Extension of a multi-criterion performance indicator model for post combustion CO_2 capture using amine solvents

by

Rochelle Fourie
B.Sc. Eng.

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School of Engineering
College of Agriculture, Engineering and Science
University of KwaZulu-Natal
Durban
South Africa

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PREFACE

The research contained in this thesis was completed by the candidate while based in the Discipline of Chemical Engineering, School of Engineering of the College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Howard College, South Africa. The research was financially supported by the South African Research Chairs Initiative (SARChI).

The contents of this work have not been submitted in any form to another university and, except where the work of others is acknowledged in the text, the results reported are due to investigations by the candidate.

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Signed: Professor D. Ramjugernath
Date:

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Signed: Professor P. Naidoo
Date:

DECLARATION: PLAGIARISM

I, Rochelle Fourie, declare that:

(i) the research reported in this dissertation, except where otherwise indicated or acknowledged, is my original work;

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Signed: Rochelle Fourie

Date: August 2018

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And lastly to God, for providing me with the motivation and strength to persevere.

ABSTRACT

Energy generation by carbonaceous fuel combustion has been identified as one of the predominant sources of CO_2 emissions. Many scientists and researchers believe that rising CO_2 levels have an adverse effect on the environment, therefore research on the capture and storage of CO_2 is ongoing. Post-combustion capture with amine-scrubbing has been identified as a practical short-term solution to the problem. The alkanolamine, monoethanolamine (MEA) is the current solvent of choice for this application. However, due to disadvantages connected to its use, there is a need to identify alternative superior solvents or solvent blends. A quick and inexpensive method to identify alternative solvents is via process simulation and modelling. These tools enable the assessment of solvent viability on a large scale and the elimination of unsuitable candidates without the expense of extensive laboratory testing.

The main units considered in a post-combustion CO_2 capture simulation are the absorber, where the amine solvent is used to remove CO_2 from a flue gas stream, and the stripper, which enables the separation of the CO_2 from the solvent to facilitate recycle of the solvent for re-use in the absorber. User inputs into these simulations include the flow rate and composition of the flue gas to be treated, the solvent composition, and the desired CO_2 capture rate.

A multi-criterion performance model for the evaluation of solvents used for CO_2 capture from a coal-fired power plant, was previously developed by Daya (2017) within the Thermodynamics Research Unit at the University of KwaZulu-Natal. The inputs to this performance indicator model are primarily solvent flow rates and equipment heat duties, which were obtained from ASPEN Plus® simulations. Among the other inputs required are price data for the various factors considered in the model, which include energy requirements, make-up flows and carbon taxes. The solvents investigated to test the performance model's viability consisted of primary, secondary, tertiary and sterically-hindered alkanolamine solvents and their blends. MEA was used as the basis of comparison.

In this study, the performance indicator model is used to evaluate the performance of the previously studied amines, n-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP), in different blends as along with an additional component, piperazine (PZ). Different concentrations of the binary blends MDEA+PZ and AMP+PZ as well as the ternary blend, MDEA+AMP+PZ, were investigated. The solvent selected as the basis for the ratings was also changed from 30 wt.% MEA to 30 wt.% AMP, as AMP was previously proven to outperform MEA. The rating for the benchmark case calculated by the performance model formulae, is one. When the same calculations are applied to the other amine blends investigated, ratings below one show a performance inferior than the benchmark, whilst a rating above one show better performance compared to the benchmark. Of the blends studied, the solvent with composition 25 wt.% AMP + 5 wt.% PZ + 70 wt.% H_2O was the best performing with an overall performance increase of approximately 35% (which corresponds to a rating of 1.359).

This solvent was further studied using alternative process configurations: the absorber intercooling (ICA) and rich solvent splitting (RSS) configurations. These configurations have been reported to noticeably reduce the energy requirements for solvent regeneration, with minimum additional equipment. A rating of 1.483 was obtained for the ICA configuration, which is a 9% improvement on the rating of the conventional configuration with the same solvent. The results for the RSS configuration, however, shows no improvement on the performance of the conventional configuration.

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NOMENCLATURE

ENGLISH LETTERS

Symbol	Description	Unit
A, B, C, D	Equilibrium constants	-
C	Cost	R/ton
C_p	Heat capacity	$J/kg \cdot K$
E	Activation energy	$J/kmol$
f	Fraction	-
H_v	Heat of vaporisation	kJ/kg
k	Pre-exponential factor	-
k_2	Second order kinetic rate constant	$m^3/mol \cdot s$
K_{eq}	Equilibrium rate constant	-
$\dot{m}$	Mass flow rate	$kg/s;\ ton/hr$
n	Temperature exponent	-
p	Pressure	kPa
P	Price	R
$\dot{Q}$	Heat duty	kW
r	Reaction rate	$kmol/s$
R	Performance rating	-
R	Universal gas constant	$m^3 \cdot Pa/K \cdot mol$
T	Temperature	K

SUBSCRIPTS

b - Benchmark case

c - Condensed

cw - Cooling water

eq - Equilibrium

ihb - Inhibitor

i - Denotes a specific factor

j - Denotes a specific case

t - Total

GREEK LETTERS

Symbol	Description	Unit
α	CO_2 Loading	$mol\ CO_2/mol\ amine$
Δ	Change	-
ε	Efficiency	-

ABBREVIATIONS

ASU	-	Air Separation Unit
CCS	-	Carbon Capture and Storage
CLC	-	Chemical Looping Combustion
CW	-	Cooling Water
DLA	-	Double Loop Absorber
eNRTL	-	Electrolyte Non-Random Two Liquid (model)
ESA	-	Electrical Swing Adsorption
FCE	-	Flue gas Compression and Expansion
HIS	-	Heat Integrated Stripper
ICA	-	Intercooled Absorber
IGCC	-	Integrated Gasification Combined Cycle
IHA	-	Inter-Heated Absorber
IHP	-	Integrated Heat Pump
IHS	-	Inter-Heated Stripper
IPCC	-	Intergovernmental Panel on Climate Change
LVC	-	Lean Vapour Compression
MES	-	Multi-Effect Stripper
MOF	-	Metal Organic Framework
MPS	-	Multi-Pressure Stripper
MWe	-	Megawatt Electric
OCB	-	Overhead Condenser Bypass
PCC	-	Post-Combustion Capture
PEA	-	Parallel Economizer Arrangement
PREOS	-	Peng-Robinson Equation of State
PSA	-	Pressure Swing Adsorption
RSF	-	Rich Solvent Flashing

RSP	-	Rich Solvent Pre-heating
RSR	-	Rich Solvent Recycle
RSS	-	Rich Solvent Split
RTIL	-	Room Temperature Ionic Liquid
RVC	-	Rich Vapour Compression
SFA	-	Split Flow Arrangement
SOC	-	Stripper Overhead Compression
TBAB	-	tetra-*n*-butylammonium bromide
TSA	-	Temperature Swing Adsorption
TSIL	-	Task-Specific Ionic Liquid
VOS	-	Vacuum Operated Stripper

SOLVENT NAMES

1,4-DMPZ	-	1,4-dimethylpiperazine
1-MPZ	-	1-methylpiperazine
2-MPZ	-	2-methylpiperazine
4A1B	-	4-amino-1-butanol
5A1P	-	5-amino-1-pentanol
AEEA	-	2-(2-aminoethylamino)ethanol
AEPD	-	2-amino-2-ethyl-1,3-propanediol
$AEPDNH_2$	-	N-(2-aminoethyl)-1,3-propanediamine
AHPD	-	2-amino-2-hydroxymethyl-1,3-propanediol
AMP	-	2-amino-2-methyl-1-propanol
AMPD	-	2-amino-2-methyl-1,3-propanediol
DEA	-	diethanolamine
DEAB	-	4-(diethylamino)-2-butanol
DEEA	-	2-(diethylamino)-ethanol
DETA	-	diethylenetriamine
DGA	-	diglycolamine
DiMAP	-	3-dimethylamino-1-propanol
DIPA	-	diisopropanolamine
DMAEOE	-	2-(2-(dimethylamino)ethoxy)ethanol
DMAP	-	1-dimethylamino-2-propanol
EEA	-	N-ethylethanolamine

HMDA - hexamethylenediamine

MAE - N-methyl-2-ethanolamine

MAPA - 3-(methylamino)propylamine

MDA - 1,8-p-menthane-diamine

MDEA - N-methyldiethanolamine

MEA - monoethanolamine

MIPA - monoisopropanolamine / 1-amino-2-propanol

MPA - monopropanolamine

PZ - piperazine

TEA - triethanolamine

TEMED - N,N,N',N'-tetramethylethylenediamine

CHAPTER 1

1 INTRODUCTION

Globally, carbon capture and storage is viewed as a potential short-term solution to curb the increase of the Earth's atmospheric temperature (Hansen *et al.*, 2008). Capturing CO_2 from large industrial sources, especially power stations, has been of particular interest because traditional methods for power generation rely mainly on the combustion of carbonaceous fuels. Alternative methods of electricity generation utilizing renewable sources, while attractive, will not be able to completely replace conventional methods in the near future (Vortmeyer *et al.*, 2013). A vast number of investigations on the modification and optimisation of existing capture materials are available in the literature. These include alkonolamines, zeolites, ionic liquids, amine-grafted silicas, carbonaceous adsorbents, and metal organic frameworks. Furthermore, technologies such as chemical absorption, pressure/ temperature swing adsorption as well as alternate and novel technologies (e.g. gas hydrates, membranes, biofixation approaches), are discussed in the literature, but there is still much scope for the improvement of existing techniques (D'Alessandro *et al.*, 2010) such as absorption, which is the focus of this study.

1.1 OVERVIEW OF INDUSTRIAL CARBON CAPTURE

There is an urgent need to reduce CO_2 emissions into the atmosphere. Excess CO_2 has been demonstrated to have a negative impact on the environment; the increase of global temperatures, commonly known as global warming, is one of the more noticeable effects (Dutcher *et al.*, 2015). The Intergovernmental Panel on Climate Change (IPCC) called for a 2 °C limit on the increase of global temperature to prevent dangerous consequences. Research shows however, that a temperature increase of no more than 1 °C relative to the global temperature in 2000, could cause irreversible ice sheet and species loss (Hansen *et al.*, 2008). This temperature increase limit corresponds to a total CO_2 atmospheric concentration of no more than 450 ppm (Hansen *et al.*, 2008). In comparison, the total CO_2 atmospheric concentration fluctuated at levels below 300 ppm for thousands of years, but eventually reached the 300 ppm mark in 1950. Since then, there has been a significant and constant rise in the total CO_2 concentration, which reached 400 ppm in 2013

(NASA, 2017). Furthermore, a forecast of CO_2 emissions showed that the global CO_2 level will near 410 ppm in 2017 (Le Page, 2017), and this level was already reached by April 2017 (Kahn, 2017).

Power generation by means of fossil fuel combustion is a major contributor to atmospheric CO_2 emissions. However, while the continued use of coal for energy generation is a major contributor to rising CO_2 levels, the Global CCS Institite (2015) predicts that a majority of the world's energy (at least 60%) will still be generated by fossil fuels until at least 2040. Figure 1-1 illustrates a forecast of changes to the global energy market from 2011 to 2030.

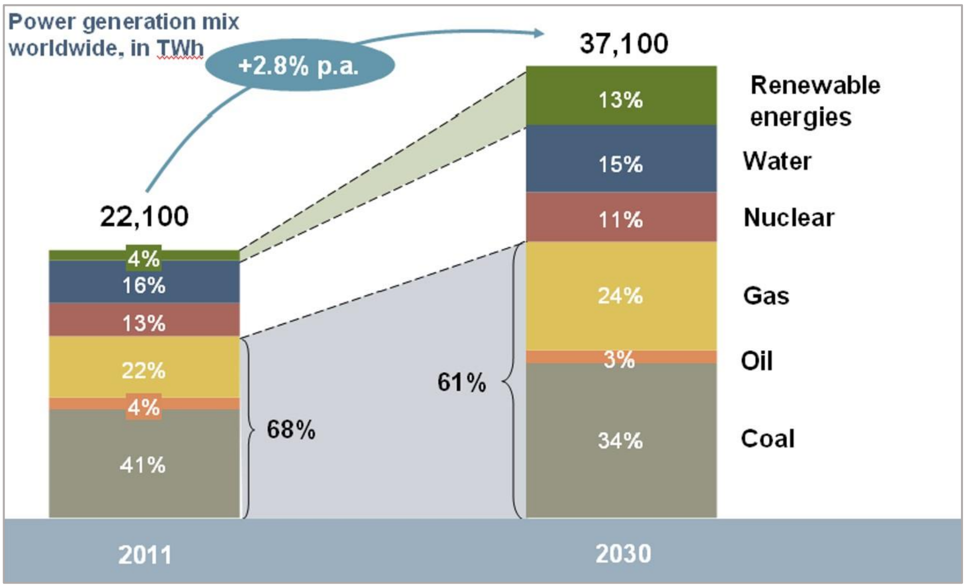


Figure 1-1: Forecast of the global electricity market to 2030 (Vortmeyer et al., 2013).

Power plants that are fuelled by coal mostly use steam-driven turbines for electricity production and the typical flue gas from the boiler contains low to moderate (13 – 15 vol %) concentrations of CO_2 (Anderson and Newell, 2003, Gupta *et al.*, 2015). While coal-fired power generation emits the largest share of the CO_2 emissions in the energy generation sector, gas-fired power stations contribute a smaller, but still significant, fraction. Other key industrial sectors, especially iron and steel production, cement manufacture, petroleum refineries and the petrochemical production industries (Kuramochi *et al.*, 2012), also contribute significantly to CO_2 emissions. The power generation sector and industrial sectors that make use of large amounts of heat or steam derived from fossil fuel combustion are prime candidates for large-scale CO_2 capture (Anderson and Newell, 2003).

The manufacture of iron and steel is one of the most energy intensive processes in the world, accounting for a reasonable portion (approximately 20%) of industrial CO_2 emissions (Zero Emissions Platform, 2013). A combined iron and steel manufacturing process consists of coking, iron ore agglomeration, a blast furnace, a basic oxygen furnace and final product manufacturing (Kuramochi *et al.*, 2012). The majority of CO_2 emissions originate from the direct combustion of fossil fuels, with a smaller portion arising from the oxidation of coke in the blast furnace. In cement manufacture, on the other hand, about half of the CO_2 emissions is due to the calcination of lime stone to produce clinker. CO_2 emissions also arise from fossil fuel combustion due to high energy requirements. The concentration of CO_2 in flue gas from this industry is relatively high (33%) due to the combination of emissions from the raw materials and significant energy requirement (Anderson and Newell, 2003, Kuramochi *et al.*, 2012).

There are various processes in petroleum refineries that emit CO_2. The majority result from energy generation by combustion of waste products such as coke or petroleum fuel, carbonaceous fuels or natural gas. The remaining CO_2 emissions come from non-combustion processes such as the production of hydrogen and the gasification of petroleum residues or waste products. CO_2 emissions primarily arise from energy production in steam boilers, but also arise from other production processes that use fossil fuels, such as the production of hydrogen (Anderson and Newell, 2003). Of all the processes in the petrochemical sector, the production of ethylene is considered to be the largest contributor to the sector's total CO_2 emissions (Kuramochi *et al.*, 2012). Other major contributors include processes for the production of propylene, butadiene and benzene (Anderson and Newell, 2003).

It is clear that the combustion of carbonaceous fuels plays a huge role in the industries mentioned. Although alternative processes that decrease combustion may be possible in some cases (such as large-scale energy production by renewable energy sources), these are often difficult and uneconomical to implement. In some cases however, no alternative to fossil fuel combustion exists. Where the use of coal for combustion is sustained, methods need to be implemented to capture and store carbon before it is emitted (Hansen *et al.*, 2008).

There are currently three methods by which carbon can be captured. These are known as post-combustion capture, pre-combustion capture and oxy-fuel combustion (which is discussed further in section 2.1). Post-combustion capture (PCC) of CO_2 by chemical absorption using amine solvents is currently favoured; but innovative research suggests that there is ample scope for improving this technology. Since next generation alternatives still have long lead times, capture by amines is generally considered the best option available in the short to medium term (Gammer, 2016, Dutcher *et al.*, 2015, Rochelle, 2009, Veawab *et al.*, 2001, Duke *et al.*, 2010).

Currently, for PCC by chemical absorption with amines, monoethanolamine (MEA) is the benchmark solvent, favoured due to its fast kinetics with CO_2 and its low cost. It does, however, have many drawbacks, which has led to investigations into more suitable amine solvents for CO_2 capture purposes. When choosing chemical solvents for PCC the main goal is to reduce the energy requirements in the desorption column. There are however additional factors to consider, such as cost of solvent and its physical properties.

The final stage of CO_2 capture is also an area of research, generally conducted separately from research about the CO_2 capture process. After the CO_2 is captured, it is compressed and transported via pipeline to storage reservoirs. Examples of reservoirs that are currently investigated for possible storage of captured CO_2 are depleted oil and gas fields, deep saline aquafiers, unmineable coal beds and even the ocean (Anderson and Newell, 2003). Captured CO_2 may also be utilized instead of stored. A few options for CO_2 utilization include usage in the food and cement industries, for enhanced oil recovery (EOR) or for the production of products such as fuels, chemicals and plastics (Chiang and Pan, 2017). Storage and utilization of the CO_2 after capture is an important developed research area. This investigation focuses on the capture of CO_2 via amine absorption only.

1.2 THIS INVESTIGATION

The aim of this investigation is to assess the performance of amine solvents and solvent blends relative to 2-amino-2-methyl-1-propanol (AMP), based on results obtained from a performance indicator model developed by Daya (2017). This study uses the results obtained from ASPEN Plus® process simulations for the absorption of CO_2 using aqueous amine solvents.

The objectives of this investigation include:

1. Determining which solvents are the most suitable for CO_2 capture based on their price and physical properties
2. Modifying the Aspen Plus simulation developed by Daya (2017), based on the flue gas feed from a coal-fired power plant and changing the column internals.
3. The results obtained from the simulations were entered into the performance indicator model, developed by Daya (2017), to assess the performance of the solvents investigated on a cost basis, considering a wide array of factors pertinent to CO_2 capture.

4. Modifications to the process configurations were identified and implemented to reduce the energy requirement and optimise the overall rating obtained from the performance indicator model.

The method of post-combustion capture in a coal-fired power plant was chosen for this investigation. In the work of Daya (2017), the performance indicator was developed to predict solvent performance in both the coal- and gas-fired power industries, as well as in the cement manufacturing industry, however the model parameters obtained for the coal-fired power plant case were better justified and supported by the literature than for the other two cases. Furthermore, CO_2 emissions from coal-fired power plants make up a significant fraction of the world's total anthropogenic CO_2 emissions, hence CO_2 capture from these power stations have the possibility of considerably reducing atmospheric CO_2 emissions. By focusing on only one type of industry also allowed for the evaluation of a greater variety of solvent blend compositions; solvent blends containing three, rather than only two amine components were also considered in this study.

Solvents were selected based on criteria that are important to the absorption process for CO_2 capture. Solvents for which data relative to CO_2 capture are available, were ranked by considering properties such as price, heat of absorption of CO_2 and physical properties: density, viscosity, surface tension and vapour pressure. The top-ranked solvents were chosen for further investigation by simulation using Aspen Plus®.

The simulation developed in Aspen Plus is a base model – the solvents used in the simulation are "dropped into" the existing model, hence the equipment specifications remained unchanged for each solvent investigated. The results obtained from the Aspen simulations are used as inputs to the performance model to determine a rating for each solvent relative to a benchmark solvent. The Aspen Plus simulation software is thus used as a tool to obtain the final result, which is a performance rating.

The major factors considered in the performance model were: cost of solvent, cost of utilities, the costs of corrosion inhibitors, reclamation and disposal, and carbon taxes. In this investigation, the performance indicator model has been used to assess amine solvents and blends not included in the study of Daya (2017), thereby increasing knowledge on the range of potential solvents available relative to the conventionally used monoethanolamine (MEA), as well as the benchmark of this study, AMP.

The performance indicator model was further extended by evaluating different process configurations for CO_2 capture by amine absorption. The best performing solvents or blends, according to the performance model, were applied in alternative configurations: intercooled absorber (ICA) and rich solvent split (RSS). These configurations, as demonstrated in the literature, show increased performance for CO_2 capture compared to the conventional process. The results from this further investigation should reveal whether alternative, modified process configurations perform better when all the factors included in this performance indicator are considered.

This thesis is structured as follows: Chapter 1 gives a general introduction to CO_2 capture which includes an overview of the industries with a potential for CO_2 capture installations. An overview of the work performed during this investigation is also included. Chapter 2 firstly presents information on CO_2 capture procedures. This includes descriptions of CO_2 capture technologies (pre-, post- and oxy-fuel combustion) as well as CO_2 capture methods and materials, with emphasis on CO_2 capture by absorption with amine solvents. Secondly, process simulation studies and process modification studies performed in the literature (for CO_2 absorption by amines) is summarized. Chapter 3 gives an explanation of the Aspen Plus® simulation setup and the methods and equations used for data analysis. Descriptions and technical details of the equipment in the Aspen flowsheet is presented. A brief explanation of the performance indicator model originally developed by Daya (2017), including an outline of the factors used as well as model equations, is also presented. Chapter 4 presents the results, and a discussion, of the work performed in this study. The method of choosing the amine solvents, simulation validation, main simulation results and results obtained from the performance indicator model are presented. Chapter 5 and 6, respectively, concludes the thesis and gives recommendations for further work.

CHAPTER 2

2 CO$_2$ CAPTURE TECHNOLOGIES AND SIMULATION STUDIES

According to the Zero Emissions Platform (2013), carbon capture is "*the most important new technology option for reducing direct emissions in industry*". Without its implementation in industry, the proposed limit of a 2 °C temperature rise will not be achieved. Before turning to the main focus of post-combustion CO$_2$ capture, the various methods by which carbon can be currently captured, as well as the technologies used, will first be outlined, to contextualise this study.

2.1 TYPES OF CARBON CAPTURE

2.1.1 POST-COMBUSTION CO$_2$ CAPTURE

Post-combustion capture refers to capturing the CO$_2$, after it has been produced by conventional combustion, and before it can be released into the atmosphere. The process is shown in figure 2-1. The flue gas resulting from combustion is available at low pressure (~ 1 bara) and has a CO$_2$ content of 7 – 8% for gas-fired and 13 – 15% for coal-fired power plants (Feron and Hendriks, 2005, Mondal *et al.*, 2012).

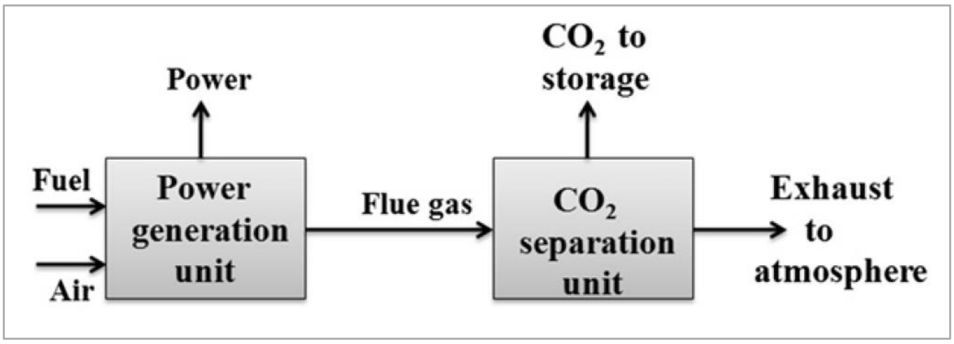


Figure 2-1: Diagram depicting a post-combustion capture process (Mondal et al., 2012).

Post-combustion CO$_2$ capture has been recognised as being the most cost-effective means for retrofitting to existing power plants. Impurities contained in post-combustion flue gas include oxides of nitrogen (NO$_x$) and sulphur (SO$_x$), as well as other sulphur compounds and particulate matter, plus large amounts of dust and incondensable gases. Due to the presence of these flue gas components, chemical absorption is considered by many to be the best capture technique for post-combustion processes; other capture technologies such as adsorption or membranes are not suitable for operation under these conditions of low CO_2 concentration in the presence of harmful impurities. Another reason why chemical absorption is considered the best option compared to other capture technologies, is due to the relatively low CO_2 content in the gas stream, which can be more efficiently removed by chemical, rather than physical, methods (Kanniche *et al.*, 2010, Mondal *et al.*, 2012).

For all of the reasons stated above, post-combustion capture processes are among the most mature of the capture methods and a number of pilot plants have been operated on a small scale. However, the successful upscale to industry-sized plants remain a challenge. Other major challenges to the implementation of post-combustion technology include a relatively low capture efficiency and energy penalty associated with solvent regeneration (Leung *et al.*, 2014).

2.1.2 PRE-COMBUSTION CO_2 CAPTURE

In pre-combustion CO_2 capture, the combustion fuel is converted to a syngas mixture of CO and H_2 prior to combustion via a gasification (for coal) or reforming (for natural gas) process. The syngas subsequently undergoes a water-gas shift reaction through the addition of steam, which forms more H_2 and converts the CO to CO_2 (Yang *et al.*, 2008, Leung *et al.*, 2014). Figure 2-2 shows an illustration of the pre-combustion process. The final gas mixture is at a higher pressure (15 – 40 bar) and contains mostly CO_2 (15 – 40%) and H_2, but other impurities, especially sulphur compounds, may also be present (Feron and Hendriks, 2005).

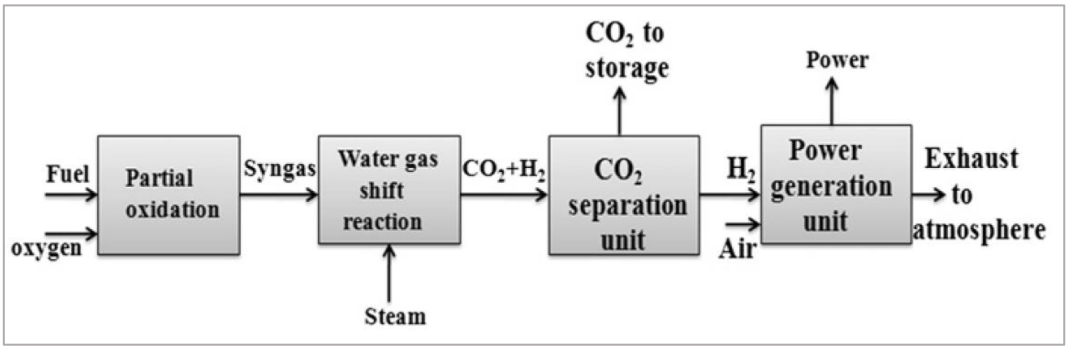


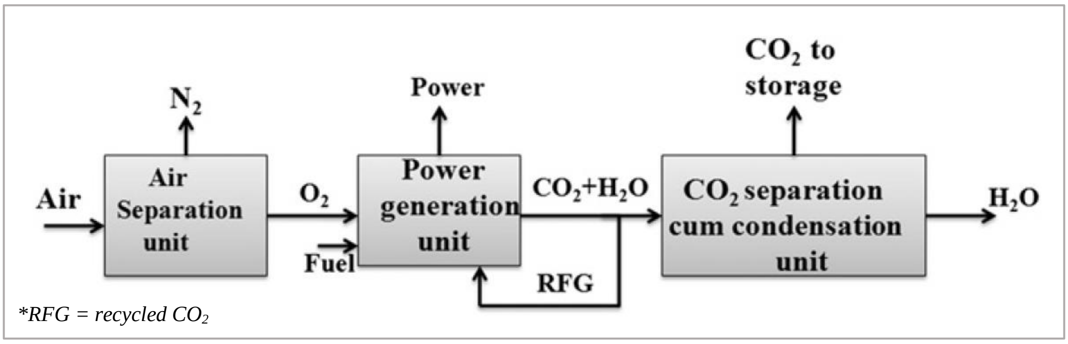
Figure 2-2: Diagram depicting a pre-combustion capture process (Mondal et al., 2012).

Low-cost physical solvents are a popular means to separate CO_2 and H_2 in a pre-combustion process, where the CO_2 is absorbed at high pressure and in turn released by means of pressure reduction (Mondal *et al.*, 2012). Other technologies that could also be used for pre-combustion capture include absorption with chemical solvents, adsorption, membranes, cryogenic distillation or gas hydrates (D'Alessandro *et al.*, 2010).

Pre-combustion capture is generally less expensive than post-combustion capture, because the physical solvents utilised are available at low cost and require less energy for regeneration (than chemical solvents); the concentration of CO_2 in the feed stream is also higher, thus increasing the efficiency of the capture process (Mondal *et al.*, 2012). However, a significant disadvantage of pre-combustion capture is the difficulty associated with constructing the capture plant upstream to the turbine (Mondal *et al.*, 2012). Pre-combustion capture units are therefore not easily retrofitted to existing power plants and are better suited for newly built power stations or Integrated Gasification Combined Cycle (IGCC) processes (Spigarelli and Kawatra, 2013).

2.1.3 OXY-FUEL COMBUSTION

Oxy-fuel combustion is a modification of the conventional combustion process, employing an oxygen-rich stream (> 95%), instead of air, to facilitate combustion of the fuel (Mondal *et al.*, 2012). Before combustion, the oxygen must be separated from an air stream in an air separation unit (ASU), which could be an energy-intensive process. An ASU can employ cryogenic distillation, adsorption or membrane technologies to facilitate the separation. Currently, the only technology proven to be viable at the scale required for power production is cryogenic separation, which requires up to 15% of the electricity generated by the power plant to operate (Spigarelli and Kawatra, 2013). A diagram depicting this process is shown in figure 2-3.



**RFG = recycled CO_2*

Figure 2-3: Diagram depicting the oxy-fuel combustion process (Mondal et al., 2012).

The oxygen rich-stream obtained from the ASU is mixed with recycled CO_2 to reduce the oxygen flame temperature from 3500 °C to about 1300 – 1400 °C for retrofitting to existing power plants, or at least 1900 °C for new oxy-combustion instalments. To reach this level of temperature reduction, the mixed gas stream should consist of 65 – 70 % CO_2, with an oxygen content of only 30 – 35 %; this is achieved by employing a CO_2 recycle (RFG). The flue gas resulting from this modified combustion process consists mainly of CO_2 (75 – 80%) with the balance mostly H_2O; impurities such as NO_x, SO_x and particulate matter are also present in trace amounts. After cleaning of this flue gas stream to remove the impurities and water vapour, a CO_2-rich stream about 80 – 90 % pure is obtained; this stream must be dried further before compression and transportation (Spigarelli and Kawatra, 2013).

A major advantage of oxy-fuel combustion is the absence of nitrogen, which significantly reduces the formation of NO_x. Disadvantages of this technology include the energy penalty of the ASU, high cost of cleaning the “flue gas” stream and the difficulty of retrofitting to existing plants (Spigarelli and Kawatra, 2013). Furthermore, while oxy-fuel combustion has been demonstrated at pilot plant scale, extensive additional research is required before a fully operational industrial-scale oxy-combustion setup can be established (Kothandaraman, 2010).

2.1.4 CHEMICAL LOOPING COMBUSTION

Chemical looping combustion (CLC) is similar to oxy-fuel combustion in that pure oxygen is used during fuel conversion and the flue gas produced consists mainly of CO_2 and H_2O. Unlike oxy-fuel combustion however, CLC utilizes O_2 obtained from metal oxides rather than from an air separation unit (Leung *et al.*, 2014).

The chemical looping process consists of successive reduction and oxidation reactions in respective reaction vessels. In the first reactor, known as the reduction reactor or fuel reactor, the metal oxide is reduced when it reacts with the fuel. This reduced product then goes to the second reactor, known as the oxidation reactor, where it is oxidised, and then recycled to the first reactor. Combining the reactions occurring in both reactors produces an overall reaction corresponding to the combustion of the fuel (Kothandaraman, 2010), as shown in Figure 2-4.

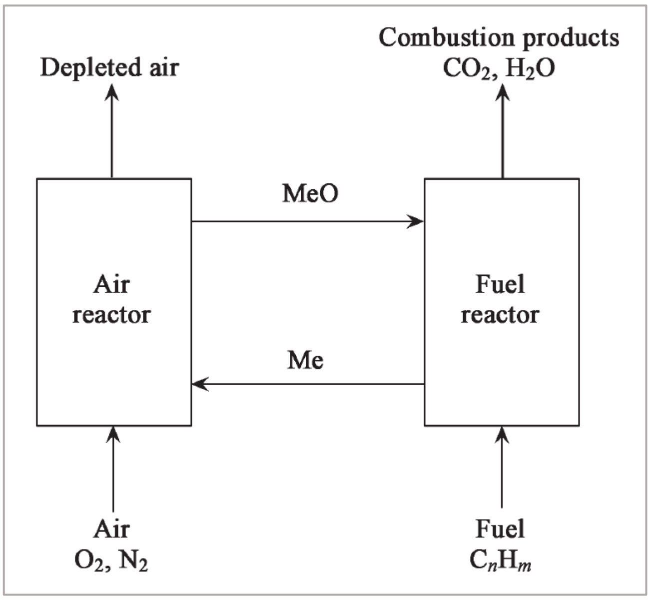


Figure 2-4: Diagram depicting the chemical looping combustion process (Yang et al., 2008).

The CO_2 and water produced can easily be separated by condensation, which eliminates the need for energy intensive separation equipment. Another advantage from a cost viewpoint is the availability of a large collection of low-cost metal oxides which are suitable for use in CLC (Leung *et al.*, 2014). Other advantages include the flexibility of the process in terms of fuel type (any carbonaceous fuel in any physical state can theoretically be used) and the restricted formation of NO_x, which is a result of the indirect contact between oxygen and fuel, as well as the moderate temperature conditions under which the oxidation reaction is able to proceed (Yang *et al.*, 2008, Spigarelli and Kawatra, 2013).

In contrast, the main drawback of this process is the lack of demonstrations or pilot plant operations to evaluate the feasibility of this technology on a larger scale (Kothandaraman, 2010). Although this technology appears very promising for CO_2 capture, there are many hurdles that must be overcome before it can be implemented for this purpose.

2.1.5 PROCESS OF CHOICE

Post-combustion capture (PCC) has been chosen for this investigation as it is considered to be the most viable option because it can be retrofitted to existing plants. Pre-combustion and oxy-fuel combustion technologies do not share this advantage. In the case of power plants, which is the focus of this investigation, the PCC plant is located after the main boiler, hence the generation of power can proceed unhindered if the capture section of the plant is malfunctioning. Nonetheless, adding a PCC plant requires a capital investment similar to that of the original facility and its operation could consume up to 20% of the power plant's energy output. Ideally, a lot less energy is required to capture the desired amount of CO_2. However, practical operation of these separation process, especially at larger scales, causes inevitable energy losses. These findings indicate the extent in the need to improve PCC technology (Gammer, 2016).

2.2 CO_2 CAPTURE TECHNOLOGIES

Within the CO_2 capture methods (pre-, post- and oxy-combustion), different capture technologies may be applied. Figure 2-5 outlines which technologies are suited for the different methods. Absorption, more specifically chemical absorption, is central to this investigation.

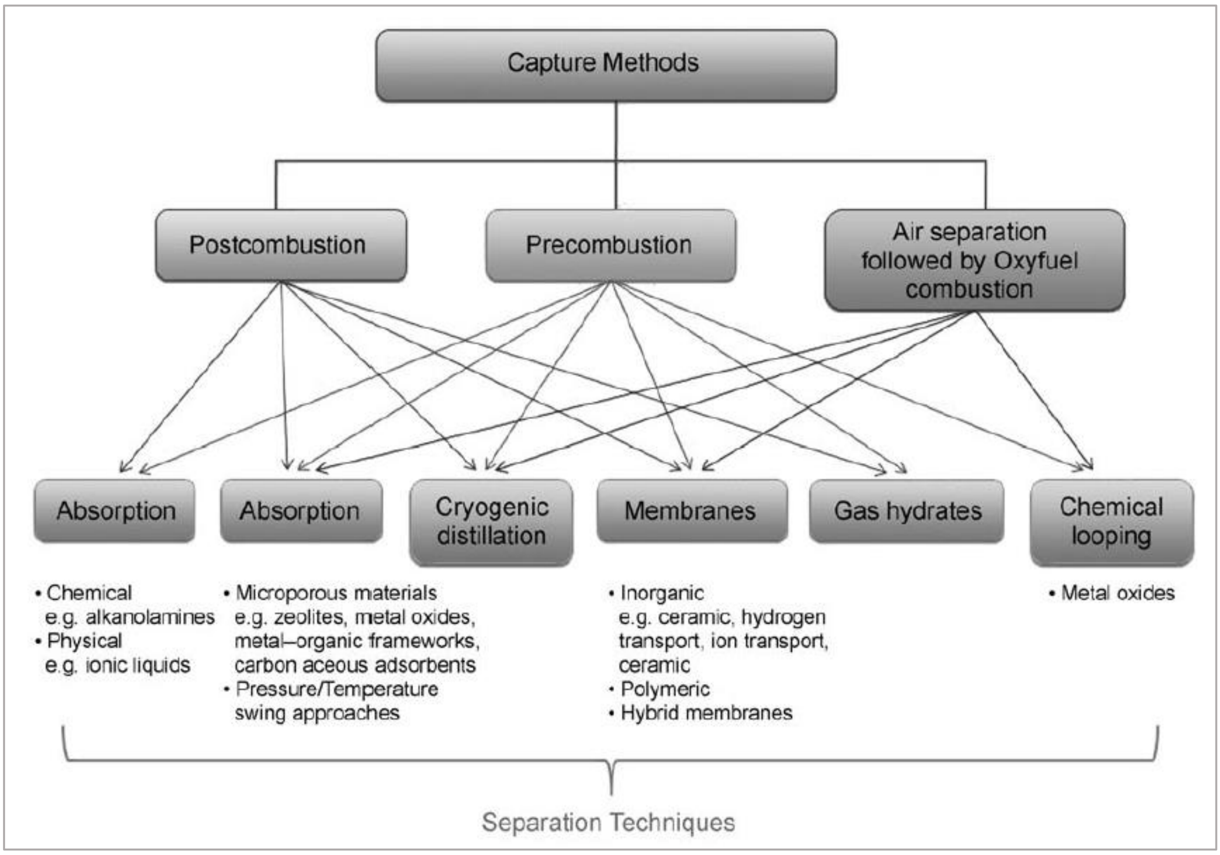


Figure 2-5: Capture technologies in relation to the various capture methods (D'Alessandro et al., 2010).

2.2.1 ABSORPTION

Both chemical and physical absorption methods are widely used in industry for the separation of CO_2 and acid gases from gas streams. During the absorption process, atoms, molecules, and ions from the gas stream are taken up into the bulk solvent phase (liquid), either chemically or physically.

Physical absorption of CO_2 usually depends on the pressure and temperature conditions of the gas stream and process, whereas chemical absorption of CO_2 relies on an acid-base neutralization reaction (Mirzaei *et al.*, 2015). Common physical absorbents include Selexol, Rectisol, Purisol and Fluor solvents; the chemical absorption process generally utilizes ammonia or amine solvents (Mirzaei *et al.*, 2015). Dual-alkali absorption and sodium carbonate slurry absorption are also possible chemical choices (Spigarelli and Kawatra, 2013). In chemical absorption, the CO_2-containing flue gas is introduced into the bottom of an absorption column, while the solvent is introduced at the top, to flow counter-currently with the gas stream. The solvent, which selectively absorbs CO_2, is then sent to a stripping column where it is regenerated and recycled back to the absorber. The desorbed CO_2 is compressed and stored (Mondal *et al.*, 2012). Solvents used for chemical absorption, which is the focus of this study, is further discussed in section 2.3.

2.2.1.1 PROCESS CONFIGURATION MODIFICATIONS

Significant energy savings could be achieved by improving the process configuration for CO_2 capture by absorption. Multiple process configurations have been proposed to improve CO_2 capture by amine absorption. As outlined in Le Moullec *et al.* (2014), all proposed process modifications can be grouped into the following categories: absorption enhancement, heat integration and heat pumps. Modifications in the absorption enhancement category facilitates an increase of the CO_2 loading at the bottom of the absorber. As a result, the required solvent flow rate for a given capture rate is reduced, which in turn causes a decrease in reboiler duty. Heat integration processes aim to integrate the heat between the different process streams of the capture plant, which ultimately causes a reduction in the reboiler duty. Process modifications which employ heat pumps on the other hand, requires additional mechanical work to increase the heating quality. This enables valorisation of heat at too low qualities and is most effective for use where increasing the heat quality level is profitable (Le Moullec *et al.*, 2014). Figure 2-6 shows how individual modifications are grouped into these categories.

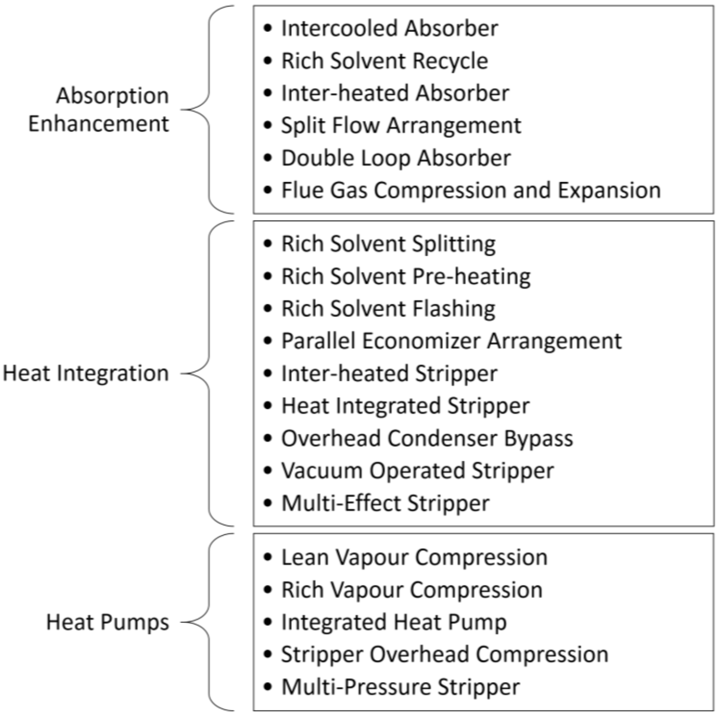


Figure 2-6: Depiction of the main categories of proposed process modifications and how individual modifications are grouped within these categories, as discussed by Le Moullec et al. (2014).

The focus of this latter part of the study was to identify the process modifications from the literature which provided adequate to significant improvement with minimal equipment modifications. The most suitable modifications that fit this description are the intercooled absorber (ICA), rich solvent split (RSS) and lean vapour compression (LVC) configurations. These are discussed in more detail in the sections which follow. The remaining alternative configurations are explained briefly in Appendix A.

2.2.1.1.1 Intercooled Absorber

When the intercooled absorber modification is applied, a fraction of the solvent in the absorber is withdrawn, cooled down, and then sent back to the absorber (Le Moullec *et al.*, 2014). This is depicted in figure 2-7 (the changes from the conventional configuration is shown in colour). In some cases, the fractional solvent stream is removed from a stage in the upper section of the absorber and returned to a stage in the bottom section. In others, the solvent is removed from, and returned to, the same stage, usually towards the bottom of the column.

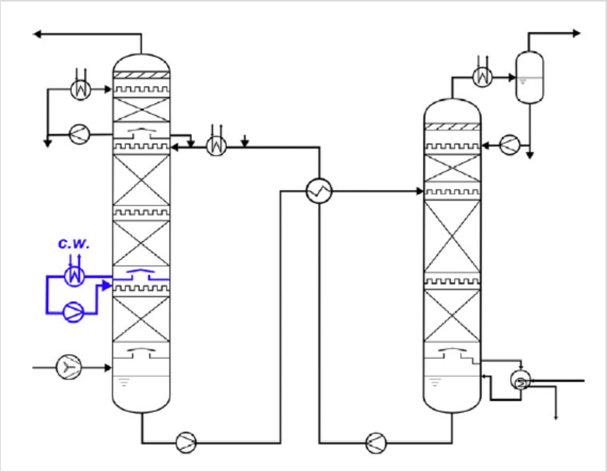


Figure 2-7: The intercooled absorber configuration (Le Moullec et al., 2014).

This modification enables an increase in the rich loading i.e. the working capacity of the solvent. The solvent flow rate required to absorb the desired amount of CO_2 is thus decreased, which further results in a reduction of the required equipment size as well as the steam demand of the reboiler (Ahn *et al.*, 2013, Le Moullec *et al.*, 2014).

When using MEA as a solvent, the savings in reboiler duty compared to the conventional process configuration, ranged from low, 1.4% - 3% (Oh *et al.*, 2016, Le Moullec and Kanniche, 2011a, Schach *et al.*, 2010) to medium, 6.4% - 11.6% (Cousins *et al.*, 2011a, Xue *et al.*, 2016, Ahn *et al.*, 2013) to a high value of 55% (Damartzis *et al.*, 2016). For AMP as solvent, Neveux *et al.* (2013) reported a 3% reduction in total equivalent work, while Damartzis *et al.* (2016) claimed a 55% saving in reboiler duty. Using solvent blends in the ICA configuration showed a 6.7% decrease in total energy usage for AMP+PZ (Zhang *et al.*, 2017), and an approximate 12.6% reduction in both total energy and reboiler duty for MDEA+PZ (Zhao *et al.*, 2017). Refer to table A-3 in appendix A for further details on studies of the ICA modification.

It seems likely that savings in energy for the ICA configuration would lie in the medium range (3% – 12%), since only Damartzis *et al.* (2016) reported very high savings (in the range 20% - 50%) and only Oh *et al.* (2016) reported very low savings (~1%). The theoretical energy savings that can be achieved with the ICA configuration is reasonable, considering that only minor changes to the equipment and process setup are required for its implementation.

2.2.1.1.2 Rich Solvent Splitting

For the rich solvent split (RSS) modification, the rich solvent stream exiting the absorber is divided into two flows. One of these streams is preheated as usual by the rich/lean heat exchanger, while the other stream remains cold. The cold stream enters the stripper at the top whilst the heated stream is injected at an appropriate location below. The optimum injection height of the heated stream becomes lower in the column as the stream temperature increases. The application of this arrangement causes the stripper temperature profile to smoothen out and maximises the heat recovered from the hot lean solvent and the stripper overhead (Le Moullec *et al.*, 2014).

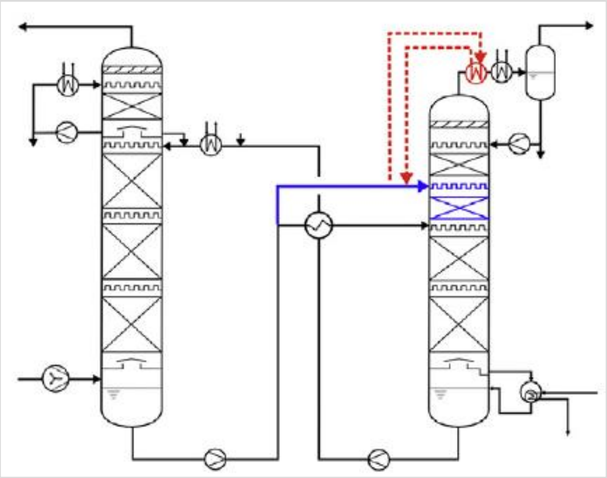


Figure 2-8: The rich solvent split configuration (Le Moullec et al., 2014).

The literature findings mostly show reboiler duty savings in the range 7% - 12% (Cousins *et al.*, 2012, Xue *et al.*, 2016, Cousins *et al.*, 2011a, Karimi *et al.*, 2011, Le Moullec and Kanniche, 2011a) when MEA is used as solvent. Total energy savings are in the 4% - 6% range (Xue *et al.*, 2016, Oh *et al.*, 2016, Neveux *et al.*, 2013). For AMP, a 6% reduction in equivalent work was reported by Neveux *et al.* (2013), and Zhang *et al.* (2017) stated a 8.5% total energy saving for an AMP+PZ blend. When considering a MDEA+PZ blend, Zhao *et al.* (2017) found a 4.7% decrease in reboiler duty, while Ehlers *et al.* (2014) showed a 15.4% reduction in total heat duty for a proprietary solvent with similar properties to MDEA+PZ. More information on studies of the RSS process modification is presented in table A-3 (appendix A).

The energy savings reported in the literature for the RSS configuration are comparable to each other, and these results can thus be assumed to be reliable. The total energy savings that can theoretically be achieved with the RSS configuration (4 – 15%) is satisfactory, and substantiates further investigation into this modification.

2.2.1.1.3 Lean Vapour Compression

The lean vapour compression modification requires the addition of a flash vessel through which the lean solvent exiting the bottom of the stripper passes in order to produce a gaseous stream composed of mainly H_2O and CO_2. This stream is compressed and fed back to the stripper, thereby reducing the reboiler steam demand (Le Moullec *et al.*, 2014). Figure 2-9 shows this modification (the changes from the conventional configuration is shown in colour).

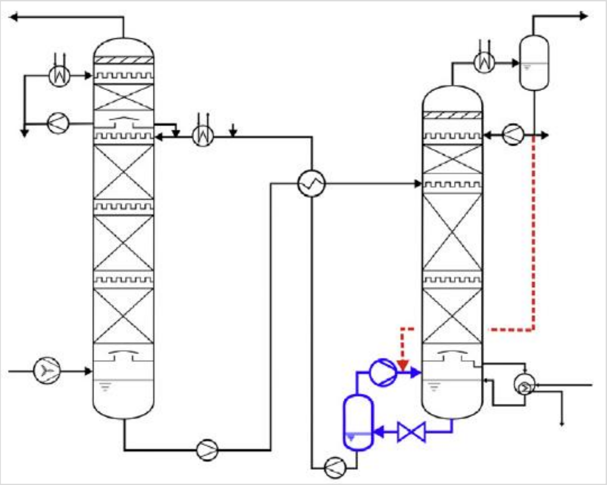


Figure 2-9: The lean vapour compression configuration (Le Moullec et al., 2014).

The LVC modification is one of the more popular modifications investigated in the literature. Simulation studies in the literature suggest that utilizing the LVC configuration with MEA can lead to a reduction of 1.4 – 11.6% in total energy requirements (Le Moullec and Kanniche, 2011b, Van Wagener and Rochelle, 2011, Cousins *et al.*, 2011b, de Miguel Mercader *et al.*, 2012, Ahn *et al.*, 2013). When considering reboiler duty only, energy savings between 13% and 28% can be achieved (Cousins *et al.*, 2011b, Karimi *et al.*, 2011, Le Moullec and Kanniche, 2011a, de Miguel Mercader *et al.*, 2012, Sanchez Fernandez *et al.*, 2012, Ahn *et al.*, 2013). There is however only a 7.6% reduction in total equivalent work reported by Neveux *et al.* (2013); this is due to the additional compression work required for this modification.

For a proprietary solvent with properties similar to a MDEA+PZ blend, Ehlers *et al.* (2014) claimed a 13.6% reduction in required heat duty, while Zhang *et al.* (2017) reported that using the LVC modification with a AMP+PZ blend requires 2.9% more total energy than the conventional configuration (this is once again probably due to the additional energy required for compression). Refer to table A-3 in appendix A for additional information on studies of LVC configurations.

2.2.2 ALTERNATIVE CAPTURE TECHNOLOGIES

Apart from absorption, there are other technologies used and currently being investigated for CO_2 capture. These do not form part of this investigation, but are briefly outlined below to contextualise the choice of chemical absorption. Examples of these include adsorption, cryogenic distillation, membranes and gas hydrates.

In an adsorption process, CO_2 molecules are removed from the flue gas stream when they adhere to the solid surface of the adsorbent. Cryogenic distillation makes use of the dew and sublimation points of CO_2 to physically separate it from the rest of the gas stream. Membranes, on the other hand, make use of the CO_2 molecule shape and size or the partial pressure of CO_2 in the gas stream to separate it from the other gaseous components present. Gas hydrate technology, the most recent technology of these mentioned here, facilitates the capture of CO_2 by trapping it within a solid crystalline structure.

Brief descriptions of these alternative technologies are presented in Appendix B.

2.3 POST-COMBUSTION CO_2 CAPTURE BY CHEMICAL ABSORPTION

Amine solvents are among the most popular chemical absorbents for CO_2 capture purposes. Amine absorption is usually facilitated by two columns, an absorber and a stripper. The absorption of CO_2 into the solvent occurs in the absorber at a temperature of approximately 40 °C. The solvent loaded with CO_2 is then sent to the stripper for regeneration. Regeneration generally occurs at temperatures exceeding 100 °C. Steam is used to provide the energy required to break the chemical bonds between the CO_2 and solvent. The CO_2 recovered is compressed and sent to storage. The regenerated solvent, containing a small amount of CO_2, is recycled to the absorber.

2.3.1 AMINE-BASED SOLVENTS

Amines are derivatives of ammonia, where one or more of the hydrogen groups have been substituted with other functional groups (Spigarelli and Kawatra, 2013). Amines with an alcohol functional group are known as alkanolamines, and they have been identified as promising solvents for CO_2 capture. Alkanolamines may be classified as primary, secondary or tertiary, depending on the position of the alcohol functional group. Common alkanolamines for CO_2 capture applications include primary alkanolamine monoethanolamine (MEA), secondary alkanolamine diethanolamine (DEA) and tertiary alkanolamine methyldiethanolamine (MDEA). MEA is the most commonly used, mainly due to its low cost, and is often used as the benchmark to assess other amine solvents. (Spigarelli and Kawatra, 2013).

Advantages of using alkanolamines or other amine-based solvents include their ability to handle streams with a low CO_2 concentration, and the maturity of the process. There are however various disadvantages related to the use of amine-based solvents. These include high energy requirements for regeneration, incomplete solvent regeneration, substantial solvent losses and degradation, and equipment corrosion. Furthermore, the scale-up of the amine absorption process to an industrial power plant capacity, is proving to be problematic due to reasons discussed (Spigarelli and Kawatra, 2013).

A literature review of aqueous amine solvents in relation to CO_2 solubility revealed a sizeable list of previously studied amines in aqueous form. Some of these are quite novel to CO_2 solubility research and not all of them revealed favourable CO_2 solubility results. The most commonly investigated (or popular) amines for CO_2 solubility in the period from 1990 to date, are 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA), N-methyldiethanolamine (MDEA), monoethanolamine (MEA) and piperazine (PZ). Figure 2-10 shows the structures of these amines.

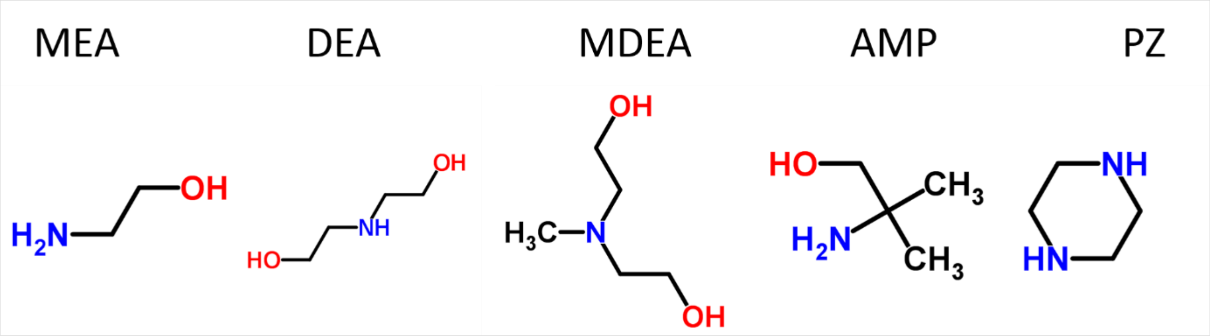


Figure 2-10: Structures of the most common amines investigated in the literature.

Table 2-1: Physical properties of the most common amines.

Property	**MEA**	**DEA**	**MDEA**	**AMP**	**PZ**
Chemical formula	C_2H_7NO	$C_4H_{11}NO_2$	$C_5H_{13}NO_2$	$C_4H_{11}NO$	$C_4H_{10}N_2$
Molecular weight	61.09	105.14	119.17	89	86.136
Melting point (°C)	10	28	−21.00	31	106
Boiling point (°C)	170	217	247	165	146
pKa (@ 25°C)	9.5	8.96	8.52	9.7	9.73
Vapor pressure (mmHg @ 20°C)	0.36	0.01	0.1	<0.10	0.8
Water solubility (wt.% @ 20°C)	Full	96.4	Full	35	15

* Data for MEA, DEA, MDEA and AMP sourced from a table compiled by (Padurean *et al.*, 2011). Data for PZ obtained from the online open chemistry database, Pubchem.

Monoethanolamine (MEA) is the most used alkanolamine solvent for the removal of CO_2 by chemical absorption (Abu-Zahra *et al.*, 2013). It is especially popular where CO_2 is present in low concentrations and in the absence of sulphurous contaminants like COS and CS_2. When MEA reacts with COS, CS_2, SO_x or NO_x irreversible heat stable salts are formed, leading to significant chemical losses. MEA is also much more corrosive than many of the other amines used in CO_2 capture applications, limiting the concentration at which the solution can be employed. Concentrations of 12% to 32% (by weight) are common, and 30 wt. % MEA has become the standard for applications where CO_2 is the only acid gas component to be removed and corrosion inhibitors are added to the solvent solution (Kohl and Nielsen, 1997). Other disadvantages of MEA include its high heat of reaction with CO_2, increasing the energy requirements in the stripper, and its high vapour pressure, causing solvent losses by vaporization in the absorber (Kohl and Nielsen, 1997). The conventional use of MEA is not unjustified; however, as it does have properties that are favourable for CO_2 capture applications. The advantages of MEA include its fast reaction rate with CO_2, low cost, and low molecular weight. This means that on a weight basis, solvent capacity is relatively high (Abu-Zahra *et al.*, 2013). Nevertheless, there is consensus in scientific research that the energy requirements for the use of MEA is too high, and thus the ongoing search for superior CO_2 capture solvents.

Diethanolamine (DEA), in aqueous form, has been used for treating refinery gases for many years. It is used especially for gases that contain considerable amounts of COS and CS_2, since secondary amines are less reactive with these impurities than primary amines, and the few reaction products that are produced are not very corrosive. DEA also has a low vapour pressure, which means it can be used in low pressure applications without significant vapour losses. Reclaiming of DEA can however be problematic since vacuum distillation might be required. The main disadvantage of

DEA in the context of CO_2 capture is the fact that DEA, when in contact with CO_2, undergoes irreversible reactions that forms corrosive degradation products. DEA is therefore not an ideal option for treating flue gas with a high concentration of CO_2 (Kohl and Nielsen, 1997).

N-methyldiethanolamine (or methyldiethanolamine) is currently the most frequently used tertiary amine for CO_2 capture research. Tertiary amines do not react directly with CO_2, but rather promote the hydrolysis of CO_2 in aqueous solutions to form bicarbonate and a protonated amine. Reaction kinetics of CO_2 with tertiary amines are however much slower than that of primary or secondary amines. The theoretical equilibrium CO_2 loading of tertiary amines is, however, higher than for primary or secondary amines as one mole of amine reacts with one mole of CO_2 and energy requirements for regeneration are reduced (Abu-Zahra *et al.*, 2013). MDEA has traditionally been used in applications where the selective capture of H_2S is a priority (Kohl and Nielsen, 1997). It has however become popular for use in CO_2 capture due to reduced energy requirements for regeneration, low tendency to degrade or corrode and ability to be used in higher concentrations than MEA (Abu-Zahra *et al.*, 2013). MDEA have been used in blends with other amines such as MEA or DEA to increase its slow reaction rate, while the blend maintains the favourable attributes of MDEA (Kohl and Nielsen, 1997). Blends of MDEA and piperazine (PZ) are also very popular and have been researched extensively (sources can be found in table C-13 of Appendix C).

Piperazine (PZ), a cyclic diamine, has been identified as a promising solvent for CO_2 capture. Due to its fast kinetics with CO_2, it is mainly used as an activator, recognised as "*the most effective would-be accelerator to conventional alkanolamines*" (Kumar, 2013). Another reason for the use of PZ in smaller quantities is its reduced solubility in water, compared to alkanolamines, due to the absence of an OH^- group. However, extensive research (Rochelle *et al.*, 2011) has concluded that piperazine, used in a concentrated, unblended form, could be the next standard for CO_2 absorption studies. Several of the disadvantages of MEA are improved or eliminated by using PZ. PZ is known for its high CO_2 capacity (which is a result of its diamine nature), low susceptibility to oxidative and thermal degradation, and high reaction rate with CO_2 (with kinetics up to ten times faster than MEA) (Abu-Zahra *et al.*, 2013). Other advantages of PZ include its low volatility and non-corrosive nature towards stainless steel. The reclamation of piperazine is also simpler than for MEA; piperazine can be reclaimed by distillation or other commercial gas-treating methods (Rochelle *et al.*, 2011).

2-Amino-2-methyl-1-propanol (AMP) is the sterically hindered form of MEA, and the most common sterically hindered alkanolamine used in CO_2 absorption studies. Sterically hindered amines are classified by alkyl groups attached to the nitrogen atom. The presence of these alkyl groups causes the formation of less stable carbamates, resulting in higher loadings and lower energy requirements for regeneration (effectively combining advantages of primary, secondary and tertiary amines). In addition, advantages include a low degradation rate and corrosivity, and decreased solvent losses and circulation rate. The most notable disadvantage of sterically hindered amines is the slow reaction with CO_2 compared to primary or secondary amines (Abu-Zahra *et al.*, 2013).

A summary of the conditions and results of the experimental CO_2 solubility investigations with these common amines are presented in tables C-1 to C-5 in Appendix C. A summarized version of these tables (with information from all sources combined) are presented in table 2-2.

Table 2-2: Data summary for the common amines.

Aqueous Amine Solvent	Common concentration(s) studied	Temperature range studied (K)	Partial CO_2 Pressure range studied (kPa)	Loading range (mol CO_2/ mol amine)
MEA	30 wt. %	303 – 443	0 – 2500	0 – 0.8
MDEA	30 – 50 wt. %	298 – 373	1 – 1500	0 – 1.5
DEA	20 – 30 wt. %	293 – 393	0 – 3000	0 – 1
PZ	10 – 40 wt. %	293 – 433	0 – 3000	0 – 3
AMP	30 wt. %	293 – 393	0 – 1500	0 – 2.5

In figure 2-11, the plot of CO_2 partial pressure versus CO_2 loading is compared for the common amines (excluding DEA, because DEA was not used in this investigation – refer to section 4.1) at a temperature of 313 K. This is a common temperature at which the solvent enters the absorber for post-combustion CO_2 applications. This graph is a depiction of the solubility data for CO_2 into the amines. On the graph, the markers represent experimental points, measured by various literature sources (refer to the graph's caption for details). The dotted lines represent trend lines inserted for ease of visual comparison, and do not relate to any models used. In such plots, the position and slope of the curves are both important. The position of the data on the graph indicate- how likely CO_2 will be absorbed; if a curve is located in the bottom right quadrant, it indicates that a greater CO_2 loading can be achieved at a lower pressure. A steep slope indicates that the change in loading ($\Delta\alpha$), is small, whereas a flatter, more gradual slope indicates that $\Delta\alpha$ is large. A large $\Delta\alpha$ is desired, as this is an indication of a greater solvent affinity for CO_2 (Li and Rochelle, 2014).

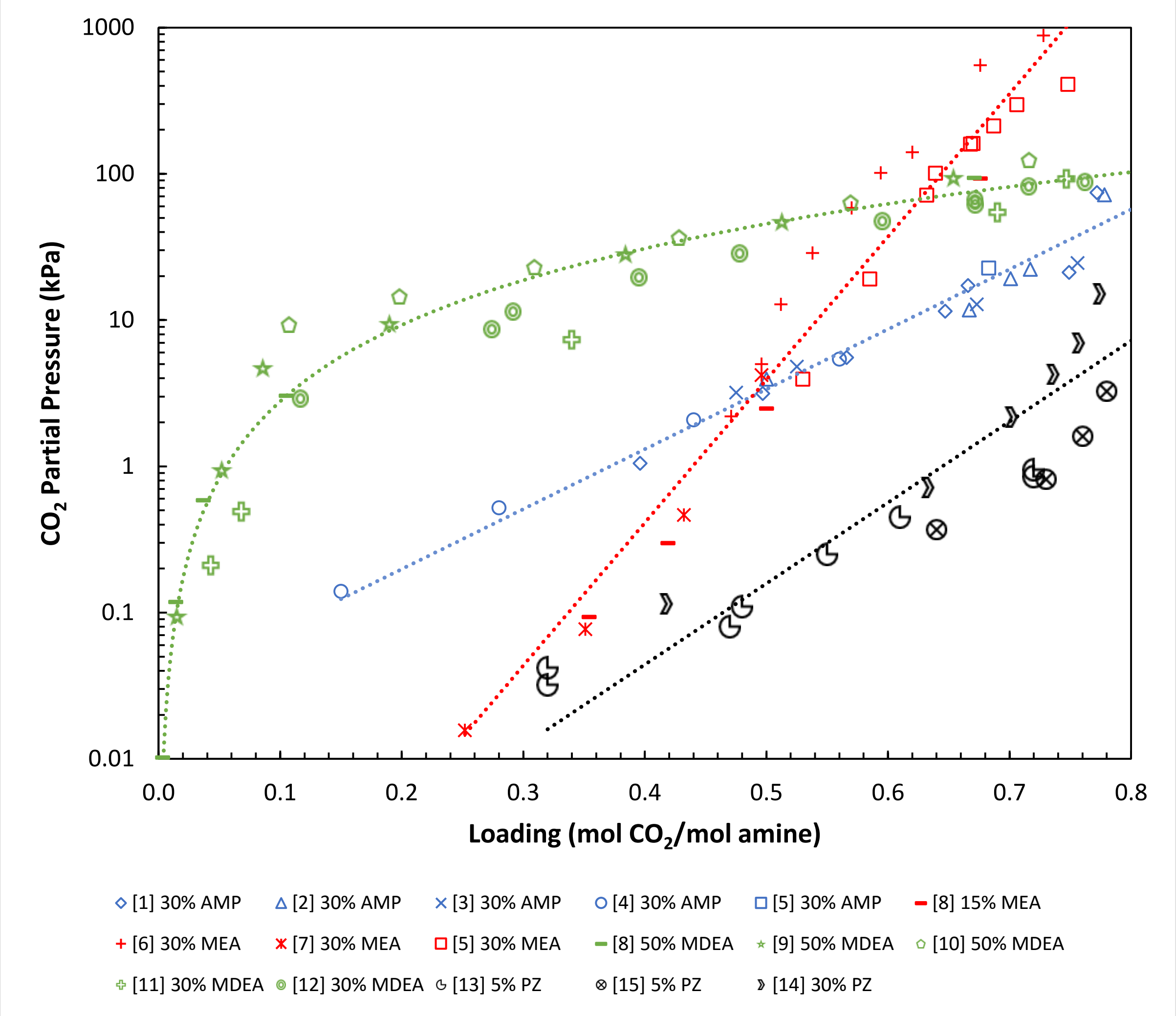


Figure 2-11: P_{CO_2} vs loading for the common amines (T=313K).

Legend (fig. 2-11): Different colours represent different amines; Red = MEA. Blue = AMP. Green = MDEA. Black = PZ. Different markers represent different sources (additionally indicated by numbers); [1] Li and Chang (1994), [2] Seo and Hong (1996), [3] Kundu *et al.* (2003), [4] Chen *et al.* (2011), [5] Tong *et al.* (2012), [6] Shen and Li (1992), [7] Dugas and Rochelle (2009), [8] Austgen *et al.* (1991), [9] Haji-Sulaiman *et al.* (1998), [10] Sidi-Boumedine *et al.* (2004), [11] Jou *et al.* (1994), [12] Dash and Bandyopadhyay (2016), [13] Bishnoi and Rochelle (2000), [14] Dash *et al.* (2011a), [15] Derks (2006), (Dash *et al.*, 2014)

From the curves in figure 2-11, it can be seen that the slopes of MDEA, AMP and PZ are all less steep than MEA, indicating that these solvents have a greater affinity for CO_2 than MEA. The cross of the MEA and AMP curves indicate that at very low pressures, CO_2 will be more easily absorbed by MEA, but as the pressure increases, AMP becomes a better choice for CO_2 capture. The PZ curve, which is most to the right, indicates that CO_2 is the most readily absorbed by PZ. The MDEA curve, while it has a flat gradient eventually (thus a large Δα is possible), has a very steep gradient at first, which indicates that a high pressure is initially required to absorb a small amount of CO_2, also indicative of the slow reaction between CO_2 and MDEA.

Considering these facts, it can be concluded that the common amines, AMP, PZ and MDEA all have a greater affinity towards CO_2 than MEA. However, due to the slow reaction of MDEA with CO_2, it would be more practical to combine it in a blend with a faster reacting amine to ensure increased performance over MEA.

Other single aqueous amines (less commonly) studied for CO_2 solubility are listed in table 2-3.

Table 2-3: A list of promising and novel amines for which CO_2 solubility data is available in the open literature.

Popular and promising solvents	Novel solvents
1-methyl piperazine (1-MPZ)	4-amino-1-butanol (4A1B)
2-methyl piperazine (2-MPZ)	5-amino-1-pentanol (5A1P)
2-(2-aminoethylamino)ethanol (AEEA)	diethylenetriamine (DETA)
2-amino-2-hydroxymethyl-1,3-propanediol (AHPD)	3-dimethylamino-1-propanol (DiMAP)
2-(diethylamino)-ethanol (DEEA)	4-(diethylamino)-2-butanol (DEAB)
diglycolamine (DGA)	N,N,N',N'-tetramethylethylenediamine (TEMED)
diisopropanolamine (DIPA)	2-(2-(dimethylamino)ethoxy)ethanol (DMAEOE)
N-ethyl-ethanolamine (EEA)	1-dimethylamino-2-propanol (DMAP)
hexamethylenediamine (HMDA)	
N-methyl-2-ethanolamine (MAE)	
3-(methylamino)propylamine (MAPA)	
1-amino-2-propanol (MIPA)	
monopropanolamine (MPA)	

HMDA was selected as a promising solvent for CO_2 capture on the basis of its structural features (Singh, 2011). The results of additional studies by Singh *et al.* (2013) as well as Mondal *et al.* (2015), further prove its superiority as a CO_2 capture solvent. A loading of 1.508 mol CO_2/mol amine can be achieved by 30% HMDA at temperatures applicable to absorber operation (40 – 60 °C) (Mondal *et al.*, 2015).

2-(2-Aminoethylamino)ethanol (AEEA), a diamine, has shown a greater CO_2 capacity and reaction rate than MEA, with a similar cyclic capacity (Ma’mun *et al.*, 2007). AEEA is a promising solvent for the absorption of CO_2 at low pressures (i.e. post-combustion conditions), in terms of both CO_2 absorption rate and CO_2 absorption capacity as well as cyclic capacity (Ma'mun, 2005). Another advantageous property of AEEA is its low vapour pressure, which would result in a decrease of solvent losses from the absorber. The increased capacity of AEEA stems from its diamine nature, which means that it can theoretically absorb two moles of CO_2 per mole of solvent; this is superior to other favourable solvents such as AMP or PZ (Najafloo *et al.*, 2015). These properties of AEEA has led to investigations using AEEA as an activator for other, more conventional alkanolamine solvents such as diethanolamine (DEA) and MDEA. Bajpai and Mondal (2013) found that AEEA, as an activator for DEA, shows superior performance compared to with PZ or MDEA. For MDEA, blends of MDEA+AEEA showed better performance than blends of MDEA with any of PZ, AMP, diisopropanolamine (DIPA) or diglycolamine (DGA) (Zoghi *et al.*, 2012). Using AEEA as a single aqueous mixture would have the potential to replace MEA if it did not have a high tendency to undergo thermal degradation at temperatures approaching 140 °C. Although the effects of thermal degradation could be lessened by reducing the regeneration temperature (Liang *et al.*, 2015), using AEEA as an activator might be a better option. More information on CO_2 solubility data for AEEA can be found in table C-7 in Appendix C.

Another promising sterically hindered alkanolamine that has been gaining interest in the field of CO_2 capture is 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), also known as TRIS which shows higher CO_2 solubility than MEA (even when used at lower weight concentrations), as well as similar sterically hindered amines, 2-amino-2-methyl-1,3-propanediol (AMPD) and 2-amino-2-ethyl-1,3-propanediol (AEPD) (Park *et al.*, 2002). Studies by Le Tourneux (2007) indicate that the CO_2 loading of a solvent increases with increased steric hindrance. AHPD, containing an amine group and three hydroxyl groups, has an increased degree of steric hindrance compared to AMP, suggesting its superiority. Limited investigation has found AHPD to have a higher CO_2 loading capacity than MEA at partial pressures above 40 kPa (Oktavian *et al.*, 2014). Table C-8 in Appendix C shows a summary of the CO_2 solubility for AHPD.

N-methyl-2-ethanolamine (MAE or MMEA) also showed better solubility of CO_2 than the common amines MEA, DEA and MDEA (Haider *et al.*, 2011, Kumar and Kundu, 2012). MAE is a moderately sterically hindered, secondary amine formed by adding a methyl group onto the amine group of MEA. It was found by Mimura *et al.* (1998) that MAE shows better kinetics with CO_2 than MEA, that it has reduced regeneration energy requirements and a low corrosion tendency. These findings have led to a further study by Kumar (2013). A significant disadvantage of MAE is its tendency to foam (Ma'mun, 2005), which decreases absorber efficiency and causes complications in process operation. Refer to table C-11 in Appendix C for a summary of the CO_2 solubility data published in the literature for MAE.

N-ethylethanolamine (EEA or EAE) is a moderately sterically hindered, secondary amine formed by adding an ethyl group onto the amine group of MEA. Like MAE, it was found by Mimura *et al.* (1998) that EEA shows kinetics with CO_2 that are comparable to that of MEA, and together with

MAE, EEA was further studied by Kumar (2013). El Hadri *et al.* (2016) identified EEA as a good alternative to MEA for CO_2 capture. EEA has also been gaining attention in CO_2 capture studies, due to the fact that it can be prepared from renewable resources (Vaidya and Kenig, 2009).

Solubility data on MAPA suggest that it would also perform well for CO_2 capture (Arshad *et al.*, 2014), but an in-depth investigation by Voice *et al.* (2013) showed that overall, MAPA actually performs worse than MEA.

2.3.2 SOLVENT BLENDS

Utilizing binary mixtures of amine solvents is a possible solution to the disadvantages of single amines (Zarogiannis *et al.*, 2015). The amine blends usually comprise an aqueous mixture of a primary or secondary amine with a tertiary or sterically hindered amine. This serves to combine the favourable properties of the primary/secondary amines (i.e. fast reaction rate) with those of tertiary and sterically hindered amines (i.e. increased CO_2 capacity and ease of regeneration). Amine blends are often less corrosive than their single component aqueous counterparts and may also require lower circulation rates for the same level of capture (Kumar, 2013).

Aqueous amine solvents for CO_2 capture are often used in blends rather than as a single aqueous amine, to benefit from the advantages of both (or all) amine components. The literature review of CO_2 solubility also included aqueous blends with two or more amine components.

Considering binary amine systems, data for numerous systems was found in the literature. Of these, aqueous systems with AMP + DEA, AMP + PZ, DEA + MDEA, MDEA + MEA and MDEA + PZ were the most studied.

One of the first blends considered, MDEA+MEA improves on the CO_2 capacity of MEA, but the discovery of superior solvents and solvent blends have caused the investigation of this blend to decrease.

Another blend that has been studied extensively is MDEA+PZ, as it combines the capacity and regeneration efficiency of MDEA with the capacity and fast absorption rate of PZ. The MDEA+PZ blend was found to have a higher CO_2 capacity than both aqueous MDEA and PZ, as well as an absorption rate comparable to PZ (Ali and Aroua, 2004, Chen *et al.*, 2011). MDEA + PZ blends are often studied in total amine concentrations of 30 wt.%, 40 wt.% or 50 wt.%. The PZ concentration does not often exceed 10%. Refer to table C-13 in Appendix C for more details.

The AMP+PZ blend, has a greater capacity for CO_2 than MEA (Brúder *et al.*, 2011, Li *et al.*, 2013). It also has a better CO_2 solubility, higher cyclic capacity and lower volatility than single aqueous mixtures of AMP or PZ (Dash *et al.*, 2012, Tong *et al.*, 2013). Furthermore, Wong *et al.* (2014) have found that this blend performs better than AMP+MDEA. AMP+PZ blends are usually studied in total amine concentrations between 20 wt.% and 50 wt.%. PZ concentrations are generally kept at 10% or below. More information can be found in table C-15 in Appendix C.

Other popular binary amine blends include 2-MPZ + PZ, AEEA + MDEA, AHPD + PZ and AMP + MDEA. Guo *et al.* (2013) and Najafloo *et al.* (2015), respectively found that a blend of AEEA with MDEA has a higher absorption rate than AEEA, and better CO_2 solubility than MDEA. The other blends mentioned all perform better than MEA.

To further increase solvent performance, some researchers have created solvent blends using three amines. These ternary amine solvents are not yet very common in the literature. Four different ternary systems have been measured. These were DIPA + AMP + PZ (Haghtalab and Izadi, 2014, Haghtalab *et al.*, 2014), 1,4-DMPZ[*] + PZ + 1-MPZ (Freeman *et al.*, 2014, Xu, 2011), MDEA + DEA + AMP (Rebolledo-Libreros and Trejo, 2004) and MDEA + AMP + PZ (Haghtalab and Izadi, 2014, Haghtalab and Ghahremani, 2015). The work by Haghtalab and Izadi (2014) revealed that tri-amine blends have a better CO_2 capture performance than binary blends of the solvent's components. As a result, blends making use of more than two amine components will most likely gain more attention in the future.

A summary of the conditions and main findings of the investigations of some blends mentioned are presented in tables C-13 to C-20 (binary blends) and tables C-21 to C-24 (ternary blends) in Appendix C.

2.3.3 AMINE SOLVENTS CONSIDERED FOR INVESTIGATION

The amine solvents investigated in this study were chosen based on the information presented in section 2.3, as well as properties of the amines such as price, density, viscosity, surface tension, vapour pressure, heat of absorption and CO_2 loading capacity. Considering all of these properties simultaneously, the top ten amines were determined to be AHPD, MDEA, PZ, DEEA, DIPA, EEA, DEA, AMP, MAE and AEEA.

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[*] 1,4-dimethyl piperazine

Another consideration was whether appropriate data for the amines were available on the Aspen Plus® simulation software used for the simulations. This, together with aspects such as popularity in the literature, highlighted MDEA, AMP and PZ as the best options for study in a post-combustion CO_2 capture simulation environment.

Kinetics were used to determine which amines would perform well in a blend. Fast-reacting amines should be paired with slower reacting amines, thus blends of AMP+PZ and MDEA+PZ were considered. In addition, aqueous solvents containing all three amine components (MDEA, AMP and PZ) were also considered.

A more thorough discussion on the choices made and the exact solvent compositions investigated is presented in section 4.1.

2.4 SIMULATION STUDIES

Many of the simulation studies on CO_2 capture use MEA as a solvent. The objective of the studies performed by Freguia and Rochelle (2003), Fisher *et al.* (2005), Abu-Zahra *et al.* (2007), Han *et al.* (2011) and Arachchige and Melaaen (2012), was to improve the process conditions or configuration (for simulation studies that aim to improve the process configuration, refer to Appendix A). Other studies, such as those by Fisher *et al.* (2007), Kothandaraman *et al.* (2009), Lee *et al.* (2009), Montenegro (2011), Molina and Bouallou (2013), Naskar *et al.* (2013), Yakub *et al.* (2014), Erfani *et al.* (2015) compared the performance of MEA to other solvents.

Other reasons for process simulation studies with MEA included: the effect that adding a capture plant had on efficiency of the parent power plant (Øi, 2007), how the results of different simulation software compare to each other and pilot plant data (Aliabad and Mirzaei, 2009, Mirzaei *et al.*, 2009, Luo *et al.*, 2009), development of an accurate model for CO_2 capture representation (Zhang *et al.*, 2009, Abu-Zahra *et al.*, 2012, Ahmadi, 2012, Øi, 2012, Lim *et al.*, 2013, Li *et al.*, 2016a) and the economic evaluation of a CO_2 capture plant (Li and Liang, 2012, Razi *et al.*, 2013).

There are also studies which focus on solvent blends. Process simulation studies of solvent blends often aim to compare the performance of the blend to pure aqueous solvents or other solvent blends (Fisher *et al.*, 2007, Padurean *et al.*, 2011, Adeosun and Abu-Zahra, 2013, Molina and Bouallou, 2013, Erfani *et al.*, 2015, Daya, 2017). One techno-economic study, performed by Jones *et al.* (2013) compares MEA with aqueous tri-amine blends consisting of MEA, MDEA and AMP; to the author's knowledge, this is the only available process simulation study using an aqueous tri-amine blend.

A summary of the conditions of process simulation studies performed in the literature is presented in table 2-4. The information in this table was compiled by the author. All solvents are of an aqueous basis and concentrations of the amines are given in wt. %. Where only a solvent name is present, the source did not disclose the exact solvent concentration.

The information presented in table 2-4 show that it is most common to achieve 90% CO_2 capture in post-combustion CO_2 capture simulations. It was thus decided that the simulations used in this investigation should achieve 90% capture. The study by Daya (2017), which this investigation is based on, only achieved 80% capture.

Table 2-4: Summary of process simulation studies performed in the literature[§].

Reference	Simulation Software	Aqueous Solvent(s) Considered (concentrations given in wt. %)	Type/ Purpose of Study	Case Studied	CO_2 Content of Flue Gas	CO_2 removal (%)
White (2002)	Aspen Plus®	MEA	Development of simulation templates for CO_2 capture technologies	Post-combustion. Coal Fired Power Plant	14.5 vol %	Not specified (CO_2 Purity = 99.9%)
Freguia and Rochelle (2003)	Aspen Plus® with RateFrac model and FORTRAN kinetic subroutine	MEA (26.6 – 33.5%)	Modelling of pilot plant data with sensitivity analysis to find optimum operating conditions for low steam usage	Post-combustion.	2.86 – 3.13%	85, 90
Alie *et al.* (2005)	Aspen Plus® with RateFrac model	30% MEA	Decoupling method for a CO_2 capture flowsheet to improve convergence issues	Post-combustion. Coal Fired Power Plant (500 MW), Natural Gas Power Plant and Cement Plant.	3, 14, 25 %	85
Chang and Shih (2005)	Aspen Plus® with RateFrac model	• 20% MEA • 25% DGA + 25% MDEA	Optimization of CO_2 capture plant, analysing conventional, split-flow and intercooled configurations	Coal-Fired and Natural-Gas-Fired Power Plant	13.2 mol % (coal); 8 mol % (gas)	90
Fisher *et al.* (2005)	• Aspen Plus® (v12.1) with RateFrac • WinSim Design II (v9.17)	MEA	Integrating MEA regeneration with CO_2 compression to reduce CO_2 capture costs. Techno-economic study with the evaluation of process modifications.	Post-combustion. Coal Fired Utility Plant (500 MW)	12.33 mol %	90, 95

Table 2-4: Summary of process simulation studies performed in the literature (contd.).

Reference	Simulation Software	Aqueous Solvent(s) Considered (concentrations given in wt. %)	Type/ Purpose of Study	Case Studied	CO_2 Content of Flue Gas	CO_2 removal (%)
Abu-Zahra *et al.* (2007)	Aspen Plus® (v13.1) with an equilibrium RADFRAC subroutine	• 20% MEA • 30% MEA • 40% MEA	Parametric study, aiming to reduce the energy requirement for solvent regeneration	Post-combustion. Fossil Fuel Fired Power Plant (600 MWe)	13.3 vol. %	80, 90, 95, 99
Fisher *et al.* (2007)	AspenOne® (v2006)	• 30% MEA • 50% MDEA • MDEA + PZ • 27% MEA + 15% PZ	Detailed analysis of energy requirements for promising solvents/ blends and process configurations	Post-combustion. Pulverised Coal Supercritical Power Plant (500 MWe)	12.38 mol %	90
Øi (2007)	Aspen HYSYS®	29% MEA	Using simulation to determine the efficiency reduction of adding a CO_2 capture plant to a gas-fired power plant	Combined Cycle Gas Power Plant	3.73 mol %	85
Aliabad and Mirzaei (2009); Mirzaei *et al.* (2009)	Aspen Plus and HYSYS	• 45% MDEA • 34% DEA	Parametric study, comparing results from Aspen and HYSYS.	Natural Gas Sweetening Plant. (Simultaneous removal of CO_2 and H_2S)	6.459 mol %	Not specified
Kothandaraman *et al.* (2009)	Aspen Plus® with RATESEP module	MEA	Parametric study with the aim to compare MEA with a potassium carbonate solvent	Post-combustion. Natural Gas-Fired and Coal-Fired Power Plants (500 MWe)	Not specified	≥ 95
Lee *et al.* (2009)	Aspen Plus® (2006.5 release)	• 30% MDEA • 30% AMP	Comparative study to compare the performance of MDEA and AMP	Post-combustion.	8.34 mol %	90

Table 2-4: Summary of process simulation studies performed in the literature (contd.).

Reference	Simulation Software	Aqueous Solvent(s) Considered (concentrations given in wt. %)	Type/ Purpose of Study	Case Studied	CO$_2$ Content of Flue Gas	CO$_2$ removal (%)
Luo *et al.* (2009)	• Aspen Plus® (v2006.5) RadFrac • Aspen Plus® RateSep • Protreat • Promax • In-house software	30% MEA	Comparing results obtained from various process simulators	Post-combustion. (Pilot Plant Scale)	4 – 8 %	Not specified
Zhang *et al.* (2009)	Aspen Plus® with RateSep	MEA	Modelling pilot plant data for model validation	Post-combustion.	15.2 – 18.0 mol %	60 – 99
Kallevik (2010)	Aspen HYSYS®	29% MEA	Parametric study	Post-combustion. Power Plant (500 MW)	5.9 wt. %	80, 85, 90
Plaza and Rochelle (2011)	Aspen Plus® RateSep, with FORTRAN kinetic subroutine	PZ (28.5 – 44 %)	Development of a model for CO$_2$ capture using PZ as solvent	Post-combustion. (Pilot Plant Scale)	Not Specified	60.7 – 92.2
Han *et al.* (2011)	Aspen Plus® RADFRAC	MEA	Parametric study with the aim of energy optimization	Post-combustion. (Pilot Plant Scale)	14 vol. %	65 – 95
Montenegro (2011)	Aspen Plus® (v2006.5), with rate-based model	• 30% MEA • 40% PZ • 30% AMP	Performance of various solvents in the conventional as well as advanced process configurations	Post-combustion. Coal Fired Power Plant	12.57 mol %	90

Table 2-4: Summary of process simulation studies performed in the literature (contd.).

Reference	Simulation Software	Aqueous Solvent(s) Considered (concentrations given in wt. %)	Type/ Purpose of Study	Case Studied	CO_2 Content of Flue Gas	CO_2 removal (%)
Padurean *et al.* (2011)	Aspen Plus®, with Rate-based models	• 30% MEA • 30% DEA • 50% MDEA • 30% AMP • 10% MEA + 20% DEA • 20% MEA + 10% DEA • 10% MEA + 20% AMP • 20% MEA + 10% AMP • 10% DEA + 20% AMP • 20% DEA + 10% AMP • 10% MDEA + 20% AMP • 20% MDEA + 10% AMP • 10% MDEA + 20% MEA • 20% MDEA + 10% MEA • 10% DEA + 20% MDEA • 20% DEA + 10% MDEA	Parametric Study. Assessment of a multi-criterial analysis and investigation of the effect of using solvent mixtures.	Coal-based IGCC Power Plant (375 - 450 MWe)	8.40 vol. %	≥ 90%
Pellegrini *et al.* (2011)	Aspen Plus®	30% MEA	Comparison of different process configurations with the aim to minimize energy usage.	Post-combustion. Coal-fired Power Plant (Pilot Plant Scale)	18.41 mol %	Not specified
Van Wagener (2011)	Aspen Plus®, RateSep	• 35% MEA • 40% PZ	Investigation of flowsheet variations pertaining to the stripper, with the aim to reduce regeneration energy consumption	Post-combustion. Coal-fired Power Plant	Not specified	Not specified

Table 2-4: Summary of process simulation studies performed in the literature (contd.).

Reference	Simulation Software	Aqueous Solvent(s) Considered (concentrations given in wt. %)	Type/ Purpose of Study	Case Studied	CO_2 Content of Flue Gas	CO_2 removal (%)
Abu-Zahra *et al.* (2012)	Aspen Plus® (v7). Equilibrium and Rate-based RADFRAC models	MEA	Comparison of pilot plant data with simulation results. Comparing the accuracy of rate-based vs. equilibrium models.	Post-combustion. Pulverised Coal-Fired Power Plant (400 MW)	12 vol. %	90
Ahmadi (2012)	• Aspen Plus® • ProMax	30% MEA	Developing a simulation model to predict pilot plant results	Post-combustion. (400 MW)	10.15 – 11.81 mol %	64.5 – 96.86
Arachchige and Melaaen (2012)	Aspen Plus®	MEA (10 – 25 %)	Optimization of the CO_2 absorption process via a sensitivity analysis.	Coal and Gas Fired Power Plants (500 MW)	13.58 mol % (coal-fired); 4.00 mol % (gas-fired)	Not specified
Li and Liang (2012)	Aspen Plus®	30% MEA	Process Simulation and Economic Analysis Study	Post-combustion. Ultra-Supercritical Pulverised Coal-Fired (USPC) Power Plant (1 GW)	13.8 wt. %	50 – 90
Øi (2012)	Aspen Plus® (v7.1 & v7.2) and Aspen HYSYS®. Equilibrium and rate-based models used for each.	30% MEA	Comparing equilibrium models with rate-based models and results on Aspen Plus and Aspen HYSYS software.	Natural Gas Fired Combined Cycle (NGCC) Power Plant (400 MW)	3.73 mol %	≥ 85

Table 2-4: Summary of process simulation studies performed in the literature (contd.).

Reference	**Simulation Software**	**Aqueous Solvent(s) Considered (concentrations given in wt. %)**	**Type/ Purpose of Study**	**Case Studied**	**CO$_2$ Content of Flue Gas**	**CO$_2$ removal (%)**
Salkuyeh and Mofarahi (2012)	Aspen Plus®, RATEFRAC	• MEA (45 – 70 %) • DGA (15 – 30 %)	Study to minimize energy requirement of a CO$_2$ capture plant	Post-combustion.	3, 5, 10 mol %	90
Adeosun and Abu-Zahra (2013)	Aspen Plus® (v7.3.2)	• 3% DEA + 27% AMP • 5% DEA + 25% AMP • 10% DEA + 20% AMP • 15% DEA + 15% AMP • 3% DEA + 27% MDEA • 5% DEA + 25% MDEA • 10% DEA + 20% MDEA • 15% DEA + 15% MDEA • 3% MEA + 27% AMP	Comparing the performance of various solvent blends.	Post-combustion. Coal-Fired Power Plant (600 MWe)	13.30 vol. %	90
Arachchige *et al.* (2013)	Aspen Plus®	40% MEA	Parametric Study	Post-combustion. Coal-Fired Power Plant (500 MW)	13.58 mol %	85
Birkelund (2013)	Aspen HYSYS®	30% MEA	Reducing energy demand by evaluating different configurations for absorption	Post-combustion.	3.3 mol %	85
Jones *et al.* (2013)	Aspen Plus®	• 30% MEA • 15% MEA + 12% MDEA + 3% AMP • 17.5% MEA + 14% MDEA + 3.5% AMP	Techno-economic study	Post-combustion. Power Plant (461 MW)	9.51 mol %	90

Table 2-4: Summary of process simulation studies performed in the literature (contd.).

Reference	Simulation Software	Aqueous Solvent(s) Considered (concentrations given in wt. %)	Type/ Purpose of Study	Case Studied	CO_2 Content of Flue Gas	CO_2 removal (%)
Lim *et al.* (2013)	Aspen Plus®, RADFRAC Rate-based module used	MEA (29.8 – 31.2 %)	Applying models to pilot plant data for model validation and improved model development	Post-combustion. (Pilot Plant Scale – 0.1 MW)	Not specified	89 – 92
Molina and Bouallou (2013)	Aspen Plus® (v7.2)	• 50% MDEA • 30% DEA • 20% MDEA + 20% DEA • 30% MDEA + 20% DEA	Comparison of solvent performance in terms of energy consumption	Post-combustion. Coal-Fired Power Plant	11.71 mol %	90
Mudhasakul *et al.* (2013)	Aspen Plus®	• 45% MDEA + 5% PZ • MDEA + PZ (0 – 7.5 % PZ) – for sensitivity study (50% total conc.)	Sensitivity analysis of S/F ratio and PZ concentration	Post-combustion	19.31 mol %	Not specified
Naskar *et al.* (2013)	Aspen Plus®, RADFRAC model	• 30% MEA • 30% DEA	Parametric Study, comparing the performance of MEA and DEA	Post-combustion. Coal-based Power Plant	24.15 wt. %	Not specified
Razi *et al.* (2013)	Aspen Plus®, RateSep	30% MEA	Techno-economic study	Coal- and Gas-Fired Power Plants (400 MWe)	3.88 vol. % (gas-fired); 13.73 vol. % (coal-fired)	90
Roussanaly *et al.* (2013)	Aspen Plus® and Aspen Process Economic Analyzer	MEA	Integrated techno-economic and environmental assessment	Post-combustion	2.5 – 20.5 % (7 cases)	90
Dash *et al.* (2014)	Aspen Plus® with RadFrac-RateSep model	• AMP + PZ (0 – 20% PZ; 30% total conc.) • AMP + PZ (0 – 26% PZ; 40% total conc.) • AMP + PZ (50% total conc.)	Parametric study, aiming to find the solvent composition that maximizes the CO_2 capture rate	Post-combustion (Pilot Plant Scale)	13 %	≥ 90%

Table 2-4: Summary of process simulation studies performed in the literature (contd.).

Reference	Simulation Software	Aqueous Solvent(s) Considered (concentrations given in wt. %)	Type/ Purpose of Study	Case Studied	CO_2 Content of Flue Gas	CO_2 removal (%)
Frailie (2014)	Aspen Plus®, RateSep with FORTRAN subroutines	• 30% PZ • 40% PZ • 41.5% MDEA + 8.5% PZ • 29% MDEA + 21% PZ	Rigorous modelling of advanced process configurations	Post-combustion.	12 %	90
Herrmann (2014)	Aspen Plus®	AMP + PZ	Developing a process modelling procedure for novel post-combustion amine solvents	Post-combustion.	13 mol %	90
Yakub *et al.* (2014)	Aspen Hysys® (v7.2)	• 16.5% MEA • 30% DEA • 50% MDEA	Techno-economic study	Post-combustion. Coal Fired Power Plant (500 MW)	15 mol %	≥ 90
Erfani *et al.* (2015)	Aspen Plus® (v7.3) and Aspen HYSYS® (v7.3)	• 60% DGA • 25% MEA • 30% DEA • 50% DIPA • 45% MDEA + 5% MEA • 45% MDEA + 5% DEA • 20% MEA + 5% DGA • 15% MEA + 10% DGA	Solvent comparison study	Post-combustion. Coal-Fired Power Plant (150 MW)	18 %	Not specified
Gupta *et al.* (2015)	Aspen Plus® with the RATEFRAC module	30% MEA	Plant Configuration Comparison; Economic Analysis	Post-combustion. Coal Fired Power Plant (550 MWe)	13.2 mol %	Not specified (> 95% purity of CO_2 in captured stream)

Table 2-4: Summary of process simulation studies performed in the literature (contd.).

Reference	**Simulation Software**	**Aqueous Solvent(s) Considered (concentrations given in wt. %)**	**Type/ Purpose of Study**	**Case Studied**	**CO_2 Content of Flue Gas**	**CO_2 removal (%)**
Mohammed (2015)	Aspen HYSYS®	DEA	Optimization and sensitivity analysis of CO_2 capture plant	Post-combustion. Coal-fired Power Plant (500MW)	15 mol %	90
Witzøe (2015)	Aspen Plus® (v8.6)	30% MEA	Simulation of pilot plant data	Post-combustion. (Pilot Plant Scale)	0 – 20 vol %	Not specified
Li *et al.* (2016a)	Aspen Plus® (v8.0)	MEA	Improving the rate-based model of a CO_2 capture plant	Post-combustion. (Pilot Plant Scale)	Not specified	Not specified (> 99% purity of CO_2 in captured stream)
Li *et al.* (2016b)	Aspen Plus® RateSep simulator	MEA (24 – 34 %)	Improving post combustion capture processes, including an investigation of process modifications	Post-combustion. Coal Fired Power Station (Pilot Plant Scale)	11.0 – 13.5 vol %	Not specified (> 97% purity of CO_2 in captured stream)
Li *et al.* (2016c)	Aspen Plus®	• 30% MEA • 35% MEA	Techno-economic assessment of a CO_2 capture plant including process improvements	Post-combustion. Coal Fired Power Station (650 MW)	17.61 wt. %	Not specified (99.5% purity of CO_2 in captured stream)
Li *et al.* (2016d)	ProTreat	• 30% MEA • 50% MDEA • 30% AMP	Verification of an optimization approach	Post-combustion.	13.3 vol %	90

Table 2-4: Summary of process simulation studies performed in the literature (contd.).

Reference	Simulation Software	Aqueous Solvent(s) Considered (concentrations given in wt. %)	Type/ Purpose of Study	Case Studied	CO$_2$ Content of Flue Gas	CO$_2$ removal (%)
van der Spek *et al.* (2016)	Aspen Plus® (v8.4)	20% AMP + 10% PZ	The development, application, and uncertainty analysis of a process simulation model for post-combustion CO$_2$ capture	Advanced Super Critical Pulverized-Coal Power Plant (833 MW)	13.6 vol %	90
Daya (2017)	Aspen Plus® (v8.6)	• 30% MEA • 30% DEA • 30% AMP • 25% MEA + 5% DEA • 20% MEA + 10% DEA • 15% MEA + 15% DEA • 10% MEA + 20% DEA • 5% MEA + 25% DEA • 25% MEA + 5% AMP • 20% MEA + 10% AMP • 15% MEA + 15% AMP • 10% MEA + 20% AMP • 5% MEA + 25% AMP • 20% DEA + 10% AMP • 10% DEA + 20% AMP • 20% MEA + 10% MDEA • 20% AMP + 10% MDEA	Development of a multi-criterion performance indicator model to compare solvent performances for CO$_2$ capture by absorption	Post-combustion. • Pulverised Coal Fired Power Plant (500 MW) • Natural Gas Power Plant (500 MW) • Cement Plant	12.01 mol % (coal); 3.83 mol % (gas); 22.36 mol % (cement)	80

[§]The information in Table 2-4 was compiled by the author.

CHAPTER 3

3 POST-COMBUSTION CO_2 CAPTURE SIMULATIONS AND DATA ANALYSIS

The simulation of a post-combustion CO_2 capture plant was created using Aspen Plus® V8.8 software. The procedure, along with the models used to calculate the performance of the solvents studied, will be discussed in this chapter.

3.1 GENERAL CONSIDERATIONS FOR SIMULATION SETUP

3.1.1 THERMODYNAMIC MODELLING

When simulating a process, it is important to have all the necessary properties and parameters to be able to represent molecular interactions accurately. Choosing the correct thermodynamic model is imperative to accurately predict these properties and interactions.

In the chemical absorption process for CO_2 capture, acid-base reactions take place. An electrolyte property model is required to describe systems of this nature. The most versatile model for acid-gas reactions, and the model recommended for use in CO_2 capture simulations, is the Electrolyte Non-Random Two-Liquid (eNRTL) model. The eNTRL model is a flexible activity coefficient model, originally developed by Chen *et al.* (1982) for single electrolyte solvent systems of aqueous nature. It was later extended by Mock *et al.* (1986) to represent mixed-solvent electrolyte systems (Al-Malah, 2017). The eNRTL model is therefore capable of representing aqueous electrolyte systems, as well as mixed solvent electrolyte systems, by calculation of activity coefficents for both ionic and molecular species over the entire range of electrolyte concentrations. If no electrolytes are present, the eNRTL model reduces to the NRTL model developed by Renon and Prausnitz (1968) (AspenTech., 2015b).

Due to the high pressures and temperatures reached in the CO_2 compression section of the flowsheet, another property model is required to describe this section. An equation of state property method is capable of predicting the behaviour of systems at these conditions. The Peng Robinson equation of State (PREOS), formulated by Peng and Robinson (1976), is a flexible model, and recommended for use at conditions of high pressure, high temperature or close to the critical point of the system. In this work, the PREOS was used in combination with the Boston-Mathias alpha function, which is applied in systems of light gases with high reduced temperatures (Boston and Mathias, 1980).

3.1.2 SYSTEM CHEMISTRY AND KINETICS

One of the most important reactions in CO_2 absorption applications is the carbamate formation reaction. For primary and secondary amines, carbamates are thought to be formed in one of two ways, via the zwitterion mechanism or via the termolecular mechanism (Kothandaraman, 2010). The Zwitterion mechanism, which assumes that a hydrogen bond is formed between an amine molecule and water molecule before any reaction between the amine and CO_2, was originally proposed by Caplow (1968). This mechanism takes place in two steps: in the first step an unstable intermediate is formed when the CO_2 molecule bonds to an amine molecule; in the second step, the carbamate is formed when the amine proton is transferred to a base molecule, which can be either an amine or water molecule (Kothandaraman, 2010). The termolecular mechanism, which was first proposed by Crooks and Donellan (1989), occurs in a single step. This mechanism assumes that the amine's proton transfer and bond formation with CO_2 occurs simultaneously. The two mechanisms are very similar – if the zwitterion (a neutral molecule with both a positive and negative charge) has a very small lifetime, the zwitterion mechanism approaches the termolecular mechanism. In the literature, the mechanism of Caplow (1968) is often used to describe amine-CO_2 reactions (Kothandaraman, 2010). For tertiary amines, on the other hand, the mechanism followed is the "base-catalyzed hydration" mechanism. Tertiary amines do not react directly with CO_2, but rather acts as a base that catalyzes the CO_2 hydration reaction (Liang *et al.*, 2016).

In the capture process, amines react with CO_2 in the absorber to form intermediate compounds which is followed by reversal of the reaction in the stripper to release the CO_2. Since this process is a reactive one, kinetics and chemical equilibrium of the system is required within the simulation to accurately simulate the process. The following reactions were taken into account for the amine chemical absorption process (AspenTech, 2014a-c):

$$CO_2 + OH^- \rightarrow HCO_3^- \tag{3-1}$$

$$HCO_3^- \rightarrow CO_2 + OH^- \tag{3-2}$$

$$2H_2O \leftrightarrow H_3O^+ + OH^- \tag{3-3}$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{-2} + H_3O^+ \tag{3-4}$$

$$MEA^{+} + H_2O \leftrightarrow MEA + H_3O^{+} \tag{3-5}$$

$$MEACOO^{-} + H_2O \leftrightarrow MEA + \ HCO_3^{-} \tag{3-6}$$

$$MDEA^{+} + H_2O \leftrightarrow MDEA + H_3O^{+} \tag{3-7}$$

$$AMP^{+} + H_2O \leftrightarrow AMP + H_3O^{+} \tag{3-8}$$

$$PZH^{+} + H_2O \leftrightarrow PZ + H_3O^{+} \tag{3-9}$$

$$PZ + CO_2 + H_2O \leftrightarrow PZCOO^{-} + H_3O^{+} \tag{3-10}$$

$$HPZCOO + H_2O \leftrightarrow PZCOO^{-} + H_3O^{+} \tag{3-11}$$

$$PZCOO^{-} + HCO_3^{-} \leftrightarrow PZ(COO^{-})_2 + H_2O \tag{3-12}$$

The kinetic reaction and equilibrium constant equations used to describe these reactions in Aspen Plus® are expressed as follows (the units of temperature is Kelvin):

$$r = kT^{n}e^{\left(\frac{-E}{RT}\right)} \tag{3-15}$$

$$\ln\left(K_{eq}\right) = A + \frac{B}{T} + C\ln(T) + DT \tag{3-16}$$

The kinetic and equilibrium constants used in conjunction with equations 3-15 and 3-16 are given in tables 3-1 and 3-2, respectively. It should be noted that the equilibrium reactions (reactions 3-3 to 3-14) are assumed to occur instantaneously because they only involve proton transfer between reacting species (Mudhasakul *et al.*, 2013).

Table 3-1: Kinetic constants used in the simulation.

Reaction	k	n	E (J/kmol)	Reference
3-1	4.3152×10^{13}	0	5.54709×10^{7}	Pinsent *et al.* (1956)
3-2	3.7486×10^{14}	0	1.05807×10^{8}	Pinsent *et al.* (1956)

Table 3-2: Equilibrium constants used in the simulation.

Reaction	A	B	C	D
3-3[1]	132.899	-13445.9	-22.4773	0
3-4[1]	216.049	-12431.7	-35.4819	0
3-5[1]	-3.03833	-7008.36	0	-0.00313489
3-6[1]	-0.52135	-2545.53	0	0
3-7[2]	-9.4165	-4234.98	0	0
3-8[3]	-3.68672	-6754.69	0	0
3-9[2]	-62.28	-2564	6.787	0
3-10[4]	466.497	1614.5	-97.54	0.2471
3-11[4]	6.822	-6066.9	-2.29	0.0036
3-12[4]	-11.563	1769.4	-1.467	0.0024

[1] Austgen (1989)
[2] AspenTech. (2015a)
[3] Dash *et al.* (2012)
[4] Dash *et al.* (2011a)

3.1.3 ASPEN PLUS SUB-MODELS

Within Aspen Plus®, there are different methods offered to simulate the various units available. For separation columns, such as the absorber and stripper column in this study, RadFrac and RateFrac models are available. The RadFrac model assumes that the column operates in total thermodynamic equilibrium, but factors for efficiency may be incorporated to account for non-idealities (Mudhasakul *et al.*, 2013). This approach is suitable for approximate designs or ideal systems. The RateFrac model, on the other hand, takes into account mass and heat transfer effects when performing calculations and assumes that equilibrium is only achieved at the gas-liquid interface. This rigorous model can therefore describe separation processes with increased accuracy, and is suitable for describing most systems (Kothandaraman, 2010). The RateFrac model was used in this study for the CO_2-solvent absorption and stripping processes.

The CO_2 capture system has inherent convergence issues due to its ionic nature and the presence of kinetic reactions. The use of rate-based calculations enhances the difficulty in convergence (Mudhasakul *et al.*, 2013). It was thus decided to model the closed-loop system with an open loop (where the recycle stream is not connected to the absorber), since highly accurate initial estimates for tear streams would be required for the alternative (Alie *et al.*, 2005). Therefore, measures had to be taken to ensure that the flow rate and composition of the lean solvent exiting the stripper matched that of the lean solvent stream entering the absorber. Design specifications and calculator blocks were used to achieve this. Firstly, a design specification was applied on the CO_2 stream exiting the stripper, to ensure that 90% capture is always maintained (this was achieved by varying the boilup ratio in the stripper). Calculator blocks were used to determine the amount of makeup solvent (amine and water components respectively) required to keep the amounts of amine and water entering and exiting, equal; the flow rates of make-up streams are determined by performing a mass balance over the CO_2 capture section (absorber and stripper).The amount of CO_2 in the system is controlled by altering the allowed amount of CO_2 in the vent stream from the absorber. In an open loop system, the rich/lean heat exchanger must also be split into one heater and one cooler. A calculator block was also used to set the heat duties of these two exchangers as equal. Since multiple absorption and stripping trains are required to achieve the desired capture (see section 3.2.2), the stream multiplication function in Aspen was used to split and recombine process streams. This splits the flow of streams equally between the number of parallel trains present, and also means that the absorber and stripper of each stream is identical. When using the performance model to analyse results, the solvent flow rate in the absorber and energy requirements in the stripper are multiplied by the number of trains in the system to obtain the total resource requirements.

3.2 FLOWSHEET SETUP

The process for post-combustion CO_2 capture by absorption can be categorised into three main sections, viz. cooling and compression of the flue gas, CO_2 absorption and solvent regeneration and CO_2 compression (Kothandaraman, 2010).

The flue gas cooling and compression section consists of a direct contact cooler (DCC) and a blower, to bring the flue gas to the required conditions before it enters the absorber. The absorption and regeneration section contains absorption and stripping columns with a pump and heat exchanger as auxiliary equipment. The CO_2 compression section contains an intercooled multistage compressor or alternatively could consist of a train of successive compressors, coolers and separators. Figure 3-1 shows the process flow diagram.

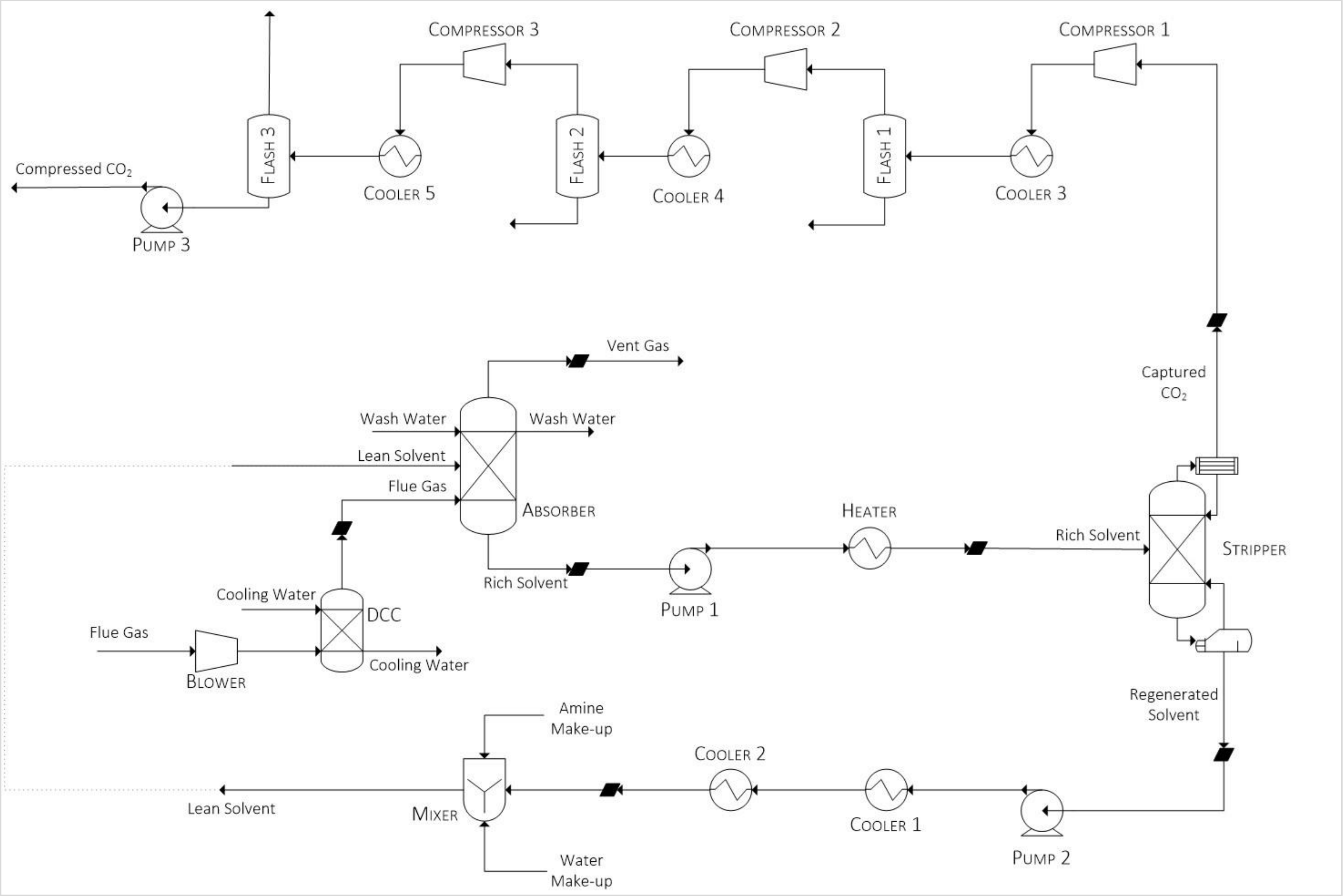

Figure 3-1: Flowsheet of the Aspen simulation for CO_2 capture by amine absorption.

3.2.1 FLUE GAS COMPRESSION AND COOLING SECTION

Flue gases derived from power plants, whether natural gas-fired or coal-fired, will require cooling before being fed to a CO_2 capture unit. A direct contact cooler is often used for this purpose. In cases where the flue gas is treated to remove SO_x (or NO_x and other impurities) cooling may not be required, since such processes generally reduce the flue gas temperature to an appropriate value for CO_2 capture (Kothandaraman, 2010). Compression of the flue gas is necessary because at a pressure of approximately 1 bar, the gas would not be able to move through the process.

3.2.1.1 GAS INLET BLOWER

The pressure of the flue gas must be increased above atmospheric pressure in order for it to be able to flow upward through the packed absorber (Kothandaraman, 2010). In the Aspen Plus® flowsheet, flue gas compression is achieved with a blower installed at the beginning of the process. Blowers are not usually used where large volumes of gas are handled, but it is absolutely necessary to overcome the pressure drops in the direct contact cooler and packing in the absorber column (Fisher *et al.*, 2007). The pressure delivered by the blower in the simulation is 111.25 kPa.

The specifications of the flue gas fed to the blower are presented in table 3-3. The flue gas composition is adapted from that given in Khalil and Gerbino (2007), which was also used by Daya (2017). Impurities with negligible concentrations such as hydrochloric acid (HCl), nitrogen dioxide (NO_2) and sulphur trioxide (SO_3) were omitted and the composition of the remaining compounds normalized.

Table 3-3: Properties of flue gas from a coal-fired power plant, used in this study.

Flow Rate (ton/hr)		2516
Temperature (°C)		125
Pressure (kPa)		101.33
Composition (mole fraction)	Nitrogen (N_2)	0.73470
	Oxygen (O_2)	0.05512
	Water vapour (H_2O)	0.07975
	Carbon Dioxide (CO_2)	0.12010
	Argon (Ar)	0.00877
	Nitrous Oxide (NO)	0.00030
	Sulphur Dioxide (SO_2)	0.00126

3.2.1.2 DIRECT CONTACT COOLER

The flue gas fed to the absorber must first be cooled to the operating temperature of the absorber, which is about 40 °C. A direct contact cooler (DCC) is usually used for this purpose. A DCC is a packed tower with counter-flow of the flue gas, which enters at the bottom, and cooling water, which enters from the top (Kothandaraman, 2010). A DCC utilizes less cooling water, has lower capital and operating costs, and a lower pressure drop than indirect coolers. The lower pressure drop is especially advantageous as it lowers the energy costs associated with the blower, since the blower must increase the pressure to overcome this pressure drop and that within the absorber (Daya, 2017).

A RadFrac column was used to simulate the DCC in Aspen Plus®. The column specifications are given in table 3-4.

Table 3-4: Specifications of the direct contact cooler.

Calculation type	Rate-based
No. of stages	10
Process stream inlet temperature (°C)	134
Process stream outlet temperature (°C)	42
Packing	250Y Standard MellaPak by Sulzer
Packed Height (m)	5
Condenser	None
Reboiler	None

3.2.2 CO_2 CAPTURE SECTION

The capture section is the main part of the capture plant. The most important equipment for CO_2 capture, the absorber and stripper columns, are found in this section.

3.2.2.1 ABSORBER

The absorber in a CO_2 capture facility is usually a packed column, with the flue gas entering from the bottom and the lean amine solvent from the top. A water wash section may be added at the top of the column to cool and clean the vent gas; alternatively a separate wash water column may be installed after the absorber (Kothandaraman, 2010).

The absorber is simulated by a RadFrac column in Aspen. Because the flue gas from a power plant has such a voluminous flow rate, multiple absorber/stripper trains are used to treat the gas. The use of multiple trains keep the column diameters at commercial sizes, which can be up to 15m (Kothandaraman, 2010). Columns with large diameters and heights are typically equipped with trays, however packed columns are preferred for CO_2 capture applications because of the corrosive and foaming nature of amine solvents. The use of packing also lowers the pressure drop, increases gas contacting efficiency and allows for higher gas flow rates than trays (Fisher *et al.*, 2007, Seader *et al.*, 2011).

Table 3-5 shows the specifications of the absorber columns (there are four identical absorbers present in the process).

Table 3-5: Specifications of the absorber.

	Section 1: **Wash water section**	**Section 2:** **Capture Section**
Calculation type	Rate-based	Rate-based
No. of stages	2	20
Top Pressure (kPa)	105	-
Packing	250Y Standard MellaPak by Sulzer	250Y Standard MellaPak by Sulzer
Packed Height (m)	2	20
Diameter (m)	12	12
Condenser	None	-
Reboiler	-	None

3.2.2.2 STRIPPER

The stripper is typically a packed column; the function of the stripper is to release the captured CO_2 from the rich amine solvent. The stripper usually operates at slightly elevated pressures (~1.8 atm). In the stripper, the reactions that took place in the absorber are essentially reversed with the heat provided by the steam in the kettle reboiler. The resulting lean solvent exits at the bottom and is recycled to the absorber. The captured CO_2 leaves at the top in a stream predominantly comprising CO_2 and H_2O (Fisher *et al.*, 2007, Kothandaraman, 2010).

Similar to the absorber setup, the stripper is modelled using a RadFrac column with rate-based calculations. There are also four identical strippers present in the process. The column specifications are given in table 3-6.

Table 3-6: Specifications of the stripper.

Calculation type	Rate-based
No. of stages	21
Top Pressure (kPa)	200
Packing	250Y Standard MellaPak by Sulzer
Packed Height (m)	17
Diameter (m)	14
Condenser	Partial
Reboiler	Kettle

3.2.2.3 AUXILIARY EQUIPMENT (PUMPS AND HEAT EXCHANGERS)

A pump is required after the absorber to increase the pressure of the solvent in order to overcome the pressure drops in the subsequent equipment and the higher operating pressure in the stripper. The increase in pressure of the rich amine solvent also prevents acid gas breakout in the heat exchanger which avoids the occurrence of corrosion problems in the heat exchanger, control valves and piping systems (Fisher *et al.*, 2005). A lean amine pump is also required after the stripper for the recycle of lean amine solvent to the absorber. The reasoning for this is similar to that explained above.

Before regeneration in the stripper, the rich amine is pre-heated with the hot lean amine from the stripper reboiler. As mentioned previously, the exchanger operates at an elevated pressure to prevent acid gas breakout and corrosion. The rich amine is heated to approximately 110 ˚C, which is based on a 10 ˚C temperature approach on the hot side of the heat exchanger (Fisher *et al.,* 2005).

Since not all of the available heat from the hot lean mine is transferred to the rich amine stream, a cooler is required in the recycle loop to cool the lean amine stream to the absorber operating temperature (±40 °C) (Fisher, et al., 2005).

3.2.3 CO_2 COMPRESSION TRAIN

The gaseous CO_2 that is released at the top of the stripper must be dried and compressed before being sent for storage via pipeline. A 4-stage reciprocating compressor, with inter-stage cooling, is generally used to achieve the compression up to 9 MPa. The supercritical liquid CO_2 is thereafter pumped to the required discharge pressure of around 13 MPa (Kothandaraman, 2010).

In the Aspen simulation, the CO_2 compression is achieved by a series of three compressors with inter-stage cooling and CO_2 separation (from the condensed H_2O), followed by a pump after the supercritical liquid phase is reached. The pressures reached by each respective compressor is 430 kPa, 1.9 MPa and 8 MPa. The final pressure of the CO_2 liquid after being pumped is 11 MPa.

3.3 PERFORMANCE INDICATOR MODEL

To determine the performance of the solvents investigated for the purpose of CO_2 capture, the results from the Aspen simulations were entered into a performance indicator model which was developed by Daya (2017). While one of the main issues regarding CO_2 capture is the high energy penalty, which is mostly associated with the solvent regeneration, many other factors also contribute to a solvent's performance. This performance indicator model considers the solvent make-up, cooling water and make-up water, steam, corrosion inhibitor, amine reclaim and disposal, and carbon taxes, all on a cost basis. A thorough explanation of all the factors considered can be found in the work of Daya (2017) and is also briefly outlined in the sections which follow.

The model is based on the cost of CO_2 avoided, rather than the cost of CO_2 captured. This is because for power plants, the electricity required for the capture section of the plant is usually sourced from the plant's electricity generation section. This approach has the effect of reducing the power output from the plant, therefore more fuel must be combusted to meet the power plant's rated output (i.e. the efficiency of the power plant decreases). Capturing CO_2 thus inevitably increases the CO_2 emitted, hence the basis of CO_2 avoided is more suitable. Figure 3-2 illustrates the concept of CO_2 captured vs CO_2 avoided.

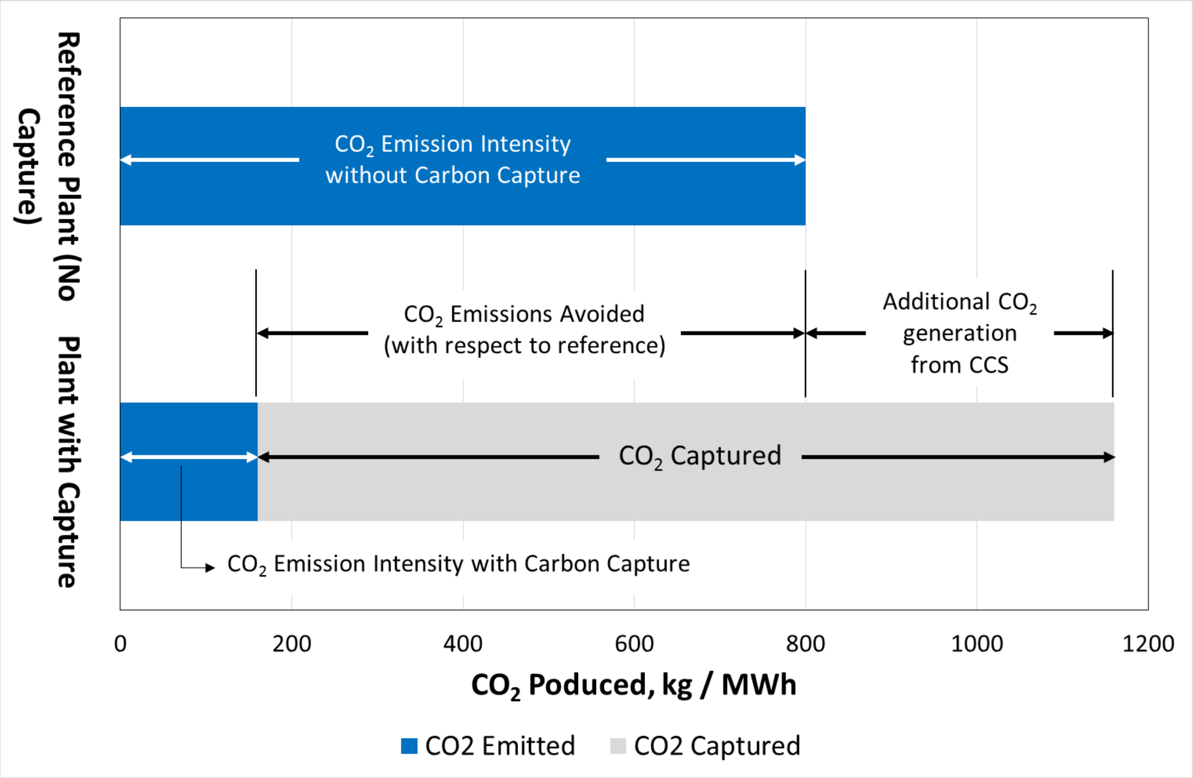

Figure 3-2: Illustrative diagram of the CO_2 captured vs CO_2 avoided concept (Canadian Clean Power Coalition, 2013).

3.3.1 FACTORS CONSIDERED IN THE MODEL

When evaluating the performance of amine solvents, many studies focus on energy considerations alone because the steam requirements for solvent regeneration could make up as much as two thirds of the operating costs. There are however other factors that influence the operating costs and this model considers some of those, which are discussed in the sections which follow. For a more thorough description of the factors considered in the model, refer to Daya (2017).

3.3.1.1 AMINE TYPE

The amine solvents considered in this study have extensively been discussed in chapter 2. The type of amine used has an impact on the model outcome because together with the variation in solvent flow rate required as the amine is changed, the various amines also have different prices. Table 3-7 shows the prices for the amines considered in this study.

Table 3-7: Prices of the amines studied.

Amine	Price (R/ton)*	Reference(s)
AMP	88374	Eachus and Bollmeier (2000); Zauba Technologies & Data (2016); Daya (2017)
MDEA	58556	Kohl and Nielsen (1997); Zauba Technologies & Data (2016)
MEA	39271	Kohl and Nielsen (1997); Sinnott (2005)
PZ	75880	Sridhar and Carter (2000); Sigma-Aldrich (2016); Zauba Technologies & Data (2016)

**The prices cited are for 2016*

Where more than one reference is cited, an average of the values from the different sources was used. If outdated prices were sourced, a ratio of the chemical consumer index of the source year and the current year was used to obtain more updated values (for the year 2016). Exchange rates and unit conversion factors also had to be used to convert all prices to a R/ton basis.

3.3.1.2 AMINE DEGRADATION RATES

Amines are susceptible to degradation throughout the CO_2 capture process. Oxidative degradation occurs mainly in the absorber due to the O_2 present in the flue gas stream. Thermal degradation can occur in the stripper because of the high temperatures reached during regeneration. Atmospheric degradation occurs when some of the amine escapes the process due to volatility, and the degradation products could potentially be harmful to the environment. The degradation products that form from oxidative and thermal degradation has a direct impact on the process because these products are found within the process streams. The reaction mechanisms that lead to the formation of degradation products are complicated due to the various factors and conditions that contribute to this formation (Fytianos *et al.*, 2016). Degradation mechanisms and kinetics are therefore rare in the literature and would severely complicate the ASPEN simulation if included. Amine degradation was thus accounted for outside of the simulations with a general degradation model, as reported by Daya (2017).

Since only oxidative and thermal degradation have an effect on the process streams, these rates were used as representative of an amine's degradation. Degradation rates for MEA, MDEA and AMP were obtained from data published by Lepaumier *et al* (2009a-c). According to Freeman *et al.* (2010) PZ does not degrade at temperatures below 140°C, thus degradation of PZ was considered negligible since the conditions of the areas of the process that contain PZ does not exceed this temperature. Table 3-8 shows the degradation rates used in this study. The values from the literature was adapted and expressed in terms of percentage amine degraded per hour. The value shown is a sum of the oxidative and thermal degradation contributions in the presence of both O_2 and CO_2 respectively.

The approach of using data from batch degradation studies for describing degradation in a full-scale industrial installations, which are continuous processes, are not completely accurate, however, it does provide a measure of comparison of the degradation levels between the different amines. This is deemed appropriate for use in the performance indicator model, since the final result is essentially a ratio.

Table 3-8: Degradation rates of the amines studied.

Amine	Combined degradation rate (%/hr)
MEA	0.3137
AMP	0.0739
MDEA	0.0970
PZ	Assumed negligible

Degradation also inevitably occurs due to the presence of trace amounts of impurities such as NO_x, SO_2, fly ash and NH_3 introduced into the process via the flue gas stream. Reactions of the amine with these compounds produces degradation products that will accumulate in the recirculating solvent if it is not removed (Rochelle *et al.*, 2011). The removal of these degradation products and other unwanted impurities such as sludge is removed in the reclaimer unit, which is commonly situated after the reboiler of the stripper. Due to the variety of degradation products which can potentially be formed and the complexity of the degradation mechanisms, the reclaimer unit was not simulated, but costs for reclamation and disposal of the degraded amines were accounted for in an Excel spreadsheet together with the other PIM calculations.

3.3.1.3 CORROSION

Some of the products which form when amines reactively absorb CO_2, can be highly corrosive. This could cause a variety of problems in the plant, such as unscheduled downtime, equipment damage and operation limitations. Corrosion inhibitors are usually added to prevent or reduce the occurrence of corrosion. Corrosion inhibitors traditionally used in amine absorption applications are arsenic and antimony, but the use of these are being discontinued as they are harmful to humans and the environment. Common alternatives are sodium metavanadate and copper carbonate, which were considered in this study (Veawab *et al.*, 2001).

The cost of corrosion inhibitor was calculated from a fraction of the recirculating solvent rate and was accounted for in the Excel spreadsheet.

3.3.1.4 ENERGY CONSUMPTION

The energy consumption in a CO_2 capture plant can be categorized as follows: electrical power consumption, steam usage and water usage.

The flue gas blower, CO_2 compressors and all pumps in the process make up the electrical power requirement of the capture plant. In this study it is assumed that the electrical requirements of the capture plant will be drawn from the power plant's output, hence the adoption of the "cost of CO_2 avoided" basis for the performance model (discussed in the start of section 3.3).

The stripper reboiler is the only consumer of steam in the process, since the compressors were modelled to be electrically driven. The steam usage of the stripper is directly related to the heat duty value obtained by the simulation, and is calculated by dividing the heat duty by the heat of vaporisation of the steam.

Cooling water is required for the direct contact cooler, stripper condenser, CO_2 compression intercoolers and the lean amine cooler. The amount of cooling water required for the condenser and coolers were once again obtained from the duties in the simulation, whereas the flow of cooling water through the DCC is directly taken from the simulation. Since the solvents used are on an aqueous basis, make-up water is also required to maintain the solvent composition.

3.3.1.5 CARBON TAX

Carbon tax is a form of pollution tax which places a levy on the amount of CO_2 released by industrial facilities. In some countries this tax has been implemented to provide an incentive to companies to reduce CO_2 emissions. In South Africa, as of 2016, the price of carbon tax has been proposed as R 120/ton with a possible 10% yearly increase in this value between 2016 and 2019 (The World Bank, 2014).

The carbon capture rate was kept constant in this study, thus the amount of carbon tax payable for each solvent blend remains constant. However, it was still included because in practice, different amines would achieve different capture rates, which would affect the value.

3.3.2 MODEL INPUTS AND OUTPUTS

The inputs required to make use of the PIM can be classified as user-defined inputs or result inputs. User-defined inputs would vary by user. In table 3-9 the user defined inputs are split into two categories “inputs into Aspen” and “external inputs”. The result inputs, which are essentially the outputs from the Aspen simulation, are labelled “inputs into PIM from Aspen”. The final output obtained from the performance model equation is the rating of a specific amine solvent or blend with regard to a specified baseline solvent.

Table 3-9: The various inputs required to use the performance indicator model (PIM).

Inputs into Aspen	Inputs into PIM from Aspen	External inputs into PIM
Flue gas flow rate	Cooler duties	Amine price(s)
Flue gas composition	Stripper condenser duty	Make-up water price
Solvent composition	Direct cooler water flow	Cooling water price
CO_2 capture rate	Stripper reboiler duty	Steam price
	Lean solvent flow from stripper	Corrosion inhibitor price
	Amine flow(s) into absorber	Amine reclaim cost
	Compressor power required	Amine disposal cost
	Pumping power required	Carbon tax rate
	Power required for blower	Amine degradation rate(s)
	Amine make-up flow(s)	Power plant efficiency
	Water make-up flow	
	CO_2 flow into process	

3.3.3 MODEL IMPLEMENTATION

The original development of the model did not combine the various contributing factors into one equation, but was rather represented as a sum of these factors. This was done to increase the flexibility of the model, as it allows for other factors to effortlessly be incorporated should the need arise in future studies (Daya, 2017). The procedure for determining the rating with the PIM follows.

The total cost of CO_2 captured is calculated as a sum of the costs of each factor i for each case j. In general, the cost factors are calculated by multiplying the price of the process chemicals or utilities with their corresponding flow rates. A sample calculation is presented in appendix D.

$$C_{T,j,captured} = \sum_{i} C_{i,j} \tag{3-17}$$

To calculate the total avoided cost, the total cost of capture is multiplied by the ratio of the original operating efficiency of the power plant without capture (ε_{OP}) and the reduced efficiency that is obtained when a capture plant is added (ε_j), which is dependent on the solvent used in case j (refer to section 3.3 and figure 3-2 for clarification on cost avoided vs. cost of capture).

$$C_{T,j,avoided} = C_{T,j,captured} \times \frac{\varepsilon_{OP}}{\varepsilon_j} \tag{3-18}$$

Multiplying by the ratio of efficiencies takes into account the additional CO_2 generated and captured as a result of the capture plant operations. The cost of CO_2 avoided will always be greater than the cost of CO_2 captured, since the original efficiency (ε_{OP}) will always be greater than the efficiency attained (ε_j) when CO_2 capture takes place.

The rating for each case j, is then determined by calculating the sum of the fraction of each factor for that case multiplied by the ratio of the avoided costs of the base case and case j, for each factor i.

$$R = \sum_i \left(x_{i,j} \times \frac{C_{i,b,avoided}}{C_{i,j,avoided}} \right) \tag{3-19}$$

The ratio of the cost avoided of the base case, to the cost avoided of each specific case, serves to compare each case to the benchmark case. If the cost avoided for case *j* is less than the benchmark case, it is an indication that the solvent in case *j* performed better in the simulation of post-combustion CO_2 capture. By multiplying with this ratio, it ensures that the rating value would be greater (than the benchmark, which has a rating of 1) for solvents that are more cost-effective, as determined by equations 3-17 and 3-18. Solvents that are less cost-effective than the benchmark, would then also have a rating of less than one.

The factor fraction, x_{ij}, used in eqn. 3-19 is calculated by dividing the cost of the factor i for case j by the total cost of CO_2 avoided for case j.

$$x_{i,j} = \frac{C_{i,j,avoided}}{C_{T,i,j,avoided}} \tag{3-20}$$

The reader is referred to Appendix D for a demonstration of the use of these equations, with sample calculations included.

The factors that the performance indicator model considers are all related to operating costs of a CO_2 capture plant. Evaluation of different solvents with this model thus require that the equipment sizes remain constant throughout all the cases being evaluated, since the model does not account for capital costs. In a real-life scenario, this would be equivalent to changing the solvent of an existing capture installation to see if it improves the plant's performance.

CHAPTER 4

4 RESULTS AND DISCUSSION

The solvent selection, results from the simulations performed in this study, and subsequent analysis of the results from the performance indicator model, are presented and discussed in this chapter. In order to validate the results obtained in this study, simulations were initially performed for 30 wt. % MEA and the aqueous blends 20% MEA + 10% MDEA and 10% MEA + 20% MDEA (all weight percentages). The results of these test systems were compared to the literature (Padurean *et al.* (2011) and Daya (2017)) for justification. Thereafter, simulations were performed on new systems comprising aqueous blends of piperazine (PZ) with 2-amino-2-methyl-1-propanol (AMP) or N-methyldiethanolamine (MDEA) as well as blends comprising all three components. In the final part of this study the results of the intercooled absorber (ICA) and rich solvent split (RSS) process modifications are presented and discussed.

4.1 CHOICE OF SOLVENTS INVESTIGATED

Over the years, a wide variety of amine solvents have been investigated for the capture of CO_2 by chemical absorption. However, not all investigated amines are necessarily suitable for this purpose. To identify amines that would theoretically perform well in a process simulation environment, the properties of amines which are important in the absorption process, were evaluated to obtain a ranking of amines in terms of potential performance.

The amine solvents were assessed in terms of their suitability for CO_2 capture based on their price, density, viscosity, surface tension, vapour pressure, heat of CO_2 absorption and CO_2 loading capacity. Similar properties were used by Papadopoulos *et al.* (2014) and Zarogiannis *et al.* (2015) in their approaches to screen and rank the performance of amines in their aqueous pure or blended forms, respectively; however, the assessment method used in this study is simpler than theirs. These properties were chosen for comparison because they are indicative of the amines' performance with regard to CO_2 capture. Amine solvents with a low cost and a high capacity for CO_2 are favourable. Vapour pressure indicates whether solvent losses would be a potential problem. Density, viscosity and surface tension are all related to the design and operation of the absorber and stripper columns. High values for density are desired as these indicate that a lower solvent flow rate and smaller columns will be required. On the other hand, a low viscosity and surface tension is preferred to increase mass transfer performance in the packing (Papadopoulos *et al.*, 2014, Zarogiannis *et al.*, 2015). A high viscosity also hinders heat transfer through the column (Freguia, 2002). Heat of absorption of CO_2 into the amine is indicative of the energy that would be required to regenerate the solvent (Chen and Rochelle, 2011), therefore low values for heat of absorption are preferred.

Using these properties as a guide, the top ten amines (all with a higher ranking than MEA) were determined to be: AHPD, MDEA, PZ, DEEA, DIPA, EEA, DEA, AMP, MAE and AEEA. Only pure aqueous amines were compared using these properties.

The following amines were rejected due to the reasons indicated:

- DEA and the majority of the solvent blends containing DEA (DEA + AMP, DEA + MDEA, DEA + MEA) have been extensively investigated (Padurean *et al.*, 2011, Daya, 2017) in a very similar way to this study.
- DIPA is known to be more selective toward H_2S than CO_2, and is therefore generally used in H_2S removal processes. According to Kohl and Nielsen (1997), DIPA is gradually being replaced by MDEA (which also appears on the shortlist).
- DEEA, while one of the better performing amines based on physical properties and price, it has slow kinetics with CO_2 (see table 4-1). It therefore should be used in blends together with a faster reacting amine; however, appropriate solubility data could only be found for pure aqueous DEEA.

To determine which amine solvent blends should be investigated, the kinetics of CO_2 with each of the listed amines were evaluated. The second order reaction constant was considered to be representative of kinetic performance (Xu *et al.*, 1996, Rayer *et al.*, 2011). Table 4-1 shows the kinetic constant values obtained (or calculated).

Table 4-1: Second order kinetic constants for the amine solvents under investigation.

Amine	k_2 (m^3/mol.s)	Reference
AEEA	1.497×10^1	Rayer *et al.* (2013)
AHPD	1.159×10^0	Paul *et al.* (2009)
AMP	1.250×10^0	Xu *et al.* (1996)
DEEA	1.166×10^{-1}	Kierzkowska-Pawlak (2015)
EEA	6.904×10^0	El Hadri *et al.* (2016)
MAE	9.889×10^0	Ali *et al.* (2002)
MDEA	4.513×10^{-2}	El Hadri *et al.* (2016)
MEA	1.077×10^1	El Hadri *et al.* (2016)
PZ	2.217×10^1	Rayer *et al.* (2011)

To obtain favourable kinetics in a blend, fast reacting amines should be paired with slower reacting amines (i.e. primary, secondary or cyclic amines paired with a tertiary or sterically hindered amines). Available solubility and kinetic data on solvent blends were collected in terms of these criteria; the most promising blends for investigation in a simulation environment were assessed to be:

- AHPD + PZ
- AMP + MAE
- AMP + MEA
- AMP + PZ
- EEA + MDEA
- MDEA + PZ

Of these, the blend AMP + MEA, like DEA, has been studied in a similar way to the present investigation. It was found by both Padurean *et al.* (2011) and Daya (2017) to be the best performing blend for CO_2 capture from coal fired power plants; hence, it will not be re-evaluated, as the focus is on expanding the performance indicator to new amines/ blends. The amines AHPD, EEA and MAE, initially intended for study, were eventually omitted due to the lack of data available in the Aspen Plus® databases. Processes containing these components as solvent, would hence not be accurately represented and the results from such investigations could not be accepted. Thus, only MDEA, AMP and PZ in various blends and compositions were considered.

From data available in the literature on CO_2 solubility and taking CO_2 reaction kinetics into account, the blends shown in table 4-2 are proposed for study (the exact blends may not have been previously investigated in all cases, but trends observed in available data suggest that these blends would perform well in terms of solubility). Total amine concentrations of 30 wt.% and 40 wt.% was selected to determine the effect of total amine concentration on the blend performance.

Furthermore, all PZ concentrations were kept at 10% or below as this is generally the norm in the literature for CO_2 solubility data.

Table 4-2: Blends proposed for investigation in this study.

Amine blend	Total amine weight concentration	Blend Compositions Proposed
AMP + PZ	30%	20% AMP + 10% PZ 25% AMP + 5% PZ
	40%	38% AMP + 2% PZ 35% AMP + 5% PZ
MDEA + PZ	30%	28% MDEA + 2% PZ 22% MDEA + 8% PZ
	40%	30% MDEA + 10% PZ 35% MDEA + 5% PZ

In addition, an aqueous solvent with three amine components, MDEA + AMP + PZ was investigated. Solubility data for this blend is only available at total concentrations above 30%. The chosen compositions were as follows:

- 25% MDEA + 10% AMP + 10% PZ
- 25% MDEA + 10% AMP + 5% PZ
- 25% MDEA + 5% AMP + 5% PZ

4.2 TEST SYSTEMS

A simulation for the benchmark case using the aqueous amine solvent of 30 wt. % MEA solution was successfully developed by adapting the simulation originally created by Daya (2017). The changes made to the original simulation created by Daya (2017) include:

- Altering flue gas composition slightly. Impurities with negligible concentrations such as hydrochloric acid (HCl), nitrogen dioxide (NO_2) and sulphur trioxide (SO_3) were omitted and the concentrations of remaining components normalized. (Refer to table 3-3 in section 3-2 for complete flue gas composition.)
- Including a calculator block to automatically set the heat duty of the cooling side of the lean-rich solvent heat exchanger (designated “cooler 1” in the process flow diagram, figure 3-1) equal to the heating side (designated “heater” in the process flow diagram, figure 3-1). One heat exchanger is thus modelled as two since the solvent recycle loop is not closed. In the work of Daya (2017), these values were matched manually.

- Addition of make-up streams for solvent(s) and water with calculator blocks to close the loops on an apparent component basis*.

The Performance Indicator Model (PIM) was set up in an Excel spreadsheet, using the guidelines provided in the thesis of Daya (2017). Major inputs to the model (for the initial base case, 30 wt.% MEA) in this study are shown in table 4-3. All prices are relevant to 2016.

Table 4-3: Main inputs to the performance model for the base case, 30% MEA

Parameter	Unit	Value
Amine Price	R/ton	39271[1]
Make-up Water Price	R/ton	11.52[2]
Cooling Tower Water Price	R/ton	0.54[2]
Steam Price	R/ton	150[2]
Corrosion Inhibitor Price	R/ton	3784[2]
Amine Reclaim Cost	R/ton	10078[2]
Amine Disposal Cost	R/ton	3008[2]
Carbon Tax Rate	R/ton	120[3]
Amine Degradation Rates	%/hr	0.3137[4]
Power Plant Efficiency	%	42.4[5]

1 (Kohl and Nielsen, 1997, Sinnott, 2005)
2 (Daya, 2017)
3 (The World Bank, 2014)
4 (Lepaumier *et al.*, 2009b, Lepaumier *et al.*, 2009c, Lepaumier *et al.*, 2009a)
5 (Gammer, 2016)

The rating for MEA (and for all the solvents and blends investigated in this study) is determined by performing the following steps: (the numbers in brackets refer to the equations presented in section 3.3.3)

1. The cost of capture, for each individual factor considered, is calculated using data as presented in table 4-3.

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* When using the eNRTL thermodynamic model in Aspen Plus, the components listed include electrolytes (ions) due to the reactions that occur in the absorber. This means that in a closed loop system, these electrolytic components are already present in the absorber before the reactions occur (due to the recycle from the stripper). A stream that shows its components in electrolyte form are said to use a "true component approach". However, these true components (which are essentially reaction products) can be reconstructed to show the non-ionic molecules that the electrolytes stem from. When considering the components in the system as the whole components instead of electrolytes, an "apparent component approach" is used. Thus, when balancing the system on an apparent component basis, the total values of the system components (CO_2, H_2O, amines) are the same, but the electrolytes which make up these components might not necessarily be 100% the same (they will be reasonably close though) (Kothandaraman, 2010).

2. The cost avoided (for each individual factor) is then calculated by multiplying the capture cost, determined in step 1, by a ratio of the plant efficiency with CO_2 capture to the original plant efficiency without capture (eqn 3-18). This takes into account the additional power that must be generated in order for the power plant to remain operating at its rated capacity.
3. The fraction of each cost factor, relative to the total cost avoided for that case, is determined (eqn 3-20) and multiplied by the ratio of cost avoided for the benchmark case, to cost avoided for the specific case investigated. Multiplication by this ratio compares the performance of the solvent investigated to the benchmark solvent.
4. Lastly, the contributions from each individual cost factor (obtained in step 3) is summed to obtain the rating of the solvent investigated (eqn 3-19).

A comprehensive sample calculation on how the rating is determined is presented in appendix D.

The optimum operating point for the benchmark case for the 30 wt.% MEA aqueous solution was found by following the method used by Daya (2017). The optimum operating point is the point at which the different costs combine to form the lowest total CO_2 capture cost (and thus the highest rating). To determine the optimum operating cost, the simulation must be performed for a range of operable lean solvent loadings – the loading which gives the lowest overall CO_2 capture cost determined by the PIM is then the optimum point for that solvent. Figure 4-1 illustrates this concept.

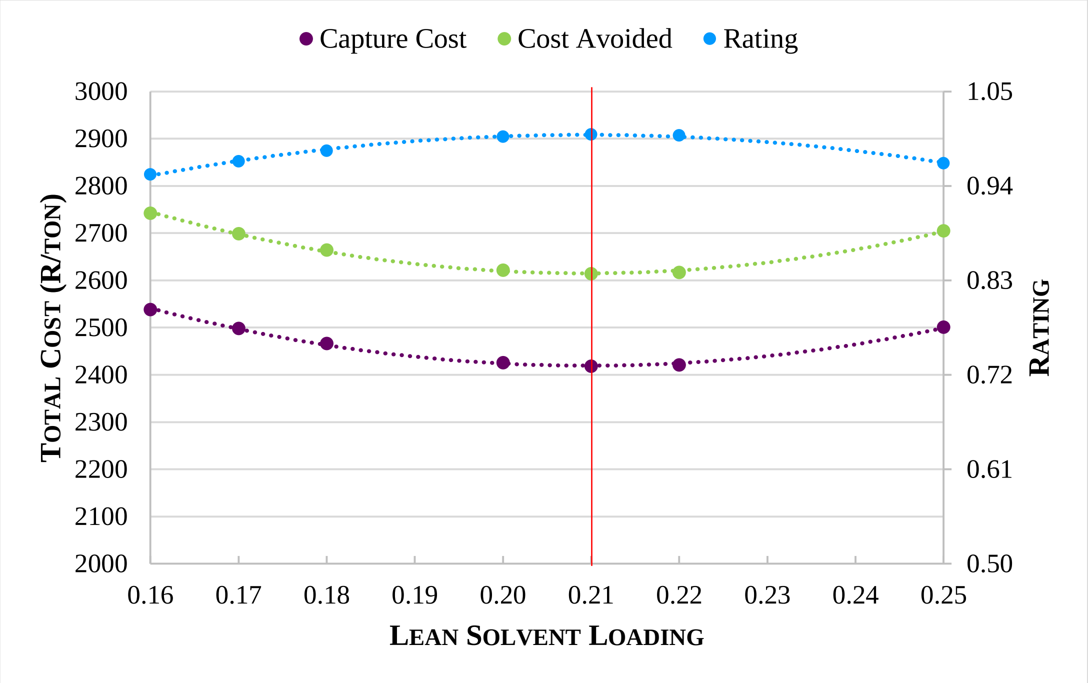

Figure 4-1: Method for determining the optimum operating point.

The major results of the process simulations for the benchmark, 30% MEA, was compared to literature results for 30% MEA simulations. This was used to validate the method used in this study to determine whether the results were comparable to that found in the literature. This comparison is presented in table 4-4.

Table 4-4: Comparison between the 30% MEA benchmarks of this work against the literature.

	This work (80% capture)	**This work (90% capture)**	**Padurean *et al* (2011)**	**Daya (2017)**	**Fisher *et al* (2007)**	**Kothandaraman (2010)**
Open/ closed Process	Open	Open	Closed	Open	Closed	Open
Solvent* Lean Loading (mol CO_2/mol amine)	0.21	0.14	n/s#	0.18	n/s	0.22
Solvent* Flowrate (ton/hr)	1484	1786	3500	2073	24237	n/s
Flue Gas CO_2 Content (mol %)	12	12	8.4	12	12.38	n/s
Flue Gas Flow Rate (ton/hr)	2283	2283	2928	2516	2448	n/s
CO_2 capture rate (%)	80	90	90.3	80	90	85
Total Energy Requirement (GJ/t CO_2)	12.4	19.6	3.29	13.00	16.82	16.61
Stripper diameter (m)	14	14	n/s	14	7.9	7
No. of trains	4	4	1	4	4	4
Energy Required per Stripper (GJ/t CO_2)	3.09	4.9	3.29	3.25	4.21	4.15

* All sources referenced in this table uses 30 wt.% MEA as a solvent
\# n/s – not specified by source

The results between this investigation and the values found in the literature differ due to the following reasons: (using reboiler duty as the main parameter for comparison)

- Variations in solvent lean loading affects the reboiler duty (Abu-Zahra, 2009, Alie *et al.*, 2005, Salkuyeh and Mofarahi, 2013)
- Increased solvent lean loading causes an increase in the required solvent flowrate for a given CO_2 capture rate, which in turn affects the required reboiler duty (Abu-Zahra, 2009, Abu-Zahra *et al.*, 2012)
- The temperature at which the lean solvent enters the absorber affects the reboiler duty (Abu-Zahra, 2009, Salkuyeh and Mofarahi, 2013, Arachchige *et al.*, 2013)
- The CO_2 content in the flue gas affects the reboiler duty (Alie *et al.*, 2005, Salkuyeh and Mofarahi, 2013, Naskar *et al.*, 2013)

- The capture rate of CO_2 can cause significant increases in required reboiler duty as it is increased (Abu-Zahra, 2009, Dash *et al.*, 2014, Arachchige *et al.*, 2013)
- An increase in the stripper pressure used causes a decrease in reboiler duty (Abu-Zahra, 2009, Kothandaraman, 2010, Dash and Wadibhasme, 2017)
- The type of column internals used affects the reboiler duty (Kothandaraman, 2010)
- The size of the columns (absorber and stripper) affects the reboiler duty (Kothandaraman, 2010, Dash and Wadibhasme, 2017, Arachchige *et al.*, 2013)

From the results obtained in this study as well as from the literature, it is implied that the number of trains (thus number of absorbers and strippers) utilized, also affects the required energy directly. Energy requirements for CO_2 capture processes with MEA are generally between 3 and 4.5 GJ/ ton CO_2 (Abu-Zahra, 2009). However, it can be seen from table 4-4 that sources which utilize multiple equipment trains require an amount in this range multiplied by the no. of trains.

Considering the information presented above, it is clear that a direct comparison between simulations performed in literature can be difficult to make. For the benchmark used to evaluate the test systems (30% MEA, 80% CO_2 capture), an energy requirement of 3.09 GJ/ ton CO_2 is reported per reboiler unit. This is 5% less than the literature source with the closest conditions, Daya (2017), which is an acceptable difference. For the MEA benchmark (30% MEA, 90% capture) used to compare the AMP benchmark to literature (refer to figure 2-4), an energy requirement of 4.9 GJ/ ton CO_2 is reported per reboiler unit. This is 16% more than the literature source with the closest conditions, Fisher *et al.* (2007), but still considered an acceptable difference when considering that not all simulation conditions match; there is especially a large difference in the column diameters used. It should also be noted that this work uses open loop simulations while Fisher *et al.* (2007) uses closed loop simulations.

Differences between the results of open and closed loop processes are not however necessarily high. Referring to table 4-4, the percentage difference between the energy requirements in the work of Fisher *et al.* (2007), which uses a closed loop, and Kothandaraman (2010), which uses an open loop, is less than 2%. Furthermore, a study by Ahmadi (2012) compared the results obtained from an open loop process simulated in Aspen Plus to a closed loop simulation in PROMAX, as well as pilot plant data. It was reported that the open loop simulation gave results very close to the other two cases. The results between the open and closed loop processes was within 3% difference on average. A maximum difference of 15% for reboiler duty was obtained between the open loop simulated data and the pilot plant data (for one run only), however, on average the difference in reboiler duty (across all runs) was only 5.2 % (Ahmadi, 2012).

This justifies that the results from open loop process simulations (like in this study) are comparable to the results obtained from simulations of closed loop processes.

After completing the simulation in assessing the benchmark case study for MEA, simulations for solvent blends previously studied were performed to ensure that results obtained from these simulations and the performance analysis model were comparable to the literature. The blends chosen were 20% MEA + 10% MDEA and 10% MEA + 20% MDEA, as both of these were studied by Daya (2017) as well as Padurean *et al.* (2011). The results are illustrated in figure 4-2.

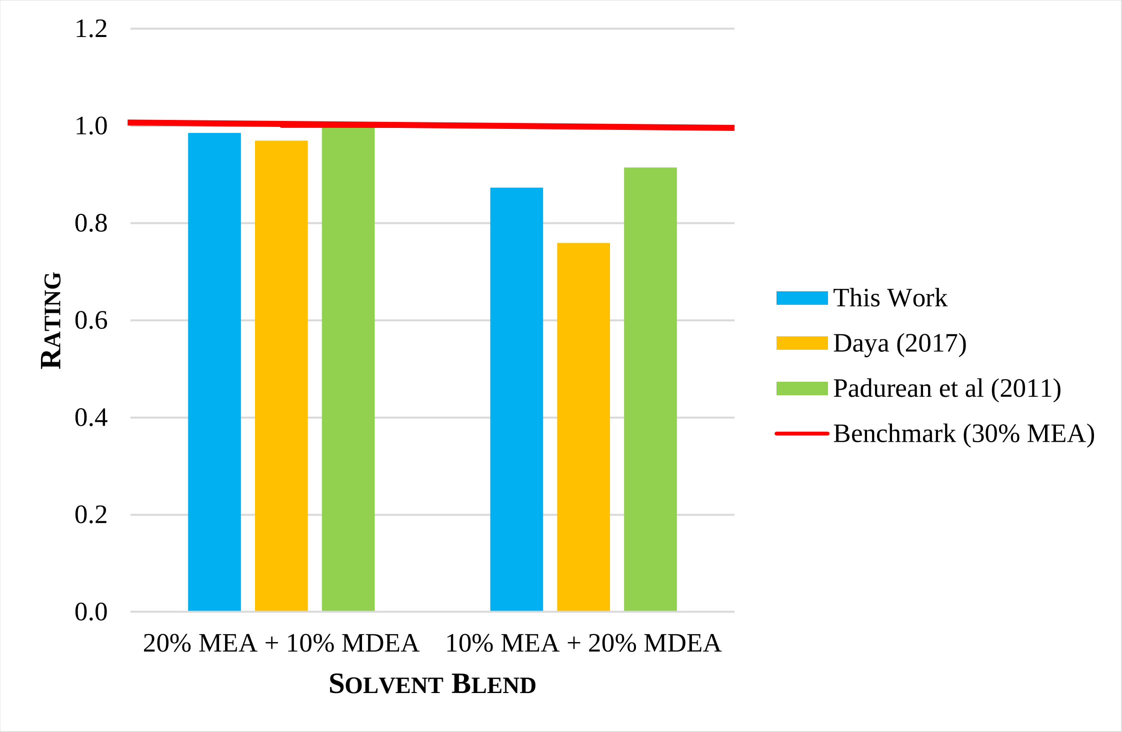

Figure 4-2: Results of the test system simulations performed for validation purposes.

Table 4-5: Differences between the ratings obtained in this work, and those in the literature, for the blend test systems.

	20% MEA + 10% MDEA		**10% MEA + 20% MDEA**	
	Rating	**% Difference**	**Rating**	**% Difference**
This Work	0.986	-	0.873	-
Daya (2017)	0.970	-1.64	0.759	-15.00
Padurean *et. al.* (2011)	1.007	2.06	0.915	4.54
Abs. Avg.		***1.85***		***9.77***

$$\%difference = \frac{literature\ value - value\ from\ this\ work}{literature\ value} \times 100$$

It can be seen from figure 4-2 and table 4-5 that the ratings obtained for the test systems in this work are comparable to that of the literature within a reasonable range (with an average percentage difference of 5.8% and a maximum of 15%). One can conclude from the comparisons made against the available literature sources that the absolute average is at most 10 %. These results were assumed indicative that the other ratings obtained in this work would be accurate and reproducible (only in one instance was the percentage difference above 5%). While the basis of this work is the same as that of Daya (2017), the work of Padurean *et al.* (2011) evaluated amine solvents and blends based on energy considerations only; heating and cooling units, as well as electrical energy consumption by pumps and compressors were considered. The work of Padurean *et al.* (2011) also included a CO_2 drying section before CO_2 compression, which was not included in this study. However, since the operations in the CO_2 drying section is dependent on the volume of CO_2 captured, and not on the solvent used, the effect of this additional section on the final results of solvent suitability was assumed to be minimal. The results of the study by Padurean *et al.* (2011), which was expressed as specific energy consumption, were converted into ratings using the PIM equations developed by Daya (2017) for comparison with the results of this work and the work of Daya (2017).

When performing the simulations for the test systems mentioned above, the conditions used in the work of Daya (2017) were followed closely (except for a slight alteration in the flue gas composition, as mentioned previously). These conditions could however be improved to conform more closely to the norms of conditions set in the literature for similar types of studies. The following changes were thus applied to the simulation specifications and process details:

- 90% capture instead of 80% capture is achieved - The capture rate was increased because a 90% capture rate is often achieved in the literature (Fisher *et al*., 2005, Lee *et al*., 2009, Padurean *et al*., 2011, Jones *et al*., 2013, Dash *et al*., 2014, Yakub *et al*., 2014, Li *et al*., 2016d) , especially when alternative solvents to MEA is used.
- The packing in the absorber and stripper were changed from Flexipac to Mellapak - The structured Mellapak packing showed an improvement in the operation of the columns and is also often used in the literature sources (Dash *et al.*, 2014, Li *et al.*, 2016b, van der Spek *et al.*, 2016).
- MEA was replaced as the benchmark by AMP - The benchmark was changed from 30% MEA to 30% AMP because both the studies of Daya (2017) and Padurean *et al.* (2011) identified AMP and blends of AMP as the best performing for post-combustion CO_2 capture from coal-fired power plants.

The simulation results using 30% AMP as the solvent, with the benchmark as 30% MEA was compared to that of Daya (2017) and (Padurean *et al.*, 2011). The MEA benchmark case for comparison here (represented by the red line in figure 4-3), was simulated with the changed capture rate (90%) and column packing (Mellapak), for a fair rating calculation. Figure 4-3 shows the comparison of the 30 wt. % AMP rating of this work (full calculation details can be found in appendix D) and that of the literature sources.

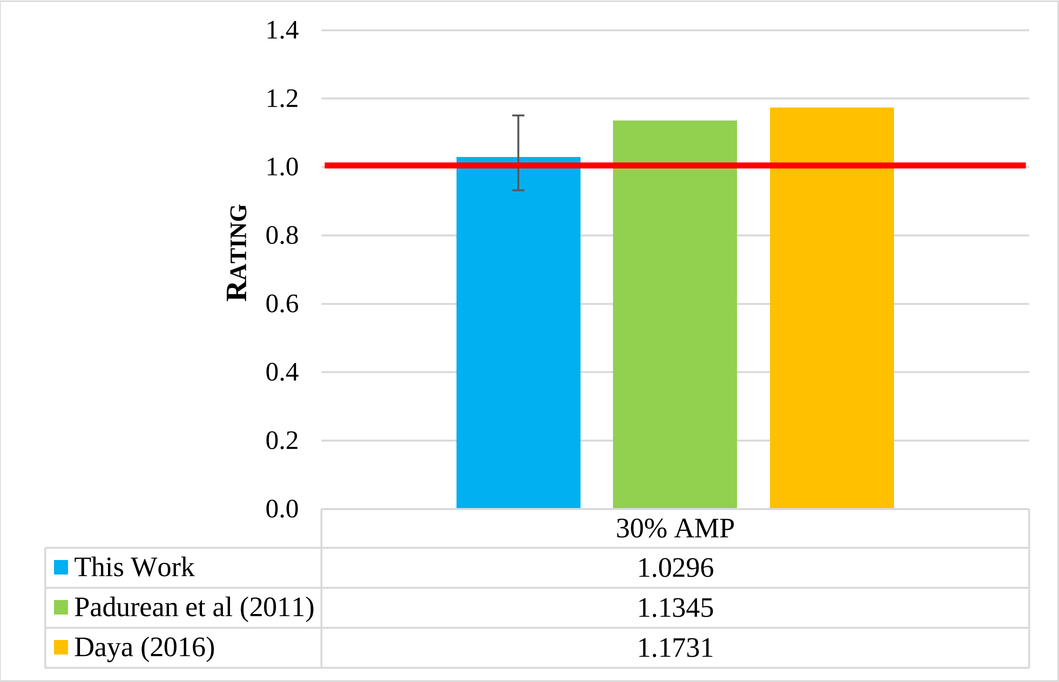

Figure 4-3: Comparison of the 30% AMP simulation results with the literature.

The initial rating calculated was not very close to the ratings obtained in the two literature sources. A sensitivity analysis (procedure explained in section 4.5) was thus performed to determine the possible range of ratings (0.932 – 1.151) that could be achieved. The upper limit of the sensitivity results lies well within range of the literature values (see the error bars on figure 4-3), and thus the rating result for the 30% AMP simulation was deemed acceptable and this case was used as the benchmark for the investigations of the study. It should be noted that in the work of Daya (2017), the initial rating obtained for 30% AMP was below 1. The rating of 1.1731, shown in figure 4-3 for the work of Daya (2017), was obtained after weighting factors were incorporated to improve the results and to make a better comparison between that work and the work of Padurean *et al.* (2011). Weighting factors were not included in this study due to the lack of literature, containing appropriate data for reasonable comparison, available for the new systems investigated.

Table 4-6 compares the 30% AMP benchmark of this study to simulations for 30% AMP published in the literature. The possible reasons given for the deviations between the results of this study and literature for MEA (table 4-4) applies to this case as well.

Table 4-6: Comparison between the AMP benchmark used in this study and AMP simulation studies found in the literature.

	This work	**Padurean *et. al.* (2011)**	**Lee et al (2009)**	**Montenegro (2011)**	**Li et al (2016d)**
Solvent Lean Loading (mol CO_2/mol amine)	0.135	n/s#	n/s	n/s	0.33
Solvent Flowrate (ton/hr)	2383	n/s	0.974	n/s	n/s
Flue Gas CO_2 Content (mol %)	12	8.4	8.34	12.57	13.3
Flue Gas Flow Rate (ton/hr)	2283	2928	0.563	324	3122
CO_2 capture rate (%)	90	93.8	95	90	90
Energy Requirement (GJ/t CO_2)	11.6	2.82	8.76	8	2.295
Stripper diameter (m)	14	n/s	n/s	7	n/s
No. of trains*	4	1	1	1	1

* If number of trains were not specified, it was assumed to be 1.
\# n/s – not specified by source

The studies of Lee *et al.* (2009) and Montenegro (2011) were performed at a smaller scale than this work, as can be inferred from the solvent and flue gas flow rates. Both of these studies also report relatively high energy requirements, which is an indication that the scale at which the studies are performed impacts the results obtained. Disregarding these two references for comparison, the maximum difference between this work and literature is 26% (considering the energy requirement per reboiler, which is 2.9 GJ/ ton CO_2 for this study) with an average percentage difference of 14.5%. These values are within an acceptable range when considering that not all conditions match.

4.3 NEW SYSTEMS

In the literature review (Chapter 2) as well as section 4.1, the reasons for choosing the solvents investigated (AMP, MDEA and PZ) were justified. Different blends of the amines AMP, MDEA and PZ were simulated in the CO_2 capture simulations. Binary solvent blends with both 30% and 40% total amine concentrations were simulated to observe whether increasing the amine concentration would increase the rating. The method adopted previously to determine the optimal concentration for the aqueous MEA solution at which the PIM produced the lowest rating was applied to each of the blends (using binary and ternary combinations of AMP, MEA and PZ) in order to determine the point which produces the best rating value. The resulting conditions then became the representative case for that specific amine blend.

The rating for the benchmark case calculated by the performance model formulae, is one. When the PIM calculations are applied for the amine blends, ratings below one shows a performance poorer than the benchmark, whilst a rating above one shows superior performance compared to the benchmark. The benchmark used for all cases is 30% AMP aqueous solution.

The results of the representative case for each blend is shown in figure 4-4 and table 4-7.

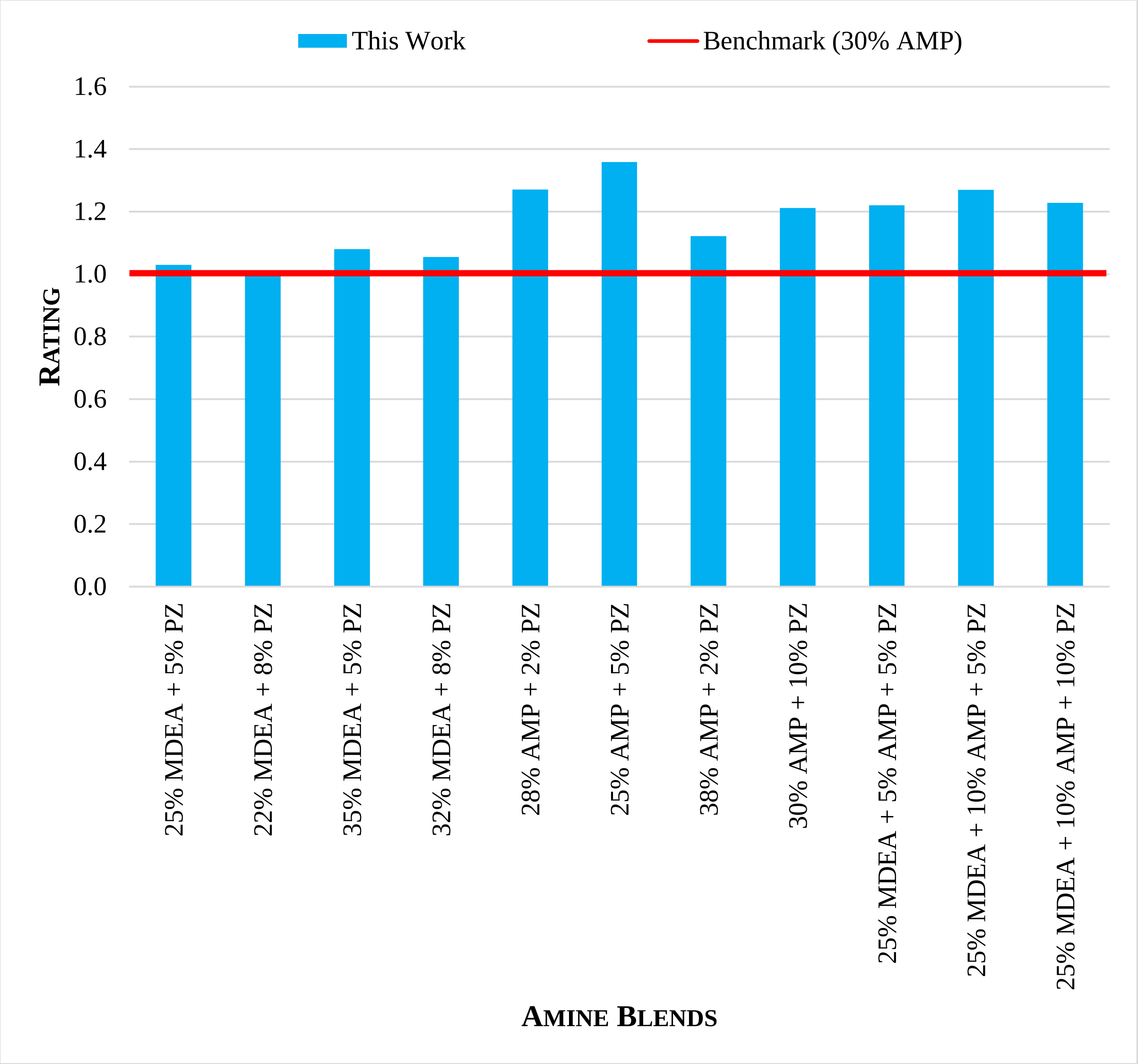

Figure 4-4: Ratings for the new systems simulated in this work.

Table 4-7: The data for the graph in figure 4-4 with the solvents investigated arranged in decreasing order of performance.

System	Ranking	Rating
25% AMP + 5% PZ	1	1.359
28% AMP + 2% PZ	2	1.270
25% MDEA + 10% AMP + 5% PZ	3	1.269
25% MDEA + 10% AMP + 10% PZ	4	1.228
25% MDEA + 5% AMP + 5% PZ	5	1.220
30% AMP + 10% PZ	6	1.212
38% AMP + 2% PZ	7	1.120
35% MDEA + 5% PZ	8	1.080
32% MDEA + 8% PZ	9	1.052
25% MDEA + 5% PZ	10	1.030
22% MDEA + 8% PZ	11	1.004
30% AMP (benchmark)	12	1.000

No current literature about simulation or pilot plant studies using the exact solvent compositions as in this study could be found, so no direct comparison to the literature can be made, i.e. no ratings can be calculated from the literature data to compare the ratings obtained in this study. The results of this study will hence be compared to trends observed in the literature of both simulation studies and solubility data studies. Factors other than rating must thus be considered for discussion. Many simulation studies focus on minimization of energy requirements, especially the energy required for regeneration, as this usually comprises the largest fraction (about two thirds) of total energy consumption; the reboiler duty is thus used here for comparison purposes. Solubility studies on the other hand, focuses on the solvent properties, hence the solvent flow rate is used here for comparison. When the CO_2 capture rate is kept constant, as in this study, a lower solvent flow rate will be required if the solvent has a greater capacity for CO_2. A summary of the relevant results for all the systems in this study is presented in table 4-8.

Table 4-8: A summary of the results obtained for the systems investigated in this work.

System	Lean Loading (mol CO_2/ mol Amine)	Rating	Reboiler Duty (MW)	Solvent Flow Rate (ton/hr)
30% AMP	0.135	1.000	296	2323
25% MDEA + 5% PZ	0.150	1.030	122	3778
22% MDEA + 8% PZ	0.215	1.004	148	3893
35% MDEA + 5% PZ	0.110	1.080	205	3345
32% MDEA + 8% PZ	0.160	1.052	147	3446
28% AMP + 2% PZ	0.170	1.270	164	1874
25% AMP + 5% PZ	0.210	1.359	136	1859
38% AMP + 2% PZ	0.170	1.120	130	1863
30% AMP + 10% PZ	0.250	1.212	91	1936
25% MDEA + 5% AMP + 5% PZ	0.125	1.220	116	2858
25% MDEA + 10% AMP + 5% PZ	0.110	1.269	107	2473
25% MDEA + 10% AMP + 10% PZ	0.177	1.228	95	2641

The results presented in table 4-8 shows that even though the reboiler duty and solvent flow rate comprise a large fraction of the rating determined by the PIM, minimal reboiler duty and solvent flow rate does not necessarily result in the best rating. The trends observed in the results as well as how the results compare to the literature will be discussed.

From solubility data published in the literature, the CO_2 capacity of the solvents investigated follows the trend MDEA < AMP < PZ. This is evident in the flow rates reported for the various blends – the flow rate shows a decreasing trend for solvents with a higher affinity for CO_2. The flow rate of the MDEA + PZ blends are significantly higher than that of the AMP + PZ blends and the flow rate of the tri-amine blends lie in between because all three components are present. Solvent flow rate is also directly linked to the reaction rate of the amine with CO_2 which also follows the trend PZ > AMP > MDEA. A higher reaction rate would lead to a lower flow rate, which is also reflected in the results shown in table 4-8.

The MDEA + PZ blends do not have very high ratings and this is mainly because of the high solvent flowrate required due to MDEA's ternary amine nature, which means it has a very slow reaction with CO_2 (refer to table 4-1). Solubility results show that an increase in PZ concentration in the blend causes the capacity for CO_2 to increase (Dash and Bandyopadhyay, 2016); the solvent flow rate trends show this. The reclaim and disposal costs of the amines, which is calculated externally, is based on the flow rate of the solvent, therefore a higher flow rate also significantly increases these costs. Therefore, even although the energy consumption for the MDEA + PZ blend is lower than the benchmark, the factors mentioned above contributes to the calculation of a lower rating for AMP + PZ blends.

For the results obtained using the AMP + PZ blends, which have the highest ratings overall, both a low reboiler duty and low solvent flow rate combines to give a high rating. The tri-amine blends show low reboiler duty, which is probably a result of combining AMP and MDEA which both have low heats of reaction with CO_2 (which implies regeneration duty will be decreased). However, due to the fact that MDEA makes up the bulk of the solvent's amine concentration, the solvent flow rate is quite high and thus the higher costs of solvent make-up and reclaim, leads to a lower rating. Therefore, whilst the tri-amine blends seem to be superior in terms of energy consumption, when considering other factors, its performance falls short of the AMP + PZ binary blends.

The blend compositions chosen for study were done by observing the norms and trends in the literature CO_2 solubility data. It is therefore possible that blends with different concentrations (that lie in between the concentrations investigated) could show better performance when evaluated by the PIM. Other blend compositions were not evaluated due to time constraints, however a recommendation regarding this issue is made in Chapter 6.

4.4 MODIFIED CONFIGURATIONS

As discussed in Chapter 2, the process modifications which require no or very little additional equipment but still show appreciable improvement in energy considerations is the intercooled absorber (ICA), rich solvent split (RSS), and lean vapour compression (LVC) configurations. The ICA and RSS configurations were simulated for the best performing solvent blend in the conventional configuration studies, which was 25% AMP + 5% PZ + 70% H_2O (wt.%).

4.4.1 INTERCOOLED ABSORBER

In the intercooled absorber configuration, a fraction of the solvent in the absorber is withdrawn, cooled down, and then sent back to the absorber (Le Moullec *et al.*, 2014).

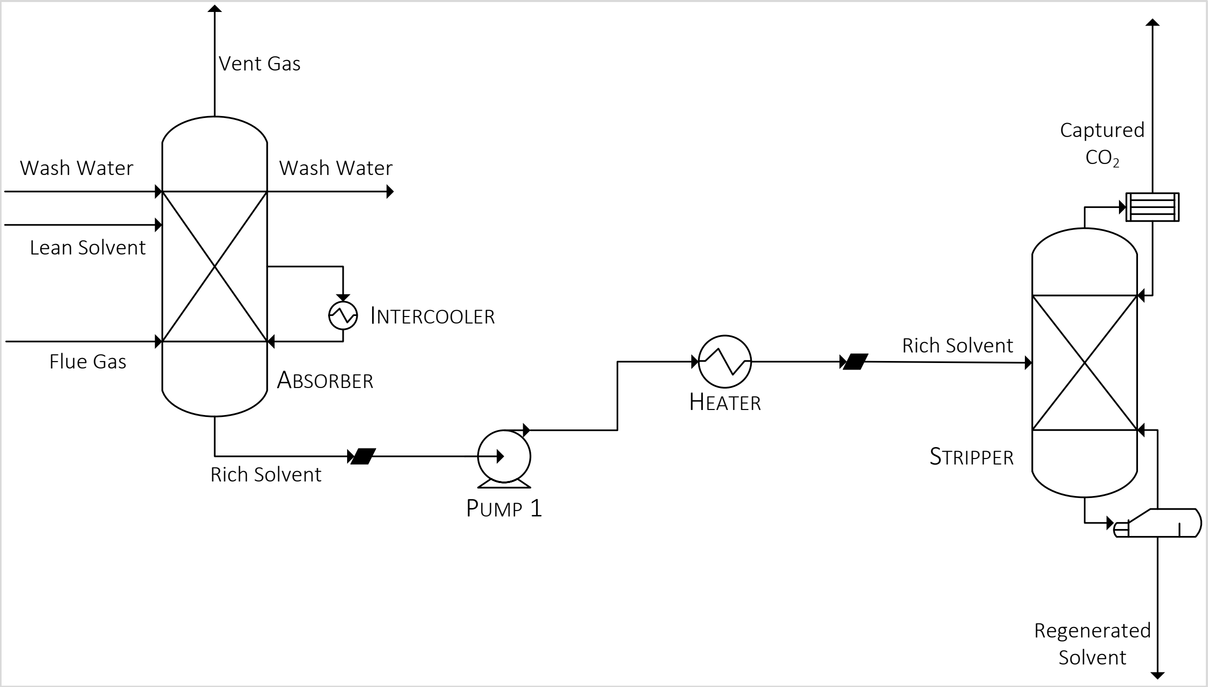

Figure 4-5: The intercooled absorber configuration as applied to the capture section of the flowsheet.

Initially, different stages were used for the take-off and re-entering of the cooled stream. This proved to be very difficult to optimize as 3 variables (cooled fraction, cooled stream exiting stage and cooled stream entering stage) needed to be optimized simultaneously. This also caused problems with the Aspen simulations as all the possible values for each variable did not always produce satisfactory results; numerous errors or failed simulation runs resulted. Using different stages for entering and exiting of the cooled stream, is less practical than using one cooling stage (where the cooled fraction exits and enters on the same stage), as it leaves a whole section of the column operates with reduced amount of solvent.

Therefore, simulations using one cooling stage were performed. These simulations proved to have overall better results than those performed previously (refer to table 4-9). Zhang *et al.* (2017) suggests that a cooling stage lower in the absorption column, where the solvent is rich in solute, is more beneficial as cooling in this region provides a higher driving force due to higher column temperatures here. In the 22 stage column used in this work (where stages are numbered from top to bottom), stage 17 was initially attempted as the cooling stage. The stage number was varied and stage 15 was selected as it resulted in the optimal performance. Due to time constraints all possible stages could not be tested for this purpose however, from table 4-9, it can be seen that results for cooling stage = 15 and cooling stage = 17 are similar, but that the simulations performed for cooling stage = 15 were more stable. This could be an indication that using stages below stage 15 as the cooling stage could result in unstable simulation runs prone to convergence errors.

Table 4-9: A summary of the intercooled absorber simulations performed under different conditions.

	Split Fraction	Entering stage	Exiting Stage	Stripper Reboiler Duty (MW)	Intercooler Duty (MW)	Solvent Flow Rate (ton/hr)	Temperature Difference in Intercooler (°C)	Estimated Rating
Case 1	0.2	20	12	142.6	-6.255	1716	19.09	1.431
Case 2	0.4	20	12	139.9	-10.48	1684	16.31	1.487
Case 3	0.55	20	12	139.3	-12.60	1679	13.66	1.509
Case 4	0.6	20	12	139.4	-13.12	1680	13.66	1.509
Case 5	0.2	17	9	142.1	-6.977	1709	21.36	1.463
Case 6	0.4	17	9	138.8	-11.51	1668	18.07	1.546
Case 7	0.55	17	9	137.8	-13.72	1656	15.79	1.577
Case 8	0.6	17	9	137.7	-14.26	1655	15.06	1.578
Case 9	0.2	17	17	141.3	-3.783	1694	11.76	1.413
Case 10*	0.3	17	17	ERRORS				
Case 11*	0.4	17	17	138.9	-6.080	1672	9.59	1.458
Case 12	0.2	15	15	142.9	-4.581	1720	14.00	1.429
Case 13	0.3	15	15	141.2	-5.953	1700	12.28	1.453
Case 14	0.4	15	15	139.9	-6.977	1684	10.90	1.471

*Convergence Errors

In table 4-9, cases 1 – 8 were performed with different exiting and entering stages for the cooled stream. Cases 9 – 14 were performed using one cooling stage only. Even though some cases from 1 – 8 have higher ratings than the cases with one cooling stage only, it was decided that having only one cooling stage is more feasible in practice, thus the results of cases 1 – 8 were disregarded and presented here only to show the progression of work.

Between the cases using stage 17 and 15 as the cooling stage, case 14 (which uses stage 15 as cooling stage) has the best rating as determined by the performance model. Using stage 17 as cooling stage brought up numerous errors (primarily related to convergence of the absorber) upon increasing the split fraction of the cooled stream above 0.2.

Using stage 15 as cooling stage was further investigated by increasing the split fraction, as well as the solvent lean loading, to obtain a maximum rating. The split fraction range was first extended to see if a maximum could be obtained at some point. This is shown in table 4-10.

Table 4-10: Further investigation into using stage 15 as cooling stage, by increasing the split fraction range.

Split Fraction	Cooling Stage	Stripper Reboiler Duty (MW)	Intercooler Duty (MW)	Solvent Flow Rate (ton/hr)	Temperature Difference in Intercooler (°C)	Estimated Rating
0.2	15	142.9	-4.581	1720	14.00	1.429
0.3	15	141.2	-5.953	1700	12.28	1.453
0.4	15	139.9	-6.977	1684	10.90	1.471
0.5	15	138.8	-7.774	1671	9.80	1.483
0.6*	15	138.0	-8.412	1660	8.90	1.483
0.7*	15	143.5	-10.09	1678	9.36	1.448

*Convergence errors

From table 4-10 it can be seen that a split fraction of 0.5 and 0.6 gives the highest rating of 1.483, however the split fraction of 0.5 was selected for further use, as using 0.6 as split fraction has no significant improvement on the results. A split fraction of 0.7 was attempted to observe the trend; simulations using stage 15 as cooling stage and 0.7 as split fraction could not run to success completion due to convergence errors. The results of this final run is shown here for illustration purposes, although they may be deemed as unreliable due to the errors in the simulations.

Using stage 15 as cooling stage and with a 0.5 split fraction, the lean loading of the solvent was varied to determine the best possible rating. The solvent used, 25% AMP + 5% PZ + 70% H_2O, showed an optimum loading of 0.21 mol CO_2/mol amine when used in the conventional configuration. Staying close to this value, a value of 0.2 mol CO_2/mol amine was used in all the simulations above. This loading produced the highest rating. A summary of the results is shown in table 4-11.

Table 4-11: The effect of the solvent lean loading on the overall rating of the solvent.

Loading	Capture Cost (R/ton)	Cost Avoided (R/ton)	Rating
0.18	2721	2984	1.308
0.20	2421	2632	1.483
0.23	3373	3669	1.064

It is therefore concluded that when using stage 15 as cooling stage, with a cooled fraction of 0.5 and a solvent lean loading of 0.2 mol CO_2/mol amine, the best rating for the ICA configuration is obtained. The rating of 1.483 obtained under these conditions is greater than the rating obtained for the same solvent in the conventional configuration (1.359), which means that this configuration shows an approximate overall improvement of 9%. This improvement is from the combined effects of reduced energy demands and reduced solvent requirements, which in turn reduces the costs of other factors such as waste disposal.

4.4.2 RICH SOLVENT SPLIT

This modification involves splitting the rich stream into two flows. One of these streams is preheated by the lean/rich heat exchanger while the other is kept cold. The cold stream enters at the top of the stripper while the heated stream is injected at an appropriate location below (Le Moullec *et al.*, 2014).

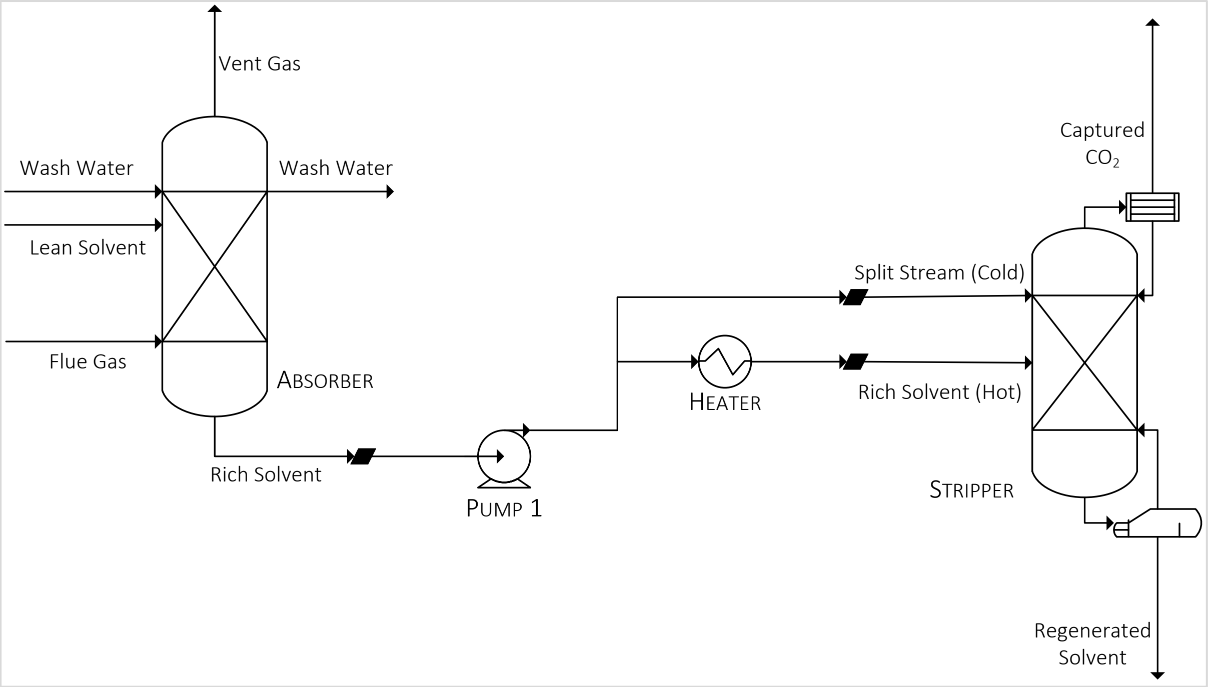

Figure 4-6: The rich solvent split configuration as applied to the capture section of the flowsheet.

In the rich solvent split configuration, the split fraction of the rich solvent stream as well as the entering stage of the heated fraction of solvent must be optimized. The aim of this study was to consider a few modifications such that minimal changes were made to the equipment specifications in the simulation. The entering stages for the cold and hot streams were set to stages 2 and 3 respectively, so that the packing in the stripper could remain unaltered (as sectioning the packing would mean installation of an entire new column). Thus, only the split was varied to find the highest rating. Table 4-12 presents the results obtained in varying the split fraction of the heated rich stream. A range of 0.1 – 0.5 was used for the split fraction because the cold stream should be of a smaller fraction than the hot stream (Zhang *et al.*, 2017).

Table 4-12: Varying the split fraction of the rich solvent split configuration to find the highest rating.

Lean Loading (mol CO_2/ mol amine)	Split Fraction	Capture Cost (R/ton)	Cost Avoided (R/ton)	Rating
0.15	0.1	2936	3190	1.2237
0.15	0.3	2936	3191	1.2236
0.15	0.5	2937	3192	1.2232

The results shown in table 4-12 show that with varying split fraction over 0.1-0.5, there is minimal change in the performance ratings; all are approximately 1.224, which is the average value calculated. The % difference from the average was within 0.02%. A split fraction of one was selected for further investigation by changing the solvent lean loading. A lean loading of 0.15 was initially chosen arbitrarily.

Table 4-13: The effect that a change in lean loading has on the rating of the solvent.

Lean Loading (mol CO_2/ mol amine)	Split Fraction	Capture Cost (R/ton)	Cost Avoided (R/ton)	Rating
0.15	0.1	2936	3190	1.224
0.18	0.1	2717	2953	1.322
0.21	0.1	2645	2877	1.357
0.216	0.1	2644	2876	1.357
0.25	0.1	2708	2948	1.324

Table 4-13 shows that a lean loading of 0.216 mol CO_2/ mol amine produced the highest rating of 1.3573. Similar to the ICA configuration, this value is very close to the optimum lean loading value obtained for the same solvent using the conventional configuration (which had a lean loading of 0.21 mol CO_2/ mol amine).

As a final check, the split fraction for the simulation with a lean loading of 0.216 mol CO_2/ mol amine was varied to observe the trends and for comparison to the simulations with a lean loading of 0.15 mol CO_2/ mol amine. Table 4-14 shows the effect that varying the split fraction has on the rating while keeping lean loading constant. It can hence be concluded that when using stage 3 as the entering stage for the hot solvent, 0.216 mol CO_2/ mol amine as lean loading and 0.1 as split fraction, the highest rating is achieved.

Table 4-14: Varying the split fraction of the rich solvent split configuration to find the highest rating.

Lean Loading (mol CO_2/ mol amine)	Split Fraction	Capture Cost (R/ton)	Cost Avoided (R/ton)	Rating
0.216	0.1	2644	2876	1.357
0.216	0.3	2647	2879	1.356
0.216	0.5	2659	2893	1.349

The highest rating achieved for this investigation was 1.356, which is very similar to the rating for the conventional configuration using the same solvent (1.359). Thus, applying this configuration makes no overall difference to the solvent performance.

4.4.3 COMPARISON TO LITERATURE

The purpose of this study is to determine a rating calculated by the performance model, to indicate the overall performance of an amine solvent or blend relative to a benchmark solvent (which was 30 wt. % AMP in this study).

It is difficult to provide a direct comparison of the results to literature; similar studies generally report their findings in percentage energy savings compared to a baseline case/benchmark solvent performance. The reboiler duty provides a good indication of performance when considering energy alone, because it accounts for a significant percentage (> 50%) of the total energy usage (Kothandaraman, 2010). Savings in reboiler duty and total energy usage were thus computed for literature comparison purposes.

Tables 4-15 and 4-16 shows a condensed summary of the results obtained using the process modifications, including comparisons between the results of the modified processes with that of the conventional process.

Table 4-15: Comparison between the main results of the conventional configuration and the process modifications.

	Conventional Configurations			Modifications	
				ICA	RSS
	30% MEA	30% AMP	25% AMP + 5% PZ	25% AMP + 5% PZ	25% AMP + 5% PZ
Reboiler Duty (MW)	564.9	295.7	136.2	138.8	131.5
Total Energy Requirements (MW)	4501	2415	1114	1146	1080
Cost of CO_2 Avoided (R/ton CO_2)	4020	3904	2873	2632	2893
Rating	0.971	1	1.359	1.483	1.349

Table 4-16: Percentage savings of the process modifications with respect to each of the conventional configuration cases presented in table 4-15.

	ICA wrt 30% MEA	ICA wrt 30% AMP	ICA wrt 25% AMP + 5% PZ	RSS wrt 30% MEA	RSS wrt 30% AMP	RSS wrt 25% AMP + 5% PZ
Reboiler Duty	75.4	53.0	-1.9	76.7	55.5	3.5
Total Energy Requirements	74.6	52.6	-2.9	76.0	55.3	3.0
Cost of CO_2 Avoided	34.5	32.6	8.4	28.0	25.9	-0.7

When comparing the savings in reboiler duty and energy and the difference in cost of CO_2 avoided (which directly affect the overall rating) for the various cases, the vales of the ICA configuration show a contradicting trend. Although reboiler duty is a main contributor to the value of the rating, solvent flow rates also have a significant influence. For the ICA configuration, the solvent make-up flows, and hence the costs of amine reclaim and disposal, is significantly reduced. This caused the overall rating to be high, even though the reboiler duty was slightly (1.9%) more than that of the conventional case using the same solvent.

Zhang *et al.* (2017) used a solvent with composition 28% AMP + 17% PZ + 55% H_2O (all wt.%) and found that energy savings of 6.7% and 8.5% for the ICA and RSS configurations could be achieved respectively. These energy savings were computed in comparison to the conventional configuration using the same solvent. Compared to the conventional configuration with the same solvent, the results of this study show that the ICA configuration requires 2.9% more energy than the conventional configuration and that RSS has a 3% energy saving. However, in terms of overall capture cost, ICA shows a 8.4% improvement while RSS is very similar to the conventional configuration. A possible reason for the discrepancies between the results of this work and that of Zhang *et al.* (2017) may be due to the optimisation of the process conditions, discrepancies resulting due to varying equipment sizes which impacts on utilities, etc. – it is possible that complete optimization of process conditions and equipment sizes could have produced results more similar to the literature.

It should however be noted that other studies in the literature (which use mainly 30% MEA as solvent) have also shown varying results. For the ICA configuration, reductions in reboiler duty range from low values (~ 3%) (Schach *et al.* (2010); Le Moullec and Kanniche (2011a); Neveux *et al.* (2013); Gupta *et al.* (2015)) to much higher values of about 55% (Damartzis *et al.*, 2016). Similarly for the RSS configuration, reductions in reboiler duty range from values between 5 and 10% (Cousins *et al.* (2011a); Cousins *et al.* (2011b); Neveux *et al.* (2013); Xue *et al.* (2016); Zhao *et al.* (2017)) to values as high as 49% (Damartzis *et al.*, 2016). Table 2-1 in Chapter 2 show these results and more information on process modifications.

These variations in the literature results leads to the conclusion that the savings obtained is very dependent on the conditions of each individual study.

4.5 SENSITIVITY ANALYSIS

A sensitivity analysis was performed to determine the possible deviations in the ratings obtained. This was done by finding at least three different values for all price factors used in the model, computing the standard deviation, and using the standard error in the prices as an uncertainty (details can be found in Appendix D). The maximum and minimum values for the rating of each case were determined by combining all the uncertainties to produce the highest and lowest possible rating, respectively. The results showed that the ratings in this work have an average error of ±4% (relative to the baseline case). The upper and lower bounds of the ratings for each solvent blend is shown in table 4-17.

Table 4-17: Results of the sensitivity analysis.

Amine Blend	Rating	Lower Bound	Upper Bound
25% MDEA + 5% PZ	1.030	0.918	1.172
22% MDEA + 8% PZ	1.004	0.896	1.142
35% MDEA + 5% PZ	1.080	0.968	1.223
32% MDEA + 8% PZ	1.055	0.945	1.194
28% AMP + 2% PZ	1.270	1.149	1.420
25% AMP + 5% PZ	1.359	1.228	1.521
38% AMP + 2% PZ	1.121	1.019	1.246
30% AMP + 10% PZ	1.212	1.099	1.351
25% MDEA + 5% AMP + 5% PZ	1.220	1.093	1.381
25% MDEA + 10% AMP + 5% PZ	1.269	1.142	1.429
25% MDEA + 10% AMP + 10% PZ	1.228	1.105	1.381
ICA 25% AMP + 5% PZ	1.483	1.341	1.659
RSS 25% AMP + 5% PZ	1.357	1.226	1.520
Standard Error		**0.0349**	**0.0475**
Average		**0.0412**	

The deviations between the presented rating value and its upper and lower bound respectively, are plotted on figure 4-7 as error bars.

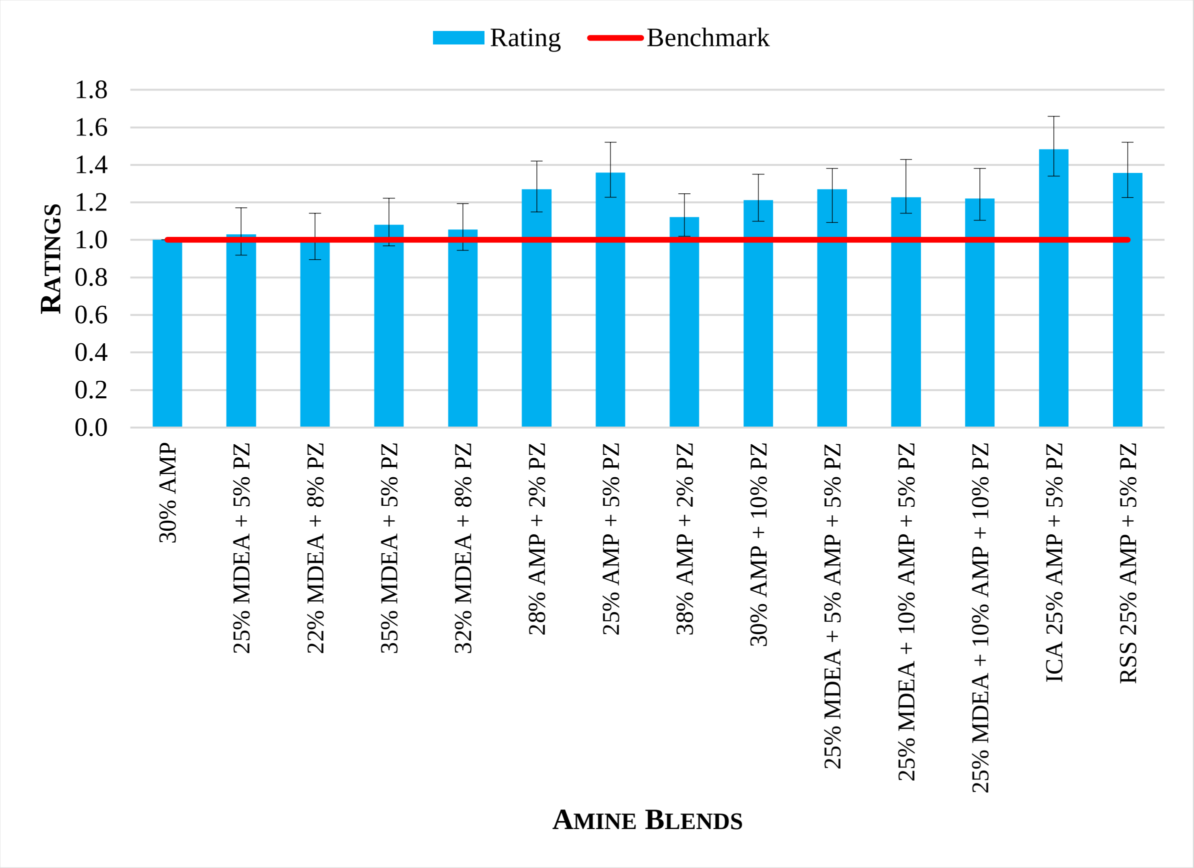

Figure 4-7: Performance ratings for the amine blends investigated.

The average standard error of the ratings in this work, 0.0412, is almost double that of the standard error in the work of Daya (2017), which was 0.0225. A very small error was obtained in the work of Daya (2017), because weighting factors were used to reduce the error between the results of that study and the literature. This led to the higher contributing factors in the PIM to have a weighting of less than one in the model, which means that a change in those factors had a reduced effect in the work of (Daya, 2017). In this work all factors had a weighting of one due to the absence of weighting factors. If more data on studies similar to this one were available with the same solvents, weighting factors could also be regressed for these systems, which could possibly lead to reduced deviations.

To summarize, the amine solvents investigated in this work were MDEA, AMP and PZ in aqueous blends of MDEA or AMP with PZ as well as aqueous tri-amine blends containing all three amine components. The PIM developed by Daya (2017) was modified, then used to evaluate the solvent blends by determining a rating of each blend relative to a baseline solvent, 30 wt. % AMP. The blend 25% AMP + 5% PZ (wt. %) was the best performing and was further used to study the process modifications, intercooled absorber (ICA) and rich solvent split (RSS). The ICA configuration showed a 9% improvement on the rating obtained from the conventional configuration with the same solvent, while applying the RSS modification had no effect on the rating. A sensitivity analysis showed that the ratings obtained are accurate within a 4% margin.

CHAPTER 5

5 CONCLUSIONS

The concept of the performance indicator model originally developed by Daya (2017) was used to determine the performance of different aqueous amine solvent blends for post-combustion CO_2 capture from a coal-fired power plant.

30 wt. % AMP, a different baseline solvent from the initial 30 wt. % MEA was selected, as the literature studies have shown that AMP is better for CO_2 capture than MEA.

Aqueous solvent blends of AMP or MDEA with piperazine were evaluated, as well as ternary amine aqueous blends with AMP, MDEA and PZ. For the binary amine blends, total amine concentrations of 30 wt.% and 40 wt.% were evaluated, while the total amine concentration of the ternary amine blends were 45 wt.%.

The best performing blends was 25% AMP + 5% PZ (wt.%), with a rating of 1.359. In comparison, the worst performing blend, 22% MDEA + 8% PZ, had a rating of 1.004. The latter is practically the same as that of the benchmark solvent AMP.

For the MDEA + PZ blends, an increase in the total amine concentration caused an increase of up to 5% in the performance rating, while for the AMP + PZ blends, increasing the total amine concentration had a negative effect (up to 21% decrease) on the performance ratings.

Furthermore, increasing the PZ concentration had a positive effect on the ratings of all binary amine blends. For AMP + PZ blends, ratings were increased with 7% and 8% for total amine concentrations of 30 wt. % and 40 wt. %, respectively. For MDEA + PZ blends, ratings increased by 2.5% and 2.7% for total amine concentrations of 30 wt. % and 40 wt. %, respectively.

The ratings of the tri-amine blends (1.220 – 1.269) were higher than that of the MDEA + PZ blends (1.004 – 1.080) and lower than AMP + PZ blends with a total amine concentration of 30 wt. % (1.270 – 1.359).

The best performing blend, 25% AMP + 5% PZ, was further used to evaluate modified process configurations; these included the intercooled absorber configuration and the rich solvent split configuration.

For the intercooled absorber configuration, with cooling on stage 15, a split fraction of 0.5 and a lean solvent loading of 0.20 mol CO_2/ mol amine a rating of 1.483 was obtained. This gave a 9% improvement on the rating of the conventional configuration.

The highest rating obtained for the rich solvent split configuration was 1.356 (where the split fraction was 0.1 and the lean solvent loading was 0.216 mol CO_2/ mol amine). This process modification showed no improvement on the rating of the solvent.

A sensitivity analysis revealed that the ratings obtained in this work has an average error of ± 4% relative to the baseline solvent.

CHAPTER 6

6 RECOMMENDATIONS

- As initially recommended by Daya (2017), it would be useful to incorporate equipment sizes (i.e. capital costs) into the performance model. In this work, the equipment sizes were kept the same in order to only determine the performances of different solvents. This would be beneficial in the event that a new solvent is to be used in an existing capture plant. However, for new installations, it would be more advantageous to know the performance of a solvent together with optimized conditions and equipment sizes. Incorporating individually designed equipment for each solvent or blend could significantly alter the ratings obtained.

- It is also recommended to evaluate more compositions for each blend. This could be achieved by developing an Aspen Plus® user interface that could automatically determine the optimum blend composition by using the performance model as an objective function (Daya, 2017). Alternatively, various blend compositions can be evaluated and the trend in ratings used to determine what the optimum solvent blend composition would be. The manual approach, similar to the one adopted in this study for determining optimum lean loading values, will be more time consuming, but also less complex than the alternative.

- As studies about CO_2 capture evolve, new promising solvents for this application will emerge. It would be advantageous to evaluate these solvents in a process simulation environment and with a performance model as developed in this work once sufficient data on a solvent is available. Data for non-established solvents are not available in the databanks of simulation software. However, from the literature data and experimental work, the required information can be obtained and entered into the simulation software. Determining how a solvent is likely to perform in large scale applications could eliminate costly tests and studies should the simulations indicate that the solvent is not a good candidate.

- Other process modifications or combinations of modifications should be investigated. The lean vapour compression modification seems promising. With respect to combinations, it would be the simplest to combine the desired process modification with heat integration.

- Evaluating the performance of more solvents and blends with more process modifications is encouraged. In this work the best performing blend for the conventional configuration was used to evaluate the process modifications. It is however possible that one of the other blends could perform better with a specific modification.

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APPENDIX A: PROCESS MODIFICATIONS

Appendix A provides an overview of process modifications reported in the literature. Tables A-1 and A-2 provide descriptions of the different process modifications. Refer to table 2-1 in Chapter 2 for a summary of the conditions and results of studies performed on different process modifications.

Table A-1: Process modifications (extracted from Le Moullec et al. (2014))

	MODIFICATION	DESCRIPTION
ABSORPTION ENHANCEMENT	Intercooled Absorber (ICA)	A fraction of the solvent in the absorber is withdrawn, cooled down, and then sent back to the absorber.
	Rich Solvent Recycle (RSR)	A fraction of solvent is withdrawn from a lower absorber level (which could include bottoms) and recycled back to an upper level.
	Inter-heated Absorber (IHA)	Inter-heated absorbers operate in the same way as inter-cooled absorbers, except that heating, instead of cooling, is applied.
	Split Flow Arrangement (SFA)	In the split flow arrangement, the solvent is regenerated at two (or more) loading ratios. One of the streams is a lean solvent stream, which is fed to the top of the absorber and the remaining stream(s) are semi-lean, and fed to the middle of the absorber. For the SFA, the rich-lean heat exchanger must be split into two (or more) exchangers for heat recovery from the lean and semi-lean stream(s) exiting the stripper.
	Double Loop Absorber (DLA)	This configuration divides the absorber into two sections, similar to the split flow process. The absorption mainly takes place in the bottom section; the upper section is used for gas treating. The main purpose of this configuration is to use different solvents in the different absorber loops.
	Flue Gas Compression and Expansion (FCE)	In this modification, the flue gas is compressed up to 3 bar, raising the CO$_2$ partial pressure to increase absorption in the solvent.
HEAT INTEGRATION	Rich Solvent Splitting (RSS)	This modification involves dividing the rich stream into two flows. One of these streams is preheated by the lean/rich heat exchanger while the other remains cold. The cold stream enters at the stripper top whilst the heated stream is injected at an appropriate location below.

Table A-1: Process modifications (extracted from Le Moullec et al. (2014)) (contd.)

	MODIFICATION	DESCRIPTION
HEAT INTEGRATION	Rich Solvent Pre-heating (RSP)	The rich solvent heated to a temperature higher than that achievable in the rich-lean exchanger by transferring heat from the hot lean solvent exiting the stripper to the cold rich solvent entering the stripper.
	Rich Solvent Flashing (RSF)	Here, the rich solvent is flashed before it is fed to the stripper, which releases some CO_2 and cools down the remaining liquid stream.
	Parallel Economizer Arrangement (PEA)	The primary aim of this modification is to optimize heat recovery between streams around the stripper and the reboiler, and streams being fed to that part of the process. This can be achieved by splitting either the rich or lean solvent and feeding each stream section to separate heat exchangers.
	Inter-heated Stripper (IHS)	As with its absorber counterpart, a semi-lean solvent stream is withdrawn from the stripper, re-heated, and then sent back into the stripper.
	Heat Integrated Stripper (HIS)	This modification eliminates lean/rich heat exchanger and fully integrates it into the stripper.
	Overhead Condenser Bypass (OCB)	Instead of feeding the liquid condensate from the stripper overhead condenser back to the stripper, it is sent directly to the absorber.
	Vacuum Operated Stripper (VOS)	In this modification the stripper operates at vacuum/ sub-ambient pressure; this makes it possible to use low pressure steam for solvent regeneration.
	Multi-effect Stripper (MES) (Matrix stripper goes here)	Multiple strippers are required for the multi-effect stripper configuration. The general principle is to use waste heat from a stripper with higher pressure to provide heat to a stripper with lower pressure.
HEAT PUMPS	Integrated Heat Pump (IHP)	An integrated heat pump provides high quality heat from low quality heat and electric power.
	Lean Vapour Compression (LVC)	The lean vapour compression modification requires the addition of a flash vessel, through which the lean solvent exiting the bottom of the stripper passes, to produce a gaseous stream composed of mainly H_2O and CO_2. This stream is compressed and recycled to the stripper.
	Rich Vapour Compression (RVC)	For RVC, the hot rich solvent is flashed, producing a gaseous and a liquid stream, respectively. The gaseous stream produced is compressed and then fed to the bottom of the stripper and the liquid stream is pumped to the top of the stripper.

Table A-1: Process modifications (extracted from Le Moullec et al. (2014)) (contd.)

	MODIFICATION	**DESCRIPTION**
HEAT PUMPS	Stripper Overhead Compression (SOC)	The gaseous stream that exits the stripper is not condensed, but rather compressed. The resulting high pressure gaseous stream is then partially condensed at high pressure (5 – 10 bar) and the heat released by condensation is used to provide heat for the reboiler.
	Multi-pressure Stripper (MPS)	In multi-pressure stripper configurations, the reboiler operates at low pressure. The pressure along the stripper is then increased by the use of dedicated compressors.

Table A-2 describes some process modifications not covered by the review of Le Moullec *et al.* (2014). Among these are heat integration modifications. Heat integration can take on many forms within the process, and different sources defines it differently. Some examples are given in table A-2.

Table A-2: More process modifications for CO_2 capture by absorption.

Modification	**Description**	**Reference**
Vapour Recompression	With vapour recompression, the stripper bottoms is used to intercool the gas stream in the multistage compressor. The purpose of vapour recompression is to recover the heat of condensation of the overhead water vapour as well as the heat of compression.	Jassim and Rochelle (2006)
Heat integration	The overhead gas from the stripping column is used to pre-heat the rich solvent entering the regenerator.	Cousins *et al.* (2011a)
	A combination of the rich solvent split and rich solvent pre-heating modifications as described by Le Moullec *et al.* (2014); refer to table A-1.	Ahn *et al.* (2013)
Compressor integration	A type of heat integration configuration where the hot CO_2 gas stream is used to provide heat to the reboiler.	Karimi *et al.* (2011)
Condensate heating	In the condensate heating configuration, energy supplied to the reboiler can be recovered by preheating the condensate with the stripper overhead stream.	Ahn *et al.* (2013)

Table A-2: More process modifications for CO$_2$ capture by absorption (contd.)

Modification	Description	Reference
Condensate evaporation	This is an improvement of the condensate heating configuration. Heat recovery from the stripper overhead stream is maximized by evaporating the condensate rather than heating it.	Ahn *et al.* (2013)
Flue gas split feed	Multiple feed streams to the absorber.	Oh *et al.* (2016)
Advanced rich split	In the advanced rich solvent split configuration, the split solvent stream is mixed directly with the vapour in the stripper. A condenser is employed to exchange heat between a cold split stream and the hot lean solvent stream from the stripper bottoms.	Zhang *et al.* (2017)

Table A-3 gives a summary of the process modification studies performed in the literature. The information in this table was compiled by the author. All studies cited are process simulation studies. The conditions (solvent, power plant output, CO$_2$ capture rate) as well as main findings are reported. The unit MWe, used in the “conditions” column, stands for megawatt electric. This is a value assigned to power plants which refer to the electricity output of the plant. Unless otherwise stated, “baseline case” refers to the conventional process configuration with aqueous MEA as solvent.

Table A-3: Summary of simulation studies of process modifications performed in the literature[#].

Reference	Modification(s)	Conditions	Results
Chang and Shih (2005)	Intercooled Absorber	• 320 MW Coal-Fired Plant • 90% CO_2 capture • Solvents: 20 wt.% MEA (LL = 0.15); 25 wt.% MDEA + 25 wt.% DGA (LL = 0.1)	• Elimination of temperature bulge; 10 – 15 °C column temperature decrease • When optimized, achieves cost reduction of 10% compared to conventional
	Split-Flow	• 320 MW Coal-Fired Plant • 90% CO_2 capture; 95% CO_2 capture • Solvents: 20 wt.% MEA (LL = 0.15); 25 wt.% MDEA + 25 wt.% DGA (LL = 0.1)	• Up to 20% reduction in stripper reboiler duty compared to conventional • When optimized, achieved cost reduction of 26% compared to conventional • Configuration more beneficial to DGA/MDEA system
Fisher *et al.* (2005)	Multi-pressure Stripping	• 500 MW Coal-Fired Plant • 90% CO_2 capture • Solvent: MEA	• 0.1% reduction in amine circulation rate • Up to 39% reduction in reboiler duty • 30% increase in total capital cost
	Vapour Recompression + Heat Recovery	• 500 MW Coal-Fired Plant • 90% CO_2 capture • Solvent: MEA	• 2% increase in amine circulation rate • Up to 36% reduction in reboiler duty • 17% increase in total capital cost
	Multi-pressure Stripping + Vapour Recompression + Heat Recovery	• 500 MW Coal-Fired Plant • 90% CO_2 capture • Solvent: MEA	• 2% increase in amine circulation rate • Up to 22% reduction in reboiler duty • 7% increase in total capital cost
Jassim and Rochelle (2006)	Vapour Recompression	• 70%, 90%, 95% CO_2 capture • 500 MW power plant • Solvent: 30 wt.% MEA • Heat exchanger approach: 5, 10 °C	• Reboiler duty (90% capture): 2.10 – 2.45 GJ/ton CO_2 • Equivalent work (90% capture): 1.04 – 1.08 GJ/ton CO_2 • 46% reduction in reboiler duty compared to simple stripper • 21% reduction in reboiler duty compared to multi-pressure stripper
	Multi-pressure Stripper	• 70%, 90%, 95% CO_2 capture • 500 MW power plant • Solvent: 30 wt.% MEA • Heat exchanger approach: 5, 10 °C	• Reboiler duty (90% capture): 3.16 – 3.35 GJ/ton CO_2 • Equivalent work (90% capture): 0.94 – 1.05 GJ/ton CO_2 • 22% reduction in reboiler duty compared to simple stripper
	Vapour Recompression + Multi-pressure stripper	• 70%, 90%, 95% CO_2 capture • 500 MW power plant • Solvent: 30 wt.% MEA • Heat exchanger approach: 5, 10 °C	• Reboiler duty (90% capture): 2.49 – 2.64 GJ/ton CO_2 • Equivalent work (90% capture): 0.95 – 1.05 GJ/ton CO_2 • At 70% capture, it has the lowest reboiler duty (2.02 GJ/ton CO_2) of all studied cases

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Aroonwilas and Veawab (2007)	Split-flow	• 500 MW power plant • Solvents: MEA • 90% CO_2 capture	• Energy penalty of the entire plant (including the power generation section) is reduced from 26% to 16% (38% reduction).
Fisher *et al.* (2007)	Double Matrix Stripper (*Multi-effect Stripper*)	• 500 MWe power plant • Solvent: MDEA+PZ; MEA+PZ • 90% CO2 capture	For MEA+PZ, compared to a conventional configuration with 30% MEA as solvent: • 10% decrease in cost of CO_2 avoided • 5% increase in derated plant capacity • 20% reduction in reboiler steam requirements For MDEA+PZ, compared to a conventional configuration with 30% MEA as solvent: • 18% decrease in cost of CO_2 avoided • 11.5% increase in derated plant capacity • 44% reduction in reboiler steam requirements
Oyenekan and Rochelle (2007)	Double Matrix Stripper *(Multi-effect Stripper)*	• 90% CO_2 capture • 500 MW power plant • Solvents: 30 wt.% MEA; MEA + PZ; MDEA + PZ	• For MEA, equivalent work is 19.3% less than the baseline • For MEA+PZ, equivalent work is 21.5% less than the baseline • For MDEA+PZ, equivalent work is 18.5% less than the baseline
	Internal exchange stripper *(Heat Integrated Stripper)*	• 90% CO_2 capture • 500 MW power plant • Solvents: 30 wt.% MEA; MEA + PZ; MDEA + PZ	• For MEA, equivalent work is 21.5% less than the baseline • For MEA+PZ, equivalent work is 20% less than the baseline • For MDEA+PZ, equivalent work is 14.2% less than the baseline
	Multi-pressure stripper with split feed	• 90% CO_2 capture • 500 MW power plant • Solvents: 30 wt.% MEA; MEA + PZ; MDEA + PZ	• For MEA, equivalent work is 18.8% less than the baseline • For MEA+PZ, equivalent work is 20.5% less than the baseline • For MDEA+PZ, equivalent work is 14.2% less than the baseline
	Flashing feed stripper *(Rich Solvent Split)*	• 90% CO_2 capture • 500 MW power plant • Solvents: 30 wt.% MEA; MEA + PZ; MDEA + PZ	• For MEA, equivalent work is 16.1% less than the baseline • For MEA+PZ, equivalent work is 16% less than the baseline • For MDEA+PZ, equivalent work is 10.9% less than the baseline

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Schach *et al.* (2010)	Intercooled Absorber	• 90% CO_2 capture • Solvent: 30 wt.% MEA	Compared to the conventional configuration: • 3% reduction in specific energy demand of the stripper (GJ/ton CO_2) • 4% reduction in total required power (MW) • 4.9% reduction in cost of CO_2 avoided (cost/ton) • 1.3% increase in the total annual cost of the power plant
	Matrix Stripper	• 90% CO_2 capture • Solvent: 30 wt.% MEA	Compared to the conventional configuration: • 5.2% reduction in specific energy demand of the stripper (GJ/ton CO_2) • 4.5% reduction in total required power (MW) • 1.5% reduction in cost of CO_2 avoided (cost/ton) • 7.4% increase in the total annual cost of the power plant
	Multi-Stripper *(Multi-effect Stripper)*	• 90% CO_2 capture • Solvent: 30 wt.% MEA	Compared to the conventional configuration: • 16.2% reduction in specific energy demand of the stripper (GJ/ton CO_2) • 6.7% reduction in total required power (MW) • 4.1% reduction in cost of CO_2 avoided (cost/ton) • 8.6% increase in the total annual cost of the power plant
Cousins *et al.* (2011a)	Absorber Intercooling	• Solvent: 30 wt.% MEA • 85% CO_2 capture	• 6.4% saving in reboiler duty (compared to conventional configuration)
	Split flow	• Solvent: 30 wt.% MEA • 85% CO_2 capture	• 11.6% saving in reboiler duty upon optimization (compared to conventional configuration)
	Rich Split	• Solvent: 30 wt.% MEA • 85% CO_2 capture	• Up to 10.3% saving in reboiler duty (compared to conventional configuration)
	Vapour Recompression *(Lean Vapour Compression)*	• Solvent: 30 wt.% MEA • 85% CO_2 capture	• 19.0% saving in reboiler duty (compared to conventional configuration)
	Heat Integration	• Solvent: 30 wt.% MEA • 85% CO_2 capture	• 2.8% saving in reboiler duty (compared to conventional configuration)

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Karimi *et al.* (2011)	Split-stream *(Rich Solvent Split)*	• 90% CO_2 capture • 150 MWe power plant • Solvent: 30% MEA	**For a heat exchanger approach of 5°C (compared to conventional configuration):** • 9.5% increase in total capital investment • 11.8% decrease in reboiler duty • 7.6% decrease in equivalent work **For a heat exchanger approach of 10°C (compared to conventional configuration):** • 6.4% increase in total capital investment • 7.6% decrease in reboiler duty • 4.9% decrease in equivalent work
	Split-stream with cooling	• 90% CO_2 capture • 150 MWe power plant • Solvent: 30% MEA	**For a heat exchanger approach of 5°C (compared to conventional configuration):** • 9.5% increase in total capital investment • 16.4% decrease in reboiler duty • 10.5% decrease in equivalent work **For a heat exchanger approach of 10°C (compared to conventional configuration):** • 6.8% increase in total capital investment • 13% decrease in reboiler duty • 8.2% decrease in equivalent work
	Multi-pressure stripper	• 90% CO_2 capture • 150 MWe power plant • Solvent: 30% MEA	**For a heat exchanger approach of 5°C (compared to conventional configuration):** • 6.9% increase in total capital investment • 32.3% decrease in reboiler duty • 8.5% decrease in equivalent work **For a heat exchanger approach of 10°C (compared to conventional configuration):** • 6.4% increase in total capital investment • 28.2% decrease in reboiler duty • 6.3% decrease in equivalent work

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Karimi *et al*. (2011)	Vapour Recompression	• 90% CO_2 capture • 150 MWe power plant • Solvent: 30% MEA	**For a heat exchanger approach of 5°C (compared to conventional configuration):** • 2.8% increase in total capital investment • 26.8% decrease in reboiler duty • 9.4% decrease in equivalent work **For a heat exchanger approach of 10°C (compared to conventional configuration):** • 1.9% increase in total capital investment • 24.6% decrease in reboiler duty • 8.4% decrease in equivalent work
	Compressor Integration	• 90% CO_2 capture • 150 MWe power plant • Solvent: 30% MEA	**For a heat exchanger approach of 5°C (compared to conventional configuration):** • 15.7% increase in total capital investment • 57.3% decrease in reboiler duty • 4.3% increase in equivalent work **For a heat exchanger approach of 10°C (compared to conventional configuration):** • 14.8% increase in total capital investment • 49.3% decrease in reboiler duty • 5.2% increase in equivalent work
	Compressor Integration with Condenser-stripper	• 90% CO_2 capture • 150 MWe power plant • Solvent: 30% MEA	**For a heat exchanger approach of 5°C (compared to conventional configuration):** • 4.7% increase in total capital investment • 6.2% decrease in reboiler duty • 4.6% increase in equivalent work **For a heat exchanger approach of 10°C (compared to conventional configuration):** • 5% increase in total capital investment • 6.6% decrease in reboiler duty • 4.2% increase in equivalent work

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Le Moullec and Kanniche (2011a)	Absorber Intercooling	- Solvent: 30 wt.% MEA - 1200 MWe capture plant	Compared to the conventional configuration: - 2.5% reduction in reboiler duty - 1.4% reduction in total equivalent work - 0.17% reduction in power plant efficiency loss
	Stripper Staged Feed *(Rich Solvent Split)*	- Solvent: 30 wt.% MEA - 1200 MWe capture plant	Compared to the conventional configuration: - 12.1% reduction in reboiler duty - 7.1% reduction in total equivalent work - 0.85% reduction in power plant efficiency loss
	Lean Vapour Compression	- Solvent: 30 wt.% MEA - 1200 MWe capture plant	Compared to the conventional configuration: - Up to 27.9% reduction in reboiler duty - Up to 7.7% reduction in total equivalent work - Up to 0.92% reduction in power plant efficiency loss
	Stripper overhead compression	- Solvent: 30 wt.% MEA - 1200 MWe capture plant	Compared to the conventional configuration: - 35.8% reduction in reboiler duty - 4.2% reduction in total equivalent work - 0.5% reduction in power plant efficiency loss
	Stripper staged feed + Internal stripper compression	- Solvent: 30 wt.% MEA - 1200 MWe capture plant	Compared to the conventional configuration: - 32.1% reduction in reboiler duty - 14.6% reduction in total equivalent work - 1.79% reduction in power plant efficiency loss
	Lean Vapour Compression + Stripper overhead compression	- Solvent: 30 wt.% MEA - 1200 MWe capture plant	Compared to the conventional configuration: - 37.2% reduction in reboiler duty - 15.4% reduction in total equivalent work - 1.94% reduction in power plant efficiency loss
Liang *et al.* (2011)	Bi-pressure stripper *(Multi-pressure Stripper)*	- 90% CO_2 capture - 600 MWe supercritical coal-fired power plant - Solvent: MEA	- Reboiler duty = 3.43 MJ/kg CO_2 (base = 3.90 MJ/kg CO_2; 12% decrease)

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Montenegro (2011)	Absorber Intercooling	• 90% CO_2 capture • Solvents: 30 wt.% MEA; 40 wt.% PZ	• For MEA, 4% reduction in reboiler duty • For PZ, 12.5% reduction in reboiler duty
	Stripper Inter-heating	• 90% CO_2 capture • Solvents: 30 wt.% MEA; 40 wt.% PZ	• For MEA, 7.2% reduction in reboiler duty • For PZ, 10.4% reduction in reboiler duty
	Adiabatic Lean Flash	• 90% CO_2 capture • Solvents: 30 wt.% MEA; 40 wt.% PZ	• For MEA, 17.5% reduction in reboiler duty • For PZ, 8.8% reduction in reboiler duty
	Absorber Intercooling + Stripper Inter-heating	• 90% CO_2 capture • Solvents: 30 wt.% MEA; 40 wt.% PZ	• For MEA, 10.9% reduction in reboiler duty • For PZ, 23.8% reduction in reboiler duty
	Absorber Intercooling + Adiabatic Lean Flash	• 90% CO_2 capture • Solvents: 30 wt.% MEA; 40 wt.% PZ	• For MEA, 19.7% reduction in reboiler duty • For PZ, 18.8% reduction in reboiler duty
Pellegrini *et al.* (2011)	Double Stripper *(Multi-effect Stripper)*	• Solvent: 30 wt.% MEA	• Reboiler duty = 102.6 kW (base = 186.39 kW) • Compression Work = 1.53 kW (base = 3.72 kW)
	Multi-pressure Stripper	• Solvent: 30 wt.% MEA	• Reboiler duty = 85.53 kW (base = 186.39 kW) • Compression Work = 9.72 kW (base = 3.72 kW)
Cousins *et al.* (2012)	Rich Solvent Split	• Pilot Plant Study • Solvent: 30 wt.% MEA • ±78% CO_2 capture efficiency	For split fractions less than 15% (mass): • 7% reduction in solvent regeneration energy • 60% reduction in condenser duty
de Miguel Mercader *et al.* (2012)	Lean Vapour Compression	• 250 MWe Capture Plant • 90% CO_2 Capture • Solvent: 30% MEA	Compared to the base case configuration: • 13.5% decrease in reboiler duty • 15.5% decrease in cooling duty • 43.2% increase in electricity requirements
	Lean Vapour Compression + Split-flow	• 250 MWe Capture Plant • 90% CO_2 Capture • Solvent: 30 wt.% MEA	Compared to the base case configuration: • 17.3% decrease in reboiler duty • 11.0% decrease in cooling duty • 43.2% increase in electricity requirements
	Stripper inter-heating	• 250 MWe Capture Plant • 90% CO_2 Capture • Solvent: 30 wt.% MEA	Compared to the base case configuration: • 10.2% decrease in reboiler duty • 8.9% decrease in cooling duty • 6.8% increase in electricity requirements

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Sanchez Fernandez *et al.* (2012)	Lean Vapour Compression	• 250 MWe Capture plant • Solvent: 30 wt.% MEA • 90% CO_2 Capture	Compared to the base case configuration: • Up to 18.0% decrease in reboiler duty • Up to 7.5% decrease in total equivalent work • Energy Saving: up to 1.24 M€/y
Ahn *et al.* (2013)	Absorber Inter-cooling	• 550 MW Power Plant • 90% CO_2 Capture • Solvent: 30 wt.% MEA	Compared to the base case configuration: • 11.6% decrease in reboiler duty • 8.9% total energy saving
	Condensate Heating	• 550 MW Power Plant • 90% CO_2 Capture • Solvent: 30 wt.% MEA	Compared to the base case configuration: • 0.3% increase in reboiler duty • -0.2% total energy saving (i.e. increased energy usage)
	Condensate Evaporation	• 550 MW Power Plant • 90% CO_2 Capture • Solvent: 30 wt.% MEA	Compared to the base case configuration: • 25.6% decrease in reboiler duty • 6.5% total energy saving
	Stripper Overhead Compression	• 550 MW Power Plant • 90% CO_2 Capture • Solvent: 30 wt.% MEA	Compared to the base case configuration: • 31.5% decrease in reboiler duty • 12.0% total energy saving
	Lean Amine Flash *(Lean Vapour Compression)*	• 550 MW Power Plant • 90% CO_2 Capture • Solvent: 30 wt.% MEA	Compared to the base case configuration: • 21.6% decrease in reboiler duty • 11.6% total energy saving
	Multi-pressure Stripping	• 550 MW Power Plant • 90% CO_2 Capture • Solvent: 30 wt.% MEA	Compared to the base case configuration: • 9.9% decrease in reboiler duty • 2.0% total energy saving
	Heat Integration	• 550 MW Power Plant • 90% CO_2 Capture • Solvent: 30 wt.% MEA	Compared to the base case configuration: • 11.9% decrease in reboiler duty • 9.1% total energy saving
	Split-amine Flow *(Split Flow Arrangement)*	• 550 MW Power Plant • 90% CO_2 Capture • Solvent: 30 wt.% MEA	Compared to the base case configuration: • 12.2% decrease in reboiler duty • 9.3% total energy saving
	Absorber Intercooling + Condensate Evaporation + Lean Amine Flash	• 550 MW Power Plant • 90% CO_2 Capture • Solvent: 30 wt.% MEA	Compared to the base case configuration: • 36.9% decrease in reboiler duty • 14.1% total energy saving

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Birkelund (2013)	Vapour Recompression	• 85% CO_2 capture • Solvent: 30% MEA	• 32.5% reduction in total energy cost • 61.8% increase in capital cost
	Vapour Recompression + Lean Split	• 85% CO_2 capture • Solvent: 30% MEA	• 29% reduction in total energy cost • 49% increase in capital cost
Jung *et al.* (2013)	Split Flow + Phase separation heat exchanger	• Solvent: MEA	• Reboiler duty = 2.48 GJ/ton CO_2 (27% less than conventional configuration) • Net energy requirement reduced by 13% compared to conventional
Neveux *et al.* (2013)	Intercooled Absorber	• Solvents: 30 wt.% MEA; 40 wt.% AMP	Compared to a conventional configuration with the same solvent: • For MEA: 0.7% reduction in equivalent work • For AMP: 3.0% reduction in equivalent work
	Stripper Split Feed *(Rich Solvent Split)*	• Solvents: 30 wt.% MEA; 40 wt.% AMP	Compared to a conventional configuration with the same solvent: • For MEA: 6.2% reduction in equivalent work • For AMP: 6.0% reduction in equivalent work
	Lean Vapour Compression	• Solvents: 30 wt.% MEA; 40 wt.% AMP	Compared to a conventional configuration with the same solvent: • For MEA: 7.6% reduction in equivalent work • For AMP: 2.3% reduction in equivalent work
	Stripper Overhead Compression	• Solvents: 30 wt.% MEA; 40 wt.% AMP	Compared to a conventional configuration with the same solvent: • For MEA: 6.2% reduction in equivalent work • For AMP: 1.9% reduction in equivalent work

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Ehlers *et al.* (2014)	Split Flow *(Rich Solvent Split)*	• Solvent: Proprietary (similar characteristics to MDEA+PZ) • 900 MW power plant • 90% CO_2 capture	Compared to the conventional configuration: • 15.4% reduction in specific heat duty • 16.4% reduction in specific cooling duty
	Vapour Recompression *(Lean Vapour Compression)*	• Solvent: Proprietary (similar characteristics to MDEA+PZ) • 900 MW power plant • 90% CO_2 capture	Compared to the conventional configuration: • 13.6% reduction in specific heat duty • 9.1% reduction in specific cooling duty
Gupta *et al.* (2015)	Absorber Intercooling	• Solvent: 30% MEA • 550 MWe Power Plant	• Cost of CO_2 avoided = 64.05 \$/tonne CO_2 (Conventional = 65.94 \$/tonne CO_2; 2.87% decrease)
	Absorber Intercooling + Double Stripper	• Solvent: 30% MEA • 550 MWe Power Plant	• Cost of CO_2 avoided = 63.09 \$/tonne CO_2 (Conventional = 65.94 \$/tonne CO_2; 4.32% decrease)
Jung *et al.* (2015)	Absorber Intercooling	• 90% CO_2 Capture • Solvent: 30 wt.% MEA	• Base case for this study (no comparative results)
	Absorber Intercooling + Cold Solvent Split *(Rich Solvent Split)*	• 90% CO_2 Capture • Solvent: 30 wt.% MEA	• 3.3% reduction in thermal energy (compared to the absorber inter-cooling configuration)
	Rich Vapour Recompression	• 90% CO_2 Capture • Solvent: 30 wt.% MEA	• 8.6% reduction in thermal energy (compared to the absorber inter-cooling configuration)
	Rich Vapour Recompression + Cold Solvent Split	• 90% CO_2 Capture • Solvent: 30 wt.% MEA	• 20% reduction in thermal energy (compared to the absorber inter-cooling configuration)
	Lean Vapour Recompression	• 90% CO_2 Capture • Solvent: 30 wt.% MEA	• 15.4% reduction in thermal energy (compared to the absorber inter-cooling configuration)
	Lean Vapour Recompression + Cold Solvent Split	• 90% CO_2 Capture • Solvent: 30 wt.% MEA	• 15% reduction in thermal energy (compared to the absorber inter-cooling configuration)

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Damartzis *et al.* (2016)	Multi-feed Absorber *(Split Flow Arrangement)*	• ≥90% CO_2 Capture • Solvents: 30 wt.% MEA; 35.4 wt.% DEA; 30 wt.% AMP; 30 wt.% MPA; 35 wt.% MPA	**Compared to the conventional configuration using 30 wt.% MEA as solvent:** • 30% MEA – ~4% reduction in reboiler energy demand & ~3% reduction in total annual costs • 35.4% DEA – ~2% increase in reboiler energy demand & ~15% reduction in total annual costs • 30% AMP – ~44% reduction in reboiler energy demand & ~22% reduction in total annual costs • 30% MPA – ~4% increase in reboiler energy demand & ~12% reduction in total annual costs • 35% MPA – ~9% reduction in reboiler energy demand & ~21% reduction in total annual costs **Compared to the conventional configuration, using the same solvent:** • 35.4% DEA – ~6% increase in reboiler energy demand & ~2% increase in total annual costs • 30% AMP – ~12% increase in reboiler energy demand & ~13% increase in total annual costs • 30% MPA – ~4% increase in reboiler energy demand & ~2% increase in total annual costs • 35% MPA – no change in reboiler energy demand or total annual costs

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Damartzis *et al.* (2016)	Intercooled Absorber	• ≥90% CO_2 Capture • Solvents: 30 wt.% MEA; 35.4 wt.% DEA; 30 wt.% AMP; 30 wt.% MPA; 35 wt.% MPA	**Compared to the conventional configuration using 30 wt.% MEA as solvent:** • 30% MEA – ~23% reduction in reboiler energy demand & ~17% reduction in total annual costs • 35.4% DEA – ~22% reduction in reboiler energy demand & ~28% reduction in total annual costs • 30% AMP – ~55% reduction in reboiler energy demand & ~35% reduction in total annual costs • 30% MPA – ~1% reduction in reboiler energy demand & ~12% reduction in total annual costs • 35% MPA – ~12% reduction in reboiler energy demand & ~19% reduction in total annual costs **Compared to the conventional configuration, using the same solvent:** • 35.4% DEA – ~19% reduction in reboiler energy demand & ~13% reduction in total annual costs • 30% AMP – ~18% reduction in reboiler energy demand & ~13% increase in total annual costs • 30% MPA – ~4% increase in reboiler energy demand & ~2% increase in total annual costs • 35% MPA – no change in reboiler energy demand or total annual costs

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Damartzis *et al.* (2016)	Double Section Stripper *(Rich Solvent Split)*	• ≥90% CO_2 Capture • Solvents: 30 wt.% MEA; 35.4 wt.% DEA; 30 wt.% AMP; 30 wt.% MPA; 35 wt.% MPA	**Compared to the conventional configuration using 30 wt.% MEA as solvent:** • 30% MEA – ~2% reduction in reboiler energy demand & ~5% reduction in total annual costs • 35.4% DEA – ~8% increase in reboiler energy demand & ~9% reduction in total annual costs • 30% AMP – ~49% reduction in reboiler energy demand & ~36% reduction in total annual costs • 30% MPA – ~3% reduction in reboiler energy demand & ~13% reduction in total annual costs • 35% MPA – ~10% reduction in reboiler energy demand & ~18% reduction in total annual costs **Compared to the conventional configuration, using the same solvent:** • 35.4% DEA – ~13% inrease in reboiler energy demand & ~10% increase in total annual costs • 30% AMP – ~2% increase in reboiler energy demand & no change in total annual costs • 30% MPA – ~3% reduction in reboiler energy demand & ~1% increase in total annual costs • 35% MPA – ~1% reduction in reboiler energy demand & ~4% increase in total annual costs

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Damartzis *et al.* (2016)	Double Section Stripper + Intercooled absorber	• ≥90% CO_2 Capture • Solvents: 30 wt.% MEA; 35.4 wt.% DEA; 30 wt.% AMP; 30 wt.% MPA; 35 wt.% MPA	**Compared to the conventional configuration using 30 wt.% MEA as solvent:** • 30% MEA – ~22% reduction in reboiler energy demand & ~18% reduction in total annual costs • 35.4% DEA – ~23% increase in reboiler energy demand & ~29% reduction in total annual costs • 30% AMP – ~56% reduction in reboiler energy demand & ~39% reduction in total annual costs • 30% MPA – ~5% reduction in reboiler energy demand & ~15% reduction in total annual costs • 35% MPA – ~10% reduction in reboiler energy demand & ~18% reduction in total annual costs **Compared to the conventional configuration, using the same solvent:** • 35.4% DEA – ~20% reduction in reboiler energy demand & ~14% reduction in total annual costs • 30% AMP – ~12% reduction in reboiler energy demand & ~5% reduction in total annual costs • 30% MPA – ~5% reduction in reboiler energy demand & ~1% reduction in total annual costs • 35% MPA – ~1% reduction in reboiler energy demand & ~4% increase in total annual costs
Li *et al.* (2016b)	Absorber Intercooling	• Solvent: 30 wt.% MEA • CO_2 purity: 99.5%	Compared to the conventional configuration: • 0.6% increase in capital cost • 1.4% reduction in reboiler duty • 0.4% reduction in total energy consumption • 0.9% decrease in cost of CO_2 avoided
	Rich Solvent Split	• Solvent: 30 wt.% MEA • CO_2 purity: 99.5%	Compared to the conventional configuration: • same capital cost • 8.3% reduction in reboiler duty • 4.8% reduction in total energy consumption • 4.4% decrease in cost of CO_2 avoided

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Li *et al.* (2016b)	Advanced Rich Solvent Split	• Solvent: 30 wt.% MEA • CO_2 purity: 99.5%	Compared to the conventional configuration: • 0.1% increase in capital cost • 10% reduction in reboiler duty • 5.5% reduction in total energy consumption • 4.9% decrease in cost of CO_2 avoided
	Stripper Inter-heating	• Solvent: 30 wt.% MEA • CO_2 purity: 99.5%	Compared to the conventional configuration: • 0.7% increase in capital cost • 6.7% reduction in reboiler duty • 4.2% reduction in total energy consumption • 3.6% decrease in cost of CO_2 avoided
	Absorber Intercooling + Rich Split + Stripper Inter-heating	• Solvent: 30 wt.% MEA • CO_2 purity: 99.5%	Compared to the conventional configuration: • 0.8% decrease in capital cost • 14.4% reduction in reboiler duty • 8% reduction in total energy consumption • 7.5% decrease in cost of CO_2 avoided
Oh *et al.* (2016)	Absorber Intercooling	• >90% CO_2 Capture • Solvent: 30 wt.% MEA • Gas-fired power plant	Upon optimization and compared to the conventional configuration: • 1.4% decrease in specific reboiler duty • 4.3% decrease in total energy cost
	Flue gas split feed	• >90% CO_2 Capture • Solvent: 30 wt.% MEA • Gas-fired power plant	Upon optimization and compared to the conventional configuration: • 5.7% decrease in specific reboiler duty • 7.4% decrease in total energy cost
	Solvent split feed *(Rich Solvent Split)*	• >90% CO_2 Capture • Solvent: 30 wt.% MEA • Gas-fired power plant	Upon optimization and compared to the conventional configuration: • 1.4% decrease in specific reboiler duty • 5.7% decrease in total energy cost
	Lean Solvent Split *(Split Flow Arrangement)*	• >90% CO_2 Capture • Solvent: 30 wt.% MEA • Gas-fired power plant	Upon optimization and compared to the conventional configuration: • 0.2% decrease in specific reboiler duty • 3.7% decrease in total energy cost

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Oh *et al.* (2016)	Combined Modifications (all above)	• >90% CO_2 Capture • Solvent: 30 wt.% MEA • Gas-fired power plant	Upon optimization and compared to the conventional configuration: • 7.1% decrease in specific reboiler duty • 7.8% decrease in total energy cost
Xue *et al.* (2016)	Intercooled Absorber	• Solvent: 30% MEA (LL = 0.25); 40% DEA (LL = 0.1) • 90% CO_2 Capture	For **MEA**, compared to the conventional configuration (same solvent): • 7.1% decrease in reboiler duty • 4.20% total energy savings For **DEA**, compared to the conventional configuration (same solvent): • 2.8% decrease in reboiler duty • 1.64% total energy savings
	Flue Gas Precooling	• Solvent: 30% MEA (LL = 0.25); 40% DEA (LL = 0.1) • 90% CO_2 Capture	For **MEA**, compared to the conventional configuration (same solvent): • 5.3% decrease in reboiler duty • 3.17% total energy savings For **DEA**, compared to the conventional configuration (same solvent): • 2.8% decrease in reboiler duty • 1.60% total energy savings
	Rich Solvent Split	• Solvent: 30% MEA (LL = 0.25); 40% DEA (LL = 0.1) • 90% CO_2 Capture	For **MEA**, compared to the conventional configuration (same solvent): • 7.7% decrease in reboiler duty • 4.61% total energy savings For **DEA**, compared to the conventional configuration (same solvent): • 7% decrease in reboiler duty • 4.06% total energy savings

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Xu *et al.* (2016)	Rich Solvent Preheating	• Solvent: 30% MEA (LL = 0.25); 40% DEA (LL = 0.1) • 90% CO_2 Capture	For **MEA**, compared to the conventional configuration (same solvent): • 0.03% increase in reboiler duty • -0.02% total energy savings (i.e. loss) For **DEA**, compared to the conventional configuration (same solvent): • 0.5% decrease in reboiler duty • 0.27% total energy savings
	Solvent Split Flow *(Split Flow Arrangement)*	• Solvent: 30% MEA (LL = 0.25); 40% DEA (LL = 0.1) • 90% CO_2 Capture	For **MEA**, compared to the conventional configuration (same solvent): • 7.6% decrease in reboiler duty • 4.45% total energy savings For **DEA**, compared to the conventional configuration (same solvent): • 7.8% decrease in reboiler duty • 4.50% total energy savings
	Rich Solvent Flashing	• Solvent: 30% MEA (LL = 0.25); 40% DEA (LL = 0.1) • 90% CO_2 Capture	For **MEA**, compared to the conventional configuration (same solvent): • 5% increase in reboiler duty • -3.03% total energy savings (i.e. loss) For **DEA**, compared to the conventional configuration (same solvent): • 4.2% increase in reboiler duty • -2.44% total energy savings (i.e. loss)
	Stripper Condensate Bypass *(Overhead Condenser Bypass)*	• Solvent: 30% MEA (LL = 0.25); 40% DEA (LL = 0.1) • 90% CO_2 Capture	For **MEA**, compared to the conventional configuration (same solvent): • 0.8% decrease in reboiler duty • 0.38% total energy savings For **DEA**, compared to the conventional configuration (same solvent): • 1.2% decrease in reboiler duty • 0.73% total energy savings

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Xu *et al*. (2016)	Stripper Condensate Heating	• Solvent: 30% MEA (LL = 0.25); 40% DEA (LL = 0.1) • 90% CO_2 Capture	For **MEA**, compared to the conventional configuration (same solvent): • 1.4% decrease in reboiler duty • 0.80% total energy savings For **DEA**, compared to the conventional configuration (same solvent): • 1% decrease in reboiler duty • 0.58% total energy savings
	Lean Vapour Compression	• Solvent: 30% MEA (LL = 0.25); 40% DEA (LL = 0.1) • 90% CO_2 Capture	For **MEA**, compared to the conventional configuration (same solvent): • 12.8% decrease in reboiler duty • 3.87% total energy savings For **DEA**, compared to the conventional configuration (same solvent): • 11.9% decrease in reboiler duty • 2.70% total energy savings
Stec *et al.* (2017)	Split Flow *(Split Flow Arrangement + Rich Solvent Split)*	• Solvent: 30 wt.% MEA • >90% CO_2 recovery	• 1.6% decrease in reboiler heat duty
Zhang *et al.* (2017)	Intercooled Absorber	• Solvent: 28% AMP + 17% PZ • 90% CO_2 capture • 660 MWe Power Plant	• 6.7% energy saving compared to the base case
	Lean Vapour Compressor	• Solvent: 28% AMP + 17% PZ • 90% CO_2 capture • 660 MWe Power Plant	• Total energy saving of -2.7% (i.e. more energy required)
	Rich Solvent Split	• Solvent: 28% AMP + 17% PZ • 90% CO_2 capture • 660 MWe Power Plant	• 8.5% energy saving compared to the base case.
	Intercooled Absorber + Lean Solvent Compressor	• Solvent: 28% AMP + 17% PZ • 90% CO_2 capture • 660 MWe Power Plant	• 8.5% energy saving

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Zhang *et al.* (2017)	Lean Solvent Compressor + Rich Solvent Split	• Solvent: 28% AMP + 17% PZ • 90% CO_2 capture • 660 MWe Power Plant	• 9.3% energy savings
	Intercooled Absorber + Rich Solvent Split	• Solvent: 28% AMP + 17% PZ • 90% CO_2 capture • 660 MWe Power Plant	• 14% energy savings
	Intercooled Absorber + Lean Vapour Compressor + Rich Solvent Split	• Solvent: 28% AMP + 17% PZ • 90% CO_2 capture • 660 MWe Power Plant	• 15.2% reduction in energy demand
Zhao *et al.* (2017)	Absorber Inter-cooling	• 650 MW Power Plant • Solvent: 30 wt.% MDEA + 20 wt.% PZ • CO_2 Capture: 90%	Compared to the conventional configuration: • Up to 12.66% decrease in reboiler duty • Up to 12.61% overall energy savings • Up to 6.7% reduction in power plant net efficiency penalty
	Simple Rich-Split *(Rich Solvent Split)*	• 650 MW Power Plant • Solvent: 30 wt.% MDEA + 20 wt.% PZ • CO_2 Capture: 90%	Compared to the conventional configuration: • 4.7% decrease in reboiler duty • 2.5% reduction in power plant net efficiency penalty
	Advanced Rich-Split	• 650 MW Power Plant • Solvent: 30 wt.% MDEA + 20 wt.% PZ • CO_2 Capture: 90%	Compared to the conventional configuration: • Up to 6.4% decrease in reboiler duty • 3.4% reduction in power plant net efficiency penalty
	Stripper Inter-heating	• 650 MW Power Plant • Solvent: 30 wt.% MDEA + 20 wt.% PZ • CO_2 Capture: 90%	Compared to the conventional configuration: • 6.58% decrease in reboiler duty • 2.83% reduction in power plant net efficiency penalty
	Absorber Inter-cooling + Rich Split	• 650 MW Power Plant • Solvent: 30 wt.% MDEA + 20 wt.% PZ • CO_2 Capture: 90%	Compared to the conventional configuration: • 15.4% decrease in reboiler duty • 8.24% reduction in power plant net efficiency penalty
	Absorber Inter-cooling + Stripper Inter-heating	• 650 MW Power Plant • Solvent: 30 wt.% MDEA + 20 wt.% PZ • CO_2 Capture: 90%	Compared to the conventional configuration: • 17% decrease in reboiler duty • 8.95% reduction in power plant net efficiency penalty

Table A-3: Summary of simulation studies of process modifications performed in the literature (contd.).

Reference	Modification(s)	Conditions	Results
Zhao *et al*. (2017)	Absorber Inter-cooling + Stripper Inter-heating + Rich Split	• 650 MW Power Plant • Solvent: 35 wt.% MEA; 30 wt.% MDEA + 20 wt.% PZ • CO_2 Capture: 85; 90%	Compared to the conventional configuration (MEA): • 18.3% decrease in reboiler duty • 9.78% reduction in power plant net efficiency penalty For the performance of MDEA+PZ compared to MEA: • 90% CO_2 removal (compared to 85% for MEA) • 27.7% decrease in reboiler duty • 16.1% reduction in overall power plant net efficiency penalty

[#] The information in Table 2-1 was compiled by the author.

APPENDIX B: ALTERNATIVE CAPTURE TECHNOLOGIES

An overview of alternate CO_2 capture technologies is provided. The reader is referred to the published works referenced in the corresponding sections.

B.1 ABSORPTION (IONIC LIQUIDS AND HYBRID SOLVENTS)

CO_2 capture by ionic liquids is one of the more recent solvent technologies considered. One type of ionic liquids, room temperature ionic liquids (RTILs) are defined by Babamohammadi *et al.* (2015) as *organic salts that form a stable liquid at room temperature*. Many of the disadvantages that hinder the performance of amine solvents in the context of CO_2 capture are eliminated by the use of ionic liquids. Ionic liquids are inherently thermally stable, have negligible vapour pressure, show high CO_2 solubility and may be "tuned" to incorporate desired physiochemical properties (Hasib-ur-Rahman *et al.*, 2010).

A more specialised type of ionic liquid, known as task-specific ionic liquids (TSILs), includes an amine within its structure. These types of ionic liquids are superior to conventional RTILs for CO_2 capture purposes. The synthesis of TSILs require many steps and they are hence not yet economically competitive with amine solvents (Babamohammadi *et al.*, 2015).

Ionic liquid can also be blended with an amine solvent to improve performance. These types of mixtures are often known as hybrid solvents as they combine the physical absorption characteristics of ionic liquids with the chemical absorption characteristics of the amine. Hybrid solvents are similar in performance to TSILs and even eliminate the disadvantage of high viscosity that is inherent to ionic liquids (Camper *et al.*, 2008).

Although the use of ionic liquids or hybrid solvents have superior performance to aqueous amine solvents, much more research is required before these solvents may be implemented on a commercial scale. One of the greatest drawbacks to these solvents are their high cost which makes them currently unviable as alternatives to amine solvents.

B.2 ADSORPTION

Adsorption entails the removal of one or more components of a gas mixture by means of their adsorption onto a solid surface. This process is based on the intermolecular forces at play between the gas components and the surface of the solid material used as adsorbent. For CO_2 capture, the adsorbent is loaded into a packed column through which the CO_2-containing gas stream is then passed, and the CO_2 molecules adhere to the surface of the solid particles. Upon reaching equilibrium, desorption takes place to remove the CO_2 so that the solid sorbent can be recycled for further adsorption. CO_2 capture by adsorption may be undertaken in one of three ways, namely, pressure swing adsorption (PSA), temperature swing adsorption (TSA) and electrical swing adsorption (ESA) (Mondal *et al.*, 2012).

Adsorption and regeneration occur under different conditions for each method. In PSA, adsorption occurs at high pressure and low temperature, while regeneration is at low pressure and higher temperature conditions. For TSA, like PSA, the regeneration temperature is higher than adsorption temperature. The increased energy requirements for TSA makes it more costly than PSA. In ESA, an electric current at low voltage is passed through the adsorbent bed (Mondal *et al.*, 2012).

Adsorbents commonly used for CO_2 capture applications include activated carbon, zeolites, mesoporous silicates, alumina, and metal-organic frameworks (MOFs) (Mirzaei *et al.*, 2015).

B.3 CRYOGENIC DISTILLATION

Commercially, cryogenic distillation is widely used for removing CO_2 from gas streams where its concentration exceeds 50% (Mondal *et al.*, 2012). In a cryogenic separation process, the CO_2 is physically separated from the gas stream on the basis of dew and sublimation points. The main advantage of cryogenic separation is that it can operate at atmospheric pressure and no chemical reagents are required. The primary disadvantage is the requirement of minimal water content in the gas stream, which means several costly steps are required to remove water until only a trace amount remains (Mondal *et al.*, 2012, Spigarelli and Kawatra, 2013).

In contrast to CO_2 removal, CO_2 capture by cryogenic separation is a relatively novel idea, since using cryogenic distillation in applications with a low CO_2 concentration, such as CO_2 removal from power plant flue gases is considered uneconomical due to the large amount of energy required for refrigeration (Mondal *et al.*, 2012).

B.4 MEMBRANE TECHNOLOGY

Capture by membrane technology is a relatively new CO_2 capture technology. Membranes are "*semi-permeable barriers able to separate substances by various mechanisms*", which include diffusion, adsorption, molecular sieve or ionic transport (Mondal *et al.*, 2012). For CO_2 capture, two types of membrane processes, known as gas separation membrane and gas absorption membrane, can be applied.

In the gas separation membrane process, components pass through the membrane according to their size or affinity. The permeability and selectivity of the membrane are important parameters, as the separation of the gas components rely on the solubility or diffusivity of the molecules into the membrane. For pre-combustion capture these membranes are efficient for separating CO_2 from H_2, whereas in post-combustion capture CO_2 is separated from N_2 (Mondal *et al.*, 2012, Mirzaei *et al.*, 2015). Metallic membranes (such as membranes made from palladium or palladium alloys) are theoretically ideal for separating mixtures of CO_2 and H_2. Another type of membrane that can be used for this purpose is inorganic membranes; silica membranes are good candidates for commercial separation of CO_2 and H_2. Zeolite membranes and metal organic framework (MOF) membranes are also investigated for CO_2/H_2 separation in carbon capture applications (Ji and Zhao, 2017). Membranes applicable to separation of CO_2/N_2 gas streams are polymer-based, which could contain cellulose acetate, polymides, polysulfone or polycarbonates. A more novel option is mixed-matrix membranes. In mixed-matrix membranes, micro- or nanoparticles of inorganic material in a discrete phase is supported by a polymeric matrix. In carbon capture applications, polymide is currently the most used pre-cursor (Ji and Zhao, 2017).

For the gas absorption membrane process, the membrane is used as a gas-liquid contacting device. A membrane as contacting device between gas and liquid phases is ideal as it is not sensitive to flooding, entrainment, channeling or foaming, like conventional contacting columns. The partial pressure of the CO_2 in the gas stream is important to the membrane performance; these membranes are appropriate for use in streams with a CO_2 concentration of at least 20% by volume (Mirzaei *et al.*, 2015).

B.5 GAS HYDRATES

Hydrate-based separation is a promising technology that has gained attention in the CO_2 capture industry. Gas hydrates are crystalline solids composed of water and gas molecules, formed under low temperature and high pressure conditions (Mondal *et al.*, 2012).

For CO_2 capture, a hydrate is first formed by exposing the gas stream containing CO_2, to water at high pressure. The CO_2 is captured within the hydrate as it forms. Pure CO_2 can be released from the hydrate by subjecting it to separation and dissociation pressure and temperature conditions (Mondal *et al.*, 2012).

To increase hydrate formation efficiency, chemical additives may be used as hydrate promoters. Hydrate promoters may be kinetic or thermodynamic promoters. Kinetic promoters are usually surfactants that do not take part in hydrate formation, but increase formation rate, while thermodynamic promoters take part in hydrate formation by competing with the gas molecules for hydrate cages (Dashti *et al.*, 2015). Research published on CO_2 capture by gas hydrate technology, using a tetra-*n*-butylammonium bromide (TBAB) aqueous solution as thermodynamic hydrate promoter, shows that semi-clathrate hydrates with (CO_2 + N_2 + TBAB) are thermodynamically stable and the addition of the promoter gives more favourable hydrate dissociation conditions. This information is valuable for CO_2 capture with hydrates under conditions of mild temperatures and low pressures (Mohammadi *et al.*, 2011, Belandria *et al.*, 2012).

APPENDIX C: SUMMARY OF AMINE SOLVENTS AND BLENDS STUDIED IN THE LITERATURE

A summary of experimental data published in the literature for CO_2 solubility in aqueous amine solvents is provided in this section. Solvent compositions, temperature and pressure conditions and the CO_2 loading range obtained are quoted. All tables in appendix C were compiled by the author.

The following notes apply to all tables in Appendix C:

- Solvent concentrations (solvent composition column) are either given in weight percentage (%), molarity (M [mol/L]) or molality (m [mol/kg]); C_t denotes total concentration. Where approximate solvent concentrations are cited (denoted by the symbol "~"), a range of concentrations close to the cited value were investigated.
- Where specified, total pressure instead of partial pressure may be recorded (Denoted by "(P_t)" after the pressure range)
- Units of CO_2 loading is given in mol CO_2/mol amine UNLESS otherwise specified

C.1 AQUEOUS SOLVENTS (SINGLE AMINE)

Table C-1: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent MDEA.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Austgen *et al.* (1991)	2M MDEA	313.15	0.0056 - 92.8	0.006 - 0.842
	4.28M MDEA	313.15	0.0102 - 93.6	0.00314 - 0.663
Shen and Li (1992)	30% MDEA	313.15 - 373.15	1.1 - 1979	0.155 - 1.108
Dawodu and Meisen (1994)	4.28M MDEA	373.15; 393.15	162 - 3832	0.091 - 0.823

Table C-1: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent MDEA (contd.).

Reference	**Solvent Composition**	**Temperature (K)**	**CO_2 Partial Pressure Range (kPa)**	**CO_2 loading range (mol CO_2/ mol amine)**
Jou *et al.* (1994)	30% MDEA	298.15 - 393.15	0.00251 - 19854	0.00114 - 1.498
Rho *et al.* (1997)	5% MDEA	323.15 - 373.15	1.051 - 39.70	0.0300 - 0.6843
	20.5% MDEA	323.15 - 373.15	1.139 - 173.4	0.0260 - 0.8478
	50% MDEA	323.15 - 373.15	0.775 - 140.3	0.0087 - 0.4529
	75% MDEA	323.15 - 373.15	10.04 - 268.3	0.0126 - 0.2728
Haji-Sulaiman *et al.* (1998)	2M MDEA	303 - 323	0.997 - 95.83	0.079 - 0.880
	4M MDEA	303 - 323	0.090 - 98.2	0.010 - 0.761
Silkenbäumer *et al.* (1998)	2.632m MDEA	313.15	12 - 4080 (P_t)	0.634 - 3.435*
Xu *et al.* (1998)	3.04M MDEA	328; 343	6.152 - 806.8	0.0692 - 0.9110
	3.46M MDEA	328 - 363	147.5 - 992.0	0.1740 - 0.8488
	4.28M MDEA	313 - 373	0.876 - 1013.0	0.0091 - 0.8806
Lemoine *et al.* (2000)	23.63% MDEA	298	0.02 - 1.636	0.0171 - 0.2625
Kamps *et al.* (2001)	3.954m MDEA	313	17.65 - 646.9 (P_t)	3.338 - 4.914*
	7.994 – 8.001m MDEA (~8m)	313 - 393	68.5 - 756.5 (P_t)	1.007 - 9.227*
Park and Sandall (2001)	50% MDEA	298.15 - 373.15	0.78 - 140.40	0.0087 - 0.4923
Ali and Aroua (2004)	2M MDEA	313.15 - 353.15	0.06 - 95.61	0.05 - 0.80
Sidi-Boumedine *et al.* (2004)	25.73% MDEA	298 - 348	2.84 - 3834	0.000 - 1.303
	46.88% MDEA	298 - 348	2.70 - 4559.5	0.000 - 1.105
Ma'mun *et al.* (2005)	50% MDEA	328.15 - 358.15	65.75 - 813.4	0.1658 - 0.8133
Ermatchkov *et al.* (2006a)	1.905 – 2.620m MDEA (~2m)	313.15 - 393.15	0.43 - 59.8	0.0179 - 1.494*
	3.918 – 4.380m MDEA (~4m)	313.15 - 393.15	0.12 - 63.8	0.0186 - 2.834*
	7.331 – 8.441m MDEA (~8m)	313.15 - 393.15	0.73 - 69.3	0.0228 - 4.695*

Table C-1: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent MDEA (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Huttenhuis *et al.* (2007)	35% MDEA	283; 298	0.054 - 6.121	0.048 - 0.327
	50% MDEA	283; 298	0.441 - 986.8	0.047 - 1.105
Jang *et al.* (2008)	40% MDEA	313.15	10 - 4619	0.2377 - 0.8610
Dell'Era *et al.* (2010)	10% MDEA	298 - 323	102.8 - 103.27 (P_t)	0.0113 - 0.0134**
	20% MDEA	298 - 333	97.94 - 102.35 (P_t)	0.0165 - 0.0300**
	49% MDEA	298 - 333	94.46 - 101.80 (P_t)	0.0413 - 0.0922**
Dicko *et al.* (2010)	50% MDEA	323.15	6 - 434	0.099 - 0.891
Wong *et al.* (2014)	25% MDEA	303; 333	400 - 1600 (P_t)	0.631 - 1.349
Haghtalab and Izadi (2014)***	45% MDEA	343	205 - 1877 (P_t); 159 - 1485 (P_{CO2})	0.2447 - 0.5908
Najafloo *et al.* (2015)	5.370m MDEA	313.15 - 358.15	5.5 - 240	0.156 - 0.381
Dash and Bandyopadhyay (2016)	30% MDEA	303 - 323	1.310 - 1306.65	0.0602 - 1.4277
	50% MDEA	303 - 323	18.62 - 725.27	0.2044 - 0.95708

* Units = mol CO_2/kg

**Mole fraction of CO_2 in the liquid phase

***Simultaneous measurement of CO_2 + H_2S solubility in the aqueous amine solvents

Table C-2: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent AMP.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Teng and Mather (1990)	2M AMP	313.15; 343.15	0.162 - 5279	0.033 - 1.265
Tontiwachwuthikul *et al.* (1991)	2M AMP	293 - 353	1.59 - 94.00	0.154 - 0.960
	3M AMP	293 - 353	1.59 - 94.00	0.126 - 0.898
Li and Chang (1994)	30% AMP	313.15 - 373.15	1.05 - 197	0.039 - 0.867
Seo and Hong (1996)	30% AMP	313.15 - 353.15	3.94 - 336.6	0.279 - 0.899
Silkenbäumer *et al.* (1998)	2.430 – 2.451m AMP	313.15 - 353.15	0.007 - 2613 (P_t)	0.375 - 2.903*
	6.135 – 6.477m AMP	313.15 - 353.15	0.007 - 2743 (P_t)	0.975 - 6.382*
Kundu *et al.* (2003)	18% AMP	303	4.41 - 90.1	0.674 - 0.966
	25% AMP	303 - 323	3.25 - 91.5	0.430 - 0.938
	30% AMP	303 - 323	3.20 - 94.0	0.412 - 0.889
Chen *et al.* (2011)	4.8m AMP	313.15 - 373.15	0.14 - 63.6	0.15 - 0.60
Dash *et al.* (2011c)	2.5M AMP	298 - 328	0.440 - 1433	0.232 - 1.100
	3.4M AMP	298 - 328	0.520 - 1449	0.282 - 1.056
	4.9M AMP	298 - 328	0.412 - 1412	0.191 - 1.032
Shariff *et al.* (2011)	1M AMP	303.15 - 333.15	520 - 6010 (P_t)	1.43 - 2.49
	2M AMP	303.15 - 333.15	560 - 6080 (P_t)	1.19 - 2.28
	3M AMP	303.15 - 333.15	530 - 6060 (P_t)	0.99 - 2.18
Ahmad (2012)	0.89% AMP	313.15 - 353.15	0.0270 - 9.0375	0.0998 - 1.0395
		373.15; 393.15	245.2 - 994.9 (P_t)	0.7615 - 1.9485
	8.9% AMP	313.15 - 353.15	0.0427 - 18.6703	0.0367 - 0.8533
		373.15; 393.15	99.9 - 1001.90 (P_t)	0 - 0.9727
	26.84% AMP	313.15 - 353.15	0.0156 - 17.3346	0.0052 - 0.7205
		353.15 - 393.15	44.9 - 968.3 (P_t)	0.0001 - 0.9236

Table C-2: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent AMP (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Dash *et al.* (2012)	40% AMP	303 - 323	0.268 - 1472	0.242 - 1.042
	50% AMP	318; 328	0.909 - 194	0.249 - 0.863
Tong *et al.* (2012)	30% AMP	313.2 - 393.2	6.0 - 632.6	0 - 0.965
Wong *et al.* (2014)	25% AMP	303; 333	400 - 1600 (P_t)	0.717 - 3.653

*Units = mol CO_2/kg

Table C-3: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent PZ.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Bishnoi and Rochelle (2000)	0.6M PZ	313; 343	0.032 - 40	0.16 - 0.96
Kamps *et al.* (2003)	1.995 – 2.035m PZ (~2m)	313.15 - 393.15	13.3 - 9131 (P_t)	0 - 3.366*
	3.950 – 3.964m PZ (~4m)	333.15 - 393.15	42.8 - 9560 (P_t)	0 - 5.369*
Aroua and Mohd Salleh (2004)	0.1M PZ	293.15 - 323.15	0.9 - 95.6	0.098 - 0.257
	0.2M PZ	293.15 - 323.15	0.9 - 95.3	0.189 - 0.328
	0.4M PZ	293.15 - 323.15	0.9 - 95.3	0.356 - 0.543
	0.6M PZ	293.15 - 323.15	0.9 - 95.6	0.460 - 0.802
	1M PZ	293.15 - 323.15	0.9 - 95.1	0.703 - 1.178
Derks (2006)	0.2M PZ	298.15 - 343.15	0.38 - 107.23	0.27 - 1.23
	0.6M PZ	298.15 - 343.15	0.27 - 111.37	0.36 - 1.08
Ermatchkov *et al.* (2006b)	8% PZ	313,15	0.57 - 30.17	0.732 - 1.105*
	15% PZ	313.15 - 393.15	0.111 - 48.42	0.193 - 1.932*
	26% PZ	333.15; 393.15	0.154 - 95.30	0.199 - 3.391*

Table C-3: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent PZ (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Dugas and Rochelle (2009)	2m PZ	313.15; 333.15	0.096 - 25.378	0.240 - 0.411
	5m PZ	313.15; 333.15	0.065 - 17.233	0.226 - 0.702
	8m PZ	313.15; 333.15	0.068 - 30.738	0.231 - 0.404
	12m PZ	333,15	0.0331 - 6.791	0.231 - 0.354
Kadiwala *et al.* (2010)	0.3M PZ	313; 343	205 - 6489	0.98 - 2.77
	1.2M PZ	313; 343	198 - 7399	0.92 - 2.03
Bougie and Iliuta (2011)	0.1m PZ	287.1 - 303.1	3.285 - 338.7 (P_t)	0.45 - 2.68
	0.5m PZ	287.1; 293.1	2.130 - 161.7 (P_t)	0.316 - 1.17
	0.63m PZ	298.1; 303.1	3.519 - 150.8 (P_t)	0.298 - 1.10
	1m PZ	287.1 - 303.1	1.931 - 195.0 (P_t)	0.193 - 1.10
	2m PZ	313.1	9.34 - 532.0 (P_t)	0.097 - 1.16
Dash *et al.* (2011a)	0.2M PZ	298 - 328	0.103 - 1362	0.288 - 2.956
	0.4M PZ	298 - 328	0.086 - 1418	0.269 - 1.898
	0.8M PZ	298 - 328	0.096 - 1420	0.263 - 1.427
	1.6M PZ	298 - 328	0.083 - 1487	0.293 - 1.336
	3.2M PZ	308 - 328	0.091 - 1473	0.268 - 1.067
	4.5M PZ	318; 328	0.107 - 1416	0.436 - 1.004
Xu (2011)	~5m PZ	373 - 464	20 - 1775	0.248 - 0.292
	~8m PZ	354 - 465	20 - 3006	0.224 - 0.451
	~10m PZ	373 - 433	25 - 2065	0.287 - 0.379
Xu and Rochelle (2011)	7.75 – 8.00m PZ	354.15 - 447	20 - 2192	0.224 - 0.451

* Units = mol CO_2/kg

Table C-4: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent MEA.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Austgen *et al.* (1991)	2.5M MEA	313.15; 353.15	0.0934 - 228.7	0.351 - 0.620
Shen and Li (1992)	30% MEA	313.15 - 373.15	1.1 - 1975	0.227 - 0.806
Dawodu and Meisen (1994)	4.2M MEA	373,15	455 - 3863	0.541 - 0.723
Daneshvar *et al.* (2004)	2M MEA	303.15 - 343.15	10.67 - 78.34	0.457 - 0.911
Ma'mun *et al.* (2005)	30% MEA	393,15	7.354 - 191.9	0.1550 - 0.4182
Dugas and Rochelle (2009)	7m MEA	313.15; 333.15	0.0157 - 16.157	0.252 - 0.496
	9m MEA	313.15; 333.15	0.0104 - 21.249	0.231 - 0.469
	11m MEA	313.15; 333.15	0.014 - 8.171	0.261 - 0.461
	13m MEA	313.15; 333.15	0.0123 - 29.427	0.252 - 0.502
Xu (2011)	~7m MEA	373.15 - 443.15	12 - 1626	0.307 - 0.520
	~10m MEA	373.15 - 443.15	40 - 2435	0.379 - 0.520
Xu and Rochelle (2011)	6.85 – 6.97m MEA (~7m)	373.15 - 443.15	12 - 1442	0.310 - 0.520
Tong *et al.* (2012)	30% MEA	313; 393	3.95 - 408.17	0.211 - 0.748
Arshad *et al.* (2014)	30% MEA	313.15 - 393.15	2.1 - 585.9	0.068 - 0.780

Table C-5: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent DEA.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Dawodu and Meisen (1994)	4.2M DEA	373.15; 393.15	93 - 3742	0.299 - 0.725
Seo and Hong (1996)	30% DEA	313.15 - 353.15	4.85 - 357.3	0.404 - 0.727
Haji-Sulaiman *et al.* (1998)	2M DEA	303 - 323	0.090 - 104.073	0.133 - 0.786
	4M DEA	303 - 323	0.095 - 102.119	0.061 - 0.671

Table C-5: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent DEA (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Sidi-Boumedine *et al.* (2004)	41.78% DEA	298.13; 348.07	2.46 - 4662.7 (P_t)	0.000 - 1.088
Barreau *et al.* (2006)	2M DEA	323.15	14 - 3798	0.45 - 1.13
	25% DEA	338.50; 366.90	1 - 923	0.098 - 0.799
Kierzkowska-Pawlak and Chacuk (2010)	10% DEA	293.15; 313.15	62.5 - 114.2	0.831 - 0.979
	20% DEA	293.15; 313.15	64.7 - 119.8	0.753 - 0.867
Li and Rochelle (2014)	7m DEA	293.15 - 353.15	0.22 - 46.84	0.188 - 0.470

Table C-6: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent 1-MPZ.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Chen and Rochelle (2011)	8m 1-MPZ	313.15 - 373.15	0.1 - 33.01	0.10 - 0.26
Xu and Rochelle (2011)	7.66 – 7.76m 1-MPZ	373.15 - 433.15	255 - 2272	0.170 - 0.246
Li *et al.* (2014)	30% 1-MPZ	313.15; 393.15	0.09 - 686	0.043 - 1.039
Rayer *et al.* (2014)	15% 1-MPZ	313; 353	216 - 7769	0.193 - 0.392
	30% 1-MPZ	313; 353	182 - 7780	0.408 - 0.670

Table C-7: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent AEEA.

Reference	**Solvent Composition**	**Temperature (K)**	**CO_2 Partial Pressure Range (kPa)**	**CO_2 loading range (mol CO_2/ mol amine)**
Ma'mun *et al.* (2006)	30% AEEA	313.15 - 393.15	0.01 - 222.4	0.013 - 0.920
Zoghi *et al.* (2012)	30% AEEA	313.2 - 368.2	122 - 4378	0.06 - 1.407
Guo *et al.* (2013)	15% AEEA	303 - 323	0.9 - 795	0.621 - 1.313

Table C-8: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent AHPD.

Reference	**Solvent Composition**	**Temperature (K)**	**CO_2 Partial Pressure Range (kPa)**	**CO_2 loading range (mol CO_2/ mol amine)**
Park *et al.* (2002)	10% AHPD	313.15 - 333.15	21.7 - 1840	0.343 - 1.423
	20% AHPD	333.15	42.1 - 1451.5	0.330 - 1.023
Le Tourneux *et al.* (2008)	0.15% AHPD	283.15 - 313.15	1.91 - 73.4	$(0.75 - 4.68)\times10^{-2*}$
	0.50% AHPD	283.15 - 313.15	2.73 - 73.6	$(1.93 - 7.34)\times10^{-2*}$
	1% AHPD	283.15 - 313.15	2.26 - 74.1	$(2.91 - 11.29)\times10^{-2*}$
	2.5% AHPD	283.15 - 313.15	2.89 - 74.8	$(6.54 - 22.26)\times10^{-2*}$
Bougie and Iliuta (2010)	0.917m AHPD	298.15 - 333.15	0.31 - 2638	0.0745 - 1.8545
	2.000m AHPD	284.5 - 333.15	0.9 - 1250	0.0940 - 1.2345
	3.000m AHPD	284.2 - 333.22	0.5 - 914.8	0.0796 - 0.9741
	4.000m AHPD	293.2 - 333.22	0.6 - 1080	0.1211 - 0.8125
Bougie and Iliuta (2013)	0.953m AHPD	313.15	1.346 – 590.9	0.207 – 0.900**
	2.097m AHPD	313.15	1.500 – 346.1	0.457 – 1.650**
	3.464m AHPD	313.15	0.5239 – 464.8	0.356 – 2.600**
	4.704m AHPD	313.15	0.8511 – 413.6	0.647 – 0.330**

Table C-8: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent AHPD (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Oktavian *et al.* (2014)	5% AHPD	318.15; 333.15	3930 - 11760	0.0206 - 0.0329***
	10% AHPD	318.15; 333.15	2310 - 10750	0.0194 - 0.0329***

* Units = mol/L (total concentration of CO_2)
**Units = mol CO_2/kg
***Units = mole fraction of CO_2

Table C-9: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent DEEA.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Monteiro *et al.* (2013)	2M DEEA	313 - 353	0.0283 - 16.091	0.0204 - 0.8215
		353 - 393	115.7 - 977.1	0.091 - 1.017
	5M DEEA	313 - 353	0.063 - 19.225	0.005 - 0.3603
		353 - 393	176.6 - 1035.3	0.0057 - 0.673
Arshad *et al.* (2014)	61% DEEA	313.15 - 393.15	0.6 - 577.1	0.015 - 1.038
Xu *et al.* (2014)	3M DEEA	333.15; 353.15	3.747 - 191.907	0.393 - 0.894
	4M DEEA	333.15; 353.15	4.944 - 68.708	0.232 - 0.537
Luo *et al.* (2016)	1M DEEA	293 - 353	5.9 - 100.8	0.353 - 0.971
	2M DEEA	293 - 353	5.9 - 100.8	0.217 - 0.950
	3M DEEA	293 - 353	5.9 - 100.8	0.103 - 0.896
	4M DEEA	293 - 353	5.9 - 100.8	0.064 - 0.912

Table C-10: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent DIPA.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Dell'Era *et al.* (2010)	10.1% DIPA	297 - 304	5.7 - 207.1 (P_t)	0 - 1.0793
	11.0% DIPA	298 - 299	2.5 - 955.6 (P_t)	0 - 1.3108
	33.9% DIPA	298 - 299	3.2 - 944.0 (P_t)	0 - 0.9925
	10% DIPA	298.45 - 353.12	93.26 - 102.86 (P_t)	0.0078 - 0.0136*
	20% DIPA	298.13 - 353.14	100.39 - 102.83 (P_t)	0.0121 - 0.0297*
	25% DIPA	298.11 - 353.11	100.01 - 102.47 (P_t)	0.0153 - 0.0373*
	35% DIPA	298.55 - 353.16	99.45 - 101.53 (P_t)	0.0170 - 0.0491*
Haghtalab and Izadi (2014)**	45% DIPA	343	173 - 1355	0.3714 - 0.5323
Haghtalab *et al.* (2014)	45% DIPA	313.15 - 343.15	107 - 4064	0.520 - 1.052

* Mole fraction of CO_2 in liquid phase

** Simultaneous measurement of CO_2 + H_2S solubility in the aqueous amine solvents

Table C-11: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent MAE.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Haider *et al.* (2011)	1M MAE	303 - 333	1.0 - 99.1	0.566 - 0.996
	2M MAE	303 - 333	1.0 - 98.8	0.548 - 0.902
	4M MAE	303	1.0 - 24.6	0.474 - 0.573
Kumar and Kundu (2012)	0.968m MAE	303.1 - 323.1	4.0 - 352.8	0.554 - 1.162
	1.574m MAE	303.1 - 323.1	0.9 - 353.3	0.345 - 1.10
	2.240m MAE	303.1 - 323.1	1.0 - 355.9	0.436 - 1.023
	3.125m MAE	303.1 - 323.1	1.0 - 341.3	0.366 - 0.988

Table C-11: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent MAE (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Kumar (2013)*	30% MAE	303.1 - 323.1	0.101 - 510.7	0.282 - 1.120
Li (2015)	7m MAE	293.15 - 373.15	0.02 - 47.76	0.208 - 0.554

*Showing only data not published in Kumar and Kundu (2012)

Table C-12: Summary of the solubility data available in the literature for CO_2 in the aqueous amine solvent MPA.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Dong *et al.* (2010)	2M MPA	313.15 - 393.15	3.9 - 695.0	0.190 - 1.024
	4M MPA	313.15 - 393.15	3.2 - 661.5	0.213 - 0.876
	5M MPA	313.15 - 393.15	3.7 - 704.9	0.200 - 0.834
Idris *et al.* (2015)	5M MPA	313.15	0.0071 - 4.2314	0.201 - 0.527
	30% MPA	313.15	0.0047 - 2.3244	0.206 - 0.524
Li and Rochelle (2014)	7m MPA	293.15 - 373.15	0.01 - 42.06	0.325 - 0.586

C.2 AQUEOUS AMINE BLENDS

Table C-13: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend MDEA + PZ.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Liu *et al.* (1999)	1.53M MDEA + 0.17M PZ	323.15; 343.16	21.18 - 688.8	0.387 - 0.980
	1.35M MDEA + 0.35M PZ	323.15; 343.16	17.60 - 586.9	0.349 - 0.955
	3.15M MDEA + 0.35M PZ	303.15 - 363.16	16.73 - 573.0	0.147 - 0.842
	2.8M MDEA + 0.7M PZ	303.15 - 363.16	15.60 - 935.3	0.198 - 0.880
	4.77M MDEA + 0.53M PZ	323.15; 343.16	35.83 - 753.7	0.193 - 0.760
	3.75M MDEA + 1.55M PZ	323.15; 343.16	13.16 - 678.3	0.247 - 0.746
Bishnoi and Rochelle (2002)	4M MDEA + 0.6M PZ	313; 343	0.33 - 7.480	0.006 - 0.285
Kamps *et al.* (2003)	1.975m MDEA + 1.966m PZ	353,14	180.7 - 6400 (P_t)	2.526 - 4.478*
Ali and Aroua (2004)	1.98M MDEA + 0.01M PZ	313.15 - 353.15	0.06 - 95.28	0.06 - 0.86
	1.90M MDEA + 0.05M PZ	313.15 - 353.15	0.06 - 95.78	0.04 - 0.82
	1.80M MDEA + 0.10M PZ	313.15 - 353.15	0.06 - 95.78	0.06 - 0.82
Hosseini Jenab *et al.* (2005)	3.00M MDEA + 0.36M PZ	313.15 - 343.15	33.99 - 3850.87	0.2268 - 1.2817
	2.50M MDEA + 0.86M PZ	313.15 - 343.15	27.79 - 3938.43	0.2817 - 1.3147
	2.00M MDEA + 1.36M PZ	313.15 - 343.15	30.54 - 3673.68	0.3811 - 1.3613
Jang *et al.* (2008)	40% MDEA + 5% PZ	313.15	3 - 4483	0.2843 - 0.9372
	40% MDEA + 7.5% PZ	313.15	2 - 4473	0.2864 - 0.9794
	40% MDEA + 10% PZ	313.15	0 - 4330	0.2406 - 0.9996
Böttger *et al.* (2009)	2.2m MDEA + 1.7m PZ	313; 393	518 - 9353 (P_t)	1.902 - 8.229*
	4.22m MDEA + 2.01m PZ	313 - 393	218 - 10260 (P_t)	2.575 - 7.230*
	7.83m MDEA + 2.07m PZ	333 - 393	294 - 8997 (P_t)	2.974 - 10.73*

Table C-13: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend MDEA + PZ (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Derks *et al.* (2010)	4M MDEA + 0.6M PZ	313	0.72 - 89.7	0.062 - 0.638
	2.8M MDEA + 0.7M PZ	303; 323	0.51 - 100.1	0.042 - 0.837
	0.5M MDEA + 1.5M PZ	298; 313	0.25 - 110	0.0948 - 0.984
Speyer *et al.* (2010)	~4m MDEA + ~4m PZ	353.15; 393.15	0.60 - 63.6	0.15 - 0.44
	~2m MDEA + ~2m PZ	313.15 - 393.15	0.11 - 66.2	0.04 - 0.83
	~4m MDEA + ~1m PZ	313.15	0.95 - 61.8	0.02 - 0.73
	~4m MDEA + ~2m PZ	313.15 - 393.15	0.62 - 99.8	0.02 - 0.71
	~2m MDEA + ~1m PZ	313.15	0.31 - 30.5	0.23 - 0.72
	~8m MDEA + ~2m PZ	313.15	0.27 - 45.9	0.07 - 0.54
	~8m MDEA + ~2m PZ	313.15 - 393.15	0.91 - 146.8	0.02 - 0.60
Chen *et al.* (2011)	7m MDEA + 2m PZ	313.15 - 373.15	0.19 - 19.8	0.027 - 0.286
	5m MDEA + 5m PZ	313.15 - 373.15	0.24 - 28.2	0.18 - 0.37
Xu (2011)	7m MDEA + 2m PZ	373.15 - 433.15	78 - 2054	0.113 - 0.236
	5m MDEA + 5m PZ	373.15 - 433.15	98 - 1776	0.197 - 0.275
Najibi and Maleki (2013)	1.6M MDEA + 0.7M PZ	363.15 - 423.15	27.3 - 204	0.117 - 0.402
	3M MDEA + 0.3M PZ	363.15 - 423.15	27.5 - 188.3	0.09 - 0.368
	2M MDEA + 0.3M PZ	363.15 - 423.15	26.3 - 204.3	0.163 - 0.491
Wong *et al.* (2014)	25% MDEA + 2% PZ	303; 333	400 - 1600 (P_t)	1.403 - 3.814
	25% MDEA + 8% PZ	303; 333	400 - 1600 (P_t)	1.769 - 4.121
	50% MDEA + 2% PZ	303; 333	400 - 1600 (P_t)	0.864 - 3.245
	50% MDEA + 8% PZ	303; 333	400 - 1600 (P_t)	1.086 - 3.496

Table C-13: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend MDEA + PZ (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Dash and Bandyopadhyay (2016)	28% MDEA + 2% PZ	303 - 323	1.584 - 1066.025	0.1613 - 1.2844
	25% MDEA + 5% PZ	303 - 323	0.4205 - 99.289	0.114 - 0.929
	22% MDEA + 8% PZ	303 - 323	0.0896 - 1246.29	0.04422 - 1.2476
	48% MDEA + 2% PZ	303 - 323	8.134 - 1364.79	0.2582 - 1.0511
	45% MDEA + 5% PZ	303 - 323	10.339 - 1358.58	0.3153 - 1.0616
	42% MDEA + 8% PZ	303 - 323	7.927 - 1426.82	0.319 - 1.0654

* Units = mol CO_2/kg

Table C-14: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend DEA + MDEA.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Austgen *et al.* (1991)	2M DEA + 2M MDEA	313.15; 353.15	0.136 - 309.3	0.0240 - 0.802
Dawodu and Meisen (1994)	0.8M DEA + 2.1M MDEA	343.15 - 453.15	65 - 3707	0.042 - 0.911
	2.1M DEA + 2.1M MDEA	343.15 - 453.15	190 - 3756	0.045 - 0.928
Murrieta-Guevara *et al.* (1998)	10% DEA + 15% MDEA	313.15	3.5 - 2612.7	0.234 - 1.119
	10% DEA + 20% MDEA	313.15; 393.15	2.8 - 2833.6	0.038 - 1.086
	20% DEA + 10% MDEA	313.15	4.5 - 2377.1	0.185 - 1.056
	10% DEA + 35% MDEA	313.15	3.8 - 2638.3	0.120 - 1.010
Rebolledo-Libreros and Trejo (2004)	12.5% DEA + 32.5% MDEA	313.15 - 393.15	0.4 - 1973.1	0.047 - 1.107
Sidi-Boumedine *et al.* (2004)	7.63% DEA + 37.59% MDEA	298.12; 348.06	2.61 - 4594.6 (P_t)	0.000 - 1.109

Table C-14: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend DEA + MDEA (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Kundu and Bandyopadhyay (2006b)	1.5% DEA + 28.5% MDEA	303 - 323	3.000 - 90.00	0.250 - 0.732
	3% DEA + 27% MDEA	303 - 323	3.875 - 90.00	0.290 - 0.696
	4.5% DEA + 25.5% MDEA	303 - 323	2.400 - 90.00	0.262 - 0.677
Kumar *et al.* (2012)	6% DEA + 24% MDEA	303.1 - 323.1	14.79 - 290.1	0.422 - 0.964
	9% DEA + 21% MDEA	303.1 - 323.1	6.496 - 346.9	0.335 - 0.961
	12% DEA + 18% MDEA	303.1 - 323.1	10.81 - 331.1	0.362 - 0.936
	15% DEA + 15% MDEA	303.1 - 323.1	6.489 - 312.0	0.347 - 0.939
Osman *et al.* (2012)	25% DEA + 25% MDEA	362.1; 412.1	49 - 1153	0.043 - 0.789
	20% DEA + 30% MDEA	362.1; 412.1	52 - 1050	0.043 - 0.344

Table C-15: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend AMP + PZ.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Yang *et al.* (2010)	2.0M AMP + 0.5M PZ	313.2 - 353.2	1.29 - 132.4	0.336 - 0.872
	2.0M AMP + 1.0M PZ	313.2 - 353.2	1.06 - 129.6	0.386 - 0.876
	2.0M AMP + 1.5M PZ	313.2 - 353.2	1.00 - 123.4	0.417 - 0.870
	3.0M AMP + 0.5M PZ	313.2 - 353.2	1.08 - 116.5	0.292 - 0.844
	3.0M AMP + 1.0M PZ	313.2 - 353.2	1.07 - 127.4	0.362 - 0.862
	3.0M AMP + 1.5M PZ	313.2 - 353.2	0.97 - 139.9	0.374 - 0.851
Brúder *et al.* (2011)	3M AMP + 1.5M PZ	313.15 - 393.15	0.016 - 536.5	0.04 - 0.83

Table C-15: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend AMP + PZ (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Dash *et al.* (2011b)	22% AMP + 8% PZ	298 - 328	0.122 - 1456	0.305 - 1.072
	25% AMP + 5% PZ	298 - 328	0.101 - 1449	0.258 - 1.064
	28% AMP + 2% PZ	298 - 328	0.101 - 1487	0.202 - 1.050
Dash *et al.* (2012)	38% AMP + 2% PZ	303 - 323	0.241 - 1433	0.259 - 1.029
	35% AMP + 5% PZ	303 - 323	0.158 - 1464	0.306 - 1.021
	32% AMP + 8% PZ	303 - 323	0.170 - 1426.2	0.34 - 1.021
	48% AMP + 2% PZ	318; 328	0.523 - 180.9	0.218 - 0.839
	45% AMP + 5% PZ	318; 328	0.615 - 178.2	0.297 - 0.826
	42% AMP + 8% PZ	318; 328	0.567 - 188.7	0.309 - 0.813
Li *et al.* (2013)	12% AMP + 26% PZ	293 - 433	120 - 3237	0.279 - 0.494
	23% AMP + 11% PZ	293 - 433	38.5 - 1912	0.268 - 0.442
Tong *et al.* (2013)	25% AMP + 5% PZ	313.2 - 393.2	5.7 - 433.6	0 - 0.952
	20% AMP + 10% PZ	313.2 - 393.2	6.1 - 463.5	0 - 0.930
Wong *et al.* (2014)	25% AMP + 2% PZ	303; 333	400 - 1600 (P_t)	1.794 - 4.260
	25% AMP + 8% PZ	303; 333	400 - 1600 (P_t)	2.125 - 4.624
	50% AMP + 2% PZ	303; 333	400 - 1600 (P_t)	0.978 - 3.555
	50% AMP + 8% PZ	303; 333	400 - 1600 (P_t)	1.197 - 3.653
Li (2015)	2.3m AMP + 5m PZ	293.15 - 373.15	0.093 - 59.91	0.31 - 0.45

Table C-16: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend MDEA + MEA.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Austgen *et al.* (1991)	2M MDEA + 2M MEA	313.15; 353.15	0.0506 - 312.9	0.0756 - 0.781
Li and Shen (1992)	24% MDEA + 6% MEA	313.15 - 373.15	1.12 - 2080.0	0.185 - 1.015
	12% MDEA + 18% MEA	313.15 - 373.15	1.37 - 1973.0	0.167 - 0.881
Shen and Li (1992)	18% MDEA + 12% MEA	313.15 - 373.15	0.9 - 2016	0.197 - 0.947
	6% MDEA + 24% MEA	313.15 - 373.15	1.5 - 1987	0.235 - 0.849
Dawodu and Meisen (1994)	3.4M MDEA + 0.8M MEA	343.15 - 453.15	190 - 3876	0.050 - 0.884
	2.1M MDEA + 2.1M MEA	343.15 - 453.15	137 - 3859	0.065 - 0.917
Jou *et al.* (1994)	28.5% MDEA + 1.5% MEA	298.15 - 393.15	0.00115 - 14952	0.00214 - 1.470
	27% MDEA + 3% MEA	298.15 - 393.15	0.00153 - 19855	0.000722 - 1.373
	20% MDEA + 10% MEA	298.15 - 393.15	0.00154 - 19933	0.00109 - 1.473
	10% MDEA + 20% MEA	298.15 - 423.15	0.00132 - 19934	0.00132 - 1.399

Table C-17: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend AMP + DEA.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Seo and Hong (1996)	24% AMP + 6% DEA	313.15 - 353.15	1.61 - 269.9	0.262 - 0.810
	18% AMP + 12% DEA	313.15 - 353.15	11.0 - 364.9	0.329 - 0.821
	12% AMP + 18% DEA	313.15 - 353.15	3.8 - 357.3	0.343 - 0.748
Murrieta-Guevara *et al.* (1998)	5% AMP + 25% DEA	313.15; 373.15	162 - 2908	0.393 - 1.200
	10% AMP + 20% DEA	313.15; 373.15	22 - 2597	0.331 - 1.00

Table C-17: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend AMP + DEA (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Kundu and Bandyopadhyay (2006a)	28.5% AMP + 1.5% DEA	303 - 323	1.925 - 89.02	0.455 - 0.864
	27% AMP + 3% DEA	303 - 323	2.00 - 90.95	0.370 - 0.806
	25.5% AMP + 4.5% DEA	303 - 323	2.22 - 90.0	0.370 - 0.788
	24% AMP + 6% DEA	303 - 323	2.2 - 92.77	0.425 - 0.778
Kumar *et al.* (2012)	24% AMP + 6% DEA	303.1 - 323.1	1.021 - 354.8	0.388 - 0.989
	21% AMP + 9% DEA	303.1 - 323.1	6.038 - 246.1	0.463 - 0.963
	18% AMP + 12% DEA	303.1 - 323.1	3.013 - 318.7	0.497 - 0.938
	15% AMP + 15% DEA	303.1 - 323.1	4.021 - 282.0	0.432 - 0.879

Table C-18: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend AEEA + MDEA.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Guo *et al.* (2013)	15% AEEA + 5% MDEA	303 - 323	0.92 - 831.5	0.483 - 1.148
	15% AEEA + 10% MDEA	303 - 323	0.81 - 784.3	0.39 - 1.080
Zoghi and Feyzi (2013)	C_t = 3.36M (AEEA/MDEA = 0.125)	308.2 - 368.2	101 - 4445	0.406 - 1.007
Najafloo *et al.* (2015)	C_t = 5.370m (n_{AEEA}/n_{MDEA} = 0.125)	313.15 - 358.15	5.5 - 240	0.256 - 0.464
	C_t = 5.370m (n_{AEEA}/n_{MDEA} = 0.100)	313.15 - 358.15	5.5 - 240	0.240 - 0.448
	C_t = 5.370m (n_{AEEA}/n_{MDEA} = 0.050)	313.15 - 358.15	5.5 - 240	0.203 - 0.414

Table C-19: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend AHPD + PZ.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Bougie and Iliuta (2010)	~1.1m AHPD + ~0.01m PZ	288.15; 333.15	2.134 - 2110.2	0.0811 - 1.5060
	~1.1m AHPD + ~0.11m PZ	288.15; 333.15	2.050 - 2310.5	0.0857 - 1.6100
	1.1345m AHPD + 0.3403m PZ	298.15	3.350 - 2253.6	0.0954 - 1.4718
	1.1633m AHPD + 0.5816m PZ	313.15	7.578 - 2195.9	0.0932 - 1.3069
	4.2294m AHPD + 0.1410m PZ	313.15	7.394 - 639.6	0.0670 - 1.0396
	3.3604m AHPD + 0.4032m PZ	298.15	3.300 - 788.2	0.0518 - 0.9984
	~2.5m AHPD + ~0.65m PZ	288.15; 333.15	1.876 - 1436.9	0.0637 - 1.1367
Bougie and Iliuta (2013)	2.712m AHPD + 1.161m PZ	313.15; 373.15	0.875 - 229.4	0.265 - 3.17*
Li (2015)	3.5m AHPD + 3.5m PZ	293.15 - 373.15	0.30 - 48.00	0.203 - 0.367

* Units = mol CO_2/kg

Table C-20: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend AMP + MDEA.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Silkenbäumer *et al.* (1998)	1.266m AMP + 1.278m MDEA	313.15	12.5 - 4020 (P_t)	1.159 - 3.411*
Haghtalab and Izadi (2014)**	20% AMP + 25% MDEA	343	261 - 1987 (P_t); 196 - 1528 (P_{CO2})	0.3869 - 0.5752
Haghtalab and Ghahremani (2015)	25% AMP + 25% MDEA	313.15 - 343.15	180.7 - 3812.4	0.3386 - 0.9064
	20% AMP + 25% MDEA	313.15 - 343.15	145 - 3850.8	0.4252 - 0.8833
	15% AMP + 25% MDEA	313.15 - 343.15	162.4 - 3861.8	0.0293 - 0.8353

Table C-20: Summary of the solubility data available in the literature for CO_2 in the aqueous solvent blend AMP + MDEA (contd.).

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Shokouhi *et al.* (2015)	5% AMP + 40% MDEA	313.2 - 353.2	10.00 - 2413	0.458 - 1.217
	22.5% AMP + 22.5% MDEA	313.2 - 353.2	29.50 - 2640	0.539 - 1.020
	35% AMP + 10% MDEA	313.2 - 353.2	44.28 - 3383	0.186 - 1.185

* Units = mol CO_2/kg

** Simultaneous measurement of CO_2 + H_2S solubility in the aqueous amine solvents

C.3 TRI-AMINE AQUEOUS BLENDS

Table C-21: Summary of the solubility data available in the literature for CO_2 in the aqueous tri-amine solvent blend MDEA + DEA + AMP.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Rebolledo-Libreros and Trejo (2004)	32.5% MDEA + 12.5% DEA + 4% AMP	313.15 - 393.15	10.0 - 1927.0	0.067 - 1.036
	32.5% MDEA + 12.5% DEA + 6% AMP	313.15 - 393.15	6.6 - 1999.1	0.113 - 1.061
	32.5% MDEA + 12.5% DEA + 10% AMP	313.15 - 393.15	3.1 - 1968.7	0.079 - 1.041

Table C-22: Summary of the solubility data available in the literature for CO_2 in the aqueous tri-amine solvent blend MDEA + AMP + PZ.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Haghtalab and Izadi (2014)*	25% MDEA + 15% AMP + 5% PZ	343	197 - 1818 (P_t); 130 - 1344 (P_{CO2})	0.3840 - 0.5902
	25% MDEA + 10% AMP + 10% PZ	343	169 - 1797 (P_t); 97 - 1272 (P_{CO2})	0.4093 - 0.6136
	25% MDEA + 5% AMP + 15% PZ	343	169 - 1714 (P_t); 93 - 1167 (P_{CO2})	0.4309 - 0.6234
Haghtalab and Ghahremani (2015)	25% MDEA + 15% AMP + 10% PZ	313.15 - 343.15	185.7 - 3849.6	0.5884 - 1.0787
	25% MDEA + 10% AMP + 15% PZ	313.15 - 343.15	200.7 - 3851.4	0.635 - 1.0825
	25% MDEA + 10% AMP + 10% PZ	313.15 - 343.15	204 - 3868.9	0.758 - 1.1188
	25% MDEA + 10% AMP + 5% PZ	313.15 - 343.15	197.2 - 3852.6	0.7939 - 1.1053
	25% MDEA + 5% AMP + 10% PZ	313.15 - 343.15	124.1 - 3882.7	0.7393 - 1.1272

* Simultaneous measurement of CO_2 + H_2S solubility in the aqueous amine solvents

Table C-23: Summary of the solubility data available in the literature for CO_2 in the aqueous tri-amine solvent blend DIPA + AMP + PZ.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Haghtalab and Izadi (2014)*	25% DIPA + 15% AMP + 5% PZ	343	128 - 1275 (P_{CO2}); 194 - 1836 (P_t)	0.4154 - 0.5733
	25% DIPA + 10% AMP + 10% PZ	343	95 - 1235 (P_{CO2}); 182 - 1882 (P_t)	0.4397 - 0.6133
	25% DIPA + 5% AMP + 15% PZ	343	76 - 1175 (P_{CO2}); 161 - 1821 (P_t)	0.4575 - 0.6281
Haghtalab *et al.* (2014)	36% DIPA + 7% AMP + 2% PZ	313.15 - 343.15	1.04 - 40.43	0.502 - 1.091
	30% DIPA + 10% AMP + 5% PZ	313.15 - 343.15	1.08 - 41.53	0.578 - 1.092
	24% DIPA + 13% AMP + 8% PZ	313.15 - 343.15	0.97 - 40.44	0.519 - 1.067

* Simultaneous measurement of CO_2 + H_2S solubility in the aqueous amine solvents

Table C-24: Summary of the solubility data available in the literature for CO_2 in the aqueous tri-amine solvent blend DMPZ + PZ + 1-MPZ.

Reference	Solvent Composition	Temperature (K)	CO_2 Partial Pressure Range (kPa)	CO_2 loading range (mol CO_2/ mol amine)
Xu (2011)	0.5m DMPZ + 3.75m PZ + 3.75m 1-MPZ	373.15 - 433.15	165 - 2771	0.221 - 0.320
Freeman *et al.* (2014)	0.5m DMPZ + 3.75m PZ + 3.75m 1-MPZ	313.15 - 433.15	0.3 - 2730	0.21 - 0.32

APPENDIX D: SAMPLE CALCULATIONS

D.1 PERFORMANCE INDICATOR MODEL CALCULATIONS

This section demonstrates how the rating of a solvent is calculated using the PIM. First, the results from the Aspen Plus® simulations must be converted to a usable form; this includes calculation of utility flow rates from duties, etc. These calculated values are then used to determine the costs of the different factors considered, so that a rating may be determined by the PIM on cost basis. Sample calculations are shown for the baseline case, 30 wt. % AMP.

Calculation of the required cooling water flow rate through coolers:

Table D-1: Duties of all coolers in the process (including condensers).

Cooler Designation	Duty (kW)
Intercooler 1	61870
Intercooler 2	13777
Intercooler 3	31046
Lean Amine Cooler	253537
Stripper Condenser	830721
TOTAL COOLING	**1190950**

$$\dot{Q} = \dot{m}_{CW} \times C_p \times \Delta T \qquad \text{(D-1)}$$

Equation D-1 is used in combination with the data in table D-2 to determine the mass flow rate of cooling water (m_{CW}), which is then converted to units of ton/hr for uniformity.

Table D-2: Data used for, and results obtained from, equation D-1.

Total Cooling (kW)	498663
Water Cp (kJ/kg.K)	4.181
ΔT (K)	20
m_{CW} (kg/s)	**5963**
m_{CW} (ton/hr)	21468

Calculating the required steam flow through the strippers:

$$\dot{Q} = \dot{m}_{steam} \times H_v \times f_c \qquad \text{(D-2)}$$

Table D-3: Data used for, and results obtained from, equation D-2.

Heating Duty (kW)	440296
Water Hv (kJ/kg)	2260
Fraction condensed	0.95
m_{steam} (kg/s)	**205.07**
m_{steam} (ton/hr)	738.27

Reclaimer calculations:

The reclaimer is a necessary operation in CO_2 capture; it was not simulated in Aspen due to the complexity of the kinetics that occur during the process. A general model for reclamation was thus adopted and accounted for in Excel.

Table D-4: Data and results for the reclaim calculations.

Reclaimer Flows	
Fraction to reclaim	0.005
Flow Rates (ton/hr)	
Total Solvent*	9239
Amine	2197
Water	6251
Flows to Reclaimer (ton/hr)	
Total Solvent*	46
Amine	11
Water	31
Reclaimer Losses	
Loss Fractions	
Amine	0.05
Water	0.9
Loss Flows (ton/hr)	
Lost Amine Flow	0.549
Lost Water Flow	28

* The flow rate for total solvent does not add up to the sum of the individual amine and water flow rates because of entrained gas particles (CO_2 and other flue gas components) as well as electrolytes and impurities present.

In table D-4, the values under “Flow Rates” were obtained from the process simulation. “Flows to Reclaimer” is calculated by multiplying the flow rates with the reclaim fraction; these are the flow rates of the individual components that will pass through the reclamation process. Losses however also occur during the process. The “Loss Flows” are calculated by multiplying the “Flows to Reclaimer” for each component with its corresponding “Loss Fraction”.

Degradation calculations:

The degradation rate is multiplied by the flow of amine in the absorber to determine the flow of degraded amine. Table D-5 shows the result.

Table D-5: Data for, and results of, the degradation calculation.

Degradation Rate	0.00097
$m_{amine,absorber}$ (ton/hr)	2074.71
$m_{degraded\ amine}$ (ton/hr)	2.013

Plant efficiency calculations:

$$\varepsilon_{old} = \frac{MW_{out}}{MW_{in}} \tag{D-3}$$

Using the rated output of the power plant (MW_{out}) and the efficiency of the power plant without capture (ε_{old}), the thermal input to the power plant (MW_{in}) can be calculated with equation D-3. Table D-6 shows the result.

Table D-6: Calculation of MW_{in}.

ε_{old}	0.424
MW_{out}	500
MW_{in}	**1179**

Using the result obtained with equation D-3, the efficiency of the power plant with an installed capture plant (ε_{new}) can be calculated with equation D-4. "$MW_{capture}$" refers to the electrical energy consumed in the power plant; a breakdown of these values are given in table D-7.

$$\varepsilon_{new} = \frac{MW_{out} - MW_{capture}}{MW_{in}} \tag{D-4}$$

Table D-7: Breakdown of the energy consumed by the electrical equipment in the capture plant.

Energy required (MW)	
Compressors	31.93
Pumps	3.119
Blower	5.754
TOTAL	**40.80**

The value of ε_{new} calculated by equation D-4 was 0.3894.

Cost Calculations:

The costs for all factors are calculated by multiplying the appropriate stream flow rates by the cost of the factor. Tables D-8 to D-15 shows the data and results of the cost calculations for each factor considered in the PIM.

Table D-8: Data for, and results of, the cost of amine make-up.

Amine Price (R/ton)	88374
Make-Up Flows (ton/hr)	
Reclaimer Amine	0.549
Degraded Amine	2.013
Amine Makeup*	1.969
TOTAL (ton/hr)	**4.531**
COST (R/hour)	**400427**

*Value obtained from Aspen simulation

The cost of inhibitor is calculated as a fraction (x_{ihb}) of the lost amine flow (as explained in chapter 3).

$$C_{ihb} = x_{ihb} \times \dot{m}_{solv\_lost} \times P_{ihb} \tag{D-5}$$

Table D-9: Data for, and results of, the calculation for the cost of inhibitor.

Amine Lost (ton/hr)	2.562
$P_{Inhibitor}$ (R/ton)	3784
Inhibitor fraction	**0.005**
COST (R/hour)	**48.48**

Table D-10: Data for, and results of, the cooling water cost calculation.

CW Price (R/ton)	0.54
CW Flow (ton/hr)	53773
COST (R/hour)	**29037**

Table D-11: Data for, and results of, the make-up water cost calculation.

Water Price (R/ton)	11.52
Make-Up Flows (ton/hr)	
Reclaimer Water	28.13
Cooling Tower Loss	2487
Water Makeup	50.65
TOTAL (ton/hr)	**2566**
COST (R/hour)	**29558**

Table D-12: Data for, and results of, the steam cost calculation.

Steam Price (R/ton)	150.02
Steam Flow (ton/hr)	1983
COST (R/hour)	**297494**

Table D-13: Data for, and results of, the reclaim cost calculation.

Reclaim Price (R/ton)	10078
Reclaimer Flow (ton/hr)	46.196
COST (R/hour)	**465572**

Table D-14: Data for, and results of, the disposal cost calculation.

Disposal Price (R/ton)	3009
Disposal Flows (ton/hr)	
Reclaimer water loss	28
Reclaimer amine loss	0.549
Degraded amine	2.013
TOTAL (ton/hr)	**30.69**
COST (R/hour)	**92345**

To calculate the amount payable as carbon taxes, the CO_2 not captured (1 – capture rate) is multiplied by the amount of CO_2 fed and the CO_2 tax rate.

Table D-15: Data for, and results of, the cost of CO_2 taxes calculation.

CO_2 Tax Rate (R/ton)	120
CO_2 fed (ton/hr)	408.9
Capture Rate	0.9
COST (R/hour)	**4906**

Calculating the total cost of capture:

The total cost of CO_2 capture is calculated by taking the sum of all the individual factor costs (equation D-6). Table D-16 shows all individual factors costs as well as the total cost of capture.

$$C_{CO_2,\ captured} = \sum C_i \tag{D-6}$$

Table D-16: Costs of all factors considered in the PIM, used to calculate the total cost of CO_2 capture.

Factors	**Costs (R/hour)**
Makeup Amine	400427
Corrosion Inhibitor	48
Cooling Water	29037
Makeup Water	29558
Steam	297494
Reclaimer	465571
Disposal	92345
CO_2 Taxes	4906
TOTAL (R/hr)	**1319387**

Calculating the cost of CO_2 avoided:

The basis of the PIM is cost of CO_2 avoided, not cost of CO_2 capture (refer to figure 3-2 in chapter 3). To convert cost of CO_2 captured to cost of CO_2 avoided, the cost of capture was first converted to units of R/ton by dividing the original cost of capture (in units of R/hr) by the flow rate of CO_2 captured. The total cost of CO_2 avoided is then calculated by equation D-7.

$$C_{CO_2,\,avoided} = \frac{C_{CO_2,\,capture}\varepsilon_{old}}{\varepsilon_{new}} \tag{D-7}$$

Table D-17: Calculation of cost of CO_2 avoided from cost of CO_2 captured.

Capture Cost (R/ton)	3586
ε_{old}	0.424
ε_{new}	0.389
Cost$_{CO2,avoided}$ (R/ton)	**3904**

For each factor, the cost of CO_2 captured is converted to the cost of CO_2 avoided using equation D-7. Table D-18 summarizes these results.

Table D-18: Cost of CO_2 captured and cost of CO_2 avoided for each factor considered in the performance indicator model.

Factor	Cost of CO_2 Captured (R/hr)	Cost of CO_2 Avoided (R/hr)	Fractions (f_i)
Makeup Amine	400427	436006	0.30349
Corrosion Inhibitor	48	53	0.00004
Cooling Water	29037	31617	0.02201
Makeup Water	29558	32184	0.02240
Steam	297494	323927	0.22548
Amine Reclaim	465571	506938	0.35287
Amine Disposal	92345	100550	0.06999
CO_2 Taxes	4906	5342	0.00372
TOTAL	**1319387**	**1436616**	

The fractions in the last column of table D-18 is the cost fraction of each individual factor with respect to the total cost; it is used in the calculation of the performance rating. The fractions are calculated by equation D-8 using the cost values of CO_2 avoided.

$$f_i = \frac{C_i}{C_{total}} \tag{D-8}$$

Rating calculations:

To illustrate the calculation of a solvent's rating, 30 wt. % MEA was used as the benchmark with which the 30 wt. % AMP solvent was compared. The values of cost of CO_2 captured and cost of CO_2 avoided is summarized in table D-19.

Table D-19: Cost of CO_2 captured and cost of CO_2 avoided for the solvent 30 wt. % MEA for each factor considered in the performance indicator model.

Factor	Cost of CO_2 Captured (R/hr)	Cost of CO_2 Avoided (R/hr)
Makeup Amine	245901	267329
Corrosion Inhibitor	96	105
Cooling Water	52526	57103
Makeup Water	52958	57573
Steam	568369	617897
Amine Reclaim	355966	386986
Amine Disposal	79904	86867
CO_2 Taxes	4906	5334
TOTAL	**1360627**	**1479193**

The rating of a solvent with respect to the benchmark is then calculated by equation D-9. This calculation is completed for each factor individually and then added up to determine the overall rating (equation D-10).

$$R_i = f_i \times \frac{C_{i,b}}{C_{i,j}} \tag{D-9}$$

$$R = \sum R_i \tag{D-10}$$

Table D-20: Ratings of individual factors and overall rating.

Factors	Ratings
Makeup Amine	0.1861
Corrosion Inhibitor	0.0001
Cooling Water	0.0397
Makeup Water	0.0401
Steam	0.4301
Amine Reclaim	0.2694
Amine Disposal	0.0605
CO_2 Taxes	0.0037
TOTAL	**1.0296**

D.2 DATA FOR SENSITIVITY CALCULATIONS

Sensitivity calculations were performed to determine what the possible range of ratings for each solvent blend could be. This was done by finding different prices for all major factors, computing the standard deviation and then the relative average deviation (%) of each of the price lists. The rating is then evaluated by applying the deviation margin in a way that would result in the best rating and worst rating, respectively. Tables D-21 to D-26 show the different prices used (all prices have been made relevant to 2016 by using price indices).

Table D-21: Prices for amine solvents from various sources for use in the sensitivity analysis.

	AMP Prices	R/ton	MEA Prices	R/ton	MDEA Prices	R/ton	PZ Prices	R/ton
	Eachus and Bollmeier (2000)	96791	Kohl and Nielsen (1997)	37156	Zauba Technologies & Data (2016)	58556	Sridhar and Carter (2000)	63792
	Zauba Technologies & Data (2016)	83476	Sinnott (2005)	41386	Kohl and Nielsen (1997)	66698	Zauba Technologies & Data (2016)	53060
	Daya (2017)	84854	Sigma-Aldrich (2016)	38427	Sigma-Aldrich (2016)	56550	Sigma-Aldrich (2016)	58766
SD		7323		2170		5374		5369
% deviation		8.3		5.6		8.9		9.2

Table D-22: Prices for make-up water from various sources for use in the sensitivity analysis.

	Water Prices	R/ton
	Eberhard (2004)	11.17
	RSA DWA (2013)	10.85
	Daya (2017)	11.52
SD		0.34
% deviation		3.0

Table D-23: Prices for steam from various sources for use in the sensitivity analysis.

	Steam Prices	R/ton
	Ulrich and Vasudevan (2006)	132.73
	US Department of Energy (2003)	160.57
	Daya (2017)	150.02
SD		14.06
% deviation		9.5

Table D-24: Prices for the corrosion inhibitor from various sources for use in the sensitivity analysis.

	Inhibitor Prices	**R/ton**
	Daya (2017)	3784
	Sigma-Aldrich (2016)	8222
	Zauba Technologies & Data (2016)	6044
SD		2219
% deviation		36.9

Table D-25: Prices of amine reclaiming from various sources for use in the sensitivity analysis.

	Reclaim Prices	**R/ton**
	Daya (2017)	10078
	Sexton *et al.* (2013)	12356
	Merikoski (2012)	11217
SD		1139
% deviation		10.2

Table D-26: Amine disposal prices from various sources for use in the sensitivity analysis.

	Disposal Prices	**R/ton**
	Daya (2017)	3009
	Merikoski (2012)	4942
	Fisher *et al.* (2005)	2965
SD		1129
% deviation		31.0

For the tax on CO_2, a 10% error margin was applied as suggested by The World Bank (2014).

The main results of the sensitivity analysis is presented in figure 4-5 and table 4-14 in Chapter 4.