



**CHALMERS**  
UNIVERSITY OF TECHNOLOGY

---



# **Techno-Economic Analysis of CO<sub>2</sub> Capture Reference System Based on Phase-Change Solvent Absorption**

Master's thesis in Sustainable Energy Systems

DIXIN WEI  
CHANG PENG

---

Department of Energy and Environment  
CHALMERS UNIVERSITY OF TECHNOLOGY  
Gothenburg, Sweden 2017



MASTER'S THESIS 2017

**Techno-Economic Analysis of CO<sub>2</sub> Capture  
Reference System Based on Phase-Change  
Solvent Absorption**

DIXIN WEI  
CHANG PENG



**CHALMERS**  
UNIVERSITY OF TECHNOLOGY

Department of Energy and Environment  
*Division of Energy Technology*  
CHALMERS UNIVERSITY OF TECHNOLOGY  
Gothenburg, Sweden 2017

Techno-Economic Analysis of CO<sub>2</sub> Capture Reference System  
Based on Phase-Change Solvent Absorption

DIXIN WEI

CHANG PENG

© DIXIN WEI & CHANG PENG, 2017.

Supervisor: Stavros Papadokostantakis

Examiner: Stavros Papadokostantakis, Department of Energy and Environment

Master's Thesis 2017

Department of Energy and Environment

Division of Energy Technology

Chalmers University of Technology

SE-412 96 Gothenburg

Telephone +46 31 772 1000

Typeset in L<sup>A</sup>T<sub>E</sub>X

Printed by [Chalmers Reproservice]

Gothenburg, Sweden 2017

# Techno-Economic Analysis of CO<sub>2</sub> Capture Reference System Based on Phase-Change Solvent Absorption

DIXIN WEI

CHANG PENG

Department of Energy and Environment

Chalmers University of Technology

## Abstract

The CO<sub>2</sub> emission into atmosphere over the past century is considered as the main reason for global warming phenomenon. The Paris Agreement target of 2 °C urged not only focus on this issue, but also effective measures for the transition period and long term. The solvent based post-combustion carbon capture, a conveniently applied process, can be costly mainly due to high reboiler heating for the solvent regeneration. If the cost can be reduced to an acceptable value for power plants, then PCC processes exhibit substantial potential in coal and natural gas fired plant emission reduction, which is a large share in global CO<sub>2</sub> emissions.

This study focuses on phase-change amines, that have reported good experimental results in phase separation, and thus reduce reboiler heating demand. It starts with checking and comparing a group of amines and selecting potential candidates. Further PCC process simulation in Aspen shows detailed results in performance of different configuration and amine type.

In general, two amines known as DIBA and HXA are seen as promising replacement, especially HXA. The results are compared with MEA reference case. With respect to reboiler duty, the two selected amines both showed more than 50% reduction. And in the best scenario, the reboiler heating demand is reduced to 0.91 GJ/ton CO<sub>2</sub> captured.

Keywords: Carbon capture, MEA, phase-changing solvent, amine, Aspen, decanter

## Acknowledgements

Sincerely, we would like to thank our supervisor and examiner, Stavros Papadokostas. His advice helped us throughout the whole project and inspired several meaningful studies. We would also thank Gulnara Shavaliyeva who helped us with sources related to our study.

We also appreciate the warm support from our friends and family, especially Yiyu from group 'Teletubbies'. Besides, great thanks to the nice and friendly environment in the department, as well as master thesis students altogether.

Dixin Wei & Chang Peng,  
Gothenburg, June 2017

# Abbreviation

<b>CCS</b>	Carbon Capture and Storage
<b>CED</b>	Cumulative energy demand
<b>CF</b>	carbamate formation
<b>CR</b>	carbamate reversion
<b>DEA</b>	Diethanolamine
<b>DGA</b>	Diglycolamine
<b>DIBA</b>	Diisobutylamine
<b>EI99</b>	Eco-indicator 99
<b>GWP</b>	Global warming potential
<b>HX</b>	Heat Exchanger
<b>HXA</b>	Hexylamine
<b>keq</b>	Reaction equilibrium constant
<b>MEA</b>	Monoethanolamine
<b>MEDA</b>	Methyl diethanolamine
<b>MW</b>	molecule weight
<b>PCC</b>	Post-combustion carbon capture
<b>RED</b>	Relative energy difference
<b>VLLLE</b>	vpour liquid liquid equilibrium





# Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Carbon Capture and Storage Background . . . . .	1
1.2	Solvent Based Post-Combustion Carbon Capture Process . . . . .	3
1.3	Aim of thesis project . . . . .	4
<b>2</b>	<b>Theory</b>	<b>5</b>
2.1	Phase Change Solvent Absorption Flowsheet . . . . .	5
2.2	Amine Absorption Reaction Mechanism . . . . .	6
2.3	Liquid Liquid Equilibrium of phase-change amine . . . . .	7
2.4	Absorption and Stripping . . . . .	8
<b>3</b>	<b>Methods</b>	<b>9</b>
3.1	Study of Phase-Change Solvents . . . . .	9
3.1.1	Property Method in Aspen Plus . . . . .	9
3.1.2	Aspen Component Specification . . . . .	10
3.1.3	Property Check and Modification . . . . .	10
3.1.4	Aspen Ternary Diagram Study . . . . .	10
3.1.5	Decanter Separation Study . . . . .	15
3.2	Define Reaction Equilibrium Constant . . . . .	18
3.2.1	Reaction Keq in MEA Flowsheet . . . . .	18
3.2.2	Reaction keq value of studied molecules . . . . .	18
3.3	Base configuration setting up . . . . .	19
3.3.1	Calculating methods for absorber and stripper . . . . .	19
3.3.2	Stream and column settings . . . . .	20
3.3.3	Close-loop mass balance and design specifications . . . . .	21
3.3.4	Flowsheet improvement - add condenser unit for recycling amine	22
3.4	Other Configurations . . . . .	23
3.4.1	Double Stripper Configuration . . . . .	23
3.4.2	Configuration with Rearranged Heat Exchanger . . . . .	24
3.5	Degradation Estimation . . . . .	24
3.6	Economic and Environmental Analysis . . . . .	25
3.7	Assumption and Limitation . . . . .	27
<b>4</b>	<b>Results</b>	<b>29</b>
4.1	Reboiler duty . . . . .	29
4.1.1	Base Case Configuration . . . . .	29

4.1.2	Add condenser for recycling amine . . . . .	30
4.1.3	Double Stripper Configuration . . . . .	31
4.1.4	Heat Exchanger Rearrange Configuration . . . . .	32
4.1.5	Summary . . . . .	33
4.2	Sensitivity Analysis . . . . .	34
4.2.1	Uncertain thermodynamic estimation . . . . .	34
4.2.2	Amine solution concentration . . . . .	39
4.3	Economic and Environment Analysis . . . . .	40
4.3.1	Operating cost . . . . .	40
4.3.2	Environmental Impact . . . . .	42
<b>5</b>	<b>Conclusion</b>	<b>45</b>
<b>A</b>	<b>Appendix 1</b>	<b>I</b>
A.1	keq value and property estimation . . . . .	I
A.2	Ternary diagram of DMCA . . . . .	IV
A.3	Column. stream input setting in flowsheets . . . . .	IV
A.4	Economic and environmental analysis parameter and results . . . . .	VIII
A.5	Sensitivity Analysis results . . . . .	X
A.6	Important stream result and stripper performance tables in all scenarios	XV

# List of Figures

2.1	MEA absorption flowsheet . . . . .	5
2.2	Phase change solvent absorption flowsheet . . . . .	6
3.1	VLLE ternary diagram DIBA . . . . .	12
3.2	VLLE ternary diagram DPA . . . . .	12
3.3	VLLE ternary diagram HXA . . . . .	13
3.4	VLLE ternary diagram CHPA . . . . .	13
3.5	VLLE ternary diagram 26-DMPD . . . . .	14
3.6	VLLE ternary diagram EPD . . . . .	14
3.7	Decanter modelling setting for amine study . . . . .	15
3.8	Water mole fraction in rich phase - Decanter Temperature . . . . .	17
3.9	Water mole fraction in rich phase - Inlet CO <sub>2</sub> flowrate . . . . .	17
3.10	Base case configuration . . . . .	20
3.11	Add condenser for amine recycling . . . . .	22
3.12	Configuration of double strippers with different operating pressure . . . . .	23
3.13	Configuration with Rearranged HX Placement . . . . .	24
3.14	CED vs Price for studied amines . . . . .	27
4.1	Reboiler duty in all scenarios, compared with MEA reference . . . . .	33
4.2	Reacted substance ratio in absorber - keq for DIBA . . . . .	35
4.3	Reacted substance ratio in absorber - keq for HXA . . . . .	35
4.4	Reboiler duty - keq value, A varies from -235.025 to -227.5 . . . . .	36
4.5	Reboiler duty - keq value, A varies from -227.5 to -226.5 . . . . .	36
4.6	Reboiler duty - water split ratio in rich loading phase compared with total water entering decanter . . . . .	37
4.7	Reboiler duty - amine split ratio in rich loading phase compared with total molecular CO <sub>2</sub> entering decanter . . . . .	38
4.8	Reboiler duty - molecular CO <sub>2</sub> split ratio in rich loading phase compared with total molecular CO <sub>2</sub> entering decanter . . . . .	38
4.9	Reboiler duty - Amine aqueous solution weight based concentration, from 30% to 44% . . . . .	39
4.10	Operating cost of scenario 3,5,7 for two amines . . . . .	40
4.11	CO <sub>2</sub> Capture cost penalty in unit electricity production . . . . .	41
4.12	EI99 indicator estimation, points/ton CO <sub>2</sub> captured . . . . .	42
4.13	Global warming potential estimation, CO <sub>2</sub> eq ton/ton captured . . . . .	43
4.14	Equivalent energy consumption . . . . .	43

## List of Figures

---

A.1	DMCA ternary mixture study diagram . . . . .	IV
A.2	Reference MEA flowsheet . . . . .	IV

# List of Tables

3.1	6 Amines which showed VLLE ternary diagram phase envelope . . . .	11
3.2	Basic Flowrate and Column Setting in Decanter Modelling . . . . .	16
3.3	Water and Amine Flowrate in Two Separated Phases . . . . .	16
3.4	Values used for calculating the equilibrium constant in equation 3.3 .	18
3.5	Estimated RED (relative energy difference) values . . . . .	18
3.6	Estimated reaction equilibrium constant values in equation 3.3 . . . .	19
3.7	Amine degradation rate estimation based on MEA . . . . .	25
3.8	reference price and environmental index for studied amines . . . . .	26
3.9	Assumptions . . . . .	28
4.1	Seven Studied Scenarios . . . . .	29
4.2	Result list for Scenario 1 (equilibrium), 2 (ratebased), and MEA ref- erence . . . . .	30
4.3	Result lists for scenario 3 . . . . .	31
4.4	Result list for configuration with two strippers, scenario 4 and 5 . . .	32
4.5	Reboiler duty result for HX rearrange configuration, scenario 6 and 7	32
4.6	Amine emission lost amount of all scenarios . . . . .	34
A.1	PLXANT parameter values . . . . .	I
A.2	Parameters for Pure Components Gained by Aspen Plus . . . . .	II
A.3	Keq Value for reactions in Carbon Capture Process based on MEA. T=340 k . . . . .	III
A.4	MEA reference flowsheet setting. stripper results . . . . .	V
A.5	Component settings for absorber and stripper with equilibrium cal- culate type . . . . .	V
A.6	Components settings for stripper in double-stripper flowsheet (sce- nario 4 and 5) . . . . .	VI
A.7	Column settings for Rate-based absorber & stripper in sifferent sce- narios . . . . .	VI
A.8	Other component settings . . . . .	VII
A.9	HX setting of all scenarios . . . . .	VII
A.10	Fluegas and leanin solution stream input setting . . . . .	VII
A.11	Estimated degradation value of two amines. in all scenarios . . . . .	VIII
A.12	Utility price used in economic analysis . . . . .	VIII
A.13	Amine CED. GWP. EI99 value used in environmental analysis . . . .	VIII
A.14	Utility CED. GWP. EI 99 value used in environmental analysis . . . .	IX
A.15	Economic analysis results of scenario 3.5.7 . . . . .	IX

A.16 GWP. EI99 results of scenario 3.5.7 . . . . .	IX
A.17 Equivalent energy consumption Results of scenario 3.5.7 . . . . .	IX
A.18 Solution concentration sensitivity analysis data . . . . .	X
A.19 Result table of sensitivity analysis in decanter using DIBA with varied temperature. unit for flow rate: kmol/h . . . . .	X
A.20 Result table of sensitivity analysis in decanter using HXA with varied temperature (unit for flow rate: kmol/h) . . . . .	XI
A.21 result table of sensitivity analysis in decanter using DIBA with varied CO <sub>2</sub> mole flow rate (unit for flow rate: kmol/h) . . . . .	XI
A.22 Result table of sensitivity analysis in decanter using HXA with varied CO <sub>2</sub> mole flow rate(unit for flow rate: kmol/h) . . . . .	XII
A.23 Keq sensitivity analysis results ( reboiler energy in GJ/ton CO <sub>2</sub> ) . . .	XIII
A.24 Decanter rich outflow mole fraction sensitivity analysis results (reboiler energy in GJ/ton CO <sub>2</sub> ) . . . . .	XIV
A.25 DIBA and HXA stripper detailed performance results in all scenarios	XVI
A.26 Stream table for DIBA Scenario 1. basecase equilibrium . . . . .	XVII
A.27 Stream table for DIBA Scenario 2. basecase ratebase . . . . .	XVIII
A.28 Stream table for DIBA Scenario 3. basecase with amine recycling . .	XIX
A.29 Stream table for DIBA Scenario 4. double strippers . . . . .	XX
A.30 Stream table for DIBA Scenario 5. double strippers with amine recycling . . . . .	XXI
A.31 Stream table for DIBA Scenario 6. heat exchanger rearrangement . .	XXII
A.32 Stream table for DIBA scenario 7. heat exchanger rearrangement with amine recycling . . . . .	XXIII
A.33 Stream table for HXA scenario 1. basecase equilibrium . . . . .	XXIV
A.34 Stream table for HXA scenario 2. basecase ratebase . . . . .	XXV
A.35 Stream table for HXA scenario 3. basecase with amine recycling . . .	XXVI
A.36 Stream Table for HXA scenario 4. double strippers . . . . .	XXVII
A.37 Stream table for HXA scenario 5. double strippers and amine recycling	XXVIII
A.38 Stream table for HXA scenario 6. heat exchanger rearrangement . . .	XXIX
A.39 Stream Table for HXA scenario 7. heat exchanger rearrangement with amine recycling . . . . .	XXX

# 1

## Introduction

### 1.1 Carbon Capture and Storage Background

The Paris Agreement, published in December 2015, introduces the 2°C target which is widely accepted by countries and districts around the world [1]. The target shows the great resolution of human beings in mitigating global warming, and from another aspect reveals the importance of reducing greenhouse gas in current situation.

Ever since the industrial revolution, the carbon dioxide, known as the most common greenhouse gas emitted by all kinds of industries was increasing dramatically due to the growth in global fossil fuel consumption. This on-going growth in global fossil fuel consumption [2], and the long road to widely replace fossil fuels with clean technologies, will be contributing to the continuous growth in the total amount of CO<sub>2</sub> if no practical strategies are utilized. One possible option for us to control the CO<sub>2</sub> emission and realize our 2°C target is the carbon capture and storage, known as the CCS technology.

CCS is the well-understood way that is able to remove CO<sub>2</sub> from flue gas released for instance by power plants. Main parts of CCS are carbon capture, carbon transport and carbon storage. The CO<sub>2</sub> capture part is studied with most focus, since it is the dominating step that could significantly add additional operating cost to the emitting power plants.

#### *Carbon Capture*

Well-understood CO<sub>2</sub> capture methods at present are post-combustion carbon capture, oxy-fuel combustion process, pre-combustion capture, and inherent separation [3].

Post-combustion capture removes CO<sub>2</sub> from exhausted gas. It is a retrofitting method to control carbon emission for combustion process, and can be applied in most of the existing power plant[4]. For post-combustion capture, proper selection of solvent and arrangement of process structure can elevate the efficiency and reduce cost, that is the mainly study area of this project. However, post-combustion capture process usually work under low pressure condition (same as ambient pressure, or slightly higher than the ambient), that means energy is required for pressurizing CO<sub>2</sub> after the process.

In oxy-fuel combustion process, air is replaced by oxygen as the oxidizing agent [5]. The exhausted gas of the oxy-fuel combustion process contains around 75%  $\text{CO}_2$ , while the rest is  $\text{H}_2\text{O}$ .  $\text{CO}_2$  concentration can reach to over 99% after condensing [6]. Compared to postcombustion capture, using oxy-fuel saves some operating cost from  $\text{CO}_2$  stripping and amine consumption, but extra cost caused by pure oxygen coming from intensive air separation needs to be account. Moreover, more sophisticated equipments using advanced material for storing oxy-fuel and withstanding reactions are needed, and the retrofitting of the emitting plant will also increase the capital cost.

Chemical-looping combustion (CLC) is a method of inherent separation that has similar principle with oxy-fuel combustion. Two interlinked reactors, air reactor and fuel reactor are occupied in a CLC system. Chosen metal oxide is oxidized by air in air reactor and then react with fossil fuel in fuel reactor. The Used metal oxide is recycled back to the air reactor [7] [8]. Similar to oxy-fuel combustion, the exhaust gas after fuel reactor contains only  $\text{CO}_2$  and water which will be handled after condensing.

The idea of pre-combustion CCS is to use steam or oxygen to react with fuel, forming synthesis gas(syngas) which contains only  $\text{CO}$  and  $\text{H}_2$ . A water-gas shift reaction with extra steam is followed, to convert  $\text{CO}$  to  $\text{CO}_2$  and produce a great amount of hydrogen at the mean time [9]. Pre-combustion CCS is mainly designed for NGCC and IGCC, the process however, needs high investment, and the running cost is also high compared to other CCS processes [6].

### *Carbon Transportation*

$\text{CO}_2$  separation and capture is the start of CCS process, the following step is carbon transportation. Pressurized  $\text{CO}_2$  can be transported by onshore truck and train, offshore ship, and pipelines. Pipeline is currently a preferable option for most of the practical CCS projects[10] that produce large amount of captured  $\text{CO}_2$ . The cost of pipeline transportation increases following the increasing of transporting distance, and in some cases, shipping can be a better  $\text{CO}_2$  method. Thus, the decisive factor of selecting carbon transportation method is the geographic conditions.

An exception is CCS projects built for oil industry. As the oil reservoirs are natural  $\text{CO}_2$  storing places,  $\text{CO}_2$  produced at these projects can be injected directly to there, thus no carbon transportation is needed [11] [12].

### *Carbon Storage*

$\text{CO}_2$  storage methods can be classified as ocean storage and geological storage, both of the methods being developed by oil and mining technologies. Carbon storage needs proper locations, but the capacity of carbon storage for spots is hard to know.  $\text{CO}_2$  can leak from the storing places unintentionally and threatening life of human beings and animals around the leaking spots. Therefore, cost of the carbon storage



contains not only the short term cost for equipment and injections, but also the long term cost for monitoring as well.

Ocean storage injects the captured CO<sub>2</sub> directly into deep ocean, and the extremely high pressure at the storing location will compress the CO<sub>2</sub> to liquid with density higher than water. The cost of ocean storage is not fixed, because of the varied cost for CO<sub>2</sub> injections, the deeper the storing location is, the higher price will be.

The other way is to store CO<sub>2</sub> geologically at places like deep saline formations, oil and gas reservoirs and unminable coal beds. For oil and gas reservoirs, injecting CO<sub>2</sub> to reservoirs can at the same time provide a force to drive out fossil fuels, a considerable amount of energy can be saved in that way.

## 1.2 Solvent Based Post-Combustion Carbon Capture Process

Post-combustion carbon capture (PCC) has high utilization and installation potential in CO<sub>2</sub> emission reduction process. One major reason is that PCC does not require main retrofitting changes on plant flowsheet or component design [13], especially in countries where abundant fossil fuel provide economic solution for large scale power production. Considering the typical large capacity sizes, PCC are highly possible to lead final emission reduction in short term. However, the integration with flue gas after-treatment process does require both technical and economic analysis. Various factors including appropriate heat source for the capture process, secure transport and storage facilities also limit the investment and implementation possibility.

In mature modern power plants, the flue gas is normally sent to after-treatment including particulate matter and desulfurization treatment. After this point the flue gas will be directed to CO<sub>2</sub> separation process, as in most PCC design cases.

There were already several solvent based industrial application of PCC in different scales. Prior to PCC, aqueous amine solution has been commonly used in natural gas sweetening field for decades [14]. Previous acquired experience of amine based absorption serve as cornerstones for the choice of appropriate absorbent molecules, as well as complete PCC process design. Among the abundant amine family, MonoEthanolAmine (MEA) has been preferred for high reactivity even at low CO<sub>2</sub> pressure [15], low cost, and relatively low thermal degradation [16].

MEA absorption demonstrates considerable 90% removal efficiency, while the main obstacle of promotion lies in high energy and cost requirement[3]. Heat required in the process mainly lies in solvent regeneration process, where steam is used to heat the solvent and strip CO<sub>2</sub> out of solution. From previous testing results, 30% weight based solution has reported an energy requirement of 3.7 GJ/ton CO<sub>2</sub> [17] to 4.3 GJ/ton CO<sub>2</sub> [18] under different plant testing and CO<sub>2</sub> loading conditions, resulting

in cost of 40-100 \$/ton CO<sub>2</sub> captured [19].

Except for considering diverse PCC process designs, increasing solvent concentration and mixing amines, there has been focus on investigation of phase change amines which possibly reduce cost to large extent. Thus the range of studied solvents has expanded to various compounds, aiming at high absorption capacity and low energy consumption. The focus of this thesis will be a group of phase-changing amines [20] which present phase separation properties at varying temperature ranges.

In the previous commonly adopted absorption process, alkanolamines including MEA were preferred, because at that stage liquid-liquid separation was considered as a shortcoming [21]. The hydroxyl structure in MEA indeed prevents phase separation from water [15]. But as the research scope expands, phase changing solvents offers considerable energy reduction potential due to its liquid-liquid equilibrium characteristic. Researchers in IFP Energies nouvelles developed a DMX<sup>TM</sup> process, which undergoes phase separation after absorption [21]. Less flow rate entering the stripper and higher solvent cyclic capacity enables the stripper to work at reduced heat duty.

Moreover, another advantage lies in possibly diminished reboiler temperature, which provides opportunity of utilizing industrial excess heat. For example, the MEA process requires heat at 120-130 °. If this could be reduced, there is significant potential to integrate industrial excess heat. This and further process integration potential contributes to energy and cost optimization [22].

### 1.3 Aim of thesis project

Based on available experimental data from recent studies in phase-changing solvents for PCC, the main object of this thesis work is searching for appropriate amine absorbents that have phase-changing property and can be used in DMX<sup>TM</sup> process or other similar process, to largely reduce reboiler energy demand for high carbon dioxide removal efficiency.

The thesis starts with study of amine candidates detailed in their performance in phase separation and desorption process. Modeling and simulation for the carbon capture process using Aspen Plus is then performed to compare the energy reduction achieved for the identified promising candidates. After that, sensitivity analysis is needed to see the reliability of the modeling result, and meanwhile understand limitations and the inaccuracy of process simulation. Different process configurations are studied to see their potential in reducing energy consumption to a greater extension.

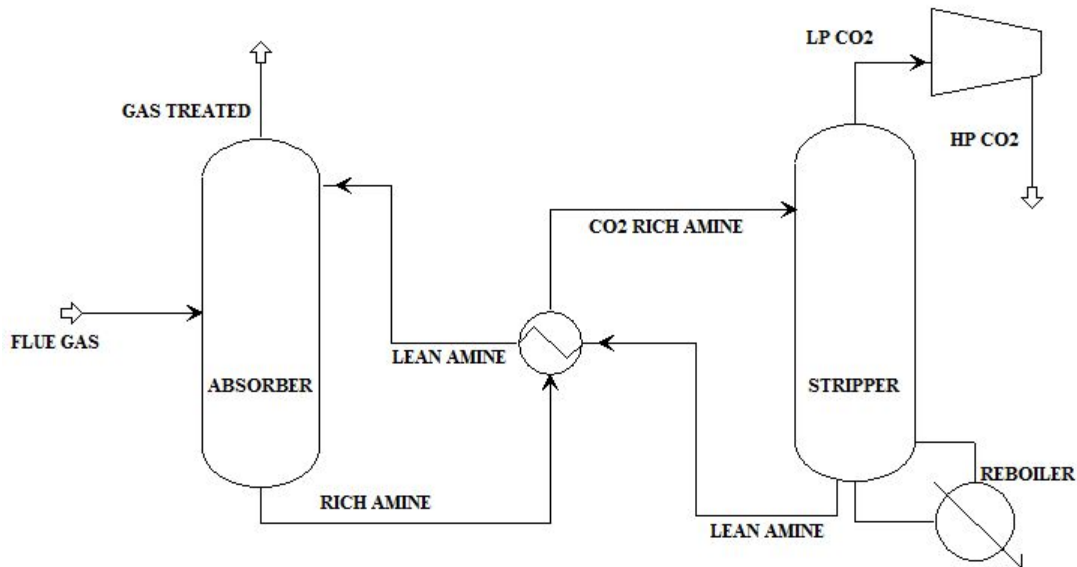
# 2

## Theory

In the following chapter, theory about amine-based absorption reaction mechanism, reaction equilibrium constant calculation, as well as VLE background used in this work are discussed.

### 2.1 Phase Change Solvent Absorption Flowsheet

*MEA Absorption*

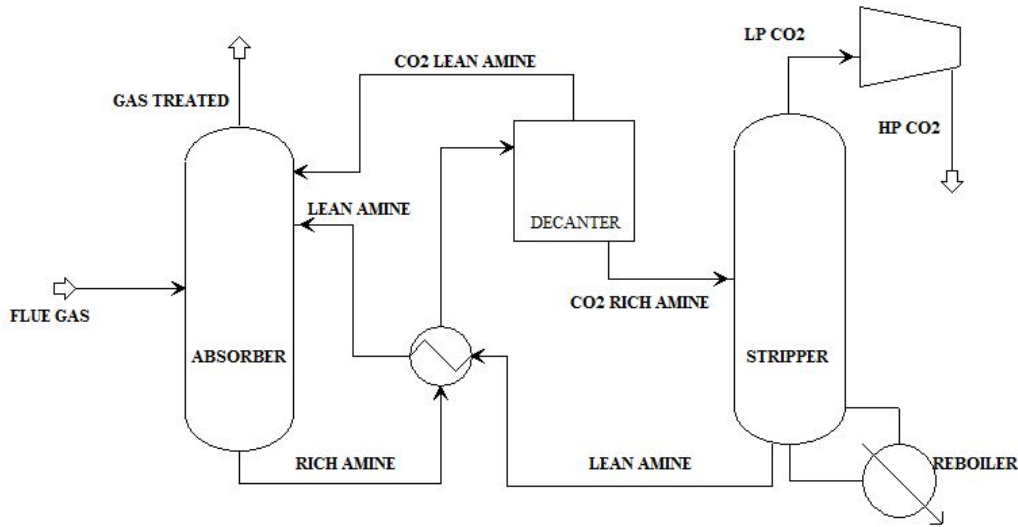


**Figure 2.1:** MEA absorption flowsheet

The MEA absorption flowsheet is shown in Figure 2.1. The process begins with reactions between flue gas and amine aqueous solution in the absorber at near ambient temperature, and subsequent heating of rich CO<sub>2</sub> loaded solution releases CO<sub>2</sub> in the stripper component. Heat exchanger utilizes the high temperature lean amine stream after stripping. Flow mixed with CO<sub>2</sub> and other vapor is condensed in the

condenser after stripper, so  $\text{CO}_2$  can reach a high purity.  $\text{CO}_2$  after the condenser will be pressurized for transportation and further storage [3].

### *DMX<sup>TM</sup> Process*



**Figure 2.2:** Phase change solvent absorption flowsheet

Compared to the MEA process, the main improvement in  $\text{DMX}^{\text{TM}}$  process is the reduced flow to the stripper because of the liquid-liquid phase separation of solvent-water- $\text{CO}_2$  mixture in a decanter [21]. After reaction with flue gas, the rich  $\text{CO}_2$  loading solution is separated into two liquid phases, where only the one with concentrated  $\text{CO}_2$  is sent to the stripper, and the lean one is recycled back to the absorber. The vapor-liquid-liquid equilibrium (VLLE) property varies according to different molecule chosen, solution concentration etc, which affects the composition and flow rate of two phases.

## 2.2 Amine Absorption Reaction Mechanism

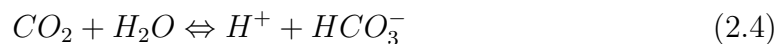
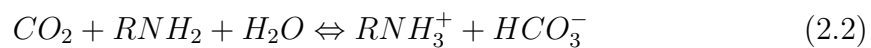
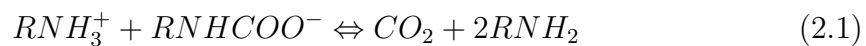
Amines suitable for phase-changing carbon capture should exhibit several important features: phase-separation performance, absorption capacity, and regenerability in stripper. The studied amines react with  $\text{CO}_2$  according to different mechanisms, considering their chemical structures. Basically amines could be divided into three groups according to the number of hydrogen atoms replaced by function groups: primary, secondary and tertiary amines represent amines categories according to one to three substituents, respectively.

As in equation 2.1, first and secondary amine aqueous solution mainly attend carbamate formation (CF) [23][20], which is the core capture and typically not reaction

rate limited. The absorption capacity is also affected by factors including amine solubility, insoluble salt formation and amine aqueous solution concentration.

For tertiary amines, the lack of free proton results in the formation of bicarbonate being the main capture equation (eq.2.2). Researchers also studied reactions including carbonic acid formation (eq.2.4). Yet formation of carbonic acid is relatively slow and negligible compared with overall reaction rate [23].

Thus in the study scope of thesis work, mainly CF reaction (2.1) is assumed for primary and secondary amines, while tertiary amine goes through bicarbonate formation (2.2) .



## 2.3 Liquid Liquid Equilibrium of phase-change amine

Total Gibbs energy and the fugacities are used as criteria when considering equilibria in a multicomponent systems. For a multicomponent system, when  $T$  and  $P$  is constant, equilibrium is reached when Gibbs energy is minimum [24] [25].

Fugacity is another alternative for chemical phase equilibrium calculation. Compared to Gibbs energy, it is a straightforward extension of its application to pure fluids. For a liquid-liquid equilibrium system, the equilibrium compositions can be given as 2.5. In the equation, the superscripts  $\alpha$  and  $\beta$  are used to mark the different liquid phase.  $\gamma$  in equations stands for the activity coefficient, and  $x$  represents the mole fraction of  $i$  in one of the liquid phases [24].

$$\hat{f}_i^\alpha = \gamma_i^\alpha x_i^\alpha P_i^{sat} = \hat{f}_i^\beta \quad (2.5a)$$

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta \quad (2.5b)$$

There is a possibility that three phases can coexist together, two liquid phase and one vapor phase. And the equation to describe this vapor-liquid-liquid equilibrium

is given as 2.6.

$$\hat{f}_i^\alpha = \gamma_i^\alpha x_i^\alpha P_i^{sat} = \hat{f}_i^\beta = y_i P = \hat{f}_i^V \quad (2.6a)$$

$$\gamma_i^\alpha x_i^\alpha P_i^{sat} = \gamma_i^\beta x_i^\beta P_i^{sat} = y_i P \quad (2.6b)$$

For vapor-liquid-liquid equilibrium, stable  $T$  and  $P$  are important factors. While for liquid-liquid equilibrium, only  $T$  affects.

## 2.4 Absorption and Stripping

Absorption and stripping are two important unit operations in solvent-based post-combustion CO<sub>2</sub> capture. Flue gas is firstly sent to a unit where one or some components are taken away by nonvolatile liquid added to the system. The process is called absorption, and the unit where the process taking place is the absorber. Absorption can be physical and chemical. Physical absorption is caused because components have higher solubility in solvents than in gas. In chemical absorption, this solubility is enhanced by chemical reactions taking place between the absorber compound and the solvent.

Chemical absorption can be reversible and irreversible. For solvent-based carbon capture, absorption is usually reversible, that is CO<sub>2</sub> can be released out in stripper, where the reverse reactions are favored because of different process operating condition [26].

# 3

## Methods

This chapter explains methods adopted in study and comparison between potential amine candidates according to performance in reaction, separation and regeneration. Details in subsequent Aspen Plus flowsheet modeling including component settings, layouts variation, reaction definition etc. are discussed as well.

### 3.1 Study of Phase-Change Solvents

There are already studies and experimental results about some phase-change solvents, stating their potential and limitation in carbon capture process. So the study starts from selecting appropriate amines and compare them using Aspen Plus, which is a cornerstone for later flowsheet setting up.

#### 3.1.1 Property Method in Aspen Plus

To start investigating available solvents in the study, the property methods are important to know. Collections of models and methods used to compute thermodynamics and transport properties in Aspen Plus are called property methods. According to the different equations used and the calculating sequences, property methods are classified into 10 groups in Aspen Plus V8.8<sup>1</sup>. These groups are recommended to be used under different conditions. Good choices of property methods will benefit the system in later simulations [27].

From equations 2.1, 2.2, and 2.3, amines studied in this project reacts with carbon dioxide, and ions are formed in the reactions. Due to the existence of ions, ELECNRTL turns to be a preferred method since it accounts for electrolytic system. But when ELECNRTL is occupied in the system, problems occurs and Aspen can't correctly process the calculation. The main reason for this is that ELECNRTL doesn't play well with the phase separation in decanter. When this methods is using, the decanter will either not recognize molecules and report errors, or not able to perform the liquid-liquid separation and give out wrong result that have only one stream out from decanter.

---

<sup>1</sup> **10 groups in Aspen:** IDEA, Refence correlations for specific components, Liquid fugacity and K-value correlations, Petroleum tuned equations of state, Equations of state for high pressure hydrocarbon application, Flexible and predictive equations of state, Liquid activity coefficients, Electrolyte activity coefficients and correlations, Solids processing, Steam tables

Since the phase separation in decanter is one of the main study aims for this thesis project, other methods are tried to see if they are suitable to be used. Among the studied methods, UNIFAC-LL turns out to be an available alternative. The method can be used to play with liquid-liquid equilibrium in decanter, and can help to plot ternary diagram in Aspen.

#### 3.1.2 Aspen Component Specification

Before processing the modelling in flowsheet, components need to be specified in the system. Most of the commonly used components have already existed in data-bank in Aspen Plus V8.8. For electrolyte problems, Elec Wizard on Select Components sheet can be used to input ionic components and relative reactions into system.

Seldom used molecules and ions that are not yet exist in Aspen data-bank can be defined by user, i.e., by providing the molecular structure <sup>2</sup>. For properties of these user-defined components, there are two methods provided by Aspen to evaluate using their structures, one is to evaluate by NIST TDE, and the other is to estimate through the property estimation tool. Both of the methods however, can only provide rough estimation for components. It is thus very important to perform cross-checking (and fitting of the underlying property models) of the most important properties for the scope of the process modelling, if experimental data are available.

#### 3.1.3 Property Check and Modification

For user-defined anions and cations, one noticeable problem is that the system still recognize them as molecules. So the molecule weight of these ions are modified to correct value.

$$\ln p_i^{*,l} = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i}\ln T + C_{6i}T^{7i} \quad \text{for } C_{8i} \leq T \leq C_{9i} \quad (3.1)$$

Another noticeable problem is incorrect vapour pressure estimation of ions in Aspen property estimation. Extended Antoine Equation (eq.3.1) is used in Aspen to calculate vapour pressure, and relevant  $C_1$  to  $C_9$  values are estimated by the property system. This is a crucial property for absorber and stripper simulation. The  $C_1$  values of molecules are modified to ensure zero ion emission. Detailed  $C_1$  to  $C_9$  values are given in Appendix A.1.

#### 3.1.4 Aspen Ternary Diagram Study

The mixture of certain amines with water in the presence of  $\text{CO}_2$  exhibits two liquid phases under certain conditions. The main object is to figure out their liquid-liquid phase separation performance and working range. Aspen Plus 8.8 works as the property estimation tool.

---

<sup>2</sup>Ions defined and imported by users are recognized as molecular form in Aspen, properties as for molecule weight need to be modified manually to avoid errors in later simulation



Ternary diagram analysis is the preliminary tool for checking VLLE behaviour. If the amine aqueous solution shows phase separation possibility, the diagram describes the separation result for diverse working conditions through tie lines and phase envelope as in Figure 3.1 below. Only mixture compositions in the envelope are separated into water and lipophilic phase, while the two ends of tie line indicate composition of corresponding outflow.

The preferred result is relatively complete separation of carbon dioxide, while water could exist in both flows. Then only the heavy CO<sub>2</sub> loaded flow is sent to further desorption. So the criteria of filtering amine at this section is that they could show phase separation envelope in the ternary diagram.

According to Zhang, Qiao, Agar [20], certain amines have shown promising experimental results on absorption capacity, regenerability and reaction rate. Based on that, 7 amines are selected for our ternary mixture diagram study. 6 of them fulfil the criteria. These 6 amines are listed in Table 3.1 below, together with respective VLLE ternary diagrams (Figure 3.1 to Figure 3.6). While study on DMCA<sup>3</sup> shows that the working envelope is close to none, which is given in the Appendix Figure A.1.

Although from the diagrams, EPD and CHPA show better phase envelope range than others, this cannot conclude they are the best performing amines. The reasons can be that ternary diagram study does not consider chemistry, and the compositions of two separated phases are also important factors.

**Table 3.1:** 6 Amines which showed VLLE ternary diagram phase envelope

Name	Amine Group	CAS no.	Exist in Aspen
Diisobutylamine(DIBA)	Secondary	110-96-3	YES
Di-n-propylamine(DPA)	Secondary	142-84-7	YES
Hexylamine(HXA)	Primary	111-26-2	YES
Cycloheptylamine(CHPA)	Primary	5452-35-7	NO
N-Ethyl piperidine(EPD)	Tertiary	766-09-6	NO
2,6-Dimethyl piperidine (26-DMPD)	Tertiary	504-03-0	NO

<sup>3</sup>DMCA : N,N-Dimethyl Cyclohexyl amine

### 3. Methods

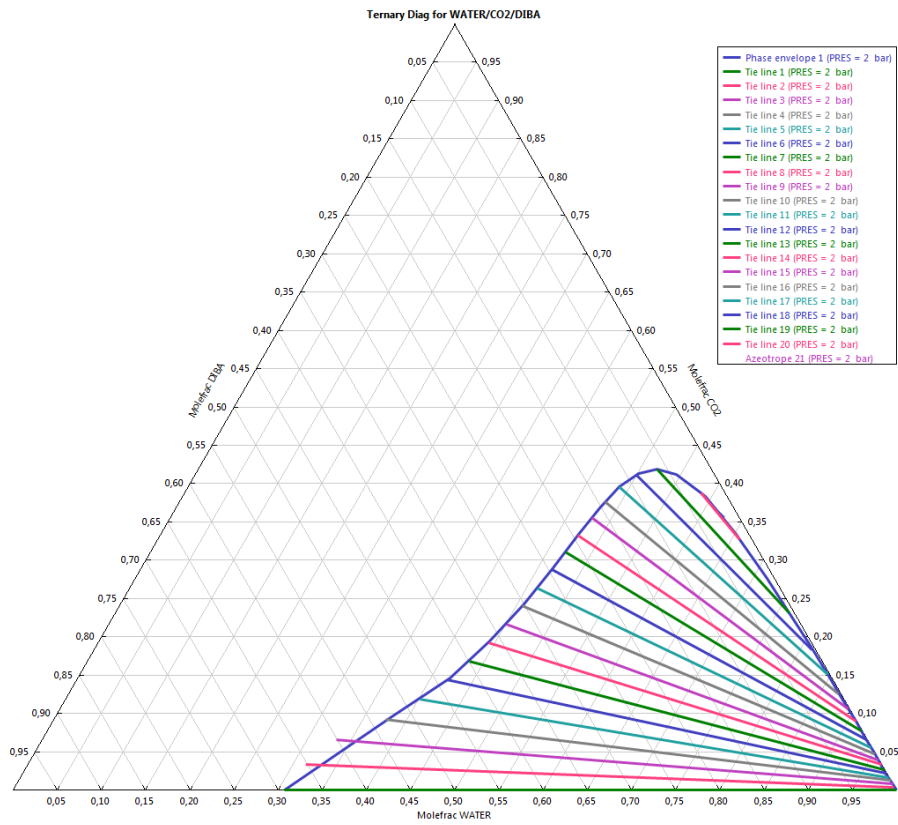


Figure 3.1: VLE ternary diagram DIBA

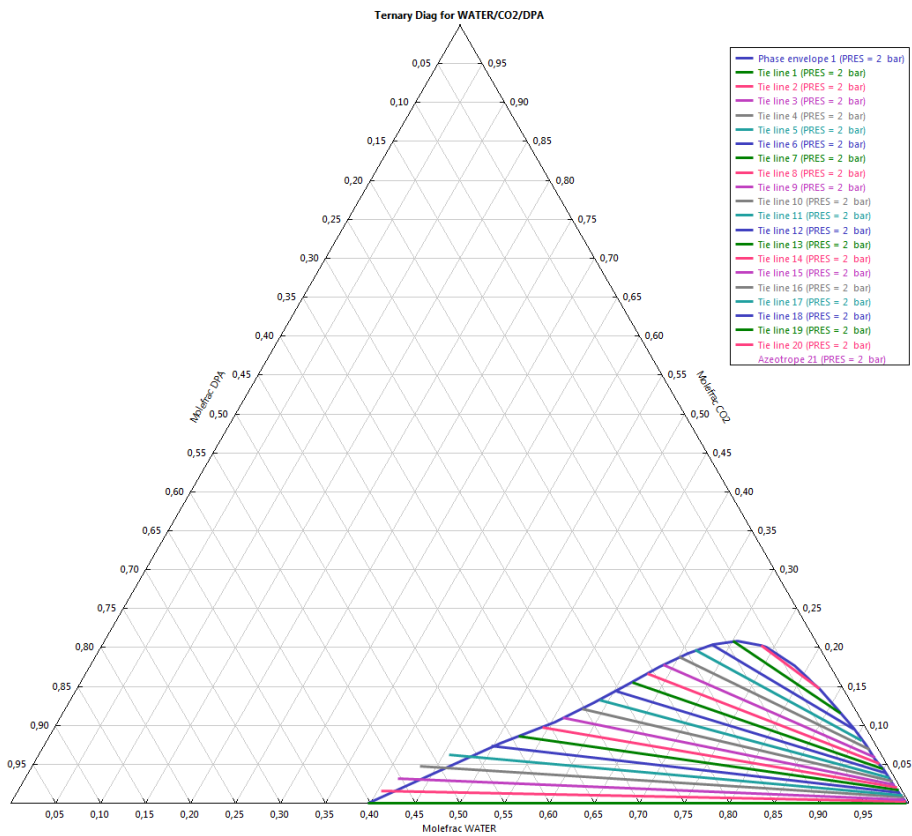


Figure 3.2: VLE ternary diagram DPA

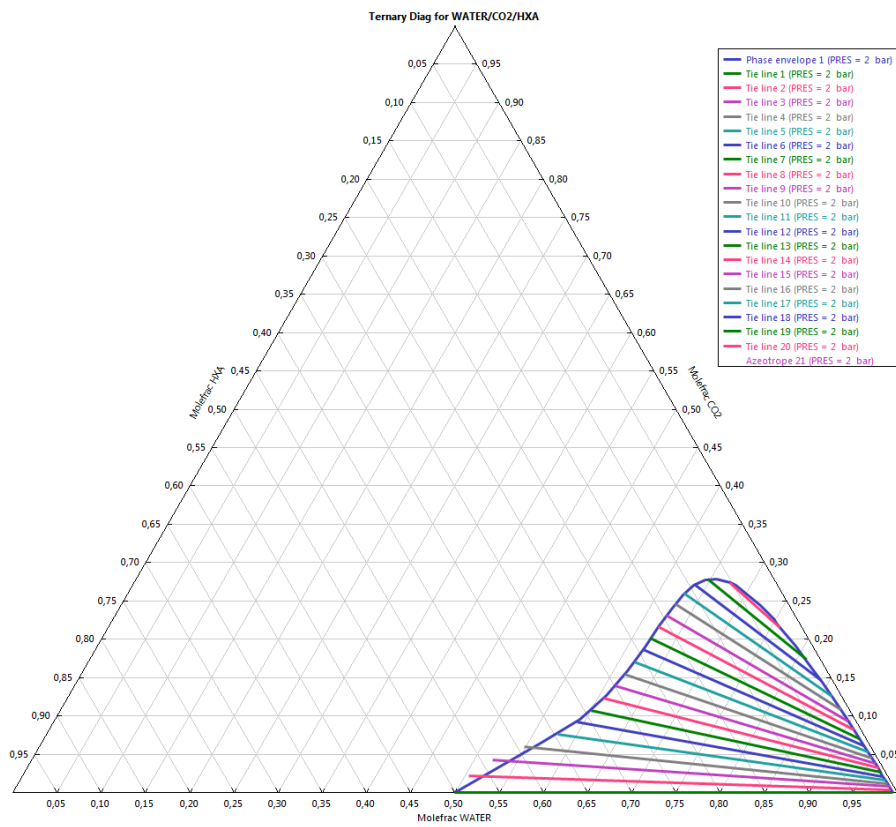


Figure 3.3: VLE ternary diagram HXA

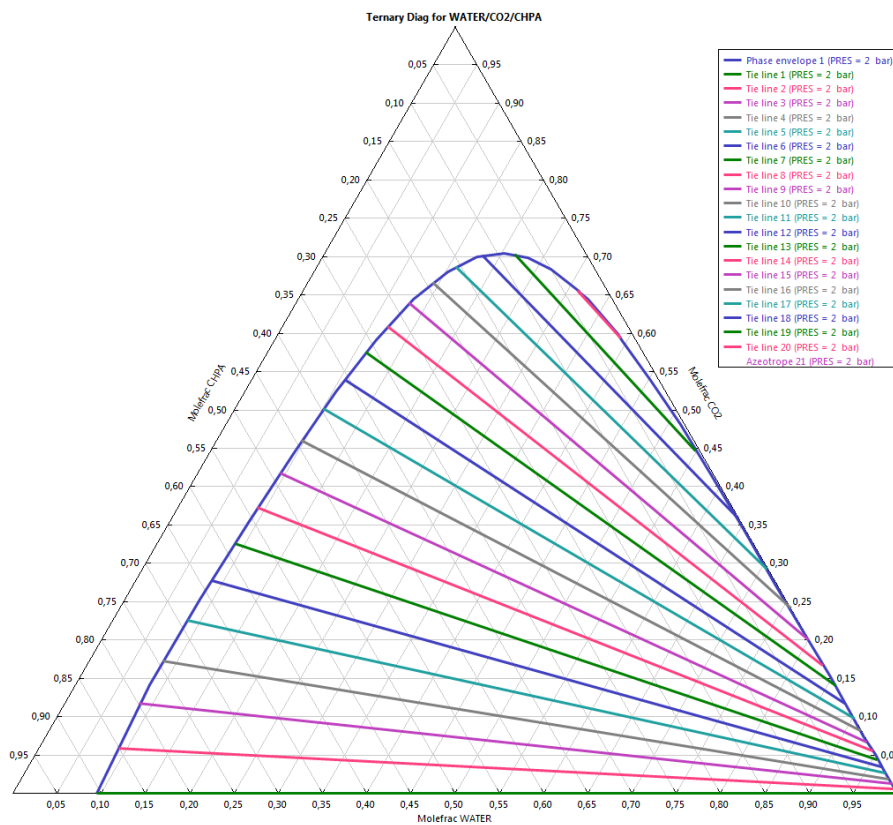


Figure 3.4: VLE ternary diagram CHPA

### 3. Methods

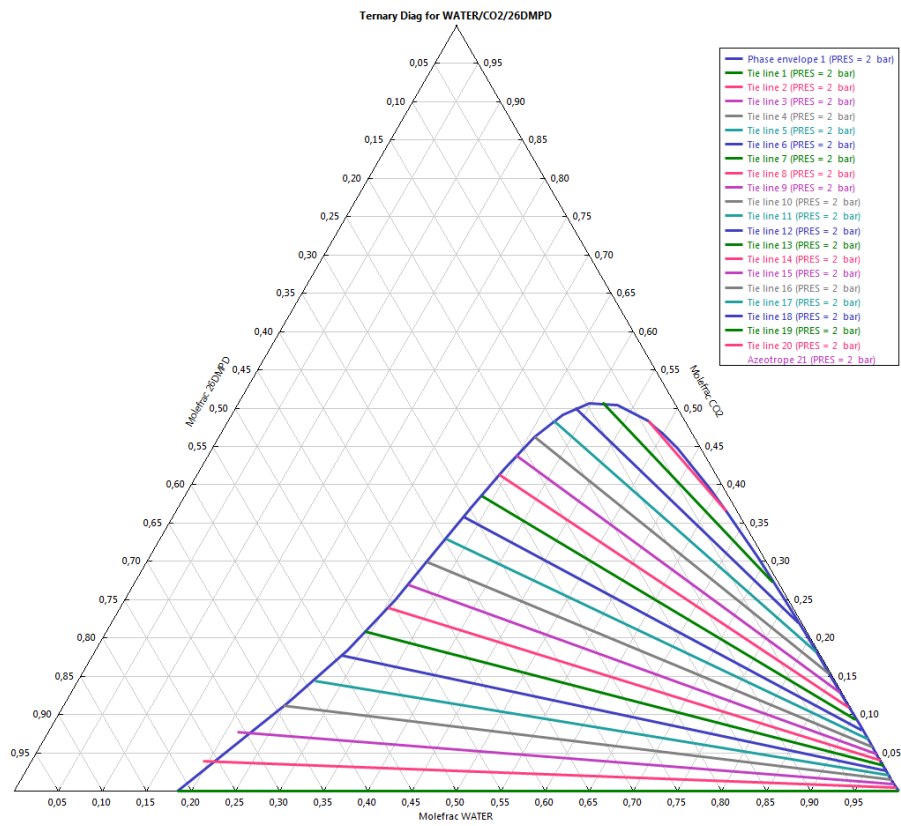


Figure 3.5: VLE ternary diagram 26-DMPD

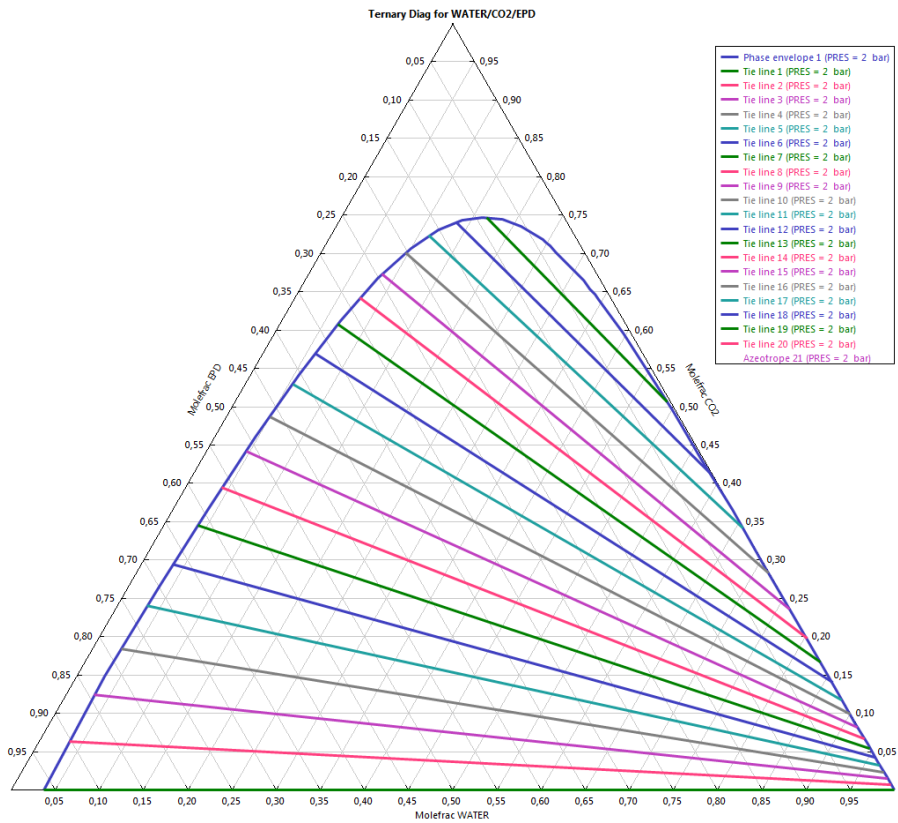


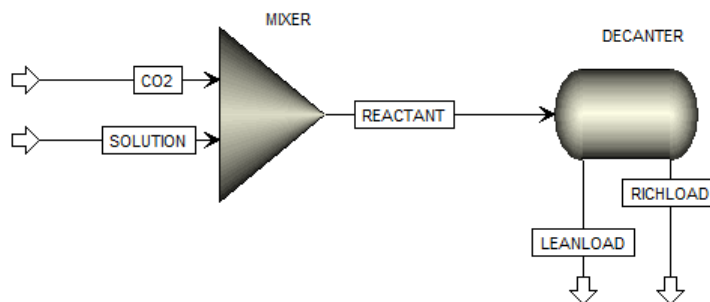
Figure 3.6: VLE ternary diagram EPD

### 3.1.5 Decanter Separation Study

Although ternary diagram is a primary property data checking tool, more detailed and accurate phase-separation modelling is indeed necessary. The decanter block in Aspen performs liquid-liquid separation according to molecule property estimation, so it is selected as the subsequent study method. As mentioned in previous chapter, UNIFAC-LL method is selected due to focus on liquid liquid equilibrium and separation.

There were trials and errors in this section. Global chemistry equation and ion definition are two most influencing factors during the modelling. The first obstacle is that, when defining chemistry in Aspen, all the relevant cations ( $\text{RNH}_3^+$ ) and anions ( $\text{RNHCOO}^-$ ) do not exist in Aspen database. When user defined ions are in the same chemical reactions with system defined ions (e.g.,  $\text{H}^+$ ,  $\text{HCO}_3^-$ ) the modelling problems appeared in Aspen. Thus the chemistry adopted is merely carbamate formation as equation 2.1 for primary and secondary amines. However, EPD and 2,6 DMPD are tertiary amines, and their chemistry is supposed to follow equation 2.2. So the user-defined ions are inevitably in same equation with system ions. The decanter is limited in estimating these two amines phase separation. The comparison mainly focuses on the other four molecules.

The other obstacle, it is discovered decanter block cannot perform phase separation calculation with chemistry definition in the decanter. So the results of the separation in the decanter are therefore serving only as first estimations and need to be refined with more accurate equilibrium data/models.



**Figure 3.7:** Decanter modelling setting for amine study

A mixer is used for modelling the absorption between  $\text{CO}_2$  and amine solution, as in Figure 3.7. Consider the above mentioned decanter limitation, the flowsheet is divided into two sections, and decanter lies in the one with no chemistry. Working conditions and inlet flow settings shown in table 3.2 are used.

Table 3.3 demonstrates the compositions of two decanter outflows of four molecules. Detailed composition of two outflows are in Appendix A.19 to A.22. The amine

**Table 3.2:** Basic Flowrate and Column Setting in Decanter Modelling

Base Case		
Flow Rate		
CO <sub>2</sub>	7.5	Kmol/hr
Amine	15	Kmol/hr
Water	50	Kmol/hr
Column		
Mixer Temp	20	C
Decanter Temp	40	C
Pressure	2	bar

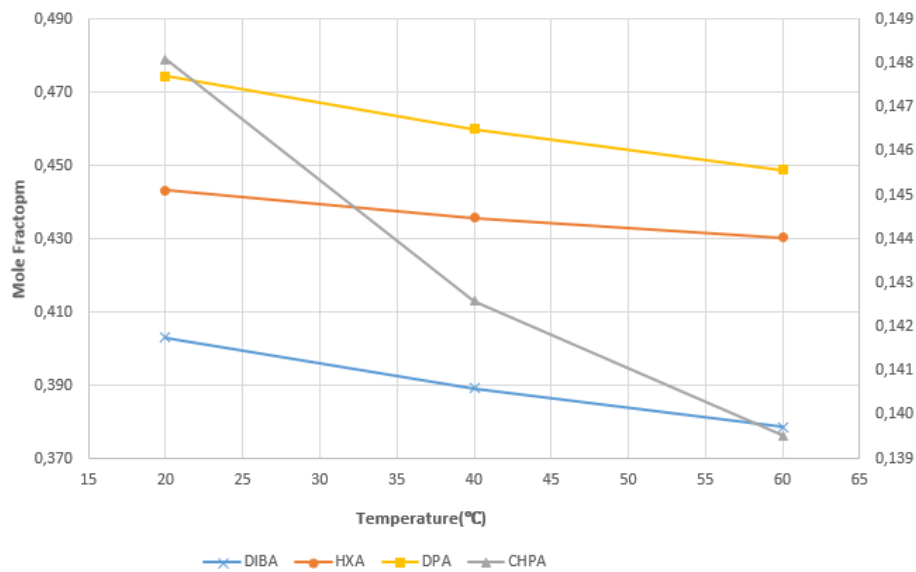
flowrate in table is the sum of amine molecule and ionic forms. Rich phase refers to rich CO<sub>2</sub> loaded phase. All molecules except for CHPA show preferred results. For molecule CHPA, almost all water exists in lean amine phase, and only 14% of rich phase composition is water. So this solvent was not considered because the concentration of water in the rich phase could be too low for dissolution purposes of the CO<sub>2</sub>-solvent system. The rest three molecules are recognized as potential candidates.

However, in this limited period of study, it is possible for us to select two amines considering the modelling time required. Another reason is that the estimated solubility data reference that is used in later steps is available temporarily for these two amines, not for HXA. Based on the various amine type, we choose DIBA (secondary) and HXA (primary) in further flowsheet modelling for wider comparison .

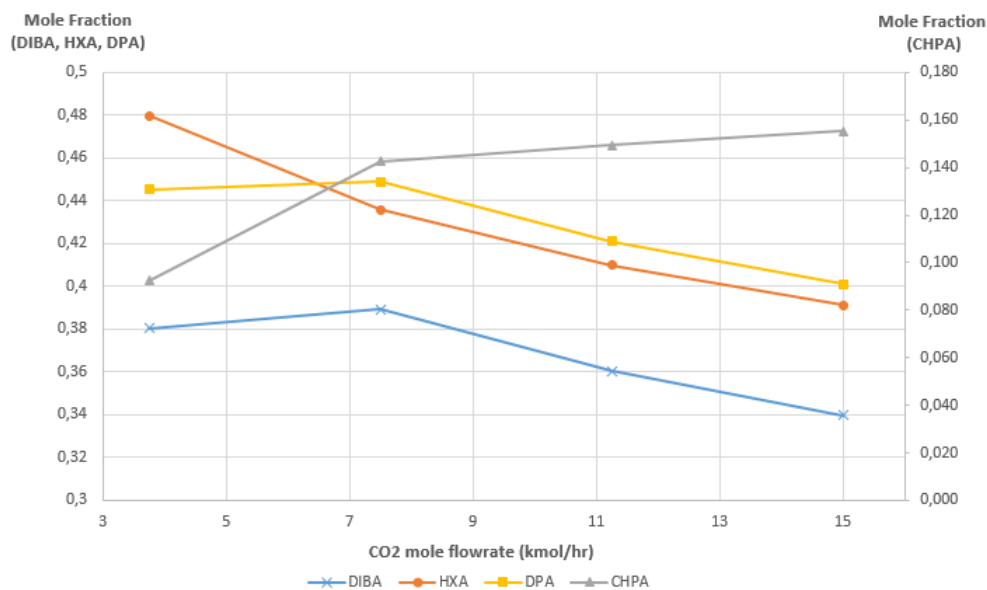
**Table 3.3:** Water and Amine Flowrate in Two Separated Phases

Kmol/hr	Lean Amine Phase			Rich Amine Phase			Fraction in Rich Phase	
	Water	Amine	Total Flow	Water	Amine	Total Flow	Water	Amine
DIBA	40.445	0.006	40.451	9.555	14.994	24.549	0.389	0.611
HXA	38.470	0.069	38.539	11.530	14.931	26.461	0.436	0.564
CHPA	47.508	0.014	47.522	2.492	14.986	17.478	0.143	0.857
DPA	37.826	0.052	37.877	12.174	14.948	27.123	0.449	0.551

Besides, the decanter temperature and inlet CO<sub>2</sub> amount values are varied to study their effect on water mole fraction in amine rich phase. Elevated decanter temperature has similar influence on all four molecules, and the result is not highly sensitive (Figure 3.8). Temperature increase of 40 °C only leads to less than 2% difference in mole fraction.



**Figure 3.8:** Water mole fraction in rich phase - Decanter Temperature



**Figure 3.9:** Water mole fraction in rich phase - Inlet CO<sub>2</sub> flowrate

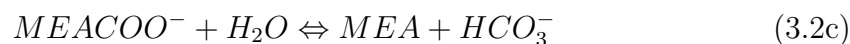
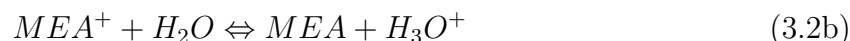
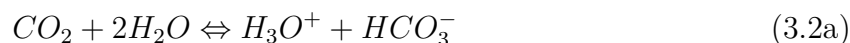
The CO<sub>2</sub> flowrate, however, affect the separation to larger extent (Figure 3.9). This is related to the calculation of CO<sub>2</sub> loading,  $n_{CO_2}/n_{amine}$ , which is indicative of the absorption. This is considered in the subsequent flowsheet modeling and decanter parameter setting.

## 3.2 Define Reaction Equilibrium Constant

Solution chemistry is needed in calculations to solve electrolyte problems. Reaction equilibrium constant -  $K_{eq}$  is specified. However, available  $keq$  value of studied amine is not available due to limited study or experiment, so they are estimated according to available MEA value.

### 3.2.1 Reaction $K_{eq}$ in MEA Flowsheet

MEA chemistry is generated from the Elec Wizard in Aspen, the process that MEA react with water and  $CO_2$  to form carbamate is described in three equations 3.2 shown below, and their  $keq$  value can be read from Aspen. They are listed in Appendix table A.3.



If we add these three equations together, we'll get equation shown as 3.3 which is used in this study (see also section 3.1.5).



The equilibrium constants of 3.3 is the product of three constants from 3.2, and the A-E values are summed. This calculation theory is given in Appendix A1. Then the MEA  $keq$  value used in equation 3.3 are shown in table below.

**Table 3.4:** Values used for calculating the equilibrium constant in equation 3.3

$\ln(K_{eq}) = A + B/T + C * \ln(T) + D * T + E * ((P - P_{ref})/P_{ref})$					
A	B	C	D	E	keq
-235.025	2538.213	36.782	-0.003	0	4.25e-8

### 3.2.2 Reaction $keq$ value of studied molecules

**Table 3.5:** Estimated RED (relative energy difference) values

MEA	DIBA	HXA
3.77	1.49	0.74



The MEA Keq value is only regarded as a reference for DIBA and HXA because of the different properties of amine structure, solubility etc. results show that DIBA and HXA have extremely good absorption and quite bad stripping when using MEA keq values. To get a more realistic CO<sub>2</sub> capture performance for these two molecules, their relative energy difference values (RED) 3.5 are compared to that of MEA.

**Table 3.6:** Estimated reaction equilibrium constant values in equation 3.3

Amine	A	B	C	D	E	Keq
HXA	-227.3	2549.61	36.8916	-0.003	0	9.4131e-5
DIBA	-228	2549.61	36.8916	-0.003	0	1.8955e-4

However the relationship between keq and relative energy difference (RED) is not linear, and it's only one of the crucial parameters that affect the reaction. It used here only to indicate the direction to adjust keq values. Chosen Keq values for HXA and DIBA are listed in table 3.6.

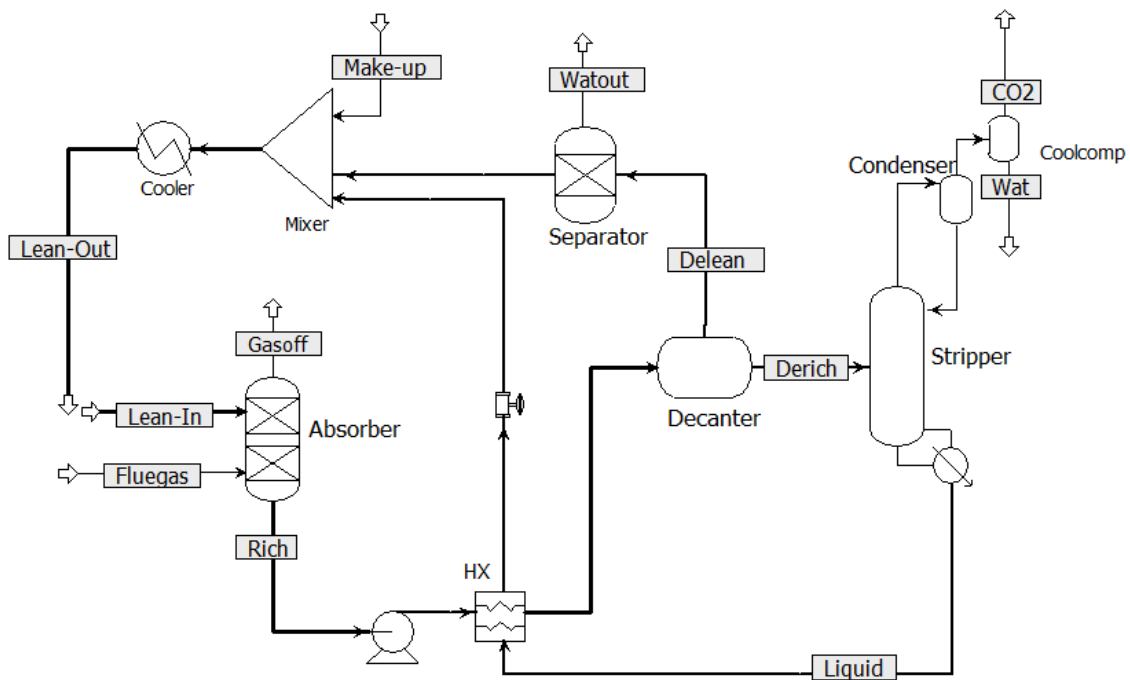
### 3.3 Base configuration setting up

In this part, the structure of flowsheet and setting of integrated columns in base configuration are discussed. A reference MEA Aspen flowsheet is used for comparison, and its flowsheeting details, parameter setting and stripper performance is given in Appendix A.2 and A.4.

The base flowsheet is shown in Figure 3.10. The absorption process occurs in the absorber unit between inlet fluegas and lean solution, and then CO<sub>2</sub> loaded solution enters heat exchanger for elevating temperature. The decanter works to separate rich loading into water and lipophilic phases, so flow with of high concentration in water is avoided from further processing in the stripper. Then the stripper and two condensers are used to separate CO<sub>2</sub> from amine as well as water. The stripper also regenerates the amine and recycles it back to absorber. Since there are losses of amine in two columns, the makeup amine solution flow is mixed with regenerated amine before cooling. Besides, the separated water flow from decanter can be recycled and used for mixing with amine lean solution to make the whole process a close loop.

#### 3.3.1 Calculating methods for absorber and stripper

For the absorber and stripper used in the flowsheet, Aspen Plus provides some unit operation models for either shortcut or rigorous calculation. Shortcut models are used for determining values as for reflux ratio and number of stages in distillation columns with one feed and two product streams . While the rigorous models is used for rigorous design and rating calculation in different kinds of columns, more inputs



**Figure 3.10:** Base case configuration

are needed to process calculation[27]. In this study, RadFrac model is selected for both absorber and stripper. RadFrac is a rigorous model for all types of multistage vapor-liquid fraction operations which include absorption and stripping, and it's suitable for multi-phase system [28].

There are two alternatives for the calculating methods in Radfrac columns, one is equilibrium-based method while the other is rate-based. In the project, equilibrium-based method is used first to process the simulation and get initial values. Then the method is changed to rate-based, and the diameter gained from the previous simulation is used as a first estimation for the rate-based calculation.

### 3.3.2 Stream and column settings

The fluegas containing  $\text{CO}_2$  enters the absorber in the bottom stage, while the *Leanin stream* loaded amine solution enters at top stage. The treated fluegas leaves column from top, while the amine solution loaded with  $\text{CO}_2$  exits the bottom. Neither condenser nor reboiler is required in absorber, and the total stage is set to 12. Top stage pressure is set to the same as the entering stream, 1.06 bar, and the total pressure drop in the column is 0.6 bar. The detailed settings for different scenarios are listed in appendix table A.5 and A.7.

The stripper uses a reboiler to heat the rich loaded solution. After sufficient regeneration, the recycled lean amine solution leaves from the bottom of the stripper while  $\text{CO}_2$  is emitted from top. Both condenser and reboiler are required in the stirpper to ensure the effective separation between liquid and vapour phase. The

reboiler heating causes substantial amount of water vapour exiting from the top, so two external condensers are added for flash procedure. They are working at 76 °C and 25°C separately. Separated water is recycled back to stripper as a reflux flow, entering the first stage.

The internal kettle reboiler is defined with reflux ratio, an initial value of 3 is tentatively defined, while later it is adjusted according to the overall flowsheet close loop requirement. Detailed input parameters stages, reflux ratio, pressure, column diameters of all scenarios are listed in table A.5, A.6, and A.7.

In order to conveniently compare the amine performance with MEA, the fluegas flowrate and composition is set as the same value as in MEA basic flowsheet: 18.4 % wt CO<sub>2</sub>, 70.2 % wt nitrogen, 7.1% wt water, and 4.3 % wt oxygen with the total mole flowrate at 213.67 kmol/hr. Fluegas temperature is set to 48 °C.

All the crucial column and stream input parameters are listed in Appendix A.8, A.9 and A.10.

### 3.3.3 Close-loop mass balance and design specifications

The recycled lean flow from stripper eventually enters the absorber after mixing with makeup flow. This changes the flowsheet from open loop to close loop, so major molecule amount (apparent component) need to reach convergence at *Lean-in* and *Lean-out* flows, i.e. water, amine and CO<sub>2</sub> flowrate. Three corresponding design specifications ensure the close loop mass balance.

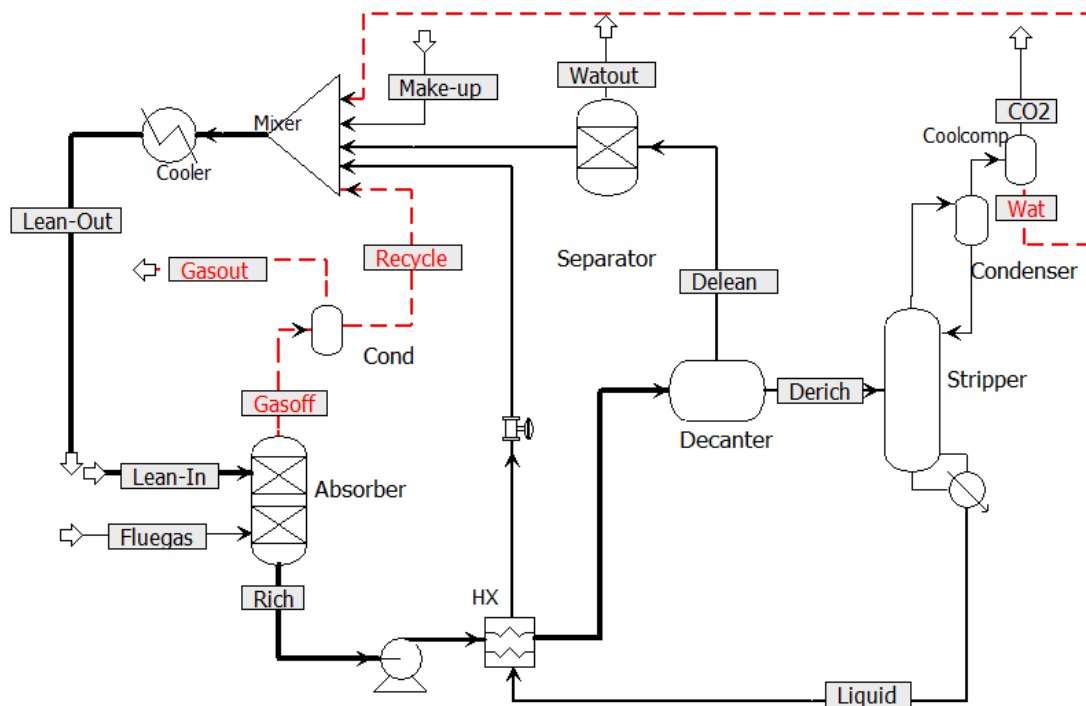
The amine and CO<sub>2</sub> amount at *Lean-out* flow is affected by the reaction in absorber and stripper, as well as inlet amine solution composition. When the reaction *keq* value is fixed, stripper settings are main influencing factors that affect the bottom product composition. Thus one design specification is used for CO<sub>2</sub> apparent component convergence. The stripper reflux ratio is mainly adjusted within 1-10, since it highly affects the stripping product.

In this shortcut flowsheet, there are only amine losses through absorber and stripper vapour outflow. Amine makeup is specified according to mass balance. In practical operation, amines are added in the form of aqueous solution in *Makeup* stream, rather than pure amine. This supplementary water amount is also considered in water mass balance.

The water loss is composed of absorber, stripper vaporization and condenser waste water. According to the simulation results, the water contained in the fluegas is absorbed into the *Rich* stream in the absorber. So there is still extra water in the *Lean-out* stream even if the *Makeup* water is adjusted to zero. To ensure overall water mass balance, waste water removal in the system is required. So a waste water separator block is added on decanter lean stream. Similar to amine mass balance, the makeup water flowrate is defined by design specification.

Apart from mass balance, another design specification is added to reach the same removal efficiency as MEA, 90 % ( $\text{CO}_2$  amount in stream  $\text{CO}_2$ /in stream *Fluegas*). *Lean-in* solution flowrate is varied, because the absorbed and stripped  $\text{CO}_2$  amount is highly sensitive to amine amount. While other parameters including  $\text{CO}_2$  loading,  $k_{eq}$  value also affect the removal and regeneration reaction in the two columns, so they are studied in subsequent process as a sensitivity analysis on capturing and stripping performance.

### 3.3.4 Flowsheet improvement - add condenser unit for recycling amine



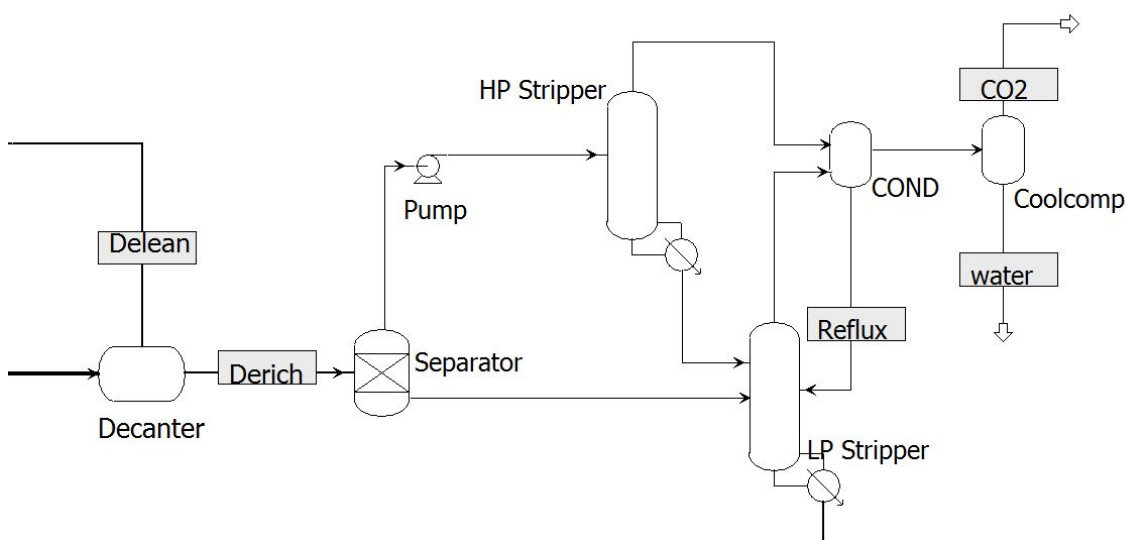
**Figure 3.11:** Add condenser for amine recycling

From the base case configuration, it is discovered that there is potential in reducing amine emission loss from the two columns, which is around 220 kg/ton  $\text{CO}_2$  for DIBA, and 100 kg/ton  $\text{CO}_2$  for HXA. In this configuration, solvent emitted from absorber and condenser are recycled to mitigate the environmental effects and reduce the operating costs (Figure 3.11). The gas out from the absorber is sent to a condenser, where the solvent and water are cooled, separated from the treated gas and sent to the mixer before the absorber. Moreover, the outlet stream of the stripper condenser, containing solvent, is sent to the same mixer instead of being released. The flowsheet can reduce more 79-99% of the solvent loss. Thus in other configurations, this procedure is also utilized as an improvement scenario.

### 3.4 Other Configurations

Some researches have studied the optimization of flowsheet for the solvent-based post combustion CO<sub>2</sub> capture to give out better performance of components and save operation cost. Two other configurations are studied, one by adopting double strippers, and the other is to rearrange heat exchanger placement [29, 30, 31].

#### 3.4.1 Double Stripper Configuration



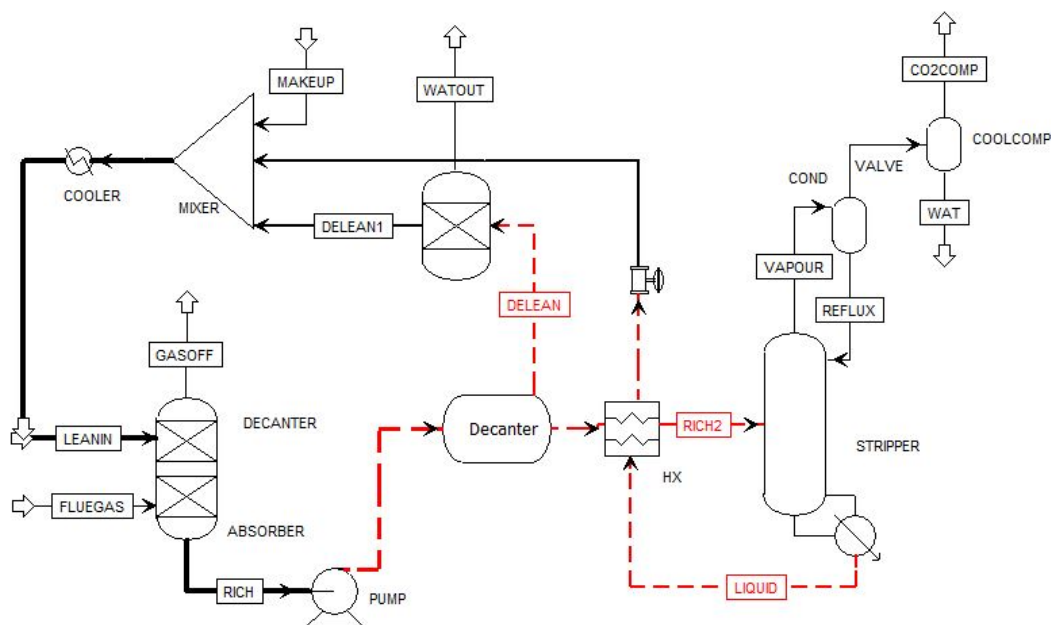
**Figure 3.12:** Configuration of double strippers with different operating pressure

Configuration with two strippers operating under different pressure are tried first, in Figure 3.12. The rich amine stream is split into two streams by a splitter in a certain ratio. Streams are sent to two strippers, and the top pressure of strippers are set to 160 and 295 kpa respectively, both with pressure drop of 6 kpa. Streams split from the separator are feed to the top stage of strippers and flow from the high pressure stripper outlet is sent to the mid stage of low pressure stripper since it has lower CO<sub>2</sub> loading.

Split ratio at the splitter has direct impact on the reboiler heat duty in strippers. For DIBA case, 25% of the separated flow is sent to the low pressure stripper while the rest of flow is sent to the other stripper. And for HXA this value is 20%. Not only the split ratio, but the solvent properties also have influence on the required heat duty of strippers. So for each amine, the split ratio and operating pressure can be optimized to obtain lower energy demand. But we should note that the double strippers used will increase the capital cost, considering their relatively high pressure.

The double stripper column input settings different from the base configuration are listed in Appendix A.6.

### 3.4.2 Configuration with Rearranged Heat Exchanger



**Figure 3.13:** Configuration with Rearranged HX Placement

The other configuration is about the heat exchanger and decanter placement. In the base configuration, heat exchanger only elevate the rich stream temperature by  $20^{\circ}\text{C}$  due to small hot and cold stream flowrate ratio. If the heat exchanger is placed after the decanter, only the  $\text{CO}_2$  rich loaded phase enters the heat exchanger, and the water phase is avoided from unnecessary heating. According to the decanter performance, water phase account for around 50% total mass flowrate, that means half of the heating demand can potentially be saved. Substantial cold stream temperature increase is expected. This configuration gives advantage in the stripper inlet stream temperature, which affects the reboiler duty. The revised flowsheet is in Figure 3.13. Relevant revised heat exchanger input parameters are listed in Appendix A.9.

## 3.5 Degradation Estimation

The solvent loss in the system consists of these major parts: emissions from the absorber and stripper, thermal and oxidative degradation. The evaporation loss could be estimated from Aspen in two column vapour off flows, and a makeup flow of amine solution is added for compensation.

The degradation estimation is not performed in Aspen because of lack of degradation data in the form of reactions and kinetics. Although there are studies about MEA degradation in the  $\text{CO}_2$  absorption process, the relevant data about new phase change amines are limited.

In this section, the degradation estimation is based on experimental and simulation results from MEA. According to Goff and Rochelle [32], under normal operation conditions, MEA oxidative degradation is assumed to be 0.29 - 0.73 kg/ton CO<sub>2</sub> captured. Badr [33] concluded amine degradation rate estimation of four amines compared to MEA, as in table A.11. According to similar amine structure and type, the estimation for DIBA and HXA take the value of 8 and 3.5 times of MEA, which gives the value of 4.08 and 1.785 kg/ton CO<sub>2</sub> captured respectively.

**Table 3.7:** Amine degradation rate estimation based on MEA

Amine	Degradation ratio <sup>a</sup>	Amine type	Source
DEA	0.71	Secondary	Freeman[34]
DGA	2.75	Primary	Freeman[34]
MDEA/Piperazine	12	Tertiary	Closmann[35]
Piperazine	5.5	Secondary	Freeman [34]

<sup>a</sup> The ratio between Amine and MEA degradation rate

Thermal degradation is simplified to be 10% of total degradation according to MEA thermal degradation value. Davis [36] reported a value of 0.019 kg/ton CO<sub>2</sub> captured. Except for direct degradation, the degradation products accumulate in the system, which requires a purge stream to remove them. The regeneration unit is assumed to be 95% efficiency, so another 5% loss is considered in this procedure. These values are used in analysing the total solvent makeup cost. The estimated values of thermal, oxidative degradation, and loss from purge are given in Appendix Table A.11.

## 3.6 Economic and Environmental Analysis

### *Operating cost*

The operating cost consists of low pressure steam cost, cost for the process water, electricity and solvent make-up. Low pressure steam is used in the reboiler for the stripping process. Amine cost include emission makeup and degradation cost. Process water is the makeup water in system. Electricity cost is from pumps and compressors installed in the system.

For solvent make-up cost, amine prices affect the results. Prices for common amine like MEA and DIBA can be gained directly from global chemical products transaction network as 'Alibaba' and 'Molbase', or supplier as Sigma-Aldrich. But for amine that is rarely used in industries, or is not yet available on market, their prices should be estimated. Also note that fluctuations of prices for the same amine are

inevitable, thus the average reference price on these supplier platforms are utilized for more objective comparison.

### *Environmental Effect*

When considering the potential of utilizing studied amines in industrial process, the environmental impact is a crucial factor, especially when the original aim of absorption process is to reduce global warming potential. Three factors are studied, CED, GWP and EI99 points.

CED is the cumulative energy demand of a product, which represents the total energy amount during the process of extraction, manufacturing and disposal [37]. The value contains energy acquired from fossil fuel as well as energy gained from renewable energy during the life cycle of a product, and the unit used here for CED is MJ/kg.

Cumulative energy demand (CED) and reference prices for several studied amines are listed on table 3.8 [38]. Since CED represents the total energy demanded during the process of producing amines, the higher CED is likely to refer to a higher price. A scatter figure of studied amines with horizontal axial of CED, and vertical axial of prices is plotted to investigate the link between these two values. The relationship between these two values, if established, could be used in predicting price of candidates available for phase-changing PCC process.

**Table 3.8:** reference price and environmental index for studied amines

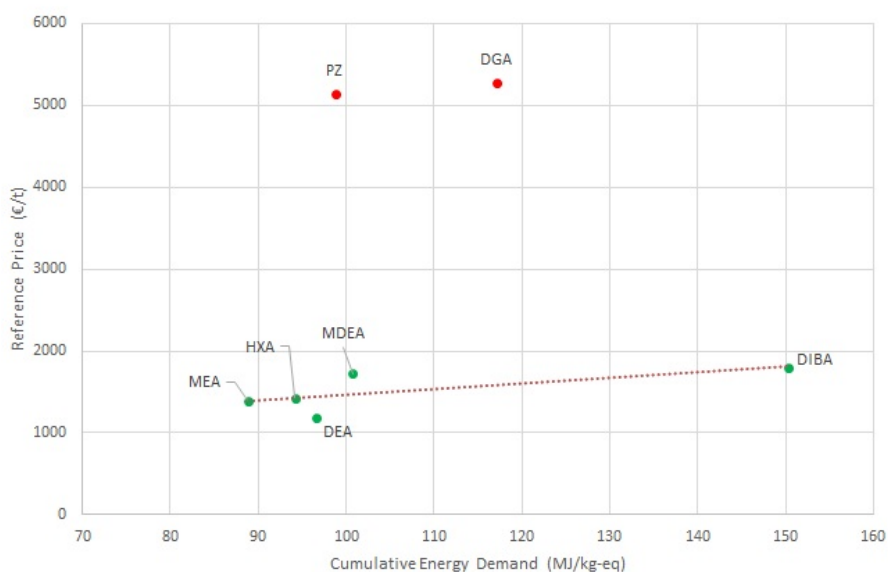
	MEA	DIBA	HXA	DEA	MDEA	DGA	PZ
CED MJ/kg-eq	88.8	150.33	94.21	96.6	100.7	117.1	98.8
price €/ton	1393	1800	1426	1175	1727	5278	5136

From figure 3.14, most of the studied amines locate close to the trending line, while DGA and PZ are away from the line. It reveals that for commonly used amines in industries, price have tighter link to the CED value, but CED is not the only factor linked to price. To predict price of amines accurately, factors such as scarcity of amine, scale of production, difficulty of transport and reservation should also be involved. So in our cost analysis, the DIBA and HXA price from reference website is directly used, as values in Table 3.8.

GWP stands for the the global warming potential, which is another important value used in LCA. It represents the cumulative radiative forcing value caused by green house gas emission for a given period of time, evaluated by the amount of CO<sub>2</sub> that could cause the equivalent impact [3]. The unit of GWP is kg CO<sub>2</sub> – eq.

EI99 is the eco-indicator 99, it is a method of weighting environmental effect. It is a comprehensive indicator integrated with various environmental effects in life cycle assessment. Higher EI 99 points expresses greater impact on environment.





**Figure 3.14:** CED vs Price for studied amines

Background data for the assessment are provided in the Appendix. Utility price in A.12, amine and utility CED, EI99, GWP in A.13 and A.14.

### 3.7 Assumption and Limitation

Crucial assumptions are made for the modelling. The most influential and sensitive assumptions are reaction equilibrium value estimation, decanter VLLE, input of user-defined molecules and all the amine ions. All the assumptions are summarized in table 3.9.

The chemistry definition for each studied amine specifies all the reactions, which could affect the performance of absorption and stripping to large extent. In our flowsheet the main assumptions are reaction in the form of equation 2.1 and equilibrium constant value. The solubility relevant RED values of DIBA, HXA and MEA indicate the relative absorption capability. However the assumed  $keq$  value lacks real data for validation. The choice of appropriate  $keq$  value lies in certain range. This assumption is the most influential factor, so a sensitivity study on the  $keq$  value is done.

Another major assumption is about VLLE in the decanter block. The phase separation are estimated by Aspen according to property estimation. However, this could differ from the actual phase separation data. It is also assumed to be no reaction in the decanter block.

User-defined molecules and ions property estimation also affect the modelling accuracy. Property estimation are performed based on structure. Aspen recognizes user-defined ions as molecules, which limits the ion estimation accuracy.

**Table 3.9:** Assumptions

Assumption	Direct Impact
Keq value (Tab.3.6)	Absorption and stripping reaction
Phase separation in decanter	Phase composition of outflows
Simplified chemistry (eq.2.1)	Carbonic acid reaction neglected
No chemistry in decanter	Phase composition of outflows
Input user-defined ions and molecules	Lack of property estimation accuracy

# 4

## Results

The three different configurations, base case, double stripper, and HX rearrangement, are studied and compared. And they result in 7 scenarios for each amine solvent, with different flowsheet or calculation modes. Description for these scenarios are listed in Table 4.1. The MEA flowsheet in Aspen is used as reference case for comparison.

**Table 4.1:** Seven Studied Scenarios

Scenario	Flowsheet setting	Columns
1	Base case configuration	Equilibrium
2	Base case configuration	Ratebased
3	Base case configuration, add amine recycling	Ratebased
4	Double stripper configuration	Ratebased
5	Double stripper configuration, add amine recycling	Ratebased
6	HX improvement configuration	Ratebased
7	HX improvement configuration, add amine recycling	Ratebased

### 4.1 Reboiler duty

The reboiler heating demand in all scenarios is discussed in this section, as it is the main part to look at when comparing different scenarios to MEA case. A summary graph of all values and amine emission loss amount is given out in Figure 4.1 at the end of this section. Detailed stripper performance results including reflux ratio, temperature for all scenarios are all given in Appendix Table A.25. Other stream data and important results are in Appendix Table A.26 to A.39.

#### 4.1.1 Base Case Configuration

The reboiler energy demand and reboiler temperature of the base case for Diisobutylamine (DIBA) and Hexylamine (HXA) is shown in Table 4.2. Both equilibrium and rate-base are used in the study. The total mass flow of CO<sub>2</sub> in flue gas is fixed, and

## 4. Results

since all scenarios have the same capture efficiency as 90%, the flow rate of captured CO<sub>2</sub> is constant as 23.28 kg/hr. Heat duty and temperature in reboiler are two important results used for comparison, they are listed in the table 4.2.

**Table 4.2:** Result list for Scenario 1 (equilibrium), 2 (ratebased), and MEA reference

	DIBA		HXA		MEA
	equilibrium	rate-base	equilibrium	rate-base	rate-base
Reboiler duty (GJ/ton CO <sub>2</sub> cap)	1.57	1.79	1.23	1.20	3.49
Reboiler temperature (°C)	112	112	111	109	123

Fresh solution concentration: 46 wt% DIBA, 40 wt% HXA

The result shows that reboiler duties required in DIBA and HXA cases are significantly lower than the MEA reference case, which is 3.49 GJ/ton CO<sub>2</sub>. When comparing the two candidate amines, HXA has better performance with respect to reboiler duty, while similar reboiler temperatures are required for both cases. Compare to the MEA temperature, there is possibly some reduction, but not enough to take these cases attractive to low-grade heat.

As mentioned in chapter 3, rate-base method provides more realistic result, to the deviation of results gained by these two methods can be reasonable. For HXA, equilibrium and rate-base methods have very close result in reboiler duty, the difference is 2%, but for DIBA, this difference is 14.3%. That means the calculation methods have greater effect on DIBA, but it is not the only decisive factor in this comparison, because the design specification also adjusts the reflux ratio differently, which could influence the reboiler duty. Considering this difference, especially for DIBA, the ratebased calculation is adopted in all other scenarios for accuracy.

### 4.1.2 Add condenser for recycling amine

The base case flowsheet showed expected reboiler duty reduction performance. But from the results gained by Aspen, the amine loss from column emissions in scenario 2 still account for 231kg/hr (2.1% of circulating amine) and 86 kg/hr (1.0%). The high supplier price of both amines makes the base case even less competitive than MEA case. So a condenser after the absorber, and amine recycling after the stripper are added on scenario 2 to reduce the solvent emission. It shows good amine recycle efficiency for both amines. The makeup amine amount due to emission loss and reboiler duty are listed in table 4.3, as well as percentage change compared with scenario 2.

Reboiler duty is affected due to these reasons :

- One design specification adjusts the stripper reflux ratio for close loop mass balance. So after recycling amine, the reflux ratio is adjusted according to new amine mass balance between *Leanout* and *Leanin*. In the stripper, this leads to the adjustment of boilup ratio, and thus the reboiler duty.
- The *Leanin* flowrate that enters absorber is adjusted by another design specification as well to ensure 90% CO<sub>2</sub> removal efficiency. As a result, the rich loading stream flowrate entering stripper changes, which in another aspect affect the reboiler duty.

**Table 4.3:** Result lists for scenario 3

	Reboiler Duty	change <sup>a</sup>	Amine Emission Makeup	change
Unit	GJ/ton CO <sub>2</sub>	%	kg/hr	%
DIBA	1.49	- 16.83	3.51	-98.35
HXA	1.20	-0.49	15.57	-79.51

<sup>a</sup>Compare with scenario 2

For DIBA the improvement on emission loss is obvious, since in the base case it vaporize more. Recycled DIBA amount also lead to more reduction on the reboiler duty, and boilup ratio is decreased from 0.40 to 0.32. HXA showed the same trend. This recycling procedure is also adopted in the other two configurations to improve the amine utilization, and lower the amine makeup.

### 4.1.3 Double Stripper Configuration

Splitting fraction of stream that goes to the low pressure stripper is set to 25% and 20% for DIBA and HXA respectively, meaning that a bigger part of the rich solvent is sent to the high pressure stripper.

The reboiler duty results are shown in table 4.4. The result shows that this configuration saves 25% and 1% reboiler duty for DIBA and HXA respectively. When the amine recycling part is integrated to double strippers flowsheet, the energy consumption for DIBA increased, mainly because high pressure stripper boilup ratio is adjusted by design specification, from 0.40 to 0.51. For HXA, the energy is 1.18 GJ/t CO<sub>2</sub>, the trend is reverse, possibly due to lower split ratio and thus different adjustment in the high pressure stripper. And boilup ratio in HP stripper decreased from 0.25 to 0.24.

The results reveal that flowsheet with double strippers can save reboiler duty in some situation, but this system must be carefully investigated or optimized with respect to the splitting ratio and stripper pressures for each solvent. Note that the additional stripper will increase the capital cost as well as the complexity of the

**Table 4.4:** Result list for configuration with two strippers, scenario 4 and 5

Reboiler Duty(GJ/ton)	LP stripper	HP stripper	total
DIBA Scenario 4	0.09	1.24	1.34
HXA Scenario 4	0.03	1.16	1.19
DIBA Scenario 5	0.11	1.45	1.56
HXA Scenario 5	0.03	1.15	1.18

system. To accept the longer pay-back period or to gain profits from the reduced reboiler duty should be further investigated into more details.

#### 4.1.4 Heat Exchanger Rearrange Configuration

When placing the heat exchanger after decanter, the temperature of stripper inlet stream is enhanced. For DIBA it's 92°C, and HXA 97 °C. This change of configuration leads to different results for the two amines. HXA shows substantial reboiler duty reduction, and is more sensitive to temperature than DIBA.

**Table 4.5:** Reboiler duty result for HX rearrange configuration, scenario 6 and 7

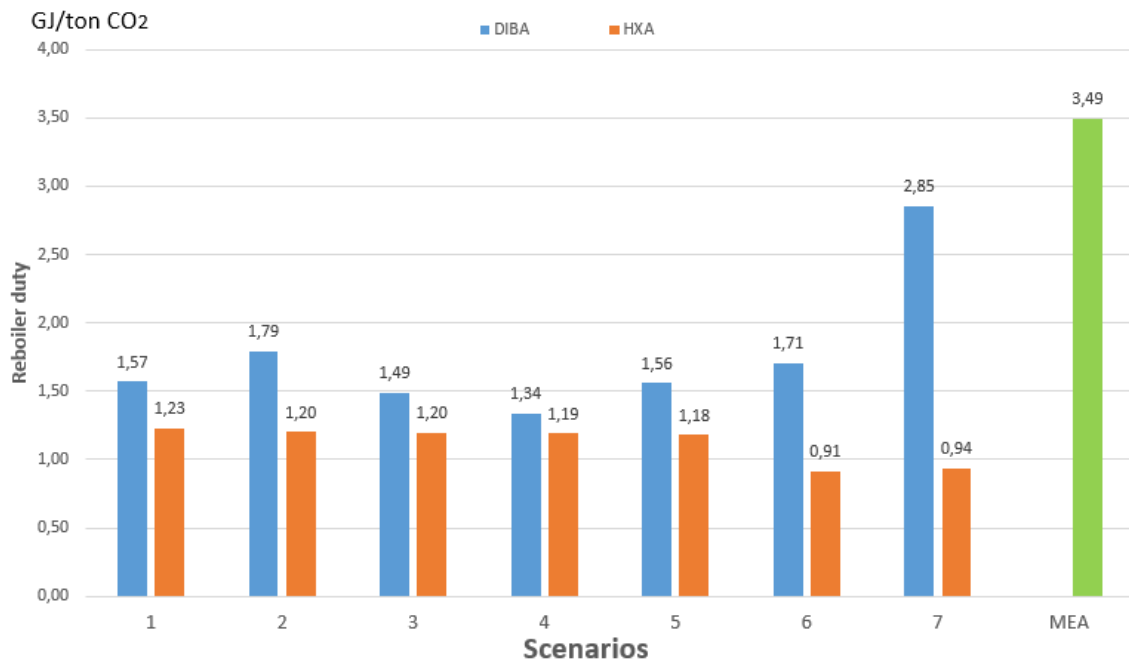
	Reboiler duty (GJ/ton CO <sub>2</sub> )	Amine Emission makeup(kg/hr)
DIBA S6	1.71	427.18
HXA S6	0.91	146.14
DIBA S7	2.85	4.71
HXA S7	0.94	7.68

The results of two scenarios with and without amine recycle condenser are listed in Table 4.5. This reboiler duty in model is affected by reflux ratio, *Leanin* flowrate and other factors including amine solubility. As mentioned before, the estimated reaction  $k_{eq}$  is assumed according to RED values, which is higher for DIBA. When checking the stripper, if the inlet temperature is increased, DIBA indeed exhibits worse regeneration ability, so to reach the 90% removal efficiency, the *Leanin* flowrate is elevated due to design specification. And thus higher volume into the stripper requires higher reboiler heating demand.

In DIBA scenario 6, the amine loss obviously increases in the stripper, and total loss is 4% of circulating amine. While HXA in scenario 6 only lose 1%. So the amine recycling in scenario 7 again lead to different adjustment on stripper boilup ratio, to ensure new amine mass balance. The heat exchanger temperature setting could be optimized to improve the performance in this configuration.

### 4.1.5 Summary

The result of all scenarios compared to MEA is shown in figure 4.1. Though several factors including amine amount, reboiler temperature also contribute to the performance in different scenario, the energy requirement is shown as the main studying target for this project.



**Figure 4.1:** Reboiler duty in all scenarios, compared with MEA reference

Apparently, all HXA scenarios are more competitive than DIBA scenarios. In scenario 6 and 7, HXA shows duty even lower than 1 GJ/ton CO<sub>2</sub> captured. HXA scenario 6, the one with the lowest energy demand, reaches to 74% reduction in energy demand compared to the 3.49 GJ/ton CO<sub>2</sub> captured in MEA reference case. This indicates the importance of the heat exchanger and decanter placement in the process design.

For DIBA, expect for scenario 7, all the others have energy requirement lower than 2 GJ/ton CO<sub>2</sub>. The best scenario is number 4, which has double strippers without amine recycling. The energy requirement for it is 1.34 GJ/ton CO<sub>2</sub>, which diminishes 62% compared with MEA.

From the aspect of energy requirement, all the scenarios studied except for HXA scenario 7 could be seen as promising. However, as the previous result of amine emission shows, amine make-up amount varies significantly between scenarios. Table 4.6 lists amine emission loss values. Compare with amine recycling in the system, these loss are within 1 -2%. But consider the price of amine which is around 1000 \$/ton amine [38], this could greatly affect the operation feasibility. Consider this

aspect, preferred scenarios are 3, 5, and 7. By rough estimation, others scenarios need solvent make-up cost above 100 \$/ton CO<sub>2</sub> cap, which is not expected.

**Table 4.6:** Amine emission lost amount of all scenarios

kg amine/ton CO <sub>2</sub> cap	S1	S2	S3	S4	S5	S6	S7
DIBA	119.14	226.11	3.42	195.23	4.65	416.91	4.59
HXA	73.21	84.91	15.20	111.61	40.98	142.63	7.49

## 4.2 Sensitivity Analysis

Several crucial parameters affecting and dominating the performance are studied, and they are chosen because either they have direct link to the modelling results, or their values are estimated with significant uncertainty. The sensitivity study is based on still the same CO<sub>2</sub> absorption rate, 90%, and scenario 2 flowsheet.

### 4.2.1 Uncertain thermodynamic estimation

#### *Reaction equilibrium constant*

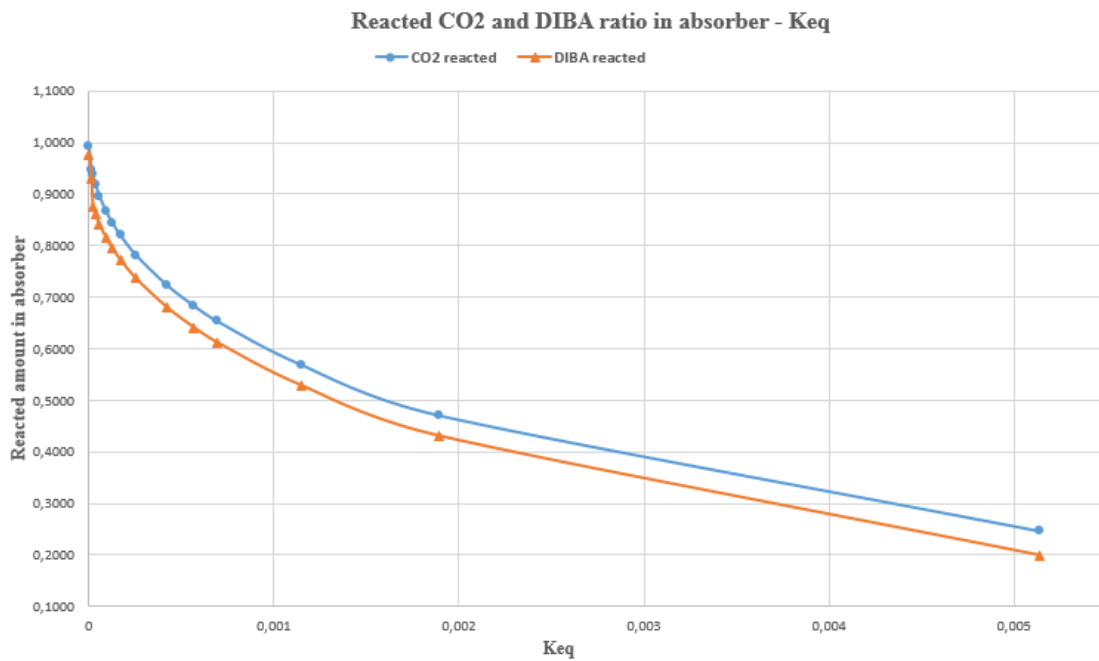
The reaction equilibrium constant assumptions in our study requires further investigation on their influence With respect to their influence on model. The A value in equation A.10 is the dominating parameter, thus it is varied while B and C are kept unchanged. The supporting detailed data is given in Appendix Table A.23.

Firstly, the effect on absorber is studied. Although the exact keq value is not available, the CO<sub>2</sub> absorption for these two amines is reported to show good performance according to Zhang,2012 [20]. Besides, from RED value given in 3.5, the two amines have lower solubility than MEA. So Keq is varied from the same value as MEA (4.25e-8) up to 5.13e-3, since the forward reaction in equation 2.1 is stripping. At these two endpoints the reaction efficiency is already far from reasonable value inside absorber.

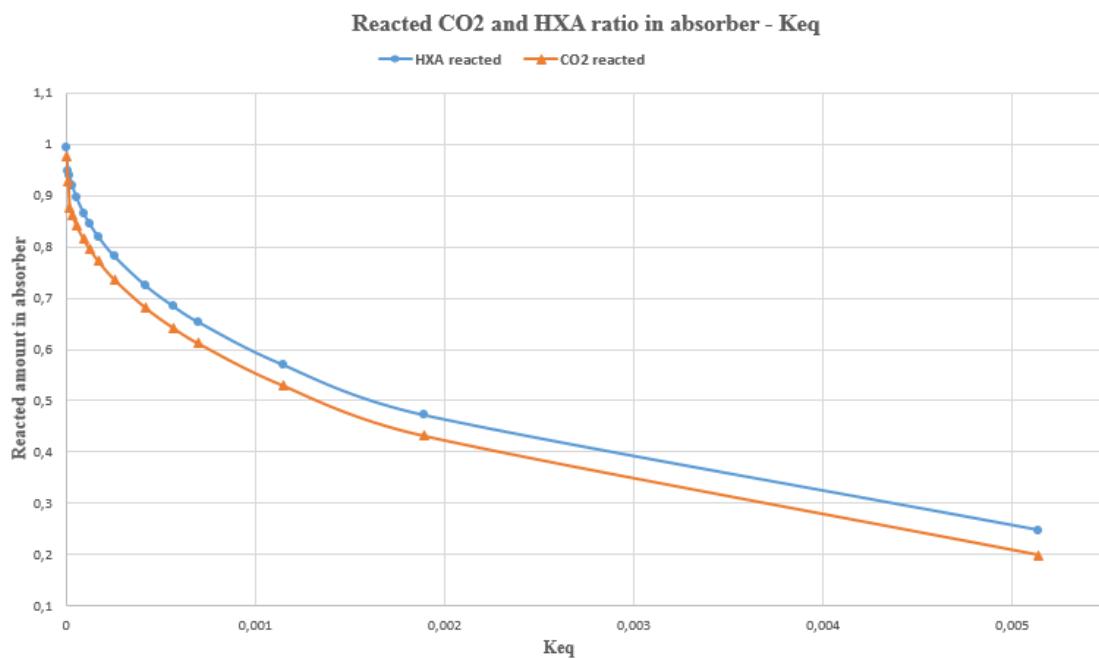
Figure 4.2 and 4.3 show almost identical performance of the two amines in absorber. It proves the significant effect of Keq value. Keq value changes the absorption ratio directly, it has greater impact on simulation than the calculation type set in absorber column.

Furthermore, the effect on stripper duty, i.e. the energy requirement per ton CO<sub>2</sub> captured is calculated for comparison, when keq is varied between 4.25e-8 and 1.27e-5. Since equation A.10 is expressed in logarithmic format, and the keq value increase in exponential scale with linear A value change, the figure is divided into Figure 4.4 and 4.5 for clear appearance.





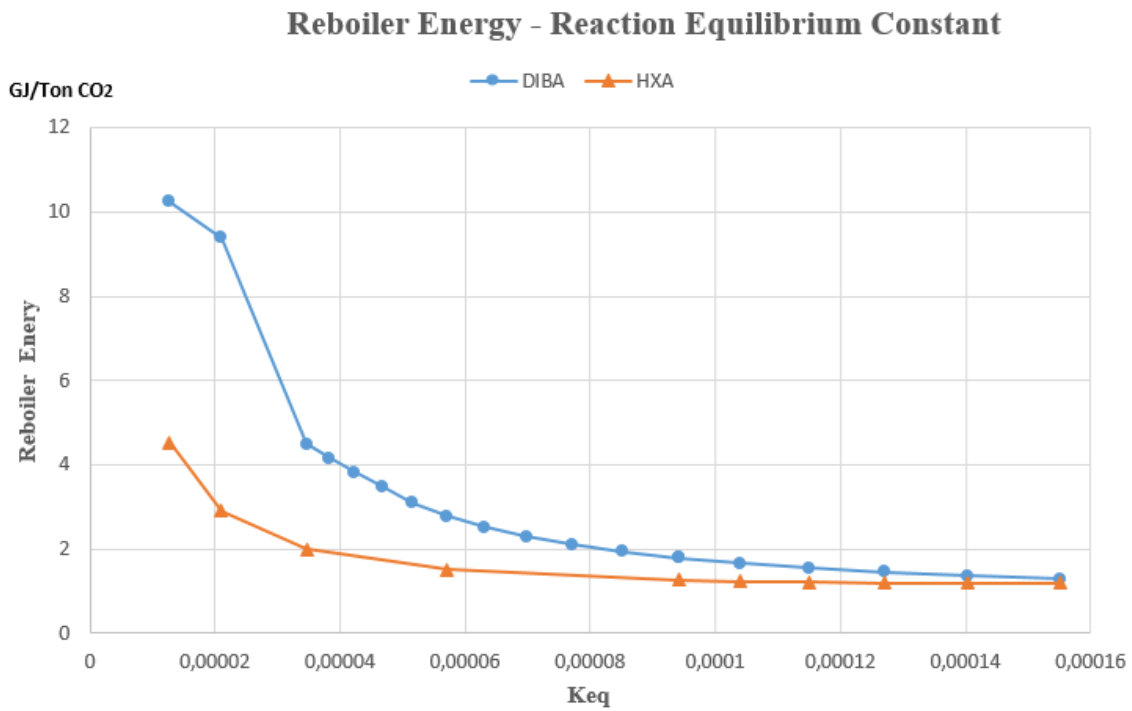
**Figure 4.2:** Reacted substance ratio in absorber - keq for DIBA



**Figure 4.3:** Reacted substance ratio in absorber - keq for HXA

Keq value has crucial influence on the process model, while for both amines there is still a range where reboiler duty is relatively stable. Further validation from possible experiment or study results can be used to improve the model accuracy.

## 4. Results



**Figure 4.4:** Reboiler duty - keq value, A varies from -235.025 to -227.5



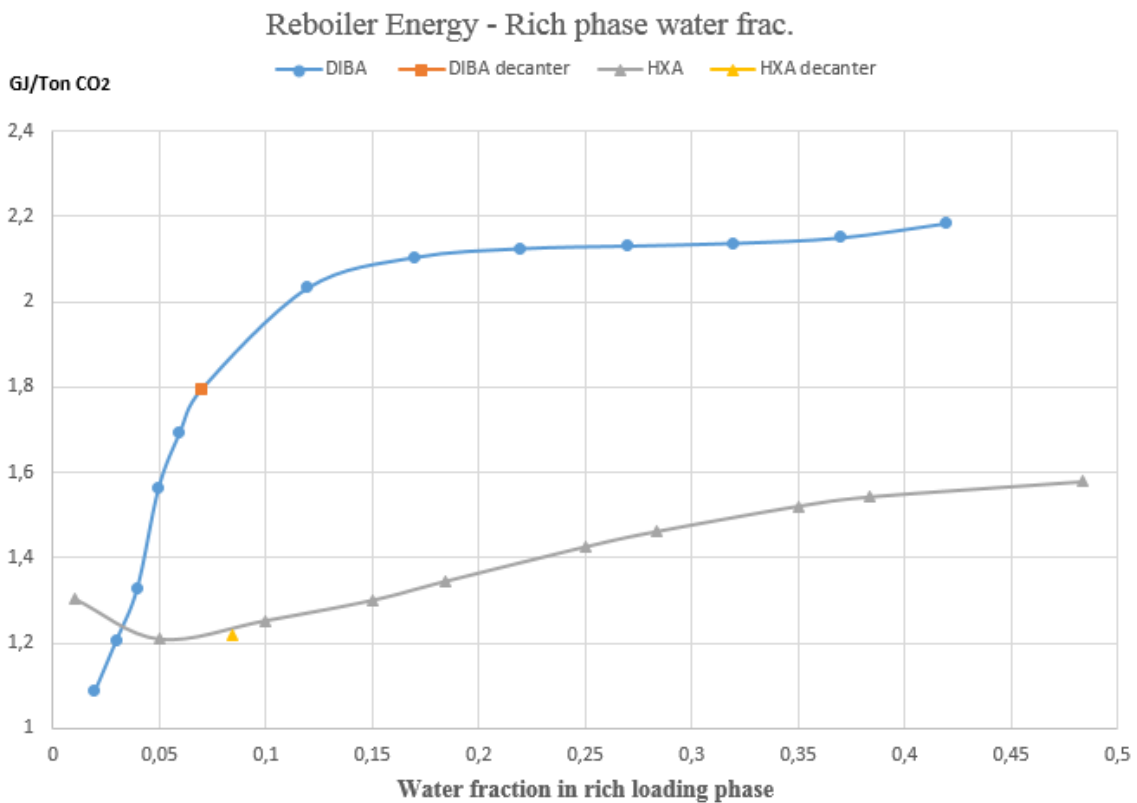
**Figure 4.5:** Reboiler duty - keq value, A varies from -227.5 to -226.5

### *Decanter block*

The decanter block performs phase separation according to VLE estimation by As-

pen, which is limited by available database resource, calculation equation in chosen method, and user-defined ions as well. So a sensitivity study on the composition of two outflows is shown in this section. A separator block is used to replace decanter, and the separation fraction is input manually. The water, CO<sub>2</sub> and amine split fraction in rich phase is varied separately. The supporting detailed data is given in Appendix Table A.18.

The first varying factor is ratio of water in rich loading phase compared with total water entering decanter. When using the decanter, less than 10% of water goes into rich phase. Thus this value is varied within 0.01 to 0.45. The original decanter calculated value is 0.06 for DIBA, and 0.08 of HXA. As in figure 4.6, DIBA is more sensitive on water separation, while HXA reboiler duty is less fluctuating at the range close to 0.08.

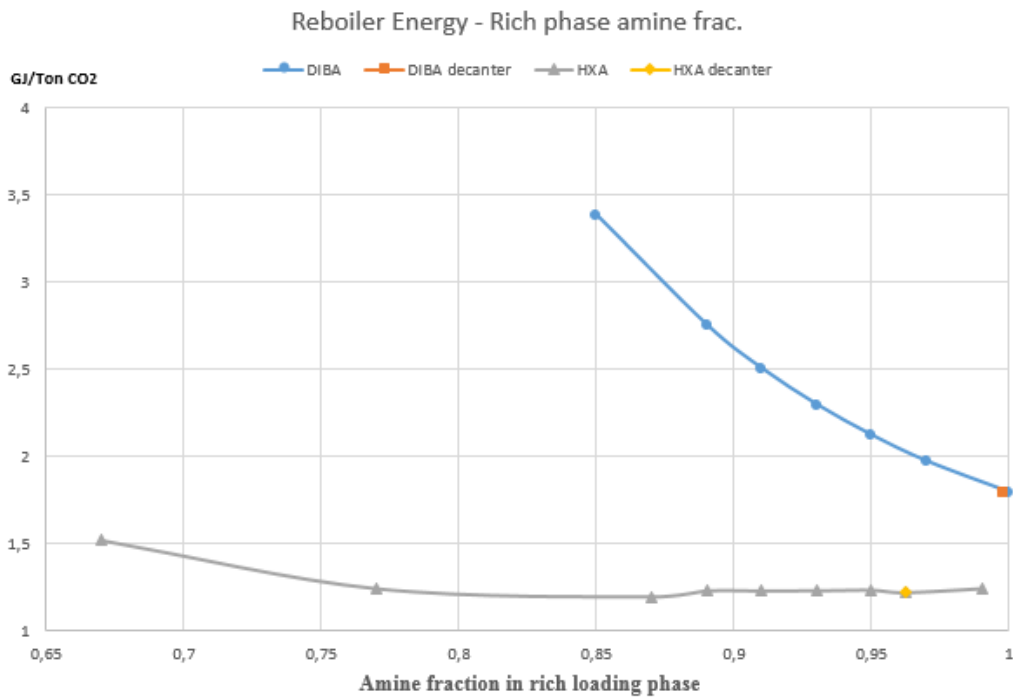


**Figure 4.6:** Reboiler duty - water split ratio in rich loading phase compared with total water entering decanter

The second parameter, the split fraction of amine (molecular and ionic) in rich phase is related to reboiler duty and the results are in Figure 4.7. When the amine concentration is lower, flow sent to decanter increases to ensure the 90% CO<sub>2</sub> removal, leading to higher energy consumed in stripper.

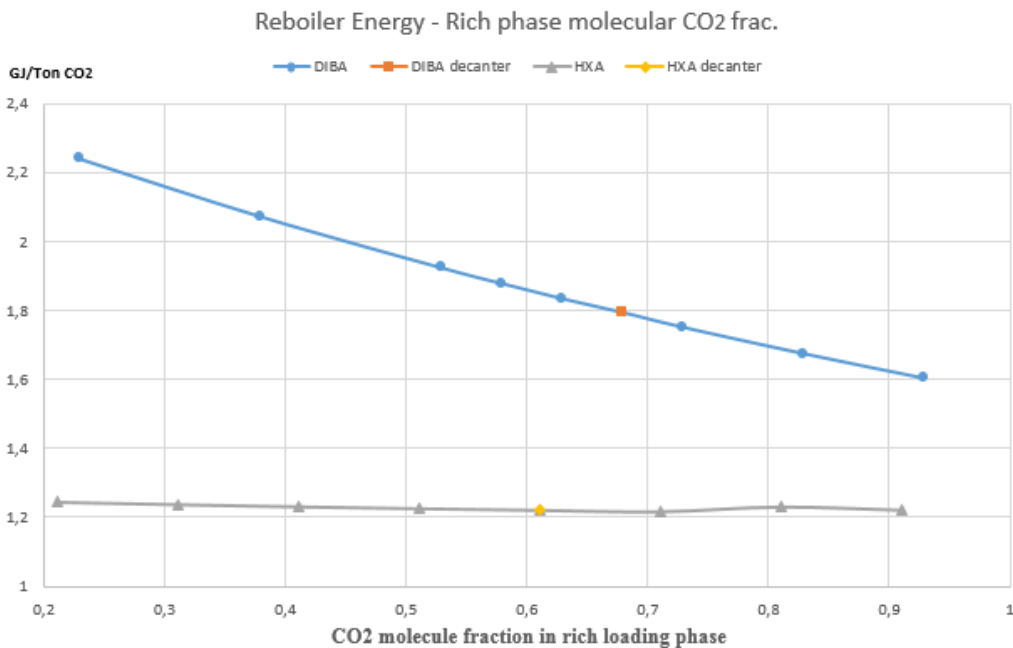
When the ratio for DIBA is decreased from the decanter estimated value 0.999, the influence on energy requirement is notable, and the duty already doubles at ratio

## 4. Results



**Figure 4.7:** Reboiler duty - amine split ratio in rich loading phase compared with total molecular CO<sub>2</sub> entering decanter

0.85. While for HXA, reboiler duty variation within the range from 0.96 to 0.75 is less than 4%, and is rising trend accelerates when ratio is lower than 0.7.

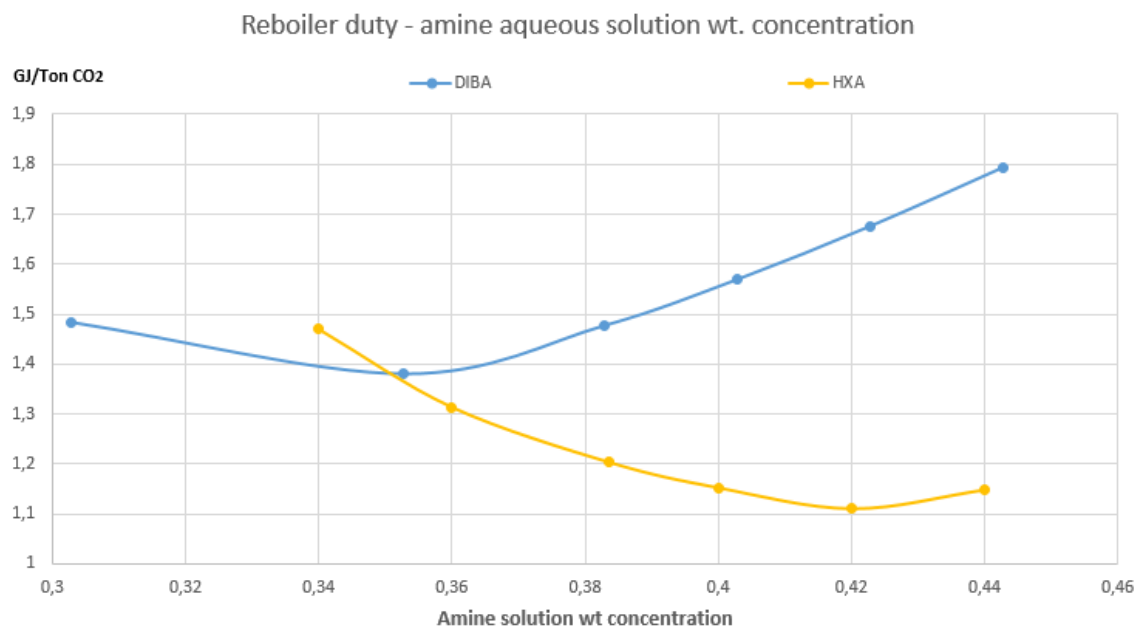


**Figure 4.8:** Reboiler duty - molecular CO<sub>2</sub> split ratio in rich loading phase compared with total molecular CO<sub>2</sub> entering decanter

The third factor, the molecular  $\text{CO}_2$  ratio in two phases is also studied, however this is expected to be less influential since the amount of molecular  $\text{CO}_2$  is very small, and decanter inlet stream is mostly composed by water (close to 50% mass fraction). The results are shown in Figure 4.8. HXA also shows more steady reboiler performance than DIBA.

These results indicate that the decanter estimation can be considered as more reliable for HXA. Especially for the amine and  $\text{CO}_2$  in separated phases, variation close to the estimated value causes performance variation within 5%. DIBA is sensitive to decanter estimation, and the amine split ratio in two phases is the most crucial value to ensure robust and solid simulation.

## 4.2.2 Amine solution concentration



**Figure 4.9:** Reboiler duty - Amine aqueous solution weight based concentration, from 30% to 44%

The amine aqueous solution utilized in all scenarios is 44% wt DIBA solution, and 38% wt HXA solution. In MEA Aspen reference case 30% wt is used. This also affects the heating demand and the amine cost. So a study on different solution concentration is performed, focusing on the influence on reboiler duty. The solution concentration has multiple effect on the performance. One is that concentration affect the absorption and regeneration reaction, as well as amine amount in the stripper inlet, which is adjusted by design specification. Besides, different solubility of the two amines also affects the stripper.

From figure 4.9, the trend of DIBA and HXA within 30% to 40% wt range seems similar (drop first, and then increase). On one side, higher concentration could indicate the total *Leanin* stream flowrate decrease, to capture same amount  $\text{CO}_2$ .

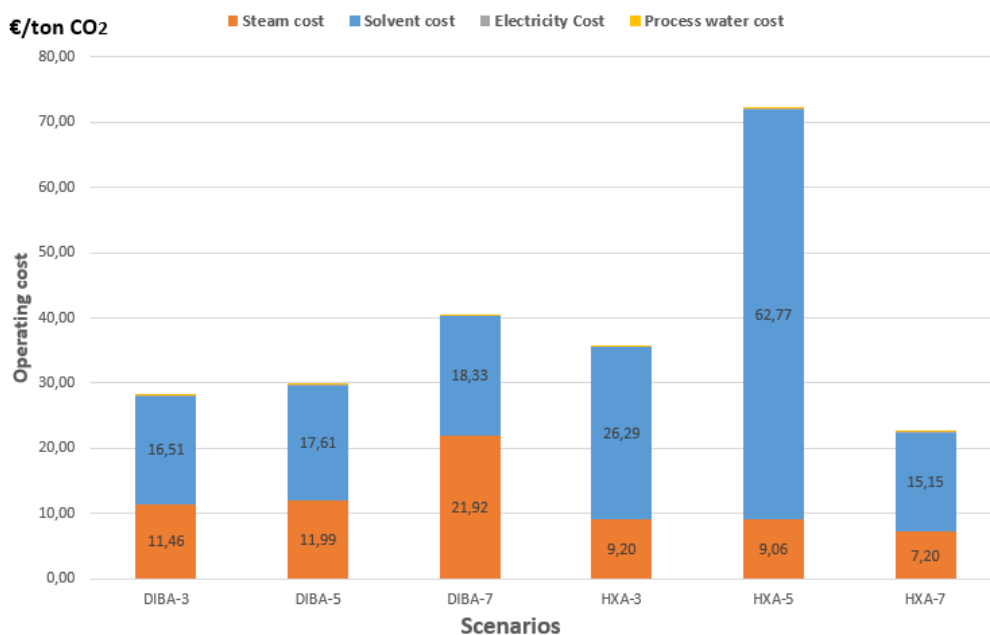
On the other side, the concentration is affecting the reversible chemistry in both absorber and stripper, and the stripper reflux ratio is adjusted to meet the mass balance. In general, there is a suitable range that reboiler duty is relatively low, which is different for two amines.

The fluctuation for HXA is obvious, when concentration is down to 32%, too much solution needed to capture CO<sub>2</sub> that the desorption becomes highly energy intensive and convergence becomes difficult. So in the figure these values of HXA are not included. Another fact to notice is that, except for reboiler duty, to capture same amount of CO<sub>2</sub>, the amine amount recycling in the system is also affected, since the flowrate and mass fraction is also changing. This is a trade-off to optimize the concentration utilized. Detailed supporting data is given in Appendix A.18.

## 4.3 Economic and Environment Analysis

### 4.3.1 Operating cost

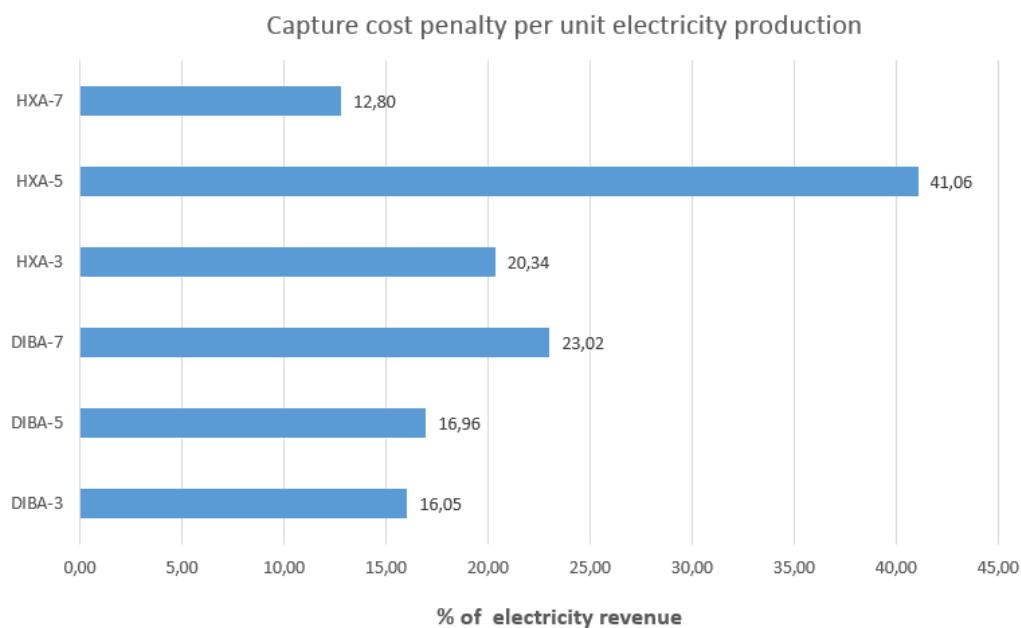
The 3 scenarios which add condenser for recycling amine have shown much significant cost reduction, while the rest with high amine emission lost cause higher operation cost than MEA reference case. MEA reference also has the amine recycling in a condenser. So the three recommended scenarios are compared with respect to mainly steam and amine cost. Amine cost includes the emission makeup and degradation cost. Steam cost refers to the reboiler required low pressure steam. The results are shown in Figure 4.10. Process water, electricity cost is close to negligible due to low amount. The supporting data for operation cost and electricity penalty is given in Appendix Table A.15.



**Figure 4.10:** Operating cost of scenario 3,5,7 for two amines

Scenario 7 with HXA is the optimum case in all studied candidates, with the cost of 22.48 €/ton CO<sub>2</sub> captured. DIBA shows best result in the scenario 3, which is the base case.

In general, DIBA amine makeup cost accounts for lower percentage in total cost than HXA. Although more than 99% of total amine is already recycled, the high price of two amines make this part not unimportant. The amine emission lost can possibly be reduced with well-designed component like scrubber and condenser in industry application. So there is indeed potential to reduce solvent cost.



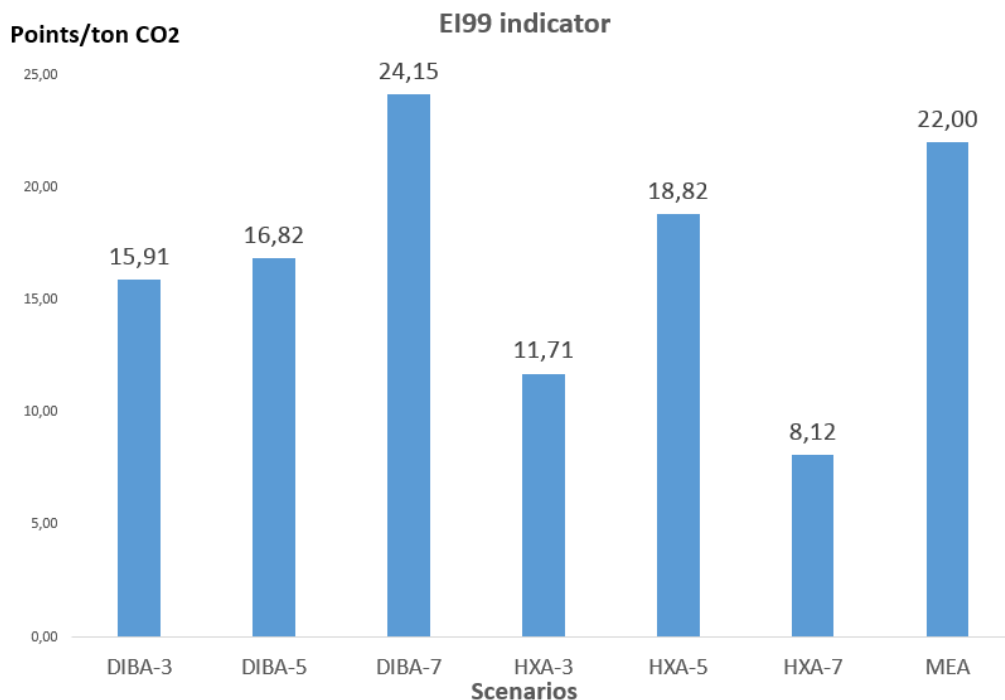
**Figure 4.11:** CO<sub>2</sub> Capture cost penalty in unit electricity production

A further investigation is to relate these values to the power plant production, to indicate the amount of cost required compared with electricity revenue. The fluegas (wet) adopted in our case is composed of 12 % volume CO<sub>2</sub>, and CO<sub>2</sub> flowrate is 1138 kg/hr. Assume the modeled plant is normal gas fired power plant [39] based on fluegas composition. According to IEA carbon capture report [40], an estimated average CO<sub>2</sub> emission from natural gas plant is 348 kg /MWh. The fluegas contained CO<sub>2</sub> flowrate in our model is 1138 kg/hr. Thus this gives estimation of the power plant size, 3.27 MW.

The cost for capturing CO<sub>2</sub> per unit electricity production is available. According to the global average electricity supplier price by IEA [41], 55 €/MWh is chosen as a reference revenue. Thus cost penalty is calculated and shown in Figure 4.11. Except for scenario 5 using HXA, all other cases need a penalty within 10-30%, which is a acceptable value for either consumer or government funding.

### 4.3.2 Environmental Impact

EI99 environment indicator factor result is shown in figure 4.12. The detailed results for GWP and EI99 are given in Appendix Table A.16. The calculation is based on estimated values for solvent, low pressure steam, electricity and process water. Different sources, production plant, and electricity type also affect the accuracy, so results are only compared between studied amines. DIBA is estimated to have larger environment impact per unit in production, so the overall indicator values are higher.

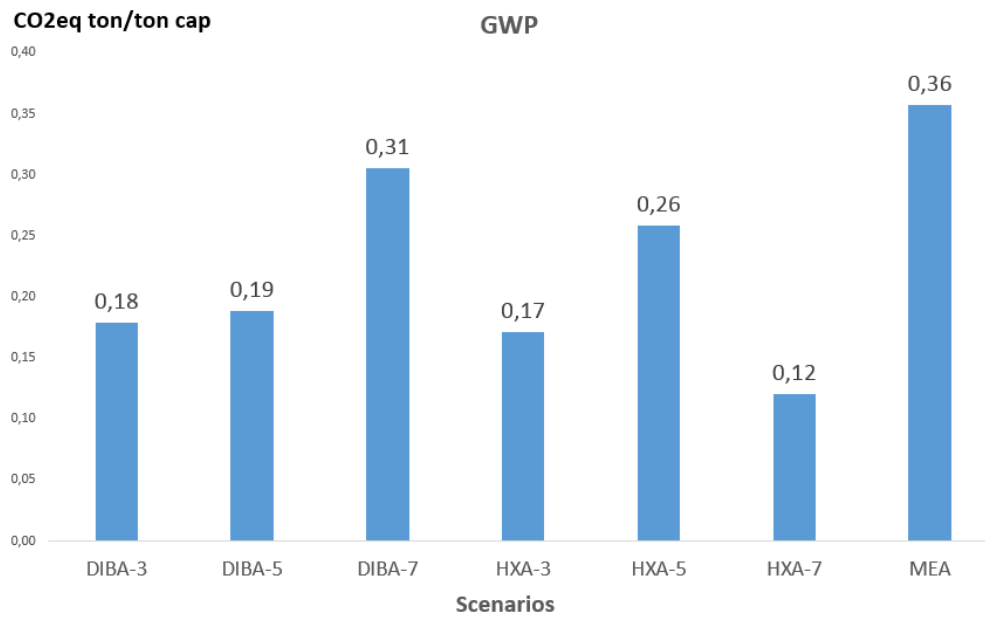


**Figure 4.12:** EI99 indicator estimation, points/ton CO<sub>2</sub> captured

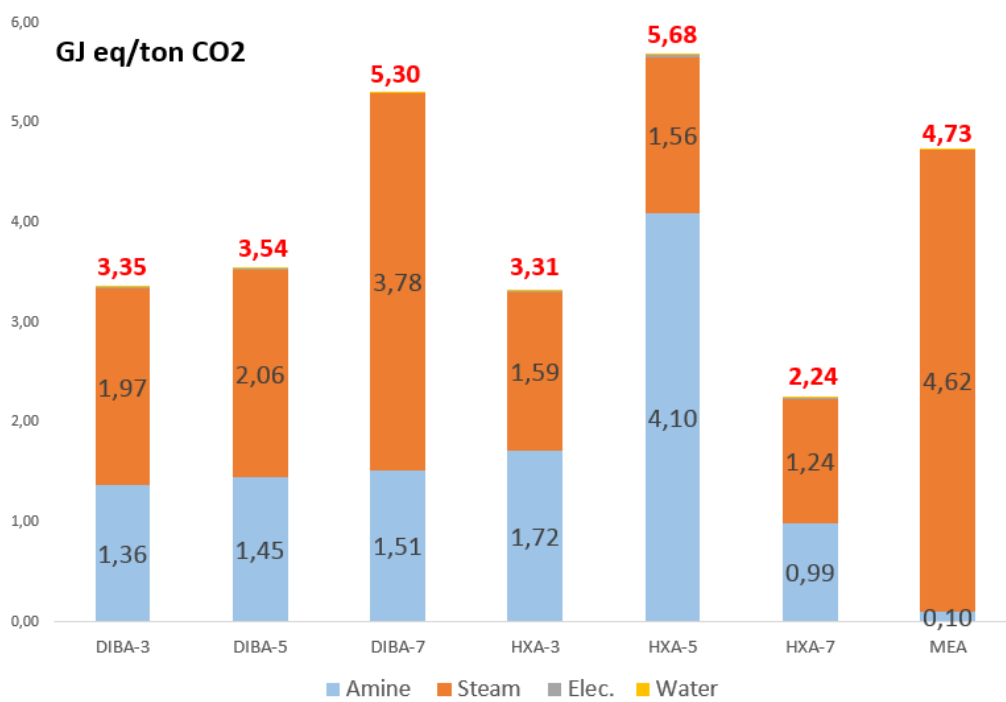
GWP is expressed in form of CO<sub>2</sub> emission caused by capture process. Even in the best case for DIBA, scenario 1, an offset of 18% occurs. HXA has advantage in scenario 7, with 12% offset value.

The energy consumption of steam, amine makeup, electricity and process water are all transferred to equivalent energy consumption, using CED values. Then they can be summed and compare with MEA reference. For MEA reference, degradation is estimated and other consumption is read from Aspen. The final result is shown in Figure 4.14. The best scenario, HXA 7 reduces more than half of consumption. However this wider comparison relies on several estimated values, so it is a rough trend analysis. The supporting data of CED is given in Appendix A.17.





**Figure 4.13:** Global warming potential estimation, CO<sub>2</sub>eq ton/ton captured



**Figure 4.14:** Equivalent energy consumption



# 5

## Conclusion

The major focus of this thesis study is to search for amine solvent, that could reach lower absorption energy demand, compared with MEA, as well as setting up suitable flowsheet layouts. It starts with study and comparison of phase change solvents. Based on previous literature and experimental data, some candidates with reported good performance and experimental results are screened, with the help of Aspen ternary diagram and decanter block simulation. Although DIBA and HXA are two amines that we finally choose, other amines from different research still exhibit good study potential.

Besides, the limitation in this stage is mainly the input of molecules and ions into Aspen. Aspen lack proper recognition of user-defined ions, which is considered as a crucial problem affect the modelling results. A potential improvement is to modify ion property estimation, from either experimental or equation calculation. However this requires reliable experimental data.

The chemistry adopted in this study is in simplified form, considering the convenience of study, and limitation of Aspen chemistry calculation, which is also a sensitive factor.

Setting up flowsheet in Aspen gives detailed stream and column results in the absorption process. In order to compare with MEA flowsheet, the initial base case flowsheet follows similar column sizing, and fluegas input. Both HXA and DIBA showed good reboiler energy reduction under the same CO<sub>2</sub> capture efficiency. To further reduce the amine emission loss, improvement on recycling amine is done. Other two configurations about HX and stripper improvement are also tried. There could also be other layouts with different absorber or stripper setting. Within totally 7 scenarios, 3, 5, and 7 all demonstrate acceptable results, the best one is HXA scenario 7.

The energy consumption results showed that - for HXA all the scenarios require less heating energy than DIBA, and the improvement on HX placement after decanter suits it best. While for DIBA the double stripper flowsheet shows better performance. For both amines, the base case configuration already reaches the energy demand of lower than 2 GJ/ton CO<sub>2</sub> captured, more than 50% reduction of MEA reference case.

Although the results fulfill the target we aim at, it is limited by assumptions and

parameter estimation. The reaction equilibrium constant,  $k_{eq}$ , which is estimated according to amine solubility, is a dominating factor. The sensitivity study shows this influence. Other sensitivity on amine solution, and the decanter performance also showed their limit on results. In general HXA is less sensitive to these parameters.

Considering the environmental and economic impact, HXA in scenario 7 showed least cost offset and environment impact.

To sum up, two chosen amines, especially HXA, shows good phase separation, absorption and regeneration performance. They both lower the energy demand compared with MEA, and the offset of electricity revenue is also reduced to 10 - 20 %. For power plant suppliers, this is a potential value if they install the CCS facility, and distribute extra cost to consumers, government support etc.

Future work in this topic can be continued in different directions.

- For the study itself, improved modeling based on more experimental data will give out more realistic results, as well as diverse process designs and validation of  $k_{eq}$  estimation.
- A larger scale of amines can be studied to find more candidates available for the process, including the DPA molecule that is excluded from the study.
- In the double stripper configuration, the splitting ratio of high and low pressure stripper, as well as working pressure could be optimized according to different amines, minimized the reboiler duty.

# Bibliography

- [1] United Nations. Paris agreement, 2015.
- [2] BP. Bp statistic review of world energy 2016, 2016.
- [3] Ellina Levina, Simon Bennett, and Sean McCoy. *Technology Roadmap: Carbon capture and storage*. OECD/IEA, 2013.
- [4] José D Figueroa, Timothy Fout, Sean Plasynski, Howard McIlvried, and Rameshwar D Srivastava. Advances in co2 capture technology—the us department of energy’s carbon sequestration program. *International journal of greenhouse gas control*, 2(1):9–20, 2008.
- [5] BJP Buhre, LKr Elliott, CD Sheng, RP Gupta, and TF Wall. Oxy-fuel combustion technology for coal-fired power generation. *Progress in energy and combustion science*, 31(4):283–307, 2005.
- [6] Mohamed Kanniche, René Gros-Bonnivard, Philippe Jaud, Jose Valle-Marcos, Jean-Marc Amann, and Chakib Bouallou. Pre-combustion, post-combustion and oxy-combustion in thermal power plant for co 2 capture. *Applied Thermal Engineering*, 30(1):53–62, 2010.
- [7] Bernhard Kronberger, Anders Lyngfelt, Gerhard Löffler, and Hermann Hofbauer. Design and fluid dynamic analysis of a bench-scale combustion system with co2 separation- chemical-looping combustion. *Industrial & Engineering Chemistry Research*, 44(3):546–556, 2005.
- [8] Anders Lyngfelt, Bo Leckner, and Tobias Mattisson. A fluidized-bed combustion process with inherent co 2 separation; application of chemical-looping combustion. *Chemical Engineering Science*, 56(10):3101–3113, 2001.
- [9] Jansen Daniel, Gazzani Matteo, Manzolini Giampaolo, van Dijk Eric, and Carbo Michiel. Pre-combustion co<sub>2</sub> capture. *Greenhouse Gas Control*, 40:167–187, 2015.
- [10] Global CCS institue. Large scale ccs projects. website.
- [11] Paulo Otávio Gomes, Bill Kilsdonk, Jon Minken, Tim Grow, and Roberto Barragan. The outer high of the santos basin, southern sao paulo plateau, brazil: pre-salt exploration outbreak, paleogeographic setting, and evolution of the syn-rift structures. *American Association of Petroleum Geologists Search and Discovery Article*, 10193, 2009.
- [12] Philip Ringrose, Mansour Atbi, David Mason, Marianne Espinassous, Øyvind Myhrer, Martin Iding, Allan Mathieson, and Iain Wright. Plume development around well kb-502 at the in salah co2 storage site. *First break*, 27(1), 2009.
- [13] Paul Feron. *Absorption-Based Post-Combustion Capture of Carbon Dioxide*. Woodhead Publishing, 2016.

- [14] Robert N Maddox, Gilbert J Mains, and Mahmud A Rahman. Reactions of carbon dioxide and hydrogen sulfide with some alkanolamines. *Industrial & engineering chemistry research*, 26(1):27–31, 1987.
- [15] Marco Aleixo, Monique Prigent, Alexandre Gibert, Fabien Porcheron, Ilham Mokbel, Jacques Jose, and Marc Jacquin. Physical and chemical properties of dmxtm solvents. *Energy Procedia*, 4:148–155, 2011.
- [16] IEA GHG. Post combustion carbon capture from coal fired plants–solvent scrubbing. *International Energy Agency Greenhouse Gas R&D Programme*, 2007.
- [17] Jacob N Knudsen, Jørgen N Jensen, Poul-Jacob Vilhelmsen, and Ole Biede. Experience with co<sub>2</sub> capture from coal flue gas in pilot-scale: Testing of different amine solvents. *Energy Procedia*, 1(1):783–790, 2009.
- [18] Prachi Singh, WPM Van Swaaij, and DWF Wim Brilman. Energy efficient solvents for co<sub>2</sub> absorption from flue gas: vapor liquid equilibrium and pilot plant study. *Energy procedia*, 37:2021–2046, 2013.
- [19] Tim C Merkel, Haiqing Lin, Xiaotong Wei, and Richard Baker. Power plant post-combustion carbon dioxide capture: an opportunity for membranes. *Journal of membrane science*, 359(1):126–139, 2010.
- [20] Jiafei Zhang, Yu Qiao, and David W Agar. Improvement of lipophilic-amine-based thermomorphic biphasic solvent for energy-efficient carbon capture. *Energy Procedia*, 23:92–101, 2012.
- [21] Ludovic Raynal, Pascal Alix, Pierre-Antoine Bouillon, Adrien Gomez, Marie le Febvre de Nailly, Marc Jacquin, Jean Kittel, Angella di Lella, Pascal Mougin, and Jean Trapy. The dmx<sup>TM</sup> process: An original solution for lowering the cost of post-combustion carbon capture. *Energy Procedia*, 4:779–786, 2011.
- [22] Hallvard F Svendsen, Erik T Hessen, and Thor Mejdell. Carbon dioxide capture by absorption, challenges and possibilities. *Chemical Engineering Journal*, 171(3):718–724, 2011.
- [23] PMM Blauwhoff, GF Versteeg, and WPM Van Swaaij. A study on the reaction between co<sub>2</sub> and alkanolamines in aqueous solutions. *Chemical Engineering Science*, 38(9):1411–1429, 1983.
- [24] J Richard Elliott and Carl T Lira. *Introductory chemical engineering thermodynamics*. Prentice Hall PTR Upper Saddle River, NJ, 1999.
- [25] Walter Greiner, Ludwig Neise, and Horst Stöcker. *Thermodynamics and statistical mechanics*. Springer Science & Business Media, 2012.
- [26] Phillip C Wankat. *Separation process engineering (third edition)*. Prentice hall, 2011.
- [27] Aspen Tech. Aspen plus v8.8 help list.
- [28] Aspen Tech. Aspen plus unit operation models reference manual.
- [29] P Seferlis and AN Hrymak. Optimization of distillation units using collocation models. *AIChE journal*, 40(5):813–825, 1994.
- [30] Theodoros Damartzis, Athanasios I Papadopoulos, and Panos Seferlis. Optimum synthesis of solvent-based post-combustion co<sub>2</sub> capture flowsheets through a generalized modeling framework. *Clean Technologies and Environmental Policy*, 16(7):1363–1380, 2014.

- 
- [31] Babatunde A Oyekan and Gary T Rochelle. Alternative stripper configurations for co<sub>2</sub> capture by aqueous amines. *AIChE Journal*, 53(12):3144–3154, 2007.
- [32] George S Goff and Gary T Rochelle. Monoethanolamine degradation: O<sub>2</sub> mass transfer effects under co<sub>2</sub> capture conditions. *Industrial & Engineering Chemistry Research*, 43(20):6400–6408, 2004.
- [33] Sara Badr. *Sustainability Assessment of Amine-based Post Combustion CO<sub>2</sub> Capture*. PhD thesis, Zürich, 2016.
- [34] Stephanie Anne Freeman. *Thermal degradation and oxidation of aqueous piperazine for carbon dioxide capture*. PhD thesis, 2011.
- [35] FB Closmann. *Oxidation and thermal degradation of methyldiethanolamine/piperazine in CO<sub>2</sub> capture*. The University of Texas at Austin. PhD thesis, Ph. D. Dissertation, 2011.
- [36] Jason Daniel Davis. Thermal degradation of aqueous amines used for carbon dioxide capture. 2009.
- [37] Mark AJ Huijbregts, Stefanie Hellweg, Rolf Frischknecht, Harrie WM Hendriks, Konrad Hungerbuhler, and A Jan Hendriks. Cumulative energy demand as predictor for the environmental burden of commodity production. *Environmental science & technology*, 44(6):2189–2196, 2010.
- [38] MOLBASE. reference price on molbase.com.
- [39] Xiaochun Xu, Chunshan Song, Ronald Wincek, John M Andresen, Bruce G Miller, and Alan W Scaroni. Separation of co<sub>2</sub> from power plant flue gas using a novel co<sub>2</sub> ‘molecular basket’ adsorbent. *Fuel Chem. Div. Prepr*, 48(1):162–163, 2003.
- [40] IEA Greenhouse Gas RD Programme. Co<sub>2</sub> capture at gas-fired power plants study report, 2011.
- [41] Fatih Birol et al. World energy outlook 2015. *Paris: International Energy Agency*, 2015.





# A

## Appendix 1

### A.1 keq value and property estimation

Aspen use relevant property estimation equations for components. The most important parameters are vapour pressure, heat capacity, viscosity, boiling temperature, liquid density. The corresponding equations that Aspen use are as follows. The Extended Antoine equation 3.1 is used for vapour pressure estimation. Equation A.2 is the ideal gas heat capacity equation, and equation A.3 is the DIPPR liquid viscosity equation. Liquid density is estimated from equation A.4. All the  $C_i$  values for each component are estimated and listed in the parameter sheet.

$$\ln p_i^{*.l} = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i}\ln T + C_{6i}T^{7i} \quad \text{for } C_{8i} \leq T \leq C_{9i} \quad (\text{A.1})$$

$$C_p^{*.lg} = C_{1i} + C_{2i} \frac{C_{3i}/T}{\sinh(C_{3i}/T)} + C_{4i} \frac{C_{5i}/T}{\cosh(C_{9i}/T)} \quad \text{for } C_{6i} \leq T \leq C_{7i} \quad (\text{A.2})$$

$$\ln \eta_i^{*.l} = C_{1i} + \frac{C_{2i}}{T} + C_{3i}\ln T + C_{4i}T^{C_{5i}} \quad \text{for } C_{6i} \leq T \leq C_{7i} \quad (\text{A.3})$$

$$\rho_i^{*.l} = C_{1i}/C_{2i}^{1+(1-T/C_{3i})^{C_{4i}}} \quad \text{for } C_{6i} \leq T \leq C_{7i} \quad (\text{A.4})$$

**Table A.1:** PLXANT parameter values

PLXANT parameter values used in equation 3.1				
Components	DIBA+	DIBACOO-	HXA+	HXACOO-
Temperature units	C	C	C	C
Property units	bar	bar	bar	bar
1	52	90	37	90
2	-8167.67158	-13830.6751	-7800.18	-14639.2
3	0	0	0	0
4	0	0	0	0
5	-7.46874067	-11.6356924	-7.29982	-12.6784
6	7.42E-18	2.87E-18	8.80E-18	3.23E-18
7	6	6	6	6
8	158.58	289.24	136.06	282.09
9	334.466636	477.237609	315.9922	470.7186

**Table A.2:** Parameters for Pure Components Gained by Aspen Plus

Parameters	Units	DIBA	DIBA+	DIBACOO-	HXA	HXA+	HXACOO-
API		58.5894			54.0425		
CHARGE		0	0	0	0	0	0
DCPLS	CAL/MOL-K				20.8073469		
DGAQFM	CAL/MOL	0	0	0	0	0	0
DGAQHG	CAL/MOL	0	0	0	14860	0	0
DGFORM	CAL/MOL	21066.2081	24121.0471	-50900.449	15608.5793	15785.33	-58865.96
DGSFRM	CAL/MOL	0	0	0	0	0	0
DHAQFM	CAL/MOL	0	0	0	0	0	0
DHAQHG	CAL/MOL	0	0	0	-46320	0	0
DHFORM	CAL/MOL	-42801.1847	-41893.5703	-124770.71	-31838.158	-30911.4	-115747.1
DHSFRM	CAL/MOL	0	0	0	0	0	0
DHVLB	CAL/MOL	9010.05541	9432.56205	14207.012	8887.55135	9237.187	14931.59
DLWC		1	1	1	1	1	1
DVBLNC		1	1	1	1	1	1
FREEZEPT	C	-70			-21.3		
HCOM	CAL/MOL	-1248447.5	0	0	-954905.895	0	0
HCTYPE		0	0	0	0	0	0
HFUS	CAL/MOL	3343.84255			5063.53301		
IONTYP		0	0	0	0	0	0
MUP	DEBYE	0.761473298			1.58890222		
MW		129.2456	130.2535	172.2475	101.19184	102.1998	144.1937
OMEGA		0.485362	0.48782927	0.815771347	0.45767	0.474466	0.9001211
OMEGHG	CAL/MOL	0	0	0	-57170	0	0
PC	BAR	25.7	26.11069	25.5333861	31.8	33.14365	31.279872
RGYR	METER	4.74E-10	4.61E-10	5.04E-10	4.07E-10	3.98E-10	4.47E-10
RHOM	GM/CC	0	0	0	0	0	0
RKTZRA		0.26938	0.24533068	0.214366511	0.25992	0.246692	0.2065708
S25HG	CAL/MOL-K	0	0	0	60.2	0	0
S025C	CAL/MOL-K	0	0	0	0	0	0
S025E	CAL/MOL-K	0	0	0	265.201801	0	0
SG		0.744387			0.762628		
TB	C	139.1	158.58	289.24	132.7	136.06	282.09
TC	C	306.85	334.466636	477.237609	310.85	315.9922	470.71859
TPT	C	-70			-21.3		
TREFHS	C	25	25	25	25	25	25
VB	CC/MOL	201.16	177.075606	185.690189	151.337	134.4842	140.71092
VC	CC/MOL	524	506.5	569.5	418	400.5	486.5
VCRKT	CC/MOL	524	506.5	569.5	418	400.5	486.5
VLSTD	CC/MOL	174.062	147.501628	137.083834	133.021	114.9078	103.72518
ZC		0.279	0.261782665	0.23307153	0.274	0.270991	0.2460505
ZWITTER		0	0	0	0	0	0

*Calculate Reaction Equilibrium Constant*

For a chemical equation shown as A.5, A and B are reactant chemical species, while C and D are the product species.  $\alpha, \beta, \gamma, \delta$  are the stoichiometric coefficients of the relative reactants and products.



When the reaction reaches equilibrium under a certain condition, the rate of reactants consuming is equal to the rate of products forming, so the concentration of both reactants and products will stay stable. The equilibrium constant of the reaction can be expressed as A.6. [A], [B], [C], [D] are the activities for the respective

species.

$$K_{eq} = \frac{[C]^\gamma * [D]^\delta}{[A]^\alpha * [B]^\beta} \quad (\text{A.6})$$

Equation A.5 will sometimes be shown as below.



Then equilibrium constants for these two equations are expressed as A.8.

$$K_{eq1} = \frac{[C]^\gamma}{[A]^\alpha} \quad (\text{A.8a})$$

$$K_{eq2} = \frac{[[D]^\delta}{[B]^\beta} \quad (\text{A.8b})$$

Therefore, the equilibrium constant of A.6 is able to be calculated out using A.9 if  $K_{eq1}$  and  $K_{eq2}$  in A.8 are given.

$$K_{eq} = K_{eq1} * K_{eq2} \quad (\text{A.9})$$

In Aspen Plus V8.8, when defining the chemical reactions, some values are needed to calculate the equilibrium constants  $K_{eq}$ . Equation that used in Aspen calculation is shown as A.10. A-E are values to be defined to determine  $K_{eq}$ .

$$\ln(K_{eq}) = A + B/T + C * \ln(T) + D * T + E * ((P - P_{ref})/P_{ref}) \quad (\text{A.10})$$

If we combine A.6 and A.10, we'll get,

$$\ln(K_{eq}) = \ln(K_{eq1} * K_{eq2}) = \ln(K_{eq1}) + \ln(K_{eq2}) \quad (\text{A.11})$$

Therefore, in a reaction written in form of separated equations, if A-E values of these equations are known, the corresponding A-E values of the combined equation can be calculated by simply adding them respectively.

**Table A.3:** Keq Value for reactions in Carbon Capture Process based on MEA. T=340 k

Equation	A	B	C	D	E	keq
3.2a	231.4654	-12092.1	-36.7816	0	0	9.26051E-09
3.2b	-3.03833	-7008.36	0	-0.00313	0	-1.0658626
3.2c	-0.52135	-2545.53	0	0		0.000332722
3.3	-235.025	2538.213	36.7816	-0.00313		-1.06586068

## A.2 Ternary diagram of DMCA

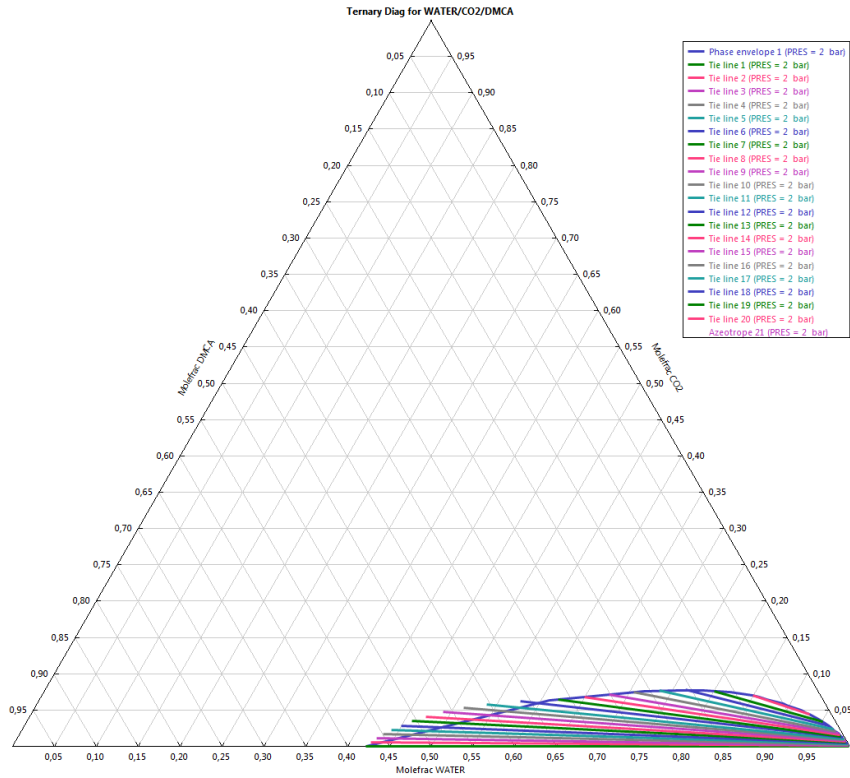


Figure A.1: DMCA ternary mixture study diagram

## A.3 Column. stream input setting in flowsheets

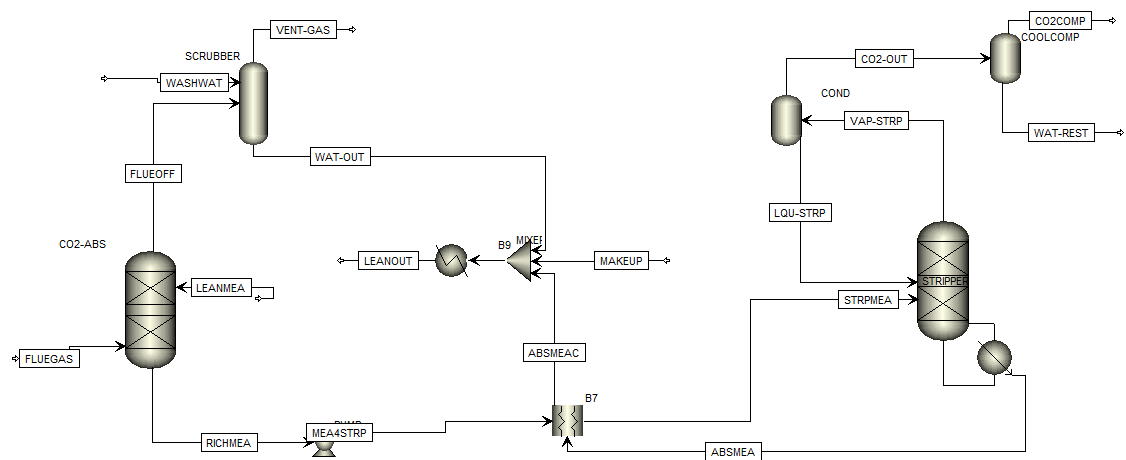


Figure A.2: Reference MEA flowsheet

**Table A.4:** MEA reference flowsheet setting. stripper results

Column setting							
	Parameter	value	unit		Parameter	value	unit
<b>Absorber</b>	No. Stages	17		<b>Stripper</b>	No. Stages	13	
	top stage pressure	1.06	bar		top stage pressure	2	bar
	pressure drop	0.06	bar		pressure drop	0.06	bar
	Fluegas feed stage	17			Fluegas feed stage	1	
	leanMEA feed stage	1			leanMEA feed stage	1	
HX and Input Stream Setting							
<b>Lean-in MEA</b>	Total flow rate	18214.3	kg/hr	<b>Makeup</b>	water	204.1	kg/hr
	mass frac MEA	0.28		<b>HX</b>	hot side temp. Change	56	c
	mass frac H2O	0.66					
	mass frac CO2	0.05					
Stripper result							
<b>Top</b>	Temperature	104.4	C	<b>Reboiler</b>	Temperature	123.4	C
	Distillate rate	51.8	kmol/hr		Heat duty	993.7	kW
	Reflux rate	753.5	kmol/hr		Bottoms rate	733.0	kmol/hr
	Reflux ratio	14.5			Boilup rate	85.5	kmol/hr
					Boilup ratio	0.1	

**Table A.5:** Component settings for absorber and stripper with equilibrium calculate type

Absorber with Equilibrium Type			Stripper with Equilibrium Type		
Condenser	none		Condenser	none	
Absorber	none		number of stages	15	
number of stages	12		Reboiler	kettle	
Fluegas feed stage	12	on-stage	Reflux ratio	3.7	Input value <sup>a</sup>
Lean-in feed stage	1	above-stage	Reflux feed stage	1	above-stage
outlet stage for rich amine	12	liquid	Derich feed stage	1	above-stage
outlet stage for gas-off	1	phase	outlet stage for liquid	15	liquid
Top stage pressure	1.06	bar	outlet stage for vapour	1	vapor
pressure drop	0.06	bar / column	Top stage pressure	2	bar
			pressure drop	0.06	bar / column
<sup>a</sup> Reflux ratio is controlled by design specification					

**Table A.6:** Components settings for stripper in double-stripper flowsheet (scenario 4 and 5)

High Pressure Stripper		
Reflux ratio	3.3	initial
Feed Stream Stage	1	above-stage
outlet stage for liquid	15	liquid
outlet stage for vapor	1	vapor
Top stage pressure	295	kPa
pressure drop	0.06	bar/column
Low pressure Stripper		
Reflux ratio	3.7	initial
Feed liquid stage	8	above-stage
Feed of stream from HP stripper stage	1	above-stage
Feed stream Reflux	1	above-stage
outlet stage for liquid	15	liquid
outlet stage for vapor	1	vapor
Top stage pressure	160	kPa
pressure drop	0.06	bar/column
General settings: Number of Stages: 15. Reboiler: kettle		

**Table A.7:** Column settings for Rate-based absorber & stripper in different scenarios

Amine	Flowsheet	AB diameter (m)	ST Diameter /HP stripper	LP stripper (If available)
DIBA	Base case	0.9295	0.54	
	base case with SR	0.9295	0.7	
	2 strippers	0.9295	0.5	0.4
	2 strippers & SR	0.9295	0.5	0.4
	HX after DC	0.9295	0.54	
	HX after DC & SR	0.9295	0.65	
HXA	Base case	0.9267	0.65	
	base case with SR	0.9267	0.65	
	2 strippers	0.9267	0.6	0.49
	2 strippers & SR	0.9267	0.6	0.49
	HX after DC	0.9267	0.65	
	HX after DC & SR	0.9267	0.65	
General : Tray type: Sieve		Tray spacing: 0.6096m		

**Table A.8:** Other component settings

Component	Parameter	value	unit/comment
HX <sup>a</sup>	Hot side temp. Change	-64	c
Condenser	temperature	76	c
	pressure	2	bar
Coolcomp condenser	temperature	25	c
	pressure	2	bar
Cooler	temperature	35	c
Waste water separator	split fraction	0.98	

<sup>a</sup> This HX input is only for basecase. different scenarios see tableA.9

**Table A.9:** HX setting of all scenarios

Scenario	Heat Exchanger		Hot side temperature Change	Value
	DIBA	HXA		Unit
1	-64	-64		c
2	-64	-64		c
3	-64	-64		c
4	-70	-60		c
5	-60	-60		c
6	-60	-60		c
7	-60	-60		c

**Table A.10:** Fluegas and leanin solution stream input setting

Stream	Parameter	value	unit/comment
Fluegas	total flow rate	83516.7	l/min
	Mole-Frac water	11.25	
	Mole-Frac CO2	11.94	
	Mole-Frac O2	3.81	
	Mole-Frac N2	71.62	
	Temp.	48	c
	pressure	1.12	bar
Leanin amine solution	total flow rate <sup>a</sup>	22950.8208	kg/hr
	Mole-Frac water	670	
	Mole-Frac CO2	14	
	Mole-Frac O2	78	
	Temp.	35	c
	pressure	1.06	bar

<sup>a</sup>Input value. Leanin flowrate is controlled by design specification

## A.4 Economic and environmental analysis parameter and results

**Table A.11:** Estimated degradation value of two amines. in all scenarios

			DIBA	HXA
Degradation	oxidative	kg/hr	4.181	1.829
	thermal	kg/hr	0.465	0.203
Loss in purge stream <sup>a</sup>	Scenario 1		1.060	1.105
	2		1.047	1.067
	3		1.136	1.057
	4	kg/hr	0.523	1.355
	5		0.498	1.355
	6		1.065	1.078
	7		0.957	1.047

<sup>a</sup> Purge loss varies in each scenario. since it's related to stripper bottom stream flowrate and amine concentration

**Table A.12:** Utility price used in economic analysis

Name	Description	FU	Price
Steam	market for steam. in chemical industry	1 kg	0.016 €
Process Water	market for water. completely softened	1 kg	0.00046 €
Electricity	market group for electricity. high voltage	1 kWh	0.0977 €

Source : Ecoinvent 3.3. all price are global average. at the point of substitution

**Table A.13:** Amine CED. GWP. EI99 value used in environmental analysis

	NR-CED (MJeq/kg)	GWP(100a) kg-CO2-eq/kg	EI99(H.A) points/kg
DIBA	150.33	5.005	0.8537
HXA	94.21	3.48	0.2821



**Table A.14:** Utility CED. GWP. EI 99 value used in environmental analysis

	NR-CED (MJeq)	GWP(100a) kg-CO <sub>2</sub> -eq	EI99(H.A) points
Steam	2.756	0.18	0.0113
Process Water	0.00027729392	0.000025472	0.0000023168
Electricity	9.967	0.733	0.055

Source : Ecoinvent 3.3. all value are global average. at the point of substitution

**Table A.15:** Economic analysis results of scenario 3.5.7

	unit	DIBA-3	DIBA-5	DIBA-7	HXA-3	HXA-5	HXA-7
Steam cost	€/ton	11.4607	11.9860	21.9213	9.2020	9.0646	7.1959
Solvent cost	€/ton	16.5090	17.6078	18.3271	26.2916	62.7690	15.1530
Electricity Cost	€/ton	0.1235	0.1731	0.1060	0.1214	0.2566	0.1212
Process water cost	€/ton	0.0858	0.0194	0.0692	0.1056	0.0158	0.0148
total capture cost	€/ton	28.1790	29.7862	40.4236	35.7205	72.1059	22.4848
cost/MWh elec <sup>ab</sup>	€/mwh	8.825655	9.329046	12.66067	11.18767	22.58357	7.042241
elec. penalty	%	16.04664	16.9619	23.01941	20.34123	41.06103	12.80407

<sup>a</sup> Reference electricity price 55€/MWh  
<sup>b</sup> NG plant CO<sub>2</sub> emission 0.348ton/MWh

**Table A.16:** GWP. EI99 results of scenario 3.5.7

	Unit	DIBA-3	DIBA-5	DIBA-7	HXA-3	HXA-5	HXA-7
GWP	CO <sub>2</sub> eq/ton CO <sub>2</sub>	179.1425	188.619	305.264	170.9698	258.3277	120.8553
EI99	points/ton CO <sub>2</sub>	15.91018	16.82431	24.14792	11.71334	18.8212	8.117627
net CO <sub>2</sub> absorption	ton/hr	0.841081	0.831371	0.711852	0.849455	0.759945	0.900804

**Table A.17:** Equivalent enegy consumption Results of scenario 3.5.7

	Equivalent Energy Consumption(GJeq./ton)						
Scenario	DIBA-3	DIBA-5	DIBA-7	HXA-3	HXA-5	HXA-7	MEA
Amine	1.36	1.45	1.51	1.72	4.10	0.99	0.10
Steam	1.97	2.06	3.78	1.59	1.56	1.24	4.62
Elec.	1.26E-02	1.77E-02	1.08E-02	1.24E-02	2.62E-02	1.24E-02	8.50E-03
Water	5.17E-05	1.17E-05	4.17E-05	6.36E-05	9.51E-06	8.91E-06	5.52E-05
Total	3.35	3.54	5.30	3.31	5.68	2.24	4.73

## A.5 Sensitivity Analysis results

**Table A.18:** Solution concentration sensitivity analysis data

DIBA	Mass Frac	0.303	0.353	0.383	0.403	0.423	0.443
Reboiler energy	GJ/ton CO <sub>2</sub>	1.484	1.380	1.476	1.569	1.676	1.793
Circulate DIBA <sup>a</sup>	Kg/s	3.942	3.309	3.093	2.984	2.896	2.823
HXA	Mass Frac	0.340	0.360	0.384	0.400	0.420	0.440
Reboiler energy	GJ/ton CO <sub>2</sub>	1.470	1.313	1.203	1.152	1.110	1.148
Circulate HXA	Kg/s	3.428	3.108	2.869	2.744	2.623	2.658
<sup>a</sup> Amount of amine circulating in the system							

**Table A.19:** Result table of sensitivity analysis in decanter using DIBA with varied temperature. unit for flow rate: kmol/h

Temperature		20	40	57	60
Phase I	Water	10.12562	9.555131	9.191053	9.13627
	CO <sub>2</sub>	8.15E-06	3.46E-06	8.09E-06	8.08E-06
	DIBA	1.86E-05	7.95E-06	1.86E-05	1.86E-05
	DIBA+	7.494419	7.494414	7.494274	7.494243
	DIBA-	7.499848	7.499761	7.499638	7.499615
	Total flow	25.11991	24.54932	24.18499	24.13015
Phase II	Water	39.87439	40.44486	40.80895	40.86373
	CO <sub>2</sub>	1.17E-06	5.13E-07	1.23E-06	1.23E-06
	DIBA	1.38E-08	5.92E-09	1.42E-08	1.43E-08
	DIBA+	0.00557	0.005585	0.005716	0.005748
	DIBA-	0.000141	0.000238	0.000352	0.000375
	Total flow	39.8801	40.45069	40.81502	40.86985
Phase I	Water Frac	0.403091	0.389222	0.380031	0.378625
	DIBA Frac	0.596908	0.610778	0.619968	0.621375
Phase II	Water Frac	0.999857	0.999856	0.999851	0.99985
	DIBA Frac	0.000143	0.000144	0.000149	0.00015
	r=w1/w2	0.403149	0.389278	0.380088	0.378681
Flow rate to decanter are constant: CO <sub>2</sub> 7.5 kmol/h. Water 50 kmol/h. DIBA 15 kmol/h.					

**Table A.20:** Result table of sensitivity analysis in decanter using HXA with varied temperature (unit for flow rate: kmol/h)

Temperature		20	40	57	60
Phase I	Water	38.10711	38.47034	38.69248	38.72481
	co2	9.66E-08	9.84E-08	9.98E-08	1E-07
	HXA	1.18E-08	1.2E-08	1.23E-08	1.24E-08
	HXA+	0.065922	0.067293	0.069008	0.069352
	HXA-	0.001198	0.001807	0.002458	0.002586
	total flow	38.17423	38.53944	38.76395	38.79675
Phase II	Water	11.89289	11.52966	11.30752	11.2752
	co2	5.74E-07	5.72E-07	5.71E-07	5.71E-07
	HXA	1.33E-06	1.33E-06	1.33E-06	1.33E-06
	HXA+	7.434078	7.432705	7.430992	7.430644
	HXA-	7.498802	7.498191	7.497542	7.497409
	total flow	26.82577	26.46056	26.23605	26.20325
Phase I	water Frac	0.998242	0.998207	0.998156	0.998146
	HXA Frac	0.443338	0.43573	0.430992	0.430298
Phase II	water Frac	0.556662	0.56427	0.569008	0.569702
	HXA Frac	0.001758	0.001793	0.001844	0.001854
	r=w1/w2	2.251648	2.290884	2.315952	2.319663

Flow rate to decanter are constant: CO<sub>2</sub> 7.5 kmol/h. Water 50 kmol/h. HXA 15 kmol/h

**Table A.21:** result table of sensitivity analysis in decanter using DIBA with varied CO<sub>2</sub> mole flow rate (unit for flow rate: kmol/h)

CO2 Mole Flow Rate		3.75	7.5	11.25	15
Phase I	Water	9.203323	9.555131	10.29391	11.0854
	CO <sub>2</sub>	0	3.46E-06	3.26979	6.549804
	DIBA	7.494573	7.95E-06	2.54E-10	5.69E-11
	DIBA+	3.747286	7.494414	7.493942	7.493446
	DIBA-	3.74987	7.499761	7.499705	7.499647
	total flow	24.19505	24.54932	28.55735	32.6283
Phase II	Water	40.79667	40.44486	39.70609	38.91459
	CO <sub>2</sub>	0	5.13E-07	0.48021	0.950199
	DIBA	0.005429	5.92E-09	2.05E-13	4.98E-14
	DIBA+	0.002715	0.005585	0.006057	0.006558
	DIBA-	0.000131	0.000238	0.000293	0.000357
	total flow	40.80495	40.45069	40.19265	39.8717
Phase I	water Frac	0.38038	0.389222	0.360464	0.339748
	DIBA Frac	0.999797	0.999856	0.987894	0.975995
Phase II	water Frac	0.61962	0.610778	0.525036	0.459512
	DIBA Frac	0.000203	0.000144	0.000158	0.000173
	r=w1/w2	0.380458	0.389278	0.364882	0.348104

Decanter temperature:40 °C. Water 50 kmol/h. DIBA 15 kmol/h

**Table A.22:** Result table of sensitivity analysis in decanter using HXA with varied CO<sub>2</sub> mole flow rate(unit for flow rate: kmol/h)

CO2 Mole Flow Rate		3.75	7.5	11.25	15
Phase I	Water	36.27445	38.47034	37.40221	36.26301
	CO <sub>2</sub>	0	9.84E-08	0.53884	1.051447
	HXA	0.072867	1.2E-08	6.49E-13	4.71E-13
	HXA+	0.036433	0.067293	0.070016	0.072625
	HXA-	0.000866	0.001807	0.002201	0.002632
	total flow	36.38462	38.53944	38.01327	37.38971
Phase II	Water	13.72555	11.52966	12.59778	13.73699
	CO <sub>2</sub>	0	5.72E-07	3.211162	6.448552
	HXA	7.427131	1.33E-06	6.88E-11	4.82E-11
	HXA+	3.713565	7.432705	7.429987	7.427373
	HXA-	3.749133	7.498191	7.497803	7.497366
	total flow	28.61538	26.46056	30.73673	35.11029
Phase I	water Frac	0.479656	0.998207	0.983925	0.969866
	HXA Frac	0.996972	0.43573	0.409861	0.391253
Phase II	water Frac	0.520344	0.56427	0.485666	0.425082
	HXA Frac	0.003028	0.001793	0.0019	0.002013
	r=w1/w2	0.481113	2.290884	2.400632	2.478875
Decanter temperature:40 °C. Water 50 kmol/h. HXA 15 kmol/h					

Table A.23: Keq sensitivity analysis results ( reboiler energy in GJ/ton CO<sub>2</sub>)

A	-228	-228.1	-228.2	-228.3	-228.4	-228.5	-228.6	-228.7
Keq	9.413E-05	8.517E-05	7.707E-05	6.973E-05	6.310E-05	5.709E-05	5.166E-05	4.674E-05
Reboiler GJ/Ton CO2	1.79	1.94	2.11	2.30	2.53	2.78	3.09	3.48
A	-228.8	-228.9	-229	-229.5	-230	-227.9	-227.8	-227.7
Keq	4.230E-05	3.827E-05	3.463E-05	2.100E-05	1.274E-05	1.040E-04	1.150E-04	1.271E-04
Reboiler GJ/Ton CO2	3.81	4.16	4.49	9.38	10.24	1.66	1.55	1.45
A	-227.6	-227.5	-227	-226.5	-226	-225.5	-225	-224.5
Keq	1.404E-04	1.552E-04	2.559E-04	4.219E-04	6.955E-04	1.147E-03	1.891E-03	3.117E-03
Reboiler GJ/Ton CO2	1.37	1.29	1.05	0.95	0.93	0.96	1.07	1.30
A	-230	-229.5	-229	-228.5	-228	-227.9	-227.8	-227.7
Keq	1.274E-05	2.100E-05	3.463E-05	5.709E-05	9.413E-05	1.040E-04	1.150E-04	1.271E-04
Reboiler GJ/Ton CO2	4.53	2.91	1.99	1.50	1.26	1.24	1.22	1.20
A	-227.6	-227.5	-227.3	-227	-226.7	-226.6	-226.5	-226
Keq	1.404E-04	1.552E-04	1.896E-04	2.559E-04	3.454E-04	3.817E-04	4.219E-04	6.955E-04
Reboiler GJ/Ton CO2	1.20	1.19	1.20	1.25	1.33	1.45	1.18	2.46
A	-225.5	-225	-224.5	-224				
Keq	1.147E-03	1.891E-03	3.117E-03	5.139E-03				
Reboiler GJ/Ton CO2	2.67	3.52	4.54	5.01				

**Table A.24:** Decanter rich outflow mole fraction sensitivity analysis results (reboiler energy in GJ/ton CO<sub>2</sub>)

WATER	Mole frac. <sup>a</sup> ,	0.069	0.019	0.029	0.039	0.049	0.059	0.069
	Reboiler GJ/ton CO <sub>2</sub>	1.795	1.088	1.206	1.331	1.565	1.695	1.795
WATER	Mole frac.	0.119	0.169	0.219	0.269	0.319	0.369	0.419
	Reboiler GJ/ton CO <sub>2</sub>	2.034	2.105	2.126	2.132	2.139	2.151	2.185
DIBA								
Amine <sup>b</sup>	Mole frac.	1.000	0.970	0.950	0.930	0.910	0.890	0.850
	Reboiler GJ/ton CO <sub>2</sub>	1.795	1.973	2.123	2.299	2.507	2.757	3.387
CO <sub>2</sub> <sup>c</sup>	Mole frac.	0.929	0.829	0.729	0.679	0.629	0.579	0.529
	Reboiler GJ/ton CO <sub>2</sub>	1.605	1.676	1.753	1.795	1.835	1.879	1.924
WATER	Mole frac.	0.010	0.050	0.100	0.150	0.184	0.250	0.284
	Reboiler GJ/ton CO <sub>2</sub>	1.305	1.210	1.254	1.301	1.345	1.426	1.462
HXNA	Mole frac.	0.010	0.050	0.100	0.150	0.184	0.250	0.284
	Reboiler GJ/ton CO <sub>2</sub>	1.305	1.210	1.254	1.301	1.345	1.426	1.462
CO <sub>2</sub>	Mole frac.	0.910	0.810	0.711	0.611	0.511	0.411	0.311
	Reboiler GJ/ton CO <sub>2</sub>	1.220	1.230	1.215	1.220	1.225	1.230	1.237
CO <sub>2</sub>	Mole frac.	0.910	0.810	0.711	0.611	0.511	0.411	0.311
	Reboiler GJ/ton CO <sub>2</sub>	1.220	1.230	1.215	1.220	1.225	1.230	1.237

<sup>a</sup> Mole fraction in decanter amine-phase outflow

<sup>b</sup> True component amine sum. i.e. molecule and ion fraction are modified together

<sup>c</sup> Molecular form CO<sub>2</sub>

## **A.6 Important stream result and stripper performance tables in all scenarios**

**Table A.25:** DIBA and HXA stripper detailed performance results in all scenarios

Scenario	Top stage					Reboiler				
	Temperature C	Distillate rate kmol/hr	Reflux rate kmol/hr	Reflux ratio	Temperature C	Heat duty kW	Bottoms rate kmol/hr	Boilup rate kmol/hr	Boilup ratio	
DIBA	1	88.80	43.92	158.65	3.61	112.39	446.98	120.04	41.96	0.35
	2	85.33	49.03	161.47	3.29	112.30	510.45	118.78	48.35	0.41
	3	77.57	38.65	160.43	4.15	111.61	424.52	128.94	41.28	0.32
HXA	4HP <sup>a</sup>	86.97	30.86	110.76	3.59	125.26	354.17	83.77	33.85	0.40
	4LP	82.72	11.58	42.85	3.70	106.30	26.53	115.88	2.32	0.02
	5HP	93.52	36.49	108.04	2.96	128.82	413.13	74.81	38.32	0.51
	5LP	84.67	12.90	47.73	3.70	106.74	30.85	110.44	2.63	0.02
HXA	6	96.42	70.97	168.03	2.37	111.49	486.64	124.20	46.25	0.37
	7	98.61	100.77	185.82	1.84	112.44	812.00	112.04	73.90	0.66
	1	57.11	26.80	194.06	7.24	110.62	349.32	179.68	35.64	0.20
	2	57.18	27.17	182.67	6.72	110.74	342.53	172.83	35.65	0.21
HXA	3	57.63	27.27	181.21	6.65	110.94	340.86	171.13	35.33	0.21
	4HP	54.02	19.61	149.34	7.61	119.34	330.51	141.84	35.53	0.25
	4LP	77.34	10.52	38.93	3.70	104.65	8.86	171.12	0.90	0.01
	5HP	54.36	19.72	148.03	7.51	119.65	327.73	140.43	35.06	0.25
	5LP	77.60	10.43	38.58	3.70	104.83	8.04	169.46	0.81	0.00
	6	95.06	48.70	192.76	3.96	110.75	259.63	173.65	26.99	0.16
	7	95.29	49.25	188.83	3.83	111.30	266.55	168.98	27.39	0.16

<sup>a</sup> High pressure and lower pressure stripper



**Table A.26:** Stream table for DIBA Scenario 1. basecase equilibrium

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out
WATER	12188.09	12188.09	24.19784	112.8841	865.7346	8.328564
CO2	0.4414977	0.4441511	0	86.35185	74.87363	1024.656
DIBA	6527.985	6527.985	122.0751	38.2727	952.6795	0.2301716
O2	5.27732	0	0	254.4255	4.327968	4.303412
N2	30.34817	0	0	4288.473	27.40613	27.34972
DIBA+	1839.844	1840.039	0	0.000208207	4618.114	0.0000172473
DIBA-	2433.283	2433.272	0	0.0000380244	6120.466	0.0000027389
Total Flow kg/hr	756.5602	755.3134	2.287705	169.5614	129.2293	24.85733
Temperature C	35	35	35	25.80515	57.64858	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction	0.0183409	0.0183727	0	-	0.0131649	-
(valid for liquid)	0.1021929	0.1023622	0.4128682	-	0.0570387	-
CO2 Loading	0.1794742	0.1794872	0	-	0.2308067	-

Table A.27: Stream table for DIBA Scenario 2. basecase ratebase

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out	
WATER	12167.41	12167.41	58.78884	145.191	864.1668	8.999158	
CO2	0.4405416	0.4433974	0	74.07071	80.65289	1024.637	
Mass Flow	DIBA	6516.909	6516.909	231.6791	101.5911	856.4069	0.1333909
kg/hr	O2	5.705118	0	0	253.6366	4.680335	4.648176
	N2	32.69334	0	0	4283.949	29.53703	29.46265
	DIBA+	1836.719	1836.917	0	0.000207537	4626.061	0.0000115908
	DIBA-	2429.153	2429.143	0	0.0000436022	6131.09	0.000001362
Total Flow kg/hr	22989.03	22950.82	290.4679	4858.439	12592.6	1067.881	
Temperature C	35	35	35	29.86919	55.8764	25	
Pressure bar	1.06	1.06	1.06	1.06	2	2	
Liquid Fraction	1	1	1	0	1	0	
mole fraction	CO2	0.0183385	0.0183727	0	0.0142351	-	
(valid for liquid)	DIBA	0.1021797	0.1023622	0.3545512	0.0514702	-	
CO2 Loading	0.179474	0.1794872	0	-	0.2765707	-	

**Table A.28:** Stream table for DIBA Scenario 3. basecase with amine recycling

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out
WATER	15406.89	15406.89	188.5099	28.69629	928.4031	8.133701
CO2	0.9723916	0.972594	0	113.8477	84.45044	1024.634
DIBA	6274.715	6274.715	3.446684	3.123152	1013.518	0.3120842
O2	0.2226934	0	0	251.8704	4.870645	4.8451
N2	1.229089	0	0	4273.575	30.78151	30.72324
DIBA+	2324.769	2324.765	0	0.0000550907	4913.291	0.000021588
DIBA-	3074.28	3074.274	0	0.00000721278	6514.446	0.00000400181
Total Flow kg/hr	27083.08	27081.61	191.9566	4671.113	13489.76	1068.648
Temperature C	35	35	35	5	54.57054	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction	0.0186657	0.0186666	0	-	0.0138963	-
(valid for liquid)	DIBA	0.0879953	0.088	0.00254207	-	0.0567887
CO2 Loading	0.2121214	0.2121212	0	-	0.2447017	-

**Table A.29:** Stream table for DIBA Scenario 4. double strippers

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out
WATER	12105.52	12105.52	94.50969	144.0429	857.3042	8.195169
CO2	0.4383088	0.4411421	0	79.71686	80.15326	1024.631
Mass Flow	DIBA 6483.761	6483.761	200.0391	97.40254	856.6082	0.2790562
kg/hr	O2 5.663198	0	0	253.7206	4.639111	4.604642
	N2 32.46285	0	0	4284.438	29.28344	29.20466
	DIBA+ 1827.382	1827.574	0	0.000208821	4602.061	0.0000198784
	DIBA- 2416.804	2416.787	0	0.0000435171	6099.28	0.00000348313
Total Flow kg/hr	22872.03	22834.08	294.5488	4859.321	12529.33	1066.914
Temperature C	35	35	35	29.71577	57.29882	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction	CO2 0.0183387	0.0183727	0	-	0.014232	-
(valid for liquid)	DIBA 0.1021801	0.1023622	0.2278162	-	0.051792	-
CO2 Loading	0.1794743	0.1794872	0	-	0.2747928	-

**Table A.30:** Stream table for DIBA Scenario 5. double strippers with amine recycling

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out
WATER	11634.92	11634.92	41.97766	27.83568	823.8526	8.723725
CO2	0.4212273	0.4239929	0	112.3905	76.53726	1024.637
DIBA	6231.707	6231.707	4.761103	4.469278	853.5231	0.1589583
O2	5.431851	0	0	254.1619	4.365711	4.326948
N2	31.07622	0	0	4287.009	27.60117	27.51152
DIBA+	1756.136	1756.527	0	0.0000705529	4418.675	0.0000131497
DIBA-	2322.835	2322.836	0.00E+00	0.0000113525	5856.213	0.00000171143
Total Flow kg/hr	21982.53	21946.42	46.73877	4685.866	12060.77	1065.358
Temperature C	35	35	35	5	58.12181	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction	0.0183367	0.0183727	0	-	0.0141254	-
(valid for liquid)	0.1021769	0.1023622	0.0155633	-	0.0536386	-
CO2 Loading	0.1794607	0.1794872	0	-	0.2633443	-

**Table A.31:** Stream table for DIBA Scenario 6. heat exchanger rearrangement

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out
WATER	12598.84	12598.84	86.68706	156.4736	948.4201	9.973854
CO2	0.4561363	0.4591194	0	35.48127	84.707	1024.626
Mass Flow kg/hr	DIBA 6747.984	6747.984	427.1791	142.3384	849.3252	0.0859634
	O2 5.979753	0	0	252.9985	5.038205	4.98688
	N2 34.15959	0	0	4280.255	31.73463	31.61501
	DIBA+ 1901.847	1902.05	0	0.000196394	4790.435	0.00000878442
	DIBA- 2515.291	2515.275	0	0.0000445134	6349.153	0.00000074215
Total Flow kg/hr	23804.56	23764.61	513.8662	4867.547	13058.81	1071.288
Temperature C	35	35	35	31.3037	32.46131	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction (valid for liquid)	CO2 0.0183383	0.0183727	0	-	0.0141451	-
	DIBA 0.102178	0.1023622	0.4071897	-	0.0482942	-
CO2 Loading	0.1794741	0.1794872	0	-	0.2928948	-

**Table A.32:** Stream table for DIBA scenario 7. heat exchanger rearrangement with amine recycling

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out
WATER	11637.82	11637.82	151.8476	27.84175	875.0498	9.903817
CO2	0.4213665	0.4240985	0	112.1004	77.16998	1024.594
DIBA	6233.26	6233.26	4.709178	4.460798	853.3954	0.0847713
O2	5.339058	0	0	254.1581	4.434027	4.372339
N2	30.43053	0	0	4286.987	28.03216	27.88744
DIBA+	1756.48	1756.965	0	0.0000703913	4420.099	0.00000912372
DIBA-	2323.427	2323.414	0	0.0000113067	5858.227	0.000000699298
Total Flow kg/hr	21987.18	21951.88	156.5568	4685.548	12116.41	1066.842
Temperature C	35	35	35	5	34.63563	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction	0.0183364	0.0183727	0	-	0.0139149	-
(valid for liquid)	0.1021788	0.1023622	0.00430417	-	0.0523983	-
CO2 Loading	0.1794546	0.1794872	0	-	0.2655611	-

**Table A.33:** Stream table for HXA scenario 1. basecase equilibrium

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out
WATER	16332.79	16332.79	57.02641	148.586	1400.202	7.141831
CO2	5.243232	5.270659	0	110.8833	72.96271	1024.636
Mass Flow kg/hr	O2 6.284099	0	0	253.6537	4.072376	4.068454
	N2 35.97008	0	0	4284.714	25.42829	25.41996
	HXA 6870.604	6870.604	75.00968	68.12329	2503.706	1.48419
	HXA+ 1920.888	1923.838	0.00E+00	0.00000000017285	3892.335	0.000000000023813
	HXACOO- 2714.433	2714.343	0.00E+00	0.0000000190736	5704.271	0.0000000130434
Total Flow kg/hr	27886.21	27846.85	132.0361	4865.961	13602.98	1062.751
Temperature C	35	35	35	31.80858	57.50322	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction	CO2 0.0183188	0.0183727	0		0.00906917	
(valid for liquid)	HXA 0.1021653	0.1023622	0.1897408		0.1353486	
CO2 Loading	0.1793059	0.1794872	0		0.067006	



Table A.34: Stream table for HXA scenario 2. basecase ratebase

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out
WATER	15792.32	15792.32	65.46505	161.4297	1347.298	7.173263
CO2	5.068691	5.096246	0	109.856	77.02648	1024.623
O2	6.369144	0	0	253.5152	4.124081	4.119093
N2	36.42792	0	0	4283.946	25.72932	25.71863
HXA	6643.247	6643.247	86.99693	77.87113	2301.064	1.230225
HXA+	1857.272	1860.176	0	0.00000000017395	3817.552	0.00000000024537
HXACOO-	2624.609	2624.522	0	0.0000000200849	5595.418	0.00000000869306
Total Flow kg/hr	26965.31	26925.36	152.462	4886.618	13168.21	1062.864
Temperature C	35	35	35	33.19484	57.18755	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction	0.018317	0.0183727	0		0.00991721	
(valid for liquid)	0.1021574	0.1023622	0.1913222		0.1288493	
CO2 Loading	0.1793025	0.1794872	0		0.0769675	

**Table A.35:** Stream table for HXA scenario 3. basecase with amine recycling

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out
WATER	15647.04	15647.04	232.2801	37.36797	1335.585	7.176775
CO2	5.0489	5.049363	0	110.591	76.26796	1024.634
Mass Flow kg/hr	0.1421239	0	0	253.5111	4.070384	4.065186
	N2	0.8301716	0	0	4283.916	25.4015
	HXA	6582.132	6582.132	15.54971	7.839584	2291.405
	HXA+	1843.064	1843.063	0	0.00000000006244	3777.968
	HXACOO-	2600.379	2600.377	0.00E+00	0.0000000000399828	5537.361
						0.000000000024376
						1.181239
						0.0000000000807193
Total Flow kg/hr	26678.63	26677.66	247.8298	4693.226	13048.06	1062.448
Temperature C	35	35	35	10	57.32386	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction	CO2	0.018372	0.0183727	0	0.00990747	
(valid for liquid)	HXA	0.1023587	0.1023622	0.0117777	0.1294573	
CO2 Loading	0.1794871	0.1794872	0		0.0765308	

Table A.36: Stream Table for HXA scenario 4. double strippers

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out
WATER	15909.6	15909.6	259.375	162.7891	1360.133	7.447043
CO2	5.102542	5.134092	0	100.6005	77.56557	1024.625
O2	6.369503	0	0	253.4015	4.170472	4.157553
N2	36.42071	0	0	4283.288	26.01207	25.9837
HXA	6692.581	6692.581	114.3559	80.97133	2308.237	0.5289539
HXA+	1869.577	1873.99	0	0.00000000017174	3849.797	0.00000000018161
HXACOO-	2644.115	2644.012	0	0.000000020227	5642.652	0.00000000216965
Total Flow kg/hr	27163.76	27125.31	373.7309	4881.05	13268.57	1062.742
Temperature C	35	35	35	33.37859	55.39695	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction	0.0183032	0.0183727	0	0.00990523		
(valid for liquid)	0.1021326	0.1023622	0.0727794		0.1281975	
CO2 Loading	0.1792108	0.1794872	0		0.0772653	

**Table A.37:** Stream table for HXA scenario 5. double strippers and amine recycling

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out	
WATER	15760.05	15760.05	33.9178	24.71087	1348.21	7.614913	
CO2	5.054283	5.085834	0	112.3341	76.89966	1024.651	
Mass Flow kg/hr	6.428649	0	0	253.4152	4.114283	4.100238	
	N2	36.71045	0	0	4283.387	25.66936	25.63827
	HXA	6629.674	6629.674	41.86257	38.4829	2299.15	0.3886353
	HXA+	1852.018	1856.375	0.00E+00	9.96E-22	3808.807	0.000000000015761
	HXACOO-	2619.273	2619.16	0.00E+00	3.0849E-17	5582.522	0.0000000013499
Total Flow kg/hr	26909.21	26870.35	75.78036	4712.33	13145.37	1062.393	
Temperature C	35	35	35	5	55.50835	25	
Pressure bar	1.06	1.06	1.06	1.06	2	2	
Liquid Fraction	1	1	1	0	1	0	
mole fraction (valid for liquid)	CO2	0.0183029	0.0183727	0	0.00990923		
	HXA	0.1021301	0.1023622	0.1801479	0.1288507		
CO2 Loading	0.1792116	0.1794872	0		0.0769047		

**Table A.38:** Stream table for HXA scenario 6. heat exchanger rearrangement

Stream Name	Lean_4	Lean_in	Make_up	Gas_off	De_rich	CO2_out
WATER	16031.9	16031.9	145.9203	164.3877	1418.49	7.696647
CO2	5.145528	5.173558	0	91.07953	78.31057	1024.591
O2	6.480153	0	0	253.28	4.246038	4.22564
N2	37.0366	0	0	4282.585	26.4691	26.42383
HXA	6744.028	6744.028	146.1404	84.58222	2315.802	0.3503442
HXA+	1885.437	1888.395	0	0.00000000016926	3883.465	0.0000000001503
HXACOO-	2664.429	2664.337	0	0.0000000203939	5692.506	0.00000000114864
Total Flow kg/hr	27374.45	27333.83	292.0607	4875.915	13419.29	1063.288
Temperature C	35	35	35	33.58955	35.68416	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction	0.0183169	0.0183727	0	0.00977916	0.00977916	
(valid for liquid)	0.102157	0.1023622	0.1513193	0.1257727	0.1257727	
CO2 Loading	0.1793018	0.1794872	0	0.0777526	0.0777526	

**Table A.39:** Stream Table for HXA scenario 7. heat exchanger rearrangement with amine recycling

Stream Name	Lean 4	Lean in	Make up	Gas off	De rich	CO2 out
WATER	15609.85	15609.85	30.18565	26.44642	1383.342	7.670696
CO2	5.00608	5.037361	0	112.4161	76.34004	1024.604
Mass Flow kg/hr	O2 6.365145	0	0	253.5155	4.086444	4.066901
	N2 36.35417	0	0	4283.948	25.496	25.45261
	HXA 6566.49	6566.487	7.683548	4.412848	2289.279	0.3561168
	HXA+ 1834.359	1838.682	0	0.000000000046812	3768.245	0.000000000015135
	HXACOO- 2594.3	2594.197	0	0.00000000266773	5523.413	0.00000000118053
Total Flow kg/hr	26652.72	26614.25	37.8692	4680.739	13070.2	1062.151
Temperature C	35	35	35	5	36.0981	25
Pressure bar	1.06	1.06	1.06	1.06	2	2
Liquid Fraction	1	1	1	0	1	0
mole fraction (valid for liquid)	CO2 0.0183028	0.0183727	0	0	0.00978021	
	HXA 0.10213	0.1023622	0.0433519		0.1275553	
CO2 Loading	0.179211	0.1794872	0		0.0766742	