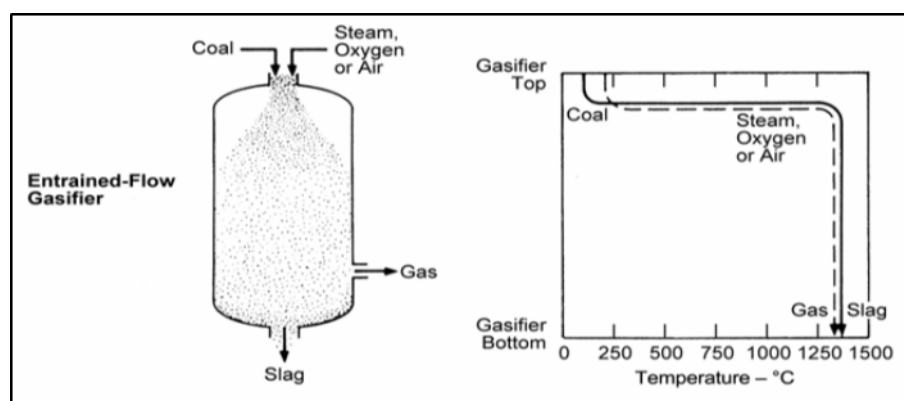


Figure 2.7. Scheme of Entrained Flow Process

After syngas is formed, next step is syngas conversion into methanol. There are some processes that is used in industry, such as ICI, Lurgi, Nissui Topsoe, Kellogg, Mitsubishi Gas Company (MGC), etc. Figure 2.8. shows the percentage usage of some processes.

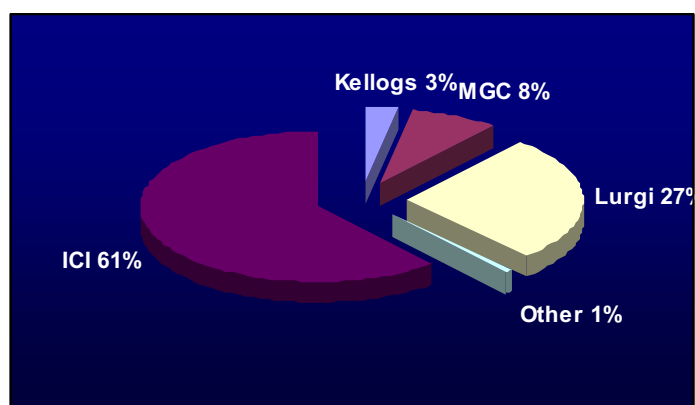


Figure 2.8. Comparison Usage of Methanol Conversion Process

Imperial Chemical Industries (ICI) process to produce methanol was introduced in the 1960s in the United Kingdom (UK). In 1963, Phineas Davies and

Frederick Snowdon filled a patent for a methanol production process operating at 30.4 – 121.6 bar. Using a copper, zinc, and chromium catalyst, they had created a process capable of producing high quantities of methanol without the need for very high pressure. The lower pressure meant that fast reaction rates could be achieved at lower temperature of 473.15 – 573.15 K, which reduced the formation of byproduct. This meant the catalyst was able to achieve a selectivity of greater than 99.5 %, based on organic impurities in the liquid methanol (Sheldon, 2017).

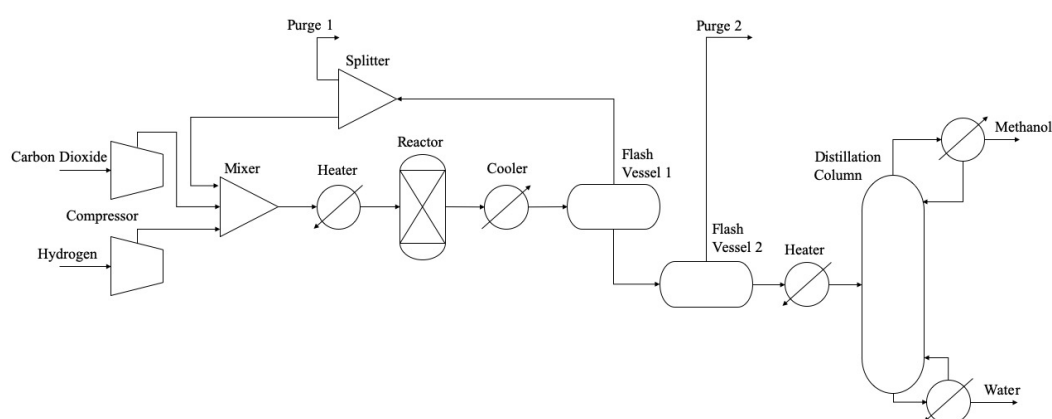


Figure 2.9. Methanol Production Process

Figure 2.9 shows typical methanol production process. Carbon dioxide that has been captured before is compressed to 50.7 – 101.3 bar and mixed with fresh hydrogen feed and recycle flow before entering ICI quench reactor, where there is catalyst bed in it and operates in approximately 513.15 – 543.15 K. Reactions of methanol synthesis are:



Effluent from reactor is then cooled to 313.15 K to condense methanol. Inert gas in the reactor is recycled back into circulator. Some purge is taken from recycle gas to take some inert gas and will be used as fuel gas. Crude methanol from separator still consists of water and other chemicals that will be separated by using two flash vessels and one distillation column. First flash vessel aims to separate methanol solution from unreacted carbon dioxide and hydrogen. Second flash vessel aims to separate methanol solution from any other impurities that still contain

in the stream and decreases pressure. Final separation of methanol solution occurs in distillation column, where purified methanol exits from top stream and water exits from bottom stream.

2.6. Former Research

There are some former researches that have been discussed about carbon capture, storage, and conversion. These section will discuss briefly about those former researches:

1. Diamante et al. have been done research titled “Unified pinch approach for targeting of carbon capture and storage (CCS) systems with multiple time periods and regions” in 2014. In their research, they used composite curve, cascade table, and grid diagram to design carbon capture and storage network in multi-region using sequential method. They have not compared sequential method grid diagram with simultaneous method grid diagram. Optimization of carbon capture and storage network based on total annual cost have not been done too.
2. Zuchrillah and Rachmawati have optimized carbon capture and storage network using pinch method in 2014. In their research, they used pinch method to simulate mass exchanger network. Reviewed system is carbon capture and storage which aims to capture carbon dioxide from sources and store it into much safer form. The research have used grid diagram to design carbon capture and storage network and done in single region only.
3. Ooi et al. have been done research titled “Planning of carbon capture and storage with pinch analysis techniques” in 2013. The research developed carbon capture and storage network using pinch method. Region used in the research was single region. Carbon storage composite curve and carbon storage cascade analysis were used to determine appropriate matching. The research only used cascade table to design carbon capture and storage network. Grid diagram to design carbon capture and storage network was not used.

This page is intentionally left blank

CHAPTER 3

RESEARCH METHODS

This research is divided by some steps, those are:

1. Literature study and data collection
2. Making of carbon capture simulation
3. Validation of carbon capture simulation
4. Generating cascade table for carbon capture and storage network
5. Generating grid diagram for carbon capture and storage network
6. Optimizing carbon capture and storage network
7. Making of carbon conversion to methanol simulation
8. Validation of carbon conversion to methanol simulation
9. Optimizing carbon capture and conversion to methanol simulation

3.1. Literature Study and Data Collection

Literature is taken from several books and journals which are relevant to the research. Literature study is done to learn some things, such as post-combustion carbon capture using absorption process using monoethanolamine (MEA) as a solvent, the amount of sources and sinks in Indonesia, and the use of carbon dioxide in a methanol production process.

Two regions are selected for this research, namely West Sumatra and East Java. Source will come from five industries in West Sumatra, while sink comes from six places, three of them are coming from West Sumatra and the other three come from East Java (Usman et al. 2014; Satyana and Purwaningsih 2003). Data that are already collected is shown in Table 3.1. for source and Table 3.2. for sink.

Table 3.1. Source Data

Code	Source Place	Start Time (y)	Duration (y)	End Time (y)	Average Production Rate (Mt/y)	Flue Gas Produced (Mt)
SR1	PLN Bukit Asam	5	25	30	1.786	44.65
SR2	RU III Plaju	7	25	32	0.619	15.475
SR3	PT. Merbau GGS	15	25	40	0.133	3.325
SR4	PT. Semen Batu Raja	10	50	60	0.501	25.05
SR5	Pusri Palembang	12	20	32	2.507	50.14
Total Flue Gas Produced (Mt)						138.64

Table 3.2. Sink Data

Code	Sink Place	Region	Start Time (y)	Duration (y)	End Time (y)	Average Injection Rate (Mt/y)	Sink Capacity (Mt)
SK1	Site I2	West Sumatra	7	25	32	0.17	4.25
SK2	Site H2		4	25	29	0.21	5.25
SK3	Site 3		2	50	52	0.96	48
SK4	Banyu Urip	East Java	10	36	46	0.0873	3.14
SK5	Sukowati		20	50	70	0.06286	3.14
SK6	Mudi		30	55	85	0.05714	3.14
Total Sink Capacity (Mt)							66.92

3.2. Making of Carbon Capture Simulation

Simulation of carbon capture is done using Aspen Plus 7.3. Simulation of carbon capture is made for post-combustion carbon capture. Simulation is made for post-combustion carbon capture using absorption process, with aqueous monoethanolamine (MEA) solution as a solvent. The simulation will use approximately 30 weight% aqueous MEA solution, since corrosion might occur in higher amine concentration.

Flow of flue gas feed used for the simulation is obtained from sources data in Table 3.1. The amount of flue gas is total flue gas produced divided by the longest duration of source. Since flue gas composition data for each stream is not available, assumption of flue gas composition is made. It is assumed that flue gas from each source is already passed through air pollution unit. First air pollution unit is particulate removal, such as baghouse filter or electrostatic precipitator, in order to eliminate particulate content. Second air pollution unit is flue gas desulfurization to decrease its sulfur dioxide (SO₂) content, so that the sulfur dioxide presence can be neglected. Another assumption is that composition of flue gas from each source is the same. Flue gas and MEA solvent specification used in the carbon capture simulation is shown in Table 3.3. and Table 3.4.

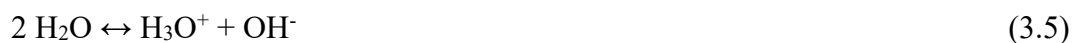
Table 3.3. Flue Gas Stream Specification

Specification	Value
Temperature (K)	320.49
Pressure (bar)	1.57
Total mass flow (kg/s)	372.43
Components	Mass Fraction
H ₂ O	0.041
CO ₂	0.232
N ₂	0.727

Table 3.4. MEA Solvent Stream Specification

Specification	Value
Temperature (K)	319.15
Pressure (bar)	1.01
Total mass flow (kg/s)	1,605.02
Components	Mass Fraction
H ₂ O	0.676
MEA	0.289
CO ₂	0.034
N ₂	0.001

As described before, in more simple way, several reactions occur during absorption and desorption of carbon dioxide from flue gas, those reaction set is described as follows (White, 2002).



The equilibrium constants for above equations can be calculated using equation below with relevant parameters are taken from literatures (Freguia, 2002).

$$\ln K_j = A_j + \frac{B_j}{T} + C_j \ln T + D_j T \quad (3.6)$$

Where

Table 3.5. Values of Equilibrium Constant Equations

Reaction	A _j	B _j	C _j	D _j
1	-3.038	-7008.3	0	-0.00313
3	216.05	-12431.7	-35.48	0
4	-0.52	-2545.53	0	0
5	132.89	-13445.9	-22.47	0

For reaction (2), at the operating condition experimental data suggests that reaction (2) is too slow to reach equilibrium. Therefore, a temperature approach to equilibrium of 280.93 K is specified (White, 2002).

Besides equilibrium approach, another way to simulate carbon dioxide absorption with aqueous monoethanolamine (MEA) is using kinetic model. The reaction between carbon dioxide and MEA is usually described using two different reaction mechanism, the zwitterion mechanism and the termolecular mechanism. Aboudheir et al. (2003) showed that the termolecular mechanism could be used to explain the observed kinetic phenomena. According to the termolecular mechanism, the complete reaction set will be given as below:



Here B represents any base present in solution and MEA, H_2O , HCO_3^- , CO_3^{2-} are the main base present in the loaded MEA solution.

The carbamate reversion reaction considered is given as:



Bicarbonate formation reaction is:



Based on researches that have been done, the rate constant expressions are given as (Putta et al. 2017):

$$k_{\text{MEA,a}}^T = 4.5191 \times 10^{11} \times \exp \left[-\frac{5851.7}{T} \right] \quad (3.10)$$

$$k_{\text{H}_2\text{O,a}}^T = 2.1105 \times 10^6 \times \exp \left[-\frac{2382.4}{T} \right] \quad (3.11)$$

Specification of each equipment used in the carbon capture simulation is shown in Table 3.6.

Table 3.6. Equipment Specification for Carbon Capture Simulation

Specification	Value
Absorber	
Condenser	No
Reboiler	No
Stages	7 equilibrium stages

Specification	Value
Top Tray Pressure	1.01 bar
Column pressure drop	0.57 bar
Heat Exchanger	
Pressure drop	0 bar
Stripper	
Condenser	Partial condenser
Reboiler	Kettle reboiler
Stages	10 equilibrium stages
Top Tray Pressure	1.21 bar
Column pressure drop	0.568 bar
Lean Solvent Cooler	
Outlet Temperature	319.15 K
Pressure drop	0 bar
Recycle Mixer	
Pressure drop	0 bar

3.3. Validation of Carbon Capture Simulation

After both simulations are done, next step is validation of simulations which have been made before. Validation is done to ensure that simulations match with the reference, such as plant data or journal. If simulations do not match with the reference, simulations is evaluated and fixed, so it can match with the reference.

3.4. Generating Cascade Table for Carbon Capture and Storage Network

Generating cascade table is the first step to calculate CCS network. Cascade table is used to calculate the amount of minimum alternative storage needed and unutilized storage and pinch point that will be used for generating grid diagram. Generating cascade table is done in following steps:

1. Prepare a table with the following column name: t, source, sink, Δt , flow rate carbon dioxide, load carbon dioxide, infeasible, and feasible cascade.
2. Plot stream line for source and sink in appropriate year.

3. Δt column is time difference
4. Flow rate carbon dioxide column is $\Sigma SK - \Sigma SR$
5. Load carbon dioxide column is flow rate carbon dioxide $\times \Delta t$
6. Calculation for shifted year for different Δt (0, 5, and 10 years) is done by adding Δt in the start and end for each sink operation

3.5. Generating Grid Diagram for Carbon Capture and Storage Network

Grid diagram will be made in two ways, simultaneous and sequential. As stated before, sources are assumed to be in one region, which is West Sumatra, while sinks are assumed to be separated in two regions, West Sumatra and East Java. In sequential method, sources and sinks from West Sumatra are paired first. The alternative storage needed is then transferred to East Java.

For simultaneous grid diagram:

1. Make a vertical line as pinch point line
2. Make horizontal lines, which each line represents each source and sink. Line direction is drawn from left (starting operation year) to right (end operation year).
3. Calculation for shifted year is done by subtracting pinch point time of sink by 0, 5, and 10 years for every Δt variable.
4. Grid diagram consists of two zones, below pinch (left side of the pinch line) and above pinch (right side of the pinch line). There are some rules for designing integration process between source and sink regarding below and above pinch zone.
 - Mass transfer in below pinch zone, flow rate source \geq sink, while in above pinch zone, flow rate source \leq sink.
 - Mass transfer is started from pinch point
 - Below pinch zone, there should be no unutilized storage and above pinch zone, there should be no alternative storage
5. Pairing process between source and sink also concerns about time difference between paired source and sink. Find pairing that has the same

or close time difference with designed Δt . To obtain suitable time difference, there is possibility that source and sink stream has to be split. Some rules for splitting stream are as follows.

- Splitting process is only be done if pairing stream does not meet the requirement of pinch rules
 - Splitting process is done by dividing one stream of source and sink to several streams with appropriate values.
 - Start and end year of the stream are not changed
6. If pairing process has been done, but there is still unutilized storage below pinch zone and alternative storage above pinch zone, the additional pairing can be done without following the rule that has been stated before.

For sequential grid diagram:

1. Grid diagram is made using simultaneous method for single region only.
2. Alternative storage that is needed, is then transferred to sinks that are located in the other region, in this case East Java.
3. Multi-region pairing also considers about time difference between paired source and sink, just like single region pairing process.
4. Multi-region pairing does not follow the pinch rules.

3.6. Optimizing Carbon Capture and Storage Network

Total annual cost (TAC), which consist of annual operating cost (AOC) and annual capital cost (ACC), based on transferred load between source and sink will be calculated. Some of main costs that will be calculated in determining total annual cost are transportation cost and penalty fee. Based on geographical location of each source and sink, transportation system is decided to use both piping and shipping. Shipping will consist of three elements, ship cost, port storage cost, and loading cost, while penalty fee consists of alternative storage and unutilized storage penalty. Therefore, there are some calculations to calculate total annual cost, which are annual capital cost (piping and shipping) and annual operating cost (piping, shipping, and penalty).

For piping ACC and AOC calculation

1. Some variables to calculate ACC and AOC for piping system are.

$P_{in} = 152$ bar, $P_{out} = 103$ bar, $T = 298.15$ K, $\rho = 884$ kg/m³, $\mu = 0.0000606$ Ns/m², surface roughness (ε) = 0.00015 m (galvanized iron), construction cost factor = \$ 826,339 /m.km, O&M cost factor = \$ 3,100 /km (Heddle et al. 2003).

2. Piping ACC calculation

- Pipe diameter calculation

Calculation is done based on pressure drop and friction factor in turbulent flow (Geankoplis 2003). Pipe diameter calculation is done by using iteration, which Reynold number is calculated first and assuming D.

$$Re = \frac{4\dot{m}}{\pi\mu D} \quad (3.12)$$

\dot{m} is carbon dioxide flow rate, which is obtained from grid diagram. Relative roughness is also calculated using formula below.

$$k = \frac{\varepsilon}{D} \quad (3.13)$$

After that, looking up friction factor (f) using friction factor chart or known as Moody chart, which correlate Reynold number (Re) and relative roughness (k) (Perry and Green, 2008).

Then, new pipe diameter is calculated using the simplified formula, combining the equations for pressure drop and head loss. The formula for calculating new diameter is shown below. The calculation is repeated until constant value of D is obtained (Heddle et al. 2003).

$$D^5 = \frac{32f\dot{m}^2}{\pi^2\rho\left(\frac{\Delta P}{L}\right)} \quad (3.14)$$

- Pipe ACC calculation

After diameter of pipe is obtained, ACC of pipe is calculated using equation below.

$$Piping\ ACC = const.\ cost\ factor \times D \times distance \times \frac{i(1+i)^n}{(1+i)^n - 1} \quad (3.15)$$

Total piping ACC is the summation of overall individual piping ACC.

3. Piping AOC calculation

Calculation of piping AOC is determined using equation below.

$$\text{Piping AOC} = \text{O\&M cost factor} \times \text{distance} \quad (3.16)$$

Total piping AOC is the summation of overall individual piping AOC.

For shipping ACC and AOC calculation

1. Some variables to calculate ACC and AOC for shipping are.

- Ship cost

Ship capacity = 10,000 ton, ship construction cost = \$ 35,000,000, Crew, Insurance, Maintenance (CIM) cost = 5 % construction cost, fuel cost = \$ 9,150 /day (Mitsubishi Heavy Industries 2004).

- Port storage cost

Storage capacity = 20,000 ton, storage construction cost = \$ 30,000,000, O&M cost = 5 % construction cost (Mitsubishi Heavy Industries 2004).

- Loading cost

Loading capacity = 20,000 ton, loading dock construction cost = \$ 8,000,000, O&M cost = 25 % construction cost, one cycle of loading carbon dioxide to ship = 2 days (Mitsubishi Heavy Industries 2004).

2. Shipping ACC calculation

Calculation for each ACC calculation is done by comparing existing system with desired system using equation below.

$$ACC A = \text{construction cost } B \times \left(\frac{\text{capacity } A}{\text{capacity } B} \right)^{0.6} \times \frac{i(1+i)^n}{(1+i)^n - 1} \quad (3.17)$$

A is desired system, which is obtained from total carbon dioxide flow rate transferred to sink in East Java each day, while B is existing system. Total shipping ACC is summation of ship cost, port storage cost, and loading cost.

3. Shipping AOC calculation

Calculation of shipping AOC is done by following equations.

- Ship AOC

$$\text{Ship AOC} = \text{ship CIM cost} + \text{fuel cost} \quad (3.18)$$

- Port storage AOC

$$\text{Port storage AOC} = \text{O\&M port storage cost} \quad (3.19)$$

- Loading AOC

$$\text{Loading AOC} = \text{O\&M loading cost} \quad (3.20)$$

Total shipping AOC is summation of those three equations.

For penalty AOC calculation

1. Variable to calculate AOC for penalty fee is.

Carbon tax = \$ 20.74 /ton CO₂ (Sofyan 2010).

2. Alternative storage penalty AOC

$$\text{Penalty AOC} = \text{carbon tax} \times \text{alternative storage flow rate} \quad (3.21)$$

3. Unutilized storage penalty AOC

$$\text{Penalty AOC} = \text{carbon tax} \times \text{unutilized storage flow rate} \quad (3.22)$$

Total penalty AOC is summation of both alternative and unutilized storage penalty AOC.

For total calculation

1. Total annual capital cost (TACC) calculation

$$TACC = \sum \text{pip ing ACC} + \sum \text{shipping ACC} \quad (3.23)$$

2. Total annual operating cost (TAOC) calculation

$$TAOC = \sum \text{pip ing AOC} + \sum \text{shipping AOC} + \sum \text{penalty AOC} \quad (3.24)$$

3. Total annual cost (TAC) calculation

$$TAC = TACC + TAOC \quad (3.25)$$

3.7. Making of Carbon Conversion to Methanol Simulation

After the amount of captured carbon dioxide is found using carbon capture and storage network, unstored carbon dioxide, which will need alternative storage is converted into methanol. Conversion of carbon dioxide into methanol will eliminate requirement of alternative storage for unstored carbon dioxide. Furthermore, since no alternative storage needed, penalty fee for alternative storage will also be eliminated. Without penalty fee for alternative storage, total annual cost

for carbon capture and storage network will be much lower, because penalty fee has the highest contribution to total annual cost needed.

Since all unstored carbon dioxide will be converted into methanol, the capacity of methanol production simulation will be adjusted to accommodate all unstored carbon dioxide conversion. ICI process is used for simulation of methanol production process. As stated before, source of carbon dioxide comes from output of carbon capture simulation. Carbon dioxide and fresh hydrogen feed specification is shown in Table 3.7. and Table 3.8.

Table 3.7. Carbon Dioxide Feed Specification

Specification	Value
Temperature (K)	307.14
Pressure (bar)	1.21
Total mass flow (kg/s)	87.92
Components	Mass Fraction
N ₂	0.001
CO ₂	0.981
H ₂ O	0.018

Table 3.8. Hydrogen Feed Specification

Specification	Value
Temperature (K)	300
Pressure (bar)	1.01
Total mass flow (kg/s)	12.29
Component	Mass Fraction
H ₂	1

Specification of each equipment used in the carbon capture conversion to methanol is shown in Table 3.9.

Table 3.9. Equipment Specification for Carbon Conversion Simulation

Specification	Value
Compressor	
Outlet pressure	65 bar
Adiabatic efficiency	100 %
Mixer	
Pressure drop	0 bar
Feed Heater	
Outlet temperature	488 K
Pressure drop	0 bar
Reactor	
Fixed duty	0 kJ/sec
Product Cooler	
Outlet temperature	320 K
Pressure drop	0 bar
Flash Vessel 1	
Outlet temperature	313 K
Outlet pressure	65 bar
Flash Vessel 2	
Outlet temperature	308 K
Outlet pressure	1.2 bar
Product Heater	
Outlet temperature	353 K
Pressure drop	0 bar
Distillation Column	
Number of stages	8
Top stage pressure	1 bar
Tray type	Valve tray
Reboiler type	Kettle reboiler
Condenser type	Partial condenser

Reactor model used in the simulation is kinetic reactor. Methanol synthesis kinetic model is proposed by Kubota et al. (2001). From the literature, the rate of methanol formation is given as:

$$R_M = \frac{k_M \left(P_{CO_2} P_{H_2} - \frac{P_{CH_3OH} P_{H_2O}}{K_M P_{H_2}^2} \right)}{A^2} \quad (3.26)$$

While the carbon monoxide production through reversed water gas shift reaction is given as:

$$R_{RWGS} = \frac{k_R \left(P_{CO_2} - \frac{P_{CO} P_{H_2O}}{K_R P_{H_2}} \right)}{A} \quad (3.27)$$

The parameter A is given as:

$$A = 1 + K_{CO_2} P_{CO_2} + K_{H_2O} P_{H_2O} \quad (3.28)$$

The rate constants and equilibrium constants are given as:

$$k_M = 3.2651 \times 10^4 \exp[-32093/(RT)] \quad (3.29)$$

$$k_R = 1.3831 \times 10^{12} \exp[-113390/(RT)] \quad (3.30)$$

$$K_M = \exp[7087/(T - 19.499)] \quad (3.31)$$

$$K_R = \exp[-4778/(T + 4.639)] \quad (3.32)$$

$$K_{CO_2} = 0.741 \quad (3.33)$$

$$K_{H_2O} = 1.44511 \times 10^{-8} \times \exp \left[\frac{82215.3}{R \times T} \right] \quad (3.34)$$

3.8. Validation of Carbon Conversion to Methanol Simulation

After all simulations of carbon dioxide conversion to methanol are done, next step is validation of simulations. Validation is done to ensure that simulations have matched with the reference, such as plant data or journal. If simulations do not match with the reference, simulations is evaluated and fixed, so it can match with the reference.

3.9. Optimizing Carbon Capture and Conversion to Methanol Simulation

Final step of this research is optimizing the simulation which have been made before. Optimization is done by varying operating condition and calculate total annual cost of the process to find the best operating condition that gives the smallest total annual cost.

Total annual cost is calculated based on capital cost and utility cost per year required for each equipment in the process. Formula for calculating capital cost are shown in Table 3.10. and price of each utility type is shown in Table 3.11 (Luyben, 2013). As for reactor methanol synthesis, it is assumed that jacketed reactor is used.

Table 3.10. Basic Calculation of Equipment

Equipment	Calculation (in \$)
Vessel	$(17,640) (\text{diameter})^{1.066} (\text{length})^{0.802}$
Heat exchanger	$(7,296) (\text{area})^{0.65}$
Compressor	$(7,429) (\text{work})^{0.82}$

Table 3.11. Utility Price

Utility Type	Utility Price
Low pressure steam	\$ 7.78 / GJ
Medium pressure steam	\$ 8.22 / GJ
High pressure steam	\$ 9.88 / GJ
Electricity	\$ 16.8 / GJ
Cooling water	\$ 0.354 / GJ

After total annual cost for the whole process is calculated, carbon capture and conversion process is then optimized. Optimization is performed in the following order, varying number of absorber stage, stripper feed inlet stage, number of stripper stage, inlet reactor temperature, and reactor pressure. Constraints are made to ensure that product specification is maintained while doing the optimization. Table 3.12. shows design variable and constraints of the process that will be varied in order to achieve the optimization that is aimed.

Table 3.12. Design Variable and Constraints for Optimization

Specification	Value	Constraints
Number of absorber stages	7 stages	4 - 9 stages
Stripper feed inlet stage	5 th stage	4 th - 7 th stage
Number of stripper stages	10 stages	8 - 12 stages
Inlet Reactor temperature	488 K	473 - 503 K
Reactor pressure	65 bar	35 - 65 bar

CHAPTER 4

RESULT AND DISCUSSION

4.1. Simulation of Carbon Dioxide Capture

4.1.1. Overview of Carbon Capture Simulation

Simulation of carbon capture absorption using monoethanolamine (MEA) is done using Aspen Plus 7.3. In carbon dioxide absorption section, carbon dioxide is absorbed using MEA in a low temperature, approximately 323.15 bar and slightly higher than ambient pressure, 1.57 bar. In carbon dioxide desorption section, carbon dioxide is released from MEA in a high temperature, approximately 413.15 bar and lower pressure than absorber pressure, 1.21 bar. In water and solvent make up section, fresh water and solvent is added to compensate water and solvent loss due to process (Arachchige, et. al., 2012).

Since the intent of the simulation is to take data from main parameter of the process, it is decided to model it as an open-loop simulation. With the open-loop flow sheet, it would allow easier convergence and can perform multiple runs quickly. However, the flow sheet is put in place to ensure that the simulation would converge in the closed-loop simulation as well (Kothandaraman, 2010). Process flow sheet of the process is shown in Figure 2.4.

4.1.2. Making of Carbon Capture Simulation

Next step of making a simulation is placing all of the equipment in the process flow sheet window in Aspen Plus 7.3. After all of the equipment are placed in the Aspen Plus, each equipment is set individually. Each of the equipment will be described below.

1. Absorber

Absorber is the main equipment for this process, alongside stripper. In the absorber, carbon dioxide in the flue gas is absorbed by MEA. The absorber is modeled in Aspen Plus using Radfrac. The absorber has two inlet streams, those are flue gas stream and lean solvent stream. Flue gas enters absorber in the 7th stage, while lean solvent enters absorber in the 1st stage. Outlet of the absorber, which are off gas and rich solvent, exit from the absorber in 1st stage and 7th stage respectively.

2. Heat Exchanger

Heat exchanger aims to exchange rich solvent stream that needs to be heated and lean solvent stream that needs to be cooled. The integration aims to reduce operating cost that comes from steam and cooling water.

3. Stripper

Stripper aims to regenerate solvent by removing carbon dioxide from the rich solvent. Same as absorber, stripper is modeled using Radfrac. Rich solvent enters from 5th stage of the stripping column, while regenerated lean solvent exits at the bottom and carbon dioxide exits at the top of the stripping column. Stripping process is an endothermic process and energy required comes from low pressure steam in the kettle reboiler. Reactions occur in stripper are similar with reactions occur in absorber, but in reverse direction.

4. Cooler

Cooler aims to cool lean solvent exits from heat exchanger, so that temperature of the solvent is acceptable for operating condition in absorber. Lean solvent will be mixed with fresh solvent make-up in the mixer before recirculated in the absorber.

5. Mixer

Mixer aims to mix lean solvent with fresh solvent make-up. Solvent make-up is needed to maintain flow and composition of the solvent that is fed to absorber, since there is some solvent loss due to process and disposal of the solvent in exhaust gas stream. Stream that exits from mixer is fed into absorber.

4.1.3. Result of Carbon Capture Simulation

After all of the equipment are set, last step is running the simulation. While running the simulation, no warning or error messages appeared. Result of carbon dioxide capture simulation can be seen in Table 4.1.

Table 4.1. Carbon Capture Simulation Result

Specification	Value
Temperature (K)	307.14
Pressure (bar)	1.21
Total mass flow (kg/s)	87.92
Components	Mass Fraction
N ₂	0.001
CO ₂	0.981
H ₂ O	0.018

From Table 4.1. above, it can be seen that simulation of carbon dioxide capture gives a good result. Amount of stream flows from top of the stripper column is 87.92 kg/s with 98.07 % or around 86.25 kg/s of carbon dioxide in the stream. Some impurities, which is N₂ and H₂O, still exists in the stream, but it can be neglected, since the amount of impurities is too small.

In terms of ability to recover carbon dioxide from flue gas, the process also gives good result. From the result of simulation, carbon dioxide exits from the process is 86.25 kg/s. Comparing with amount of carbon dioxide enters the process, which is 86.40 kg/s, it means that carbon dioxide capture process can absorb up to 99.83 % of carbon dioxide.

With those results, it can be said that simulation of carbon dioxide capture process has been done appropriately, and product from carbon dioxide capture process can be used for the next step, either injected into sink or used as a reactant for methanol production process.

4.2. Simulation of Carbon Dioxide Storage Network

Next step after capturing carbon dioxide from flue gas is store it into sinks. This research uses minimum time difference (Δt) variable, because there is possibility that operation time of CCS is delayed. Delay of the process can happen because of some reasons, such as sink is not ready to be injected with carbon dioxide. Variable that will be used are 0, 5, and 10 years. This variable will affect

in optimum time that can be implemented CCS, and the amount of alternative storage needed and unutilized storage.

4.2.1. Carbon Capture and Storage Network using Simultaneous Method

Cascade table, as described before, is made to determine the amount of alternative and unutilized storage needed of the system, and to determine the pinch point of the system. Generating the correct cascade diagram is crucial, since the result of cascade table will be used for creating grid diagram later on. Cascade table for minimum time difference 0 years is shown in Figure 4.1.

t (year)	Source, $S_{i,t}$ (Mt/y)	Sink, $D_{j,t}$ (Mt/y)	Δt	Flowrate CO_2 (Mt/y)	Load CO_2 (Mt)	CO_2 cascade (Mt)	
						Infeasible	Feasible
2		SK3				0	82.459
		0.96	2	0.960	1.920		
4		SK2				1.920	84.379
		0.21	1	1.170	1.170		
5	SR1					3.090	85.549
	1.786		2	-0.616	-1.232		
7	SR2	SK1				1.858	84.317
	0.619	0.17	3	-1.065	-3.195		
10		SK4				-1.337	81.122
		0.0873	2	-1.479	-2.957		
12		SR5				-4.294	78.164
		2.507	3	-3.986	-11.957		
15	SR3					-16.252	66.207
	0.133		5	-4.119	-20.594		
20		SK5				-36.845	45.614
		0.06286	9	-4.056	-36.503		
29						-73.348	9.111
			1	-4.266	-4.266		
30		SK6				-77.613	4.845
		0.05714	2	-2.423	-4.845		
32						-82.459	0
			8	0.533	4.266		(PINCH)
40						-78.192	4.266
			6	0.666	3.998		
46						-74.195	8.264
			6	0.579	3.474		
52						-70.721	11.738
			8	-0.381	-3.048		
60						-73.769	8.690
			10	0.120	1.200		
70						-72.569	9.890
			15	0.057	0.857		
85						-71.712	10.747

Figure 4.1. Cascade Table for Δt 0 Years Using Simultaneous Method

From Figure 4.1., we can see pinch point of the system is obtained in year 32. It is shown also that in Δt 0 years, alternative storage needed is 82.549 Mt while unutilized storage of the system is 10.747 Mt. From data that are obtained from cascade table, grid diagram of the carbon capture and storage (CCS) network can be made and is shown in Figure 4.2.

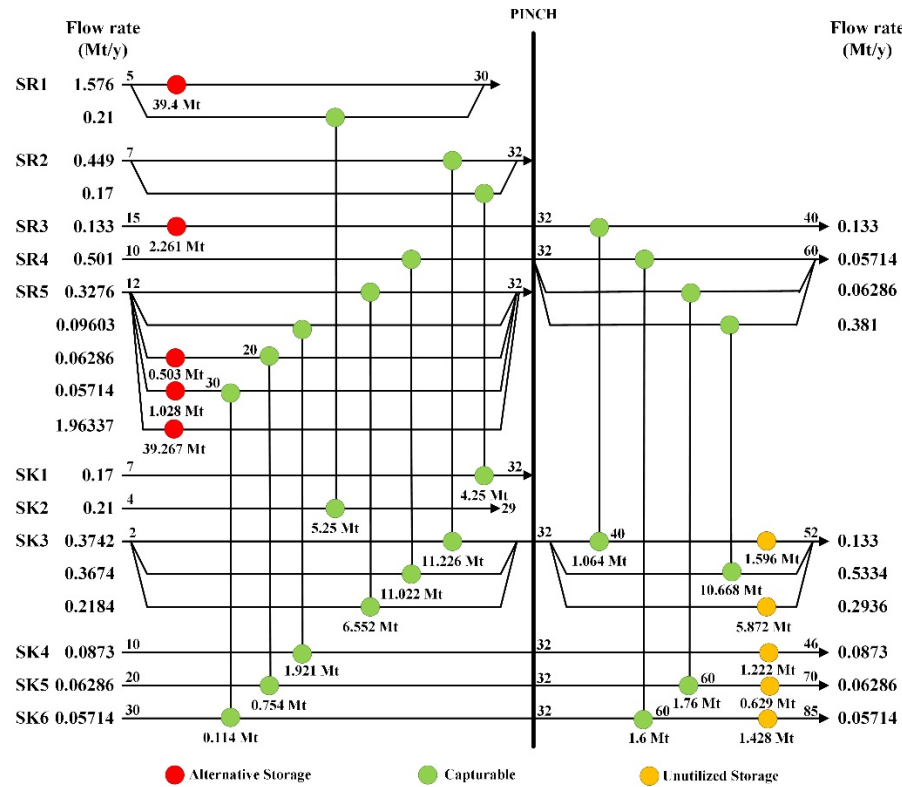


Figure 4.2. Grid Diagram for Δt 0 Years Using Simultaneous Method

As shown in Figure 4.2., pinch point is divided grid diagram into two zones, below pinch point, where carbon dioxide needs storage, and above pinch point, where there is excess sink. Those phenomena are a common problem that will happen in real life, and therefore needs to be minimized. It is shown in Figure 4.2. that SK1 receive carbon dioxide from SR2 from year 7 until year 32 with the amount of carbon dioxide is 4.25 Mt, while carbon dioxide from SR1 is transported to SK2, which will end in year 29, with the amount of carbon dioxide transferred is 5.25 Mt. The other pairings are shown in Figure 4.2. Grid diagram above gives exactly the same amount of alternative and unutilized storage as cascade table that has been made before. Alternative storage needed comes from SR1, SR3, and SR5 with 39.4 Mt, 2.261 Mt, and 40.798 Mt of carbon dioxide need alternative storage respectively, while all carbon dioxide comes from SR2 and SR4 is stored in available sink. Unutilized storage comes from SK3, SK4, SK5, and SK6 with 7.468 Mt, 1.222 Mt, 0.629 Mt, and 1.428 Mt of storage is unutilized.

t (year)	Source, $S_{i,t}$ (Mt/y)	Sink, $D_{j,t}$ (Mt/y)	Δt	Flowrate CO_2 (Mt/y)	Load CO_2 (Mt)	CO_2 cascade (Mt)	
						Infeasible	Feasible
5	SR1					0	89.394
	1.786		2	-1.786	-3.572		
7	SR2	SK3				-3.572	85.822
	0.619		2	-1.445	-2.890		
9		SK2				-6.462	82.932
		0.21	1	-1.235	-1.235		
10	SR4					-7.697	81.697
	0.501		2	-1.736	-3.472		
12		SK1				-11.169	78.225
		2.507	3	-4.073	-12.219		
15	SR3					-23.388	66.006
	0.133		10	-4.119	-41.187		
25		SK5				-64.575	24.819
		0.06286	5	-4.056	-20.279		
30						-84.854	4.540
			2	-2.270	-4.540		
32						-89.394	0
			2	0.856	1.712		(PINCH)
34						-87.682	1.712
			1	0.646	0.646		
35		SK6				-87.035	2.358
		0.05714	2	0.703	1.407		
37						-85.629	3.765
			3	0.533	1.600		
40						-84.029	5.365
			11	0.666	7.329		
51						-76.700	12.694
			6	0.579	3.474		
57						-73.226	16.168
			3	-0.381	-1.143		
60						-74.369	15.025
			15	0.120	1.800		
75						-72.569	16.825
			15	0.057	0.857		
90						-71.712	17.682

Figure 4.3. Cascade Table for Δt 5 Years Using Simultaneous Method

Cascade table for Δt 5 years is shown in Figure 4.3. The amount of alternative storage needed for the system is 89.394 Mt, while unutilized storage is 17.682 Mt. Pinch point for the system remains the same from Δt 0 years, which is year 32. From cascade table that has been generated, grid diagram for the system is made as shown in Figure 4.4.

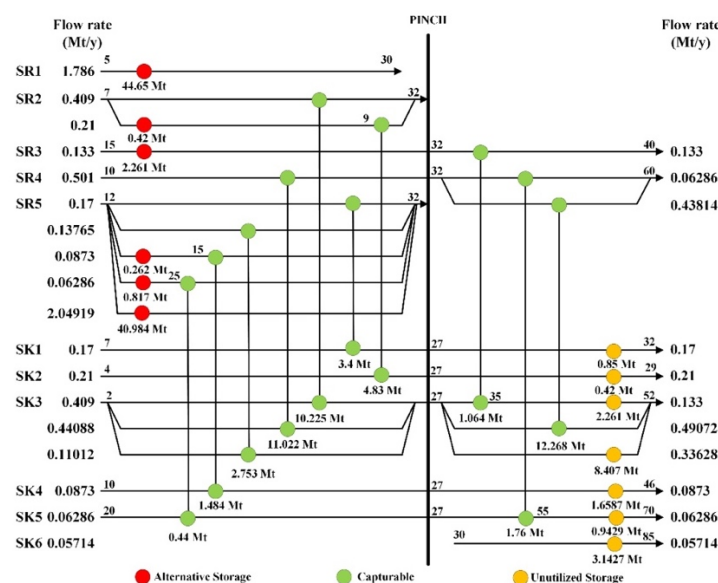


Figure 4.4. Grid Diagram for Δt 5 Years Using Simultaneous Method

It is shown in Figure 4.4. that there are some differences between grid diagram for Δt 0 and 5 years, especially in grid line. In grid diagram for Δt 0 years, grid line for SK1 and SK2 are below pinch point, while in grid diagram Δt 5 years, line of SK1 and SK2 cross pinch point, because of the time difference. Some notable pairings are all of carbon dioxide from SR1, which is 44.65 Mt, is not captured at all. SK1 receives 3.4 Mt of carbon dioxide from SR5, and SK2 receives 4.83 Mt of carbon dioxide from SR2. Because of the time difference, there are unutilized storage from SK1 and SK2. The other pairings are shown in Figure 4.4. Alternative storage comes from SR1, SR2, SR3, and SR5, with 44.65 Mt, 0.42 Mt, 2.261 Mt, and 42.063 Mt of carbon dioxide needs alternative storage respectively. Unutilized storage comes from all of the sink, with 0.85 Mt of carbon dioxide from SK1, 0.42 Mt of carbon dioxide from SK2, 10.668 Mt of carbon dioxide from SK3, 1.6587 Mt of carbon dioxide from SK4, 0.9429 Mt of carbon dioxide from SK5, and 3.1427 Mt of carbon dioxide from SK6.

t (year)	Source, $S_{i,t}$ (Mt/y)	Sink, $D_{j,t}$ (Mt/y)	Δt	Flowrate CO ₂ (Mt/y)	Load CO ₂ (Mt)	CO ₂ cascade (Mt)	
						Infeasible	Feasible
5	SR1					0	96.845
7	1.786		2	-1.786	-3.572	-3.572	93.273
10	0.619		3	-2.405	-7.215	-10.787	86.058
12	0.501		2	-2.906	-5.812	-16.599	80.246
14	2.507	SK3 0.96	2	-4.453	-8.906	-25.505	71.340
15		SK2 0.21	1	-4.243	-4.243	-29.748	67.097
17	0.133		2	-4.376	-8.752	-38.500	58.345
20		SK1 0.17	3	-4.206	-12.618	-51.118	45.727
30		SK4 0.0873	10	-4.119	-41.187	-92.305	4.540
32		SK5 0.06286	2	-2.270	-4.540	-96.845	0
39			7	0.856	5.993	-90.852	5.993
40		SK6 0.05714	1	0.646	0.646	-90.205	6.639
42			2	0.836	1.673	-88.533	8.312
56			14	0.666	9.328	-79.205	17.640
60			4	0.579	2.316	-76.889	19.956
62			2	1.080	2.160	-74.729	22.116
80			18	0.120	2.160	-72.569	24.276
95			15	0.057	0.857	-71.712	25.133

Figure 4.5. Cascade Table for Δt 10 Years Using Simultaneous Method

The last cascade table for simultaneous method, which is Δt 10 years, is shown in Figure 4.5. As predicted before, the amount of alternative storage needed and unutilized storage is increasing. For Δt 10 years, the amount of alternative storage needed is 96.845 Mt of carbon dioxide, while the amount of unutilized storage is 25.113 Mt of carbon dioxide. Pinch point for Δt 10 years is year 32, similar with the other minimum time differences. Grid diagram is made based on cascade table that has been generated before, and is shown in Figure 4.6.

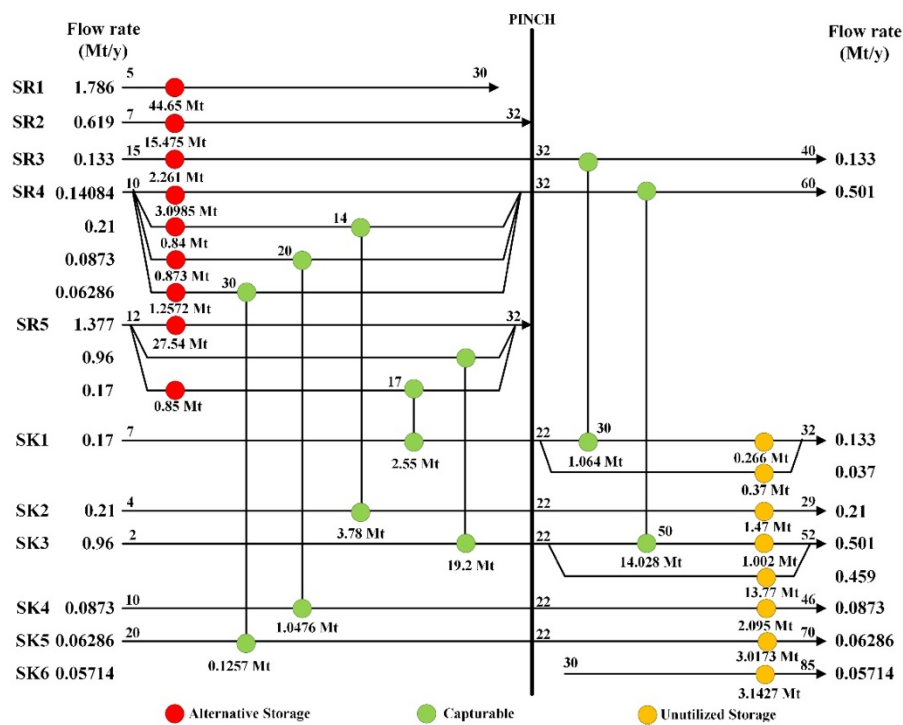


Figure 4.6. Grid Diagram for Δt 10 Years Using Simultaneous Method

In Δt 10 years, every stream, either source or sink, needs either alternative storage or unutilized storage. SR1 and SR2 in Δt 10 years do not transfer any carbon dioxide to any sinks, which leads to requirement of alternative storage as big as 44.65 Mt of carbon dioxide for SR1 and 15.475 Mt of carbon dioxide for SR2. SK6 also does not receive any carbon dioxide from any sources, so there is 3.1427 Mt of carbon dioxide storage unutilized. The other requirement of alternative storage come from SR3, SR4, and SR5, with 2.261 Mt, 6.0687 Mt, and 28.39 Mt of carbon dioxide respectively. Unutilized storage comes from SK1, SK2, SK3, SK4, and

SK5, with 0.636 Mt, 1.47 Mt, 14.792 Mt, 2.095 Mt, and 3.0173 Mt of carbon dioxide respectively.

Increasing uncaptured carbon dioxide and excess sink with increasing minimum time difference, as mentioned before, is caused by the increasing possibility that sink has not been ready yet, while source of carbon dioxide has already started its capture process. Although Δt 0 years gives the best result in simultaneous method, it is very hard to be achieved in real world. Every aspect of CCS project needs to be perfect in order to achieve Δt 0 years. However, the presence of minimum time difference generally acceptable, since there must be a little delay in planning of CCS project.

4.2.2. Carbon Capture and Storage Network using Sequential Method

After CCS network is calculated using simultaneous method, next step is calculating mass transfer of CCS network using sequential method. This method is done by generating cascade table and grid diagram for single region, which is West Sumatra in this case, then the amount of alternative storage is transported to another region, in this case is East Java. Sequential method needs to be done in order to lower the amount of alternative and unutilized storage needed (Diamante et al. 2014).

Single region cascade table and multi-region grid diagram for Δt 0 years are shown in Figure 4.7. and Figure 4.8.

t (year)	Source, $S_{i,t}$ (Mt/y)	Sink, $D_{j,t}$ (Mt/y)	Δt	Flowrate CO ₂ (Mt/y)	Load CO ₂ (Mt)	CO ₂ cascade (Mt)	
						Infeasible	Feasible
2		SK3				0	85.248
		0.960	2	0.960	1.920		
4		SK2				1.92	87.168
		0.210	1	1.170	1.170		
5	SR1					3.09	88.338
	1.786		2	-0.616	-1.232		
7	SR2	SK1				1.858	87.106
	0.619	0.170	3	-1.065	-3.195		
10		SR4				-1.337	83.911
		0.501	2	-1.566	-3.132		
12		SR5				-4.469	80.779
		2.507	3	-4.073	-12.219		
15		SR3				-16.688	68.56
		0.133	14	-4.206	-58.884		
29						-75.572	9.676
			1	-4.416	-4.416		
30						-79.988	5.26
			2	-2.630	-5.260		
32						-85.248	0
			8	0.326	2.608		(PINCH)
40						-82.64	2.608
			12	0.459	5.508		
52						-77.132	8.116
			8	-0.501	-4.008		
60						-81.14	4.108

Figure 4.7. Single Region Cascade Table for Δt 0 Years

Figure 4.7. shows cascade table for single region CCS network with Δt 0 years. Pinch point is obtained in year 32, same as simultaneous method. The amount of alternative storage needed is 85.248 Mt, while unutilized storage is 4.108 Mt. The carbon dioxide stream that needs alternative storage is then transported to another region. Result from cascade table are used to generate grid diagram, which is shown in Figure 4.8.

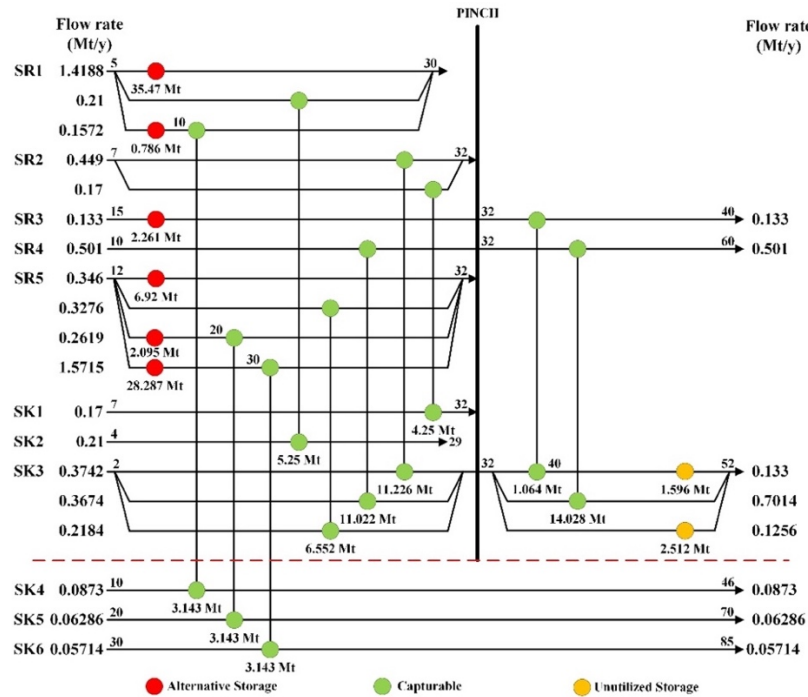


Figure 4.8. Grid Diagram for Δt 0 Years Using Sequential Method

Figure 4.8. shows that SR2, from year 7 to year 32 sends 11.226 Mt of carbon dioxide to SK3 and 4.25 Mt of carbon dioxide to SK1. SR4 sends 11.022 Mt of carbon dioxide to SK3 from year 10 until year 32, and continues sending 14.028 Mt of carbon dioxide to the same sink from year 32 until year 60. The other pairings are shown in Figure 4.15. Alternative storage needed, based on grid diagram, is 75.819 Mt, which consists of 36.256 Mt, 2.261 Mt, and 37.301 Mt of carbon dioxide from SR1, SR3, and SR5 respectively. Unutilized storage needed is 4.108 Mt of carbon dioxide, which comes from SK3.

Figure 4.9. shows single region cascade table for Δt 5 years. Similar with simultaneous method, in sequential method there is a tendency that alternative storage needed and unutilized storage is increasing with the increasing minimum time difference. In Δt 5 years, the amount of alternative storage needed is 85.032 Mt of carbon dioxide and unutilized storage is 13.321 Mt of carbon dioxide. Grid diagram is then generated and shown in Figure 4.10.

t (year)	Source, $S_{i,t}$ (Mt/y)	Sink, $D_{j,t}$ (Mt/y)	Δt	Flowrate CO ₂ (Mt/y)	Load CO ₂ (Mt)	CO ₂ cascade (Mt)	
						Infeasible	Feasible
5	SR1					0	91.318
	1.786			2	-1.786	-3.572	
7	SR2	SK3				-3.572	87.746
	0.619	0.960	2	-1.445	-2.89		
9		SK2				-6.462	84.856
		0.210	1	-1.235	-1.235		
10	SR4					-7.697	83.621
	0.501		2	-1.736	-3.472		
12	SR5	SK1				-11.169	80.149
	2.507	0.170	3	-4.073	-12.219		
15	SR3					-23.388	67.93
	0.133		15	-4.206	-63.09		
30						-86.478	4.84
			2	-2.42	-4.84		
32						-91.318	0
			2	0.706	1.412		(PINCH)
34						-89.906	1.412
			3	0.496	1.488		
37						-88.418	2.9
			3	0.326	0.978		
40						-87.44	3.878
			17	0.459	7.803		
57						-79.637	11.681
			3	-0.501	-1.503		
60						-81.14	10.178

Figure 4.9. Single Region Cascade Table for Δt 5 Years

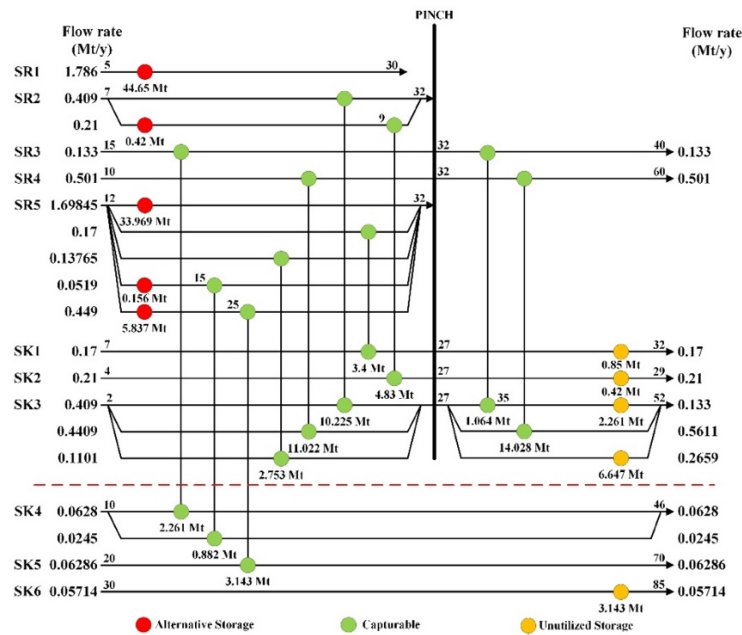


Figure 4.10. Grid Diagram for Δt 5 Years Using Sequential Method

As shown in Figure 4.10., SR1 does not transfer any carbon dioxide to sink, which leads to 44.65 Mt of carbon dioxide needs an alternative storage. SR3 and SR4 transfer all of its carbon dioxide to several sinks and do not need any alternative storage. SR3 and SR5 transfer some of its carbon dioxide to sink in

another region. SR3 transfers 2.261 Mt of carbon dioxide to SK4, while SR5 transfers 0.982 Mt of carbon dioxide to SK4 and 3.143 Mt of carbon dioxide to SK5. Beside SR1, alternative storage comes from SR2 with 0.42 Mt of carbon dioxide and SR5 with 39.962 Mt of carbon dioxide. Unutilized storage in the system comes from SK1, SK2, SK3, and SK6, with 0.85 Mt, 0.42 Mt, 8.908 Mt, and 3.143 Mt of carbon dioxide respectively.

t (year)	Source, $S_{i,t}$ (Mt/y)	Sink, $D_{j,t}$ (Mt/y)	Δt	Flowrate CO ₂ (Mt/y)	Load CO ₂ (Mt)	CO ₂ cascade (Mt)	
						Infeasible	Feasible
5	SR1					0	98.018
	1.786		2	-1.786	-3.572		
7	SR2					-3.572	94.446
	0.619		3	-2.405	-7.215		
10	SR4					-10.787	87.231
	0.501		2	-2.906	-5.812		
12	SR5	SK3				-16.599	81.419
	2.507	0.960	2	-4.453	-8.906		
14		SK2				-25.505	72.513
		0.210	1	-4.243	-4.243		
15	SR3					-29.748	68.27
	0.133		2	-4.376	-8.752		
17		SK1				-38.5	59.518
		0.170	13	-4.206	-54.678		
30						-93.178	4.84
			2	-2.420	-4.84		
32						-98.018	0
			7	0.706	4.942		(PINCH)
39						-93.076	4.942
			1	0.496	0.496		
40						-92.58	5.438
			2	0.629	1.258		
42						-91.322	6.696
			18	0.459	8.262		
60						-83.06	14.958
			2	0.960	1.92		
62						-81.14	16.878

Figure 4.11. Single Region Cascade Table for Δt 10 Years

Single region cascade table is shown in Figure 4.11. As predicted before, the amount of alternative storage needed and unutilized storage is increasing. Now, for Δt 10 years, alternative storage needed is 91.732 Mt of carbon dioxide and unutilized storage is 20.021 Mt of carbon dioxide. Pinch point for this system, remains the same with the other systems. Grid diagram based on cascade table for Δt 10 years is shown in Figure 4.12.

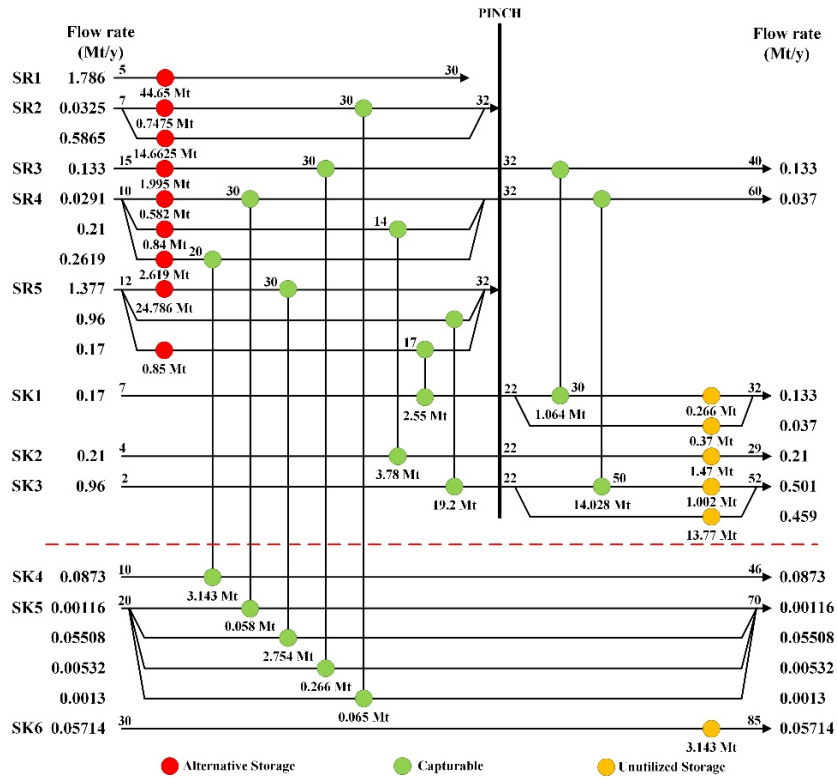


Figure 4.12. Grid Diagram for Δt 10 Years Using Sequential Method

In Δt 10 years, every source needs alternative storage, similar with simultaneous method for Δt 10 years. SR1, SR2, SR3, SR4, and SR5 need 44.65 Mt, 15.41 Mt, 1.995 Mt, 4.021 Mt, and 25.636 of carbon dioxide alternative storage. The difference between simultaneous method is SK4 and SK5 do not have unutilized storage. All of the storage capacity of those sinks is filled with carbon dioxide from SR3 and SR5. Unutilized storage from the system comes from SK1 with 0.636 Mt, SK2 with 1.47 Mt, SK3 with 14.772 Mt, and SK6 with 3.143 Mt of carbon dioxide. Summary of results, either for simultaneous method and sequential method are shown in Table 4.2.

Table 4.2. Summary of Carbon Capture and Storage Network Result

Δt	Alternative Storage (Mt)	Injected (Mt)	Unutilized Storage (Mt)	% Utilized Sink
Simultaneous Method				
0	82.459	56.181	10.747	83.94
5	89.394	49.246	17.682	73.58
10	96.845	41.795	25.133	62.45
Sequential Method				
0	75.819	62.821	4.108	93.86
5	85.032	53.608	13.321	80.1
10	91.732	46.908	20.021	70.09

Based on table above, CCS using sequential method gives a better result in term of sink utilization. For the same Δt , sequential method gives smaller amount of both alternative and unutilized storage. This is because in sequential method, sink in East Java region is utilized more, compared with simultaneous method. By utilizing more sink in East Java, alternative storage requirement will be lower and utilized storage will be higher, affecting amount of capturable carbon dioxide.

Unstored carbon dioxide that needs alternative storage, as stated before, will be converted into methanol in the later chapter of this research. Because of that conversion process, technically alternative storage is no more needed. As for unutilized storage, it may be sold to the other sources, as long as its duration and flow rate are matched with sink capacity. However, this research will not discuss about selling unutilized storage to the other sources and will leave unutilized storage as it is.

4.2.3. Optimization of Carbon Capture and Storage Network

Based on carbon capture and storage network design result, there are six schemes of mass transfer network that can be used. From each scheme, economic analysis based on total annual cost is used and will consist of total annual operating cost and total annual capital cost of piping, shipping, and penalty. The total annual

cost will vary for each scheme, which is caused by different minimum time difference. Based on formula that has been described before, calculation of total annual cost is shown in Table 4.3.

Table 4.3. Total Annual Cost Calculation

Δt	Total Annual Operating Cost (million USD)	Total Annual Capital Cost (million USD)	Total Annual Cost (million USD)
Simultaneous Method			
0	17.13	64.29	81.42
5	29.97	38.85	68.82
10	32.68	37.81	70.49
Sequential Method			
0	20.66	129.43	150.09
5	29.17	54.15	83.32
10	45.66	180.21	225.87

As predicted before, total annual cost for each scheme varies. In total annual capital cost side, each minimum time difference will give different pairing between sources and sinks, as shown in grid diagram above. Because of that, requirement for piping and shipping will be diverse, since total annual capital cost is significantly affected by capital cost of piping, the further the distance, bigger flow rate, and shorter operation time of carbon dioxide transportation will give bigger total annual capital cost.

For total annual capital cost in simultaneous method, the longer minimum time difference of the system, the amount of total annual capital cost is decreasing, while for sequential method, there is a fluctuation regarding the amount of total annual capital cost. This fluctuation happens because in minimum time difference 10 years, carbon capture and storage network has a bigger number of multi-region mass transfer and shorter time operation for each source and sink pairing. Because of shorter time operation, total annual capital cost for minimum time difference 10

years is bigger than minimum time difference 5 years, even though overall total capital cost for minimum time difference 10 years is smaller.

In total annual operating cost side, the value of total annual operating cost is increasing for each minimum time difference variable, either for simultaneous or sequential method. Increasing total annual operating cost is mainly affected by penalty fee. Bigger value of minimum time difference means more alternative storage needed and unutilized storage. Those increasing amount of alternative storage needed and unutilized storage means that more penalty fee must be paid as total annual operating cost of carbon capture and storage network. Since captured carbon dioxide that is not stored will be used as a reactant for methanol synthesis process, penalty fee is not calculated for alternative storage needed. As for unutilized storage, as described before, it can be sold to the other sources outside the boundary. However, since selling unutilized storage is outside the scope of work, the income that will be obtained for selling unutilized storage is not calculated, and therefore penalty fee must be paid for unutilized storage.

Based on Table 4.10., graph between minimum time difference and total annual operating cost, total annual capital cost, and total annual cost can be generated to find the best and optimum minimum time difference.

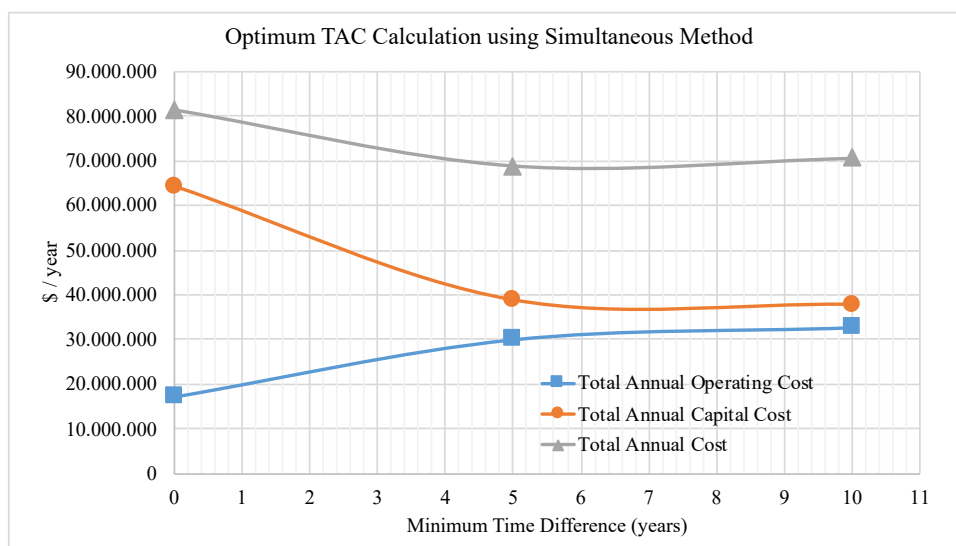


Figure 4.13. Optimum Total Annual Cost Calculation Using Simultaneous Method

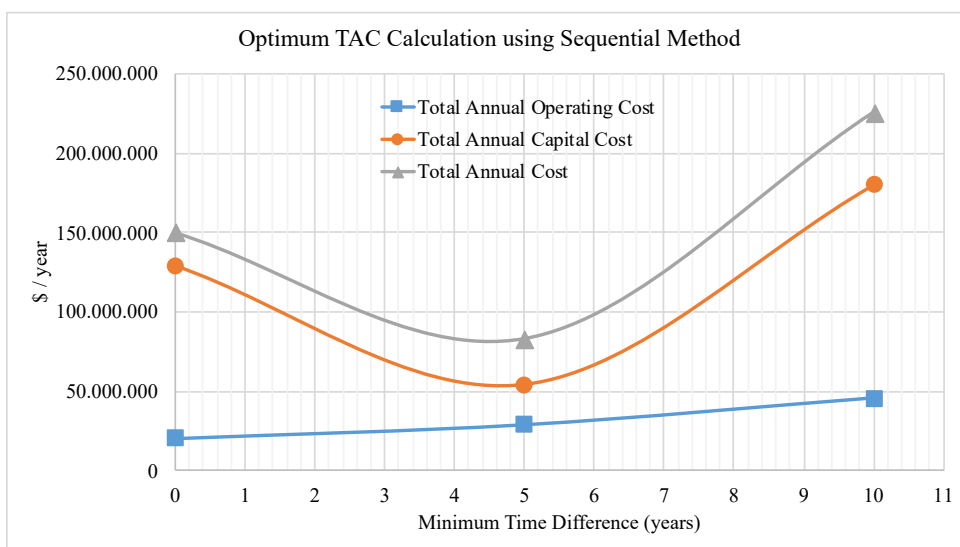


Figure 4.14. Optimum Total Annual Cost Calculation Using Sequential Method

From Figure 4.13. and 4.14. above, optimum minimum time difference is obtained, both for simultaneous and sequential method. Based on the graph, it is obtained that optimum minimum time difference for simultaneous method is 6 years with total annual cost amount \$ 67,857,256. In sequential method, although there is fluctuation in total annual capital cost result, optimum minimum time difference is obtained in 4.5 years with total annual cost amount \$ 78,233,875.

4.3. Simulation of Carbon Dioxide Conversion to Methanol

4.3.1. Overview of Methanol Synthesis Simulation

Simulation of methanol synthesis process is done based on Fjellerup's work in 2015. Feed of carbon dioxide used for reactant comes from unstored carbon dioxide in carbon capture and storage network. Fresh hydrogen is fed into system using 3:1 mole ratio to carbon dioxide feed.

Carbon dioxide and hydrogen feed are compressed to 65 bar. Those reactants are then mixed with the recycled unreacted carbon dioxide and hydrogen. After all of the reactants are mixed, the stream will be heated to 488 K before entering the synthesis reactor.

After exiting the reactor, the stream that consists of product of methanol, unreacted carbon dioxide and hydrogen, and some impurities are cooled to 300 K.

After being cooled, the stream is then separated through flash vessel. Most of methanol product and water exits from the bottom of the vessel while the unreacted carbon dioxide and hydrogen exits from top of the vessel. The unreacted carbon dioxide and hydrogen is then recycled back to the reactor.

After being separated through first vessel, the stream than contains methanol product is separated again in the second flash vessel. In this vessel, the other impurities that still contain in the stream are separated. After exiting the second flash vessel, the bottom stream will contain mostly methanol and water.

The stream than will be heated before entering distillation column. In the distillation column, purified methanol will exit from top of the distillation column. Waste water will exit from bottom of the distillation column. Flowsheet of the process can be seen in Figure 2.8.

4.3.2. Making of Methanol Synthesis Simulation

All of the process blocks are placed and set individually before connected to each other after all of the required inputs are complete. Each of the equipment used in the simulation is described below.

1. Compressor

In this process, two compressors are used. One for compressing carbon dioxide from carbon dioxide capture process and one for compressing fresh hydrogen feed. Both compressors compress each of the feed to 65 bar. The adiabatic efficiency of each compressor is assumed to be 100 %.

2. Mixer

Mixer is used to mix the carbon dioxide, fresh hydrogen feed, and unreacted carbon dioxide and hydrogen. Those feeds are mixed before entering the reactor.

3. Feed Heater

Feed heater aims to heat feed before entering the reactor. Since the feed needs to be heated to 488 K, the heater uses direct fired heater for the heating process.

4. Reactor

Reactor for methanol synthesis is modeled using kinetic reactor. Kinetic model used is proposed by Kubota et al. (2010) and has already been described before. In the reactor, two reactions occur, those are:



The first reaction is the main reaction, which produces methanol product. The second reaction produces carbon monoxide as a by-product, and therefore is avoided.

5. Product Cooler

Product cooler aims to cool the stream that exits from reactor. The stream needs to be cooled to 320 K before processed further. The stream that is cooled contains methanol product, by-product, and unreacted carbon dioxide and hydrogen.

6. Flash Vessel 1

First flash vessel aims to separate most of methanol product with the unreacted carbon dioxide and hydrogen. Methanol product will exit from bottom of the vessel, while unreacted carbon dioxide and hydrogen will exit from top of the vessel.

7. Flash Vessel 2

Second flash vessel aims to separate methanol from any other impurities that still contain in the stream. The impurities such as carbon dioxide, carbon monoxide, and hydrogen are discarded. The methanol is then processed further for final purification. Pressure of the stream is also decreased using the flash vessel.

8. Product Heater

Product heater aims to heat the methanol stream before being purified in the distillation column. The stream is heated to 353 K before entering the distillation column.

9. Distillation Column

Distillation column separates methanol product from the water. The methanol product will exit from top of the column while the waste water will exit

from bottom of the column. There are 8 stages in the column and feed is fed in the 5th stage of the column.

In the simulation, calculator and controller block are used. Calculator and controller block aim to control the fresh hydrogen feed that enter the system. Since the mass ratio between hydrogen and carbon dioxide needs to be maintained in 3:1, and also some unreacted carbon dioxide and hydrogen are recycled back to the reactor, calculator and controller block are needed to keep the process satisfied.

4.3.3. Result of Methanol Synthesis Simulation

After required inputs have been completed and all of the process blocks have been set, the simulation is then run. The simulation has been converged without no error and warning. Some important results of the simulation are taken to be discussed. The results are shown in Table 4.4

Table 4.4. Result of Simulation

Specification	Value
Temperature (K)	337.81
Pressure (bar)	1.003
Total mass flow (kg/s)	52.96
Components	Mass Fraction
H ₂	trace
CO	trace
CO ₂	0.001
Methanol	0.996
H ₂ O	0.003

From the table above, it can be seen that the result of the simulation, in terms of methanol product, is good. The simulation gives 52.96 kg/s of methanol product with 99.6 % purity that exits from top of the distillation column. With those purity, the methanol has already passed the grade for being a fuel, which is 98 % purity of methanol.

4.3.4. Optimization of Carbon Capture and Conversion to Methanol Process

Based on the results that are obtained before, simulation of carbon capture and conversion to methanol process needs to be optimized. Optimization aims to find optimum operating condition based on total annual cost needed for the process. As stated before, optimization is done by varying operating conditions and calculate total annual cost.

Formula for calculating each equipment and the price of each utility are shown in Table 3.3. and Table 3.4. Calculation of total annual cost is shown in Table 4.5., capital cost and utility cost are shown separated in order to determine how much capital cost or utility cost is needed for each equipment. For calculation of total annual cost, it is assumed that payback period for the process is 3 years.

Table 4.5. Total Annual Cost of Base Case

Equipment	Type	Capital Cost	Utility Cost (per year)
Absorber (incl. trays)	Vessel	\$ 5,827,580	-
Heat Exchanger	Heat exchanger	\$ 3,864,325	-
Stripper (incl. trays)	Vessel	\$ 3,153,726	-
Stripper condenser	Heat exchanger	\$ 569,664	\$ 4,277,745
Stripper reboiler	Heat exchanger	\$ 1,151,150	\$ 88,444,717
Cooler	Heat exchanger	\$ 2,365,853	\$ 2,178,364
CO ₂ compressor	Compressor	\$ 50,471,731	\$ 13,912,097
H ₂ compressor	Compressor	\$ 150,355,839	\$ 52,665,873
Reactor heater	Heat exchanger	\$ 723,503	\$ 14,655,523
Reactor (jacketed)	Reactor	\$ 3,370,642	-
Reactor cooler	Heat exchanger	\$ 1,990,642	\$ 3,202,200
Flash drum 1	Vessel	\$ 955,150	-
Flash drum 2	Vessel	\$ 510,065	-
Distillation pre-heater	Heat exchanger	\$ 464,800	\$ 7,115,778
Distillation column (incl. trays)	Vessel	\$ 1,723,921	-

Equipment	Type	Capital Cost	Utility Cost (per year)
Column condenser	Heat exchanger	\$ 774,744	\$ 1,536,539
Column reboiler	Heat exchanger	\$ 309,717	\$ 45,312,782
Solvent make-up	-	-	\$ 6,514,238
Total		\$ 228,582,903	\$ 239,815,857
Total annual cost (Capital cost : 3 years) + Utility cost		\$ 316,010,158	

From Table 4.5. above, capital cost, utility cost, and total annual cost for each equipment and the whole process are shown. Table 4.5. shows that for capital cost, H₂ compressor, which compress H₂ feed to 65 bar, is responsible for the biggest capital cost needed, which is \$ 150,355,839. Carbon dioxide compressor, which compress purified carbon dioxide to 65 bar, gives second biggest capital cost with \$ 50,471,731. For utility cost, reboiler in the stripper column has the biggest utility cost, which is \$ 88,444,717/year.

Total capital cost for the whole process is \$ 228,582,903 and total utility cost is \$ 239,815,857/year. It is assumed before that payback period is set to be 3 years. Therefore, to calculate total annual cost needed, total capital cost is divided by three before added with total utility cost. Total annual cost for the process is then determined, and it is \$ 316,010,158.

After calculating total annual cost for the whole process, process is then optimized. Steps for optimizing simulation has been described in Chapter 3.9. Effect of changing operating conditions to total annual cost of carbon capture and simulation process are shown below.

1. Number of Absorber Stage

Table 4.6. shows the effect of changing number of absorber stages to capital cost, utility cost, and total annual cost needed for the process. By increasing number of absorber stages, total annual cost also increases, except for 4 stages, while total annual cost increases from 5 stages. From the result, 5 stages of absorber give the smallest total annual cost.

Table 4.6. Total Annual Cost for Changing Number of Absorber Stages

Number of Absorber Stages	Total Annual Cost
4	\$ 315,948,446
5	\$ 315,757,457
6	\$ 315,845,243
7	\$ 316,010,158
8	\$ 316,192,328
9	\$ 316,368,557

A figure to illustrate trend of total annual cost needed for the process as impact of changing number of absorber stages is shown in Figure 4.15.

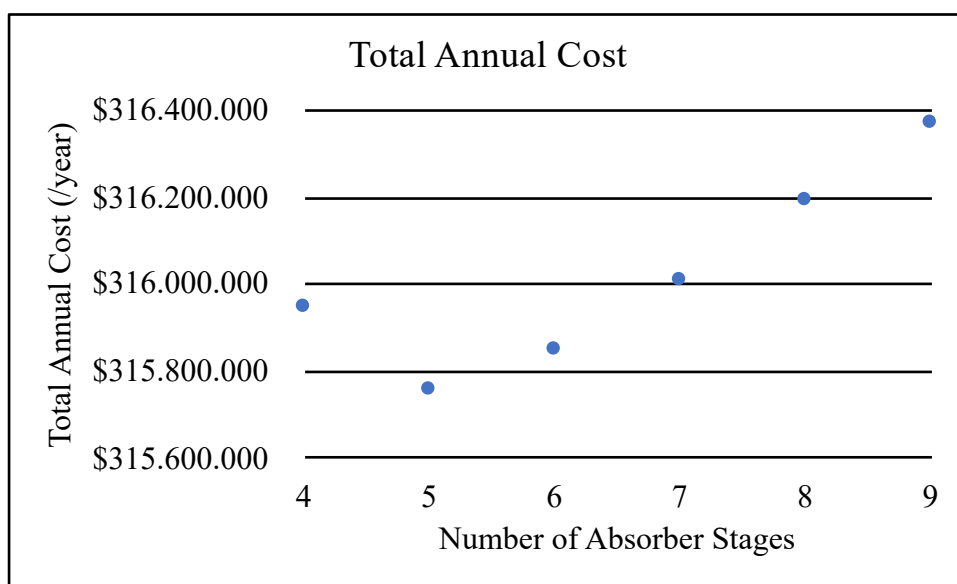


Figure 4.15. Number of Absorber Stage Effect to Total Annual Cost

2. Stripper Feed Inlet Stage

Stripper feed inlet stage is varied from 4 stage to 7 stage. Table 4.7. shows the effect of stripper feed inlet stage to total annual cost. Feed inlet at 5th stage gives the best result in terms of total annual cost. The result means that optimized condition is the same with base case condition, which is feed inlet at 5th stage.

Table 4.7. Total Annual Cost for Changing Stripper Feed Inlet Stage

Stripper Feed Inlet Stage	Total Annual Cost
4	\$ 322,390,750
5	\$ 315,757,457
6	\$ 317,858,269
7	\$ 322,808,043

A figure to illustrate trend of total annual cost needed for the process as impact of changing stripper feed inlet stage is shown in Figure 4.16.

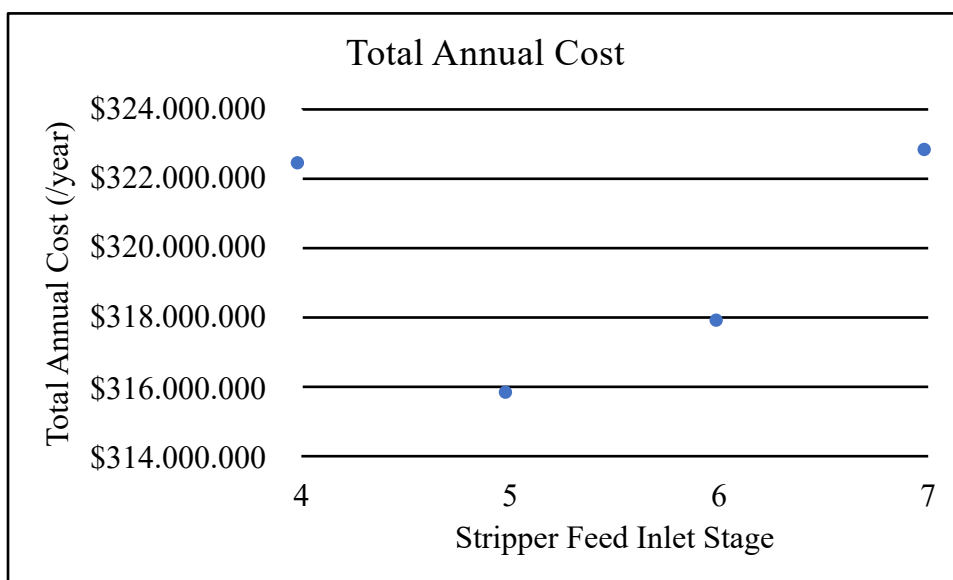


Figure 4.16. Stripper Feed Inlet Stage Effect to Total Annual Cost

3. Number of Stripper Stages

Number of stripper stages is varied from 8 stages to 12 stages. The result obtained shows that the smallest total annual cost is given while number of stripper stages is 11 stages. By increasing number of stripper stages, total annual cost decreases, except for 12 stages, which total annual cost increases compared to 11 stages. Detailed result of optimization is shown in Table 4.8.

Table 4.8. Total Annual Cost for Changing Number of Stripper Stages

Number of Stripper Stages	Total Annual Cost
8	\$ 325,690,716
9	\$ 319,333,104
10	\$ 315,757,457
11	\$ 313,540,830
12	\$ 314,761,897

A figure to illustrate trend of total annual cost needed for the process as impact of changing number of stripper stages is shown in Figure 4.17.

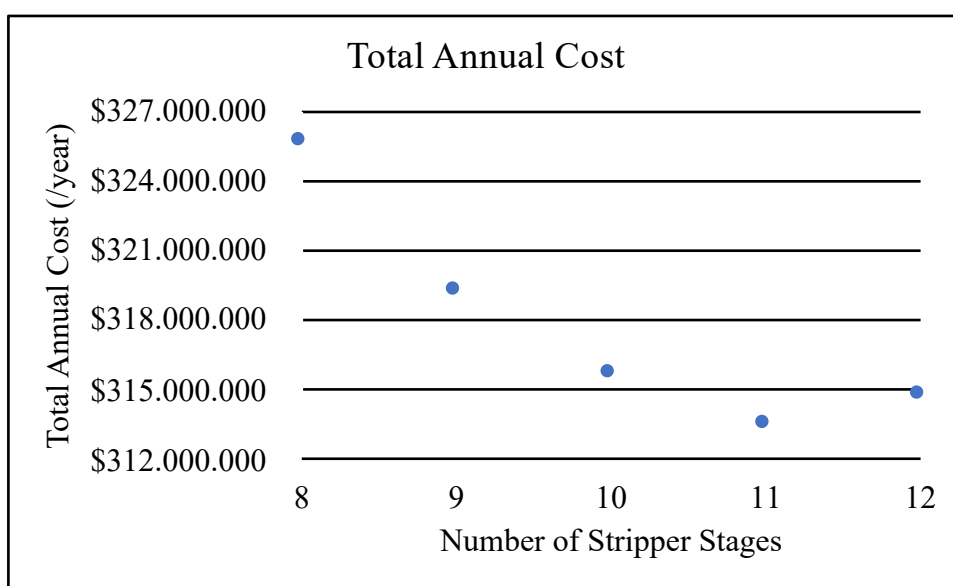


Figure 4.17. Number of Stripper Stages Effect to Total Annual Cost

4. Inlet Reactor Temperature

Temperature for inlet reactor stream is varied from 473 K to 503 K. Lower bound for inlet reactor temperature is to be 473 K. That value comes from a literature that state minimum inlet temperature for methanol synthesis is 473 K (Kubota et al., 2001). Table 4.9. shows that by decreasing inlet reactor temperature, total annual cost also decreases. Therefore, the smallest total annual cost is given while inlet reactor temperature is set to be 473 K.

Table 4.9. Total Annual Cost for Changing Inlet Reactor Temperature

Inlet Reactor Temperature (K)	Total Annual Cost
473	\$ 311,526,988
488	\$ 313,540,830
503	\$ 314,751,803

A figure to illustrate trend of total annual cost needed for the process as impact of changing inlet reactor temperature is shown in Figure 4.18.

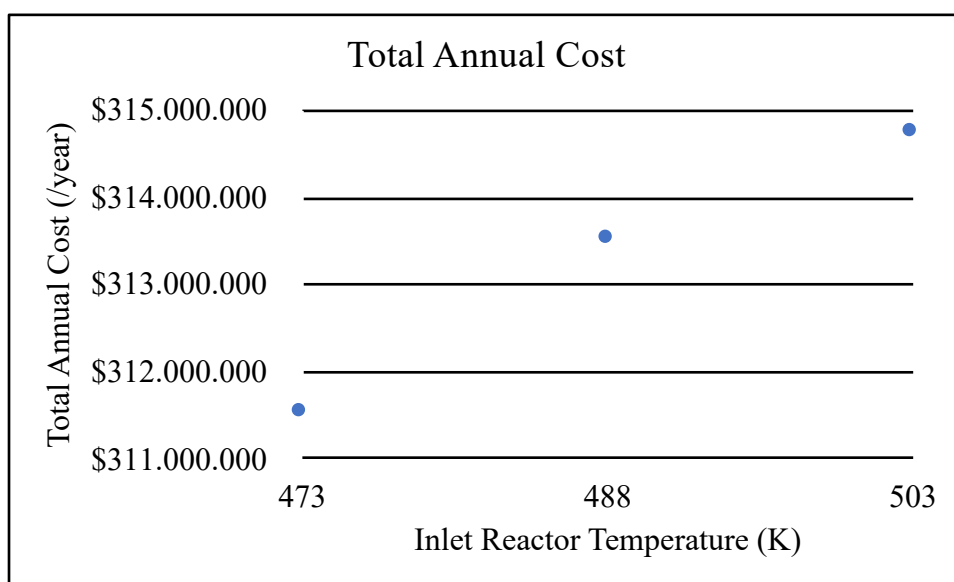


Figure 4.18. Inlet Reactor Temperature Effect to Total Annual Cost

5. Reactor Pressure

Changing reactor pressure gives the biggest effect of total annual cost. It is due to high requirement of both capital cost and utility cost for compressing hydrogen and carbon dioxide to desired pressure. 40 bar of reactor pressure gives the smallest amount of total annual cost. Total annual cost needed for reactor pressure at 40 bar \$ 291,550,576, compared to \$ 311,526,988 from 65 bar reactor pressure. Detailed result of total annual cost is shown in Table 4.10.

Table 4.10. Total Annual Cost for Changing Reactor Pressure

Reactor Pressure (bar)	Total Annual Cost
65	\$ 311,526,988
60	\$ 308,098,241
55	\$ 304,382,934
50	\$ 300,489,126
45	\$ 296,130,201
40	\$ 291,550,576
35	\$ 310,289,378

A figure to illustrate trend of total annual cost needed for the process as impact of changing reactor pressure is shown in Figure 4.19.

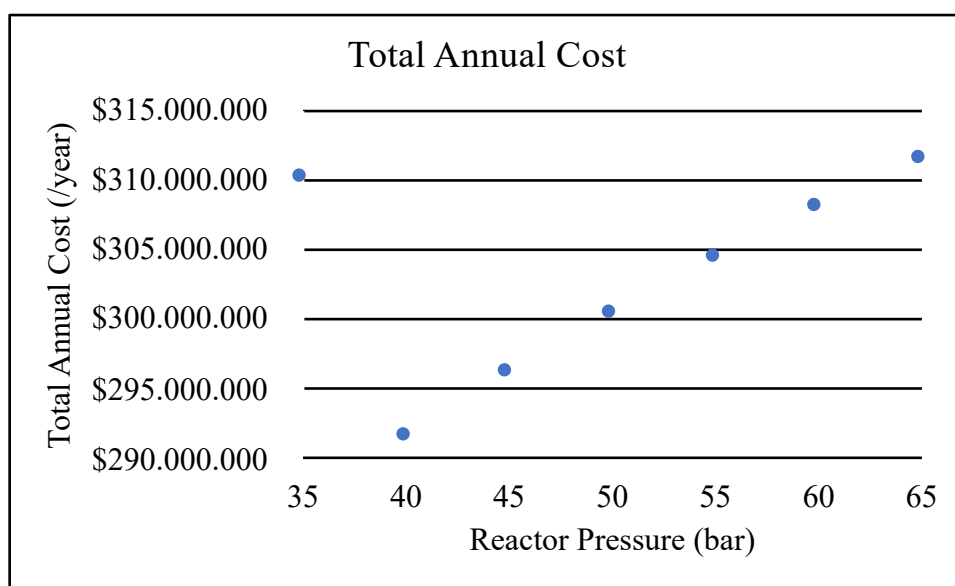


Figure 4.19. Reactor Pressure Effect to Total Annual Cost

After variation of base case has been done, Table 4.11. shows the summary of the optimization. Almost all of the parameter has been changed from base case. The only parameter that is not changed is stripper feed inlet stage. Total annual cost needed also decreases significantly. Total annual cost needed for base case is \$ 316,010,158, while total annual cost for optimized process is \$ 291,550,576.

Approximately \$ 25,000,000.00 can be saved through the optimization. Together with increasing methanol produced before, decreasing total annual cost needed can give a more economical process.

Table 4.11. Summary of Optimization

Specification	Value	
	Old design	New design
Number of absorber stage	7 stages	5 stages
Stripper feed inlet stage	5 th stage	5 th stage
Number of stripper stage	10 stages	11 stages
Inlet Reactor temperature	488 K	473 K
Reactor pressure	65 bar	40 bar
Total annual cost	\$ 316,010,158	\$ 291,550,576

This page is intentionally left blank

CHAPTER 5

CONCLUSION

After doing a research, there are some conclusions that can be concluded, those are:

1. Carbon Dioxide Capture
 - Simulation of carbon capture absorption process using monoethanolamine (MEA) has been made and converged. Simulation gives satisfying result with total flow of stream exits from top of stripper is 87.92 kg/s and purity of carbon dioxide is 98.1 %
2. Carbon Dioxide Storage Network
 - Carbon capture and storage network using sequential method can capture more carbon dioxide than simultaneous method. In sequential method, maximum capturable carbon dioxide is 93.86 %, while in simultaneous method is 83.94 %.
 - The most efficient cost is obtained in simultaneous method with optimum minimum time difference 6 years, which needs cost \$ 67,857,256, compared to sequential method with optimum minimum time difference 4.5 years, which needs cost \$ 78,233,875.
3. Carbon Dioxide Conversion to Methanol
 - Simulation of methanol synthesis process has been made and converged. The simulation gives a good result with 52.96 kg/s of product stream with 99.6 % methanol purity.
 - Optimization of carbon dioxide capture and conversion to methanol process has been done. Varying operating condition can reduce total annual cost needed from \$ 316,010,158 to \$ 291,550,576.

This page is intentionally left blank

REFERENCES

- Aboudheir, A., Tontiwachwuthikul, P., Chakma, A., Idem, R. (2003), “**Kinetics of the Reactive Absorption of Carbon Dioxide in High CO₂-loaded, Concentrated Aqueous Monoethanolamine Solutions**”. *Chemical Engineering Science*, Vol. 58, Pages 5195-5210.
- Arachchige, U.S.P.R., Muhammad, M., Melaaen, M.C. (2012), “**Optimized Carbon Dioxide Removal Model for Gas Fired Power Plant**”. *European Journal of Scientific Research*, Vol. 86, Pages 348-359.
- Arnold, D.S., Barrett, D.A., Isom, R.H. (1982), “**CO₂ can be Produced from Flue Gas**”. *Oil & Gas Journal*, Pages 130-136.
- Austgen, D.M., Rochelle, G.T., Peng, X., Chen, C. (1989), “**Model of Vapor-liquid Equilibria for Aqueous Acid Gas-alkanolamine System Using the Electrolyte-NRTL Equation**”. *Industrial and Engineering Chemistry Research*, Vol. 28, Pages 1060-1073.
- Bachu, S. (2008), “**Legal and Regulatory Challenges in the Implementation of CO₂ Geological Storage: An Alberta and Canadian Perspective**”. *International Journal of Greenhouse Gas Control*, Vol. 2, Pages 259-273.
- Bailey, D.W., & Feron, P.H.M. (2005), “**Post-combustion Decarbonisation Processes**”. *Oil & Gas Science and Technology – Rev. IFP*, Vol. 60(3), Pages 461–474.
- Barakat, H.Z., & Clark, J.A. (1966), “**On the Solution of the Diffusion Equation by Numerical Methods**”. *Journal of Heat Transfer, Transactions of ASME*, Vol. 88, Pages 421-427.
- BERR (2009), “**Energy Trends**”. London: Department of Energy and Climate Change.
- Crooks, J.E., & Donnellan, J.P. (1989), “**Kinetics and Mechanism of the Reaction Between Carbon Dioxide and Amines in Aqueous Solution**”. *Journal of Chemical Society of Perkin Transactions*, Vol. II, Pages 331-333.
- Danckwerts, P.V. (1970), “**Gas Liquid Reactions**”. New York: The McGraw-Hill Companies, Inc.

- Danckwerts, P.V. (1979), **“The Reaction of CO₂ with Ethanolamines”**. *Chemical Engineering Science*, Vol. 34, Pages 443-446.
- Diamante, J.A.R., Tan, R.R., Foo, D.C.Y., Ng, D.K.S., Aviso, K.B., Bandyopadhyay, S. (2014), **“Unified Pinch Approach for Targeting of Carbon Capture and Storage (CCS) Systems with Multiple Time Periods and Regions”**. *Journal of Cleaner Production*, Vol. 71, Pages 67-74.
- Edwards, J.T., Maurer, G., Newman, J., Prausnitz, J.M. (1978), **“Vapor-liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes”**. *AIChE Journal*, Vol. 24, Pages 966-976.
- EIA (2008), **“International Energy Outlook 2008”**. Washington DC: Energy Information Administration, US Department of Energy.
- Fjellerup, K. (2015), **“Sustainable Process Networks for Carbon Dioxide Conversion”**. Master Thesis, Technical University of Denmark, Denmark.
- Freguia, S. (2002), **“Modelling of CO₂ Removal from Flue Gas with Mono-ethanolamine”**. Master Thesis, University of Texas, USA.
- Furman, K.C., & Sahinidis, N.V. (2002), **“A Critical Review and Annotated Bibliography for Heat Exchanger Network Synthesis in the 20th Century”**. *Industrial & Engineering Chemistry Research*, Vol. 41, Pages 2335-2370.
- Geankoplis, C.J. (2003), **“Transport Processes and Separation Process Principles 4th Edition”**. New Jersey: Prentice Hall.
- Gibbins, J., & Chalmers, H. (2008), **“Carbon Capture and Storage”**. *Energy Policy*, Vol. 36, Pages 4317-4322.
- Gough, C., & Shackley, S. (2005), **“An Integrated Assessment of Carbon Dioxide Capture and Storage in the UK”**. Manchester: Tyndall Centre for Climate Change Research.
- Heddle, G., Herzog, H., Klett, M. (2003), **“The Economics of CO₂ Storage”**. Cambridge: Massachusetts Institute of Technology, Laboratory for Energy and the Environment.
- Higman, C., & van der Burgt, M. (2003), **“Gasification”**. Oxford: Gulf Professional Publishing.

- IPCC (2005), **“IPCC Special Report on Carbon Dioxide Capture and Storage, Working Group III of the Intergovernmental Panel on Climate Change”**. Cambridge: Cambridge University Press.
- IPCC (2007), **“Climate Change 2007: Mitigation, Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change”**. Cambridge: Cambridge University Press.
- IRGC (2008), **“Policy Brief: Regulation of Carbon Capture and Storage”**. Geneva: International Risk Governance Council (IRGC).
- Kent, R.L., & Eisenberg, B. (1976), **“Better Data for Amine Treating”**. *Hydrocarbon Processing*, Vol. February, Pages 87-90.
- Kothandaraman, A. (2010), **“Carbon Dioxide Capture by Chemical Absorption: A Solvent Comparison Study”**. Ph.D. Thesis, Massachusetts Institute of Technology, USA.
- Kubota, T., Hayakawa, I., Mabuse, H., Mori, K., Ushikoshi, K., Watanabe, T., Saito, M. (2001), **“Kinetic Study of Methanol Synthesis from Carbon Dioxide and Hydrogen”**. *Applied Organometallic Chemistry*, Vol. 15, Pages 121-126.
- Luyben, W.L. (2013), **“Comparison of Extractive Distillation and Pressure Swing Distillation for Aceton/Chloroform Separation”**. *Computers & Chemical Engineering*, Vol. 50, Pages 1-7.
- Maroto-Valer, M.M. (2010), **“Developments and Innovation in Carbon Dioxide (CO₂) Capture and Storage Technology”**. Cambridge: Woodhead Publishing.
- McKinsey & Company (2008), **“Carbon Capture and Storage: Assessing the Economics”**. McKinsey & Company.
- Mitsubishi Heavy Industries (2004), **“Report on Ship Transport of CO₂”**. Paris: IEA Greenhouse Gas R&D Programme.
- Ooi, R.E.H., Foo, D.C.Y., Ng, D.K.S., Tan, R.R. (2013), **“Planning of Carbon Capture and Storage with Pinch Analysis Techniques”**. *Chemical Engineering Research and Design*, Vol. 91, Pages 2721-2731.
- Orr Jr., F.M. (2009), **“CO₂ Capture and Storage: Are We Ready?”**. *Energy & Environmental Science*, Vol. 2, Pages 449–458.

- Perry, R.H. and Green, D.W. (2008), **“Perry’s Chemical Engineers’ Handbook Eight Edition”**. New York: The McGraw-Hill Companies, Inc.
- Putra, A.A., Gani, R., Juwari, Handogo R. (2016), **“Evaluation and Comparison of Carbon Dioxide Capture Using MEA and DEA”**. *International Journal of Applied Chemistry*, Vol. 12, Pages 88-92.
- Putra, A.A., Juwari, Handogo R. (2017), **“Technical and Economical Evaluation of Carbon Dioxide Capture and Conversion to Methanol Process”**. *AIP Conference Proceedings*, Vol. 1840, Pages 070007-1-6.
- Putra, A.A., Juwari, Handogo R. (2018), **“Multi Region Carbon Capture and Storage Network in Indonesia Using Pinch Design Method”**. *Process Integration and Optimization for Sustainability*, Vol. 2, Pages 321-341.
- Putra, K.R., Svendsen, H.F., Knuutila, H.K. (2017), **“Kinetics of CO₂ Absorption in to Aqueous MEA Solutions Near Equilibrium”**. *Energy Procedia*, Vol. 114, Pages 1576-1583.
- Romeo, L.M., Bolea, I., Escosa, J.M. (2008), **“Integration of Power Plant and Amine Scrubbing to Reduce CO₂ Capture Costs”**. *Applied Thermal Engineering*, Vol. 28, Pages 1039–1046.
- Satjana, A.H. & Purwaningsih, M.E.M. (2003), **“Geochemistry of The East Java Basin: New Observations on Oil Grouping, Genetic Gas Types and Trends of Hydrocarbon Habitats”**. Proceedings, Indonesian Petroleum Association.
- Sheldon, D. (2017), **“Methanol Production – A Technical History”**. *Johnson Matthey Technology Review*, Vol. 61, Pages 172-182.
- Sofyan, L. (2010), **“Distributional Impact of A Carbon Tax Indonesia Case”**. Master Thesis, Waseda University, Japan.
- Tsai, T., Ko, J., Wang, H., Lin, C., Li, M. (2000), **“Solubility of Nitrous Oxide in Alkanolamine Aqueous Solution”**. *Journal of Chemical & Engineering Data*, Vol. 45, Pages 341-347.
- Usman, Iskandar, U.P., Sugihardjo, Lastiadi, H. (2014), **“A Systematic Approach to Source-Sink Matching for CO₂ EOR and Sequestration in South Sumatra”**. *Energy Procedia*, Vol. 63, Pages 7750-7760.

- van Alphen, K., van Voorst tot Voorst, Q., Hekkert, M., Smits, R.E.H.M. (2007), **“Societal Acceptance of Carbon Capture and Storage Technologies”**. *Energy Policy*, Vol. 35, Pages 4368–4380.
- Versteeg, G.F., van Dijck, L.A., van Swaaij, P.M. (1996), **“On the Kinetics Between CO₂ and Alkanolamines Both in Aqueous and Non-aqueous Solutions, An Overview”**. *Chemical Engineering Communications*, Vol. 144, Pages 113-158.
- White, C.W. (2002), **“Aspen Plus Simulation of CO₂ Recovery Process – Final Report”**. West Virginia: EG&G Technical Service, Inc.
- Wilson, M., Tontiwachwuthikul, P., Chakma, A., Idem, R., Veawab, A., Aroonwilas, A., Gelowitz, D., Barrie, J., Mariz, C. (2004), **“Test Results from a CO₂ Extraction Pilot Plant at Boundary Dam Coal-fired Power Plant Station”**. *Energy*, Vol. 29, Pages 1259–1267.
- Wu, X., Yu, Y., Qin, Z., Zhang, Z. (2014), **“The Advances of Post-Combustion CO₂ Capture with Chemical Solvents: Review and Guidelines”**. *Energy Procedia*, Vol. 63, Pages 1339-1346.
- Zuchrillah, D.R. & Rachmawati, A.D. (2014), **“Optimasi Jaringan Carbon Capture and Storage (CCS) System dengan Menggunakan Metode Pinch”**. Undergraduate Thesis, Institut Teknologi Sepuluh Nopember, Indonesia.

This page is intentionally left blank

ATTACHMENTS

1. Carbon Dioxide Capture Simulation Result

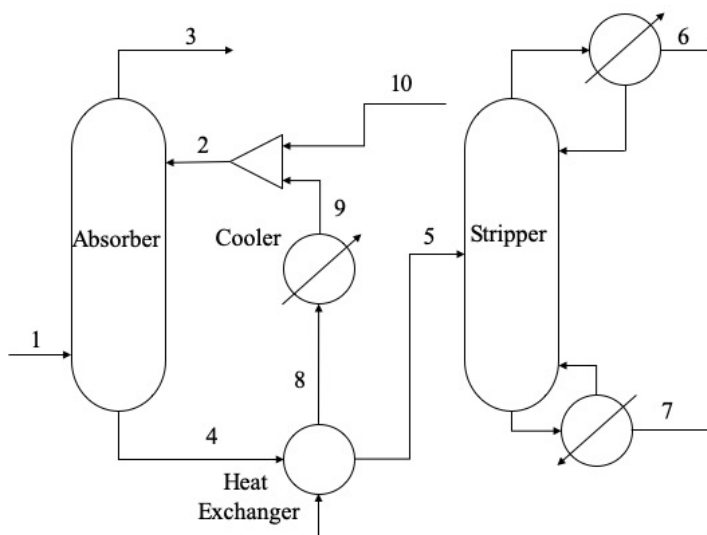


Figure A.1. Carbon Capture Simulation Flowsheet

Table A.1. Detailed Stream Specification in Carbon Capture Simulation

Stream No.	1	2	3	4	5	6	7	8	9	10
Temp. (K)	320.49	319.15	318.15	344.15	384.15	307.14	392.15	351.98	319.15	319.15
Press (bar)	1.57	1.01	1.01	1.58	1.58	1.21	1.78	1.78	1.78	1.01
Flow rate (kg/s)	372.43	1605.02	286.94	1689.92	1689.92	87.92	1602.00	1602.00	1602.00	2.43
Component Mass Fraction										
H ₂ O	0.041	0.676	0.061	0.641	0.641	0.018	0.675	0.675	0.675	0.927
CO ₂	0.232	0.034	trace	0.083	0.083	0.981	0.034	0.034	0.034	-
N ₂	0.727	0.001	0.939	0.001	0.001	0.001	0.001	0.001	0.001	-
MEA	-	0.289	trace	0.275	0.275	trace	0.290	0.290	0.290	0.073

2. Carbon Dioxide Conversion Simulation Result

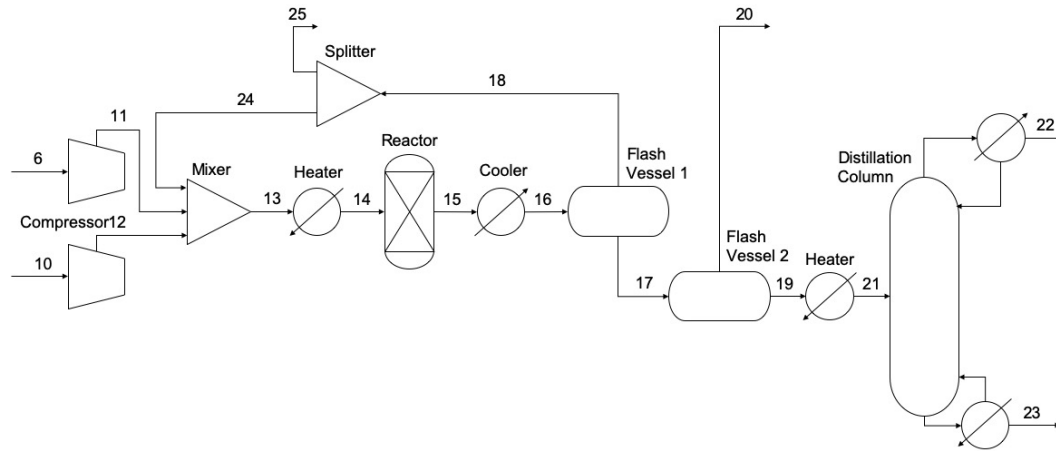


Figure A.2. Carbon Conversion Simulation Flowsheet

Table A.2. Detailed Stream Specification in Carbon Conversion Simulation

Stream No.	6	10	11	12	13	14	15	16	17
Temp. (K)	307.14	300	641.67	907.1	351.97	488	539	320	313
Press (bar)	1.21	1.01	65	65	65	65	65	65	65
Flow rate (kg/s)	87.92	12.29	87.92	12.29	1265.32	1265.32	1265.32	1265.32	88.02
Component Mass Fraction									
H ₂ O	0.018	-	0.018	-	0.003	0.003	0.029	0.029	0.385
CO ₂	0.981	-	0.981	-	0.818	0.818	0.758	0.758	0.009
CO	-	-	-	-	0.037	0.037	0.037	0.037	trace
N ₂	0.001	-	0.001	-	0.002	0.002	0.02	0.02	trace
MEA	trace	-	trace	-	trace	trace	trace	trace	trace
H ₂	-	1.00	-	1.00	0.128	0.128	0.120	0.120	trace
Methanol	-	-	-	-	0.012	0.012	0.054	0.054	0.606

Table A.3. Detailed Stream Specification in Carbon Conversion Simulation (cont.)

Stream No.	18	19	20	21	22	23	24	25
Temp. (K)	313	308	308	353	337.81	371.36	313	313
Press (bar)	65	1.2	1.2	1.2	1.003	1.32	65	65
Flow rate (kg/s)	1177.30	87.05	0.97	87.05	52.96	34.09	1165,11	12.19
Component Mass Fraction								
H ₂ O	0.002	0.389	0.026	0.389	0.003	0.989	0.002	0.002
CO ₂	0.814	0.001	0.727	0.001	0.001	0.001	0.814	0.814
CO	0.040	trace	trace	trace	trace	trace	0.040	0.040
N ₂	0.002	trace	trace	trace	trace	trace	0.002	0.002
MEA	trace	trace	trace	trace	trace	trace	trace	trace
H ₂	0.129	trace	trace	trace	trace	trace	0.129	0.129
Methanol	0.013	0.610	0.247	0.610	0.996	0.010	0.013	0.013

This page is intentionally left blank

AUTHOR BIOGRAPHY



Aditya Anugerah Putra, or usually called Adit, was born in Surabaya, December 6th 1991. The author started his formal education in SDN Pucang I Sidoarjo in 1998 – 2004, the author continued his formal education in SMP Negeri 6 Surabaya in 2004 – 2007 and took acceleration class in SMA Negeri 15 Surabaya in 2007 – 2009. After graduated from senior high school in 2009, the author continued his study by taking bachelor degree in Chemical Engineering Department, Institut Teknologi Sepuluh Nopember Surabaya and was graduated in 2013 with cum laude predicate. During his bachelor time in Chemical Engineering Department, the author chose Process System Engineering Laboratory to focus on his bachelor research about usage of ratio control in the industry.

After graduated from bachelor degree, the author continued his study in Doctoral Program in Chemical Engineering Department by joining Program Magister Menuju Doktor Sarjana Unggul under his former bachelor supervisor, Prof. Ir. Renanto, M.Sc., Ph.D. His study in doctoral program mainly focused on mitigation of carbon dioxide in order to reduce greenhouse gas effect. During his study, author have joined sandwich programs to get experience studying and living in international environment. The author went to Technical University of Denmark in 2015 under supervision of Prof. Rafiqul Gani and to Yeungnam University, South Korea in 2016 under supervision of Prof. Moonyong Lee for his sandwich program. The author have published two international journals and attended several national and international seminars.

Stay safe and stay healthy,

Aditya Anugerah Putra

0811 325 0201

adityanugerah@gmail.com