



# **DEVELOPMENT OF A PERFORMANCE INDICATOR MODEL FOR CARBON CAPTURE APPLICATIONS**

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## Abstract

A performance indicator model has been developed, based on absorption studies with amines as a CO<sub>2</sub> capture technique. The main purpose behind establishing a performance indicator was to create a scheme for the performance rating of aqueous amine solvents and their blends in a given process, where their performance could be ranked and compared to determine the most efficient solvent for the specific process. The amine solvents used in the development of the model were monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP). Three post-combustion capture application case studies were chosen and simulated using Aspen Plus® in order to develop the model under diverse process operating parameters. A natural gas combined cycle (NGCC) power plant, pulverised coal (PC) power plant and cement plant were selected as the case studies, which had flue gas CO<sub>2</sub> concentrations of 4%, 13% and 33% by volume, respectively.

The performance indicator model is novel in terms of the number and type of factors taken into account in the measurement of the performance indicator, where each solvent is judged based on the associated cost of CO<sub>2</sub> captured. Adjustable weighting factors attached to each parameter were included in the model to improve the accuracy of the ratings attained from the model. The influence of energy requirements, make-up water/amine requirements, amine degradation, corrosion inhibitors, amine reclamation, amine disposal and carbon taxes were included in the model.

It was determined that two critical characteristics exist for any given solvent: the regeneration energy and the solvent recirculation rate. In order for an amine or blend to achieve a high performance rating, it has to balance the costs associated with these two counteracting effects. In the NGCC power plant, the benchmark solution of 30 wt. % MEA and 70 wt. % water attained the highest performance rating due to its higher reaction rate, which was of benefit in a system with a very low CO<sub>2</sub> concentration. In the PC power plant, blends of MEA/AMP achieved better rating values: the combined blend of a solvent with a lower regeneration energy of 30 wt. % MEA with one with a lower solvent recirculation rate of 30 wt. % AMP. In the cement plant, 30 wt. % AMP obtained the highest rating. Here, the high CO<sub>2</sub> concentration increased the reaction rate with CO<sub>2</sub> and hence reduced the solvent recirculation rate, such that the solvent could fully benefit from its lower regeneration energy.

Since the performance indicator was developed on the basis of the cost benefit of CO<sub>2</sub> avoided, it leaves the model susceptible to fluctuations in prices. A sensitivity analysis was therefore undertaken. By combining the uncertainties in commodity prices and data from literature, an uncertainty of 2.5% for the model was determined.

The weighting factors for all case studies were regressed against a multi criterial analysis study from a PC power plant, since they do not exist in literature for NGCC and cement plants. The error between the results achieved in this study and that of literature improved by 87.3% upon introduction of the weighting factors in the PC power plant case study. However, the improvements in error for the NGCC and cement plant were only 26.1% and 0.2% respectively.

Future work around the performance indicator model could include introducing the effect of capital cost and increasing the number of amines considered. The Aspen Plus® simulation could be automated, which not only assists in introducing the factors mentioned above, but also allows for more distinct blend compositions to be investigated and optimised.

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# Nomenclature

## Abbreviations

AMP	2-Amino-2-methyl-propanol
CCS	Carbon capture and storage
DEA	Diethanolamine
DIPA	Diisopropylamine
DGA	Diglycol amine
DRI	Direct reduced iron
EAF	Electric arc furnace
EDA	Ethylene diamine
EOS	Equation of state
E-NRTL	Electrolyte Non-Random Two Liquid
ESA	Electric swing adsorption
FCC	Fluid catalytic cracker
GtC	Gigatons of carbon
HETP	Height equivalent of a theoretical plate
IGCC	Integrated gasification combined cycle
ISM	Integrated steel mill
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
NGCC	Natural gas combined cycle
NRTL	Non-Random Two Liquid
PC	Pulverised coal
PPM	Parts per million

PR	Peng Robinson
PSA	Pressure swing adsorption
PZ	Piperazine
RK	Redlich Kwong
RTIL	Room temperature ionic liquid
SRK	Soave Redlich Kwong
TSA	Temperature swing adsorption
VPSA	Vacuum pressure swing adsorption

## Chemical compounds

CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
H <sub>2</sub> S	Hydrogen sulphide
NO	Nitrogen monoxide
NO <sub>2</sub>	Nitrogen dioxide
NO <sub>x</sub>	Nitrogen oxide derivatives
O <sub>2</sub>	Oxygen
SO <sub>2</sub>	Sulphur dioxide
SO <sub>x</sub>	Sulphur oxide derivatives

## English Letters

$a_0$	Closest approach parameter	m
$A_\phi$	Debye-Huckel parameter	
B	Blow down losses	Tons/hr
C	Cooling tower water flow rate	Tons/hr
C	Cost	ZAR, \$, €
$C_p$	Heat capacity	J/kg.K
$D_s$	Dielectric constant of mixed solvent	
$D_w$	Dielectric constant of water	
e	Charge of an electron	Coulombs
E	Evaporation losses	Tons/hr
$E_a$	Activation energy	J/kmol
$g^E$	Molar excess gibbs free energy	kJ
$g^{E,Born}$	Born molar excess gibbs free energy	kJ
$g^{E,LR}$	Long range molar excess gibbs free energy	kJ
$g^{E,PDH}$	Pitzer-Debye-Huckel excess gibbs free energy	kJ
$g^{E,SR}$	Short range molar excess gibbs free energy	kJ
$g_{ij}$	Gibbs interaction energy parameter	
$H_v$	Heat of vapourisation	kJ/kg
$I_x$	Ionic strength	mol/kg
k	Rate constant	
$k_B$	Boltzmann constant	J/K
$k_{ij}$	Binary interaction parameter	
M	Make up water flow rate	Tons/hr

$\dot{m}_{cw}$	Mass flow rate of cooling water	Tons/h
$\dot{m}_s$	Mass flow rate of steam	Tons/hr
$M_s$	Solvent molecular weight	g/mol
$N_o$	Avogadro's number	
$P$	Pressure	bar
$P$	Purge losses	Tons/hr
$\dot{Q}_{cool}$	Cooling duty	J, kJ, MJ
$\dot{Q}_{heat}$	Heating duty	J, kJ, MJ
$r$	Reaction rate	mol/dm <sup>3</sup> .s
$R$	Performance rating	
$R$	Universal gas constant	J/mol.K
$r_k$	Born radius	m
$T$	Temperature	K
$V_m$	Molar volume	m <sup>3</sup> /mol
$w$	Weighting factor	
$x$	Mass fraction	
$z$	Charge	Coulomb

## Greek Letters

$\alpha$	Attractive parameter	
$\beta$	Boltzmann factor	J/K
$\Delta$	Change in	
$\varepsilon$	Efficiency	
$\lambda_{ij}$	Binary adjustable energy interaction parameter	

$\rho$	Density	$\text{kg/m}^3$
$\tau_{ij}$	Non-random factor	
$\omega$	Acentric factor	

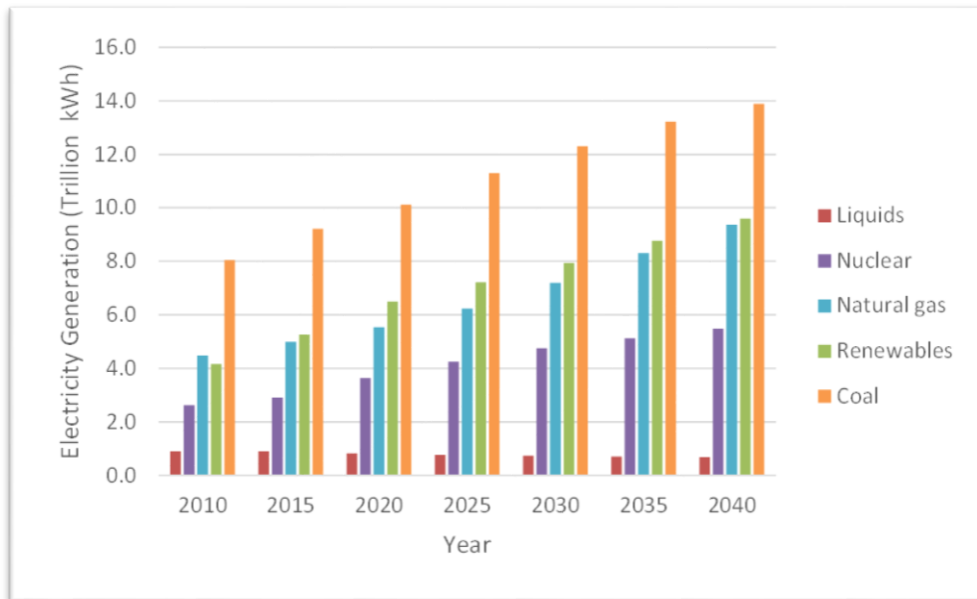
# Chapter 1

## Introduction

In today's highly industrialised economy the emission of CO<sub>2</sub> is inevitable, and alone is responsible for approximately 64% of the enhanced greenhouse effect (Mondal, et al., 2012). At present, the global atmospheric concentration of CO<sub>2</sub> is at 402 ppm and is increasing at a rate of 2.1 ppm per year, which is three times faster than the rate of increase in the late 1950's and more than one hundred times faster than the rate of increase that occurred at the end of the last ice age (Griffin, 2013). Climatologists had originally stated that CO<sub>2</sub> levels would need to be brought back down below 350 ppm in order to preserve a world similar to that which existed when civilisation developed and to which life on Earth is adapted. However, with this goal looking unlikely in the near future, new targets suggest that CO<sub>2</sub> levels will need to be maintained below 450 ppm in order to limit the global warming temperature increase to below 2°C (relative to pre-industrial global temperature) and avoid irreversible environmental damage (Hansen, et al., 2008).

The energy sector is the main contributors of CO<sub>2</sub> emissions, where 86% of the world's energy use still relies on fossil fuels (Mudhasakul, et al., 2013). Figure 1-1 shows the predicted utilisation of the different fuel types for world electricity generation. The amount of fossil fuels used as an energy source is expected to increase as the global energy demand increases due to the rapid population growth rate in large countries such as India, China and Brazil, as well as a result of people emerging from poverty and demanding the same commodities that exist in first world countries (Zero Emission Resource Organization, 2014). This attraction to the continued use of fossil fuels in the future is due to their inherent advantages as an energy source: advantages such as availability, ease of transport and affordability (Gupta, et al., 2003).





**Figure 1-1: Expected World Electricity Generation by Fuel Type, 2010-2030. Data adapted from (U.S. Energy Information Administration, 2013).**

Although renewable energy alternatives such as solar, nuclear, and biomass are available, their current state of development, risk level and cost do not allow for them to meet the world's energy demand. Furthermore, a rapid change to alternative energy sources would create large disruptions to the energy supply infrastructure with adverse consequences to the global economy.

Whilst the energy sector is the main contributor of CO<sub>2</sub> emissions, it is not the only target for the implementation of carbon capture and storage (CCS) technologies, since there are other industries where CO<sub>2</sub> emissions could be reduced by improving the processes, but never completely eliminated.

An example of another industrial sector where CO<sub>2</sub> is released is the cement industry. In the production process, limestone is heated to release some of its carbon, which is liberated in the form of CO<sub>2</sub>. At present, no suitable alternative to this process exists. Thus, to eliminate CO<sub>2</sub> emissions, the CO<sub>2</sub> has to either be captured or cement production has to stop, the latter being an impractical alternative. This is also the case in the production of steel, petroleum and chemicals such as methanol and ammonia. The method called carbon capture and storage (CCS) is widely viewed as a viable, current option for reducing CO<sub>2</sub> emissions from these industries (Zero Emission Resource Organization, 2014).

With the consequences of greenhouse gas emissions becoming more threatening, there is an increasing urgency to implement greenhouse gas mitigation technology. CCS is a technology that is currently available, and although it will not eliminate all CO<sub>2</sub> emissions, it has the potential to significantly reduce CO<sub>2</sub> emissions that would have otherwise been released into the atmosphere. For this reason, techniques of implementing CO<sub>2</sub> capture methods will be an important topic well into the 21<sup>st</sup> century in order to allow for the utilisation of fossil fuels to meet the world's growing energy demands, as well as continue other industrial processes without further increasing the concentration of CO<sub>2</sub> in the atmosphere (Berge, et al., 2011).

Presently, there is no one technology that is a clear-cut option to be deployed as a CO<sub>2</sub> capture technology. Although various processes are envisaged to be employed as a CO<sub>2</sub> separation technique, not all are at adequate stages of development or equal in terms of feasibility. For example, cryogenic separation is deemed to be too expensive to implement due to the high energy requirement and suitable membranes have not yet been developed for large scale industrial applications (Kanniche & Bouallou, 2007).

The present scale of global investment in fossil fuel related infrastructure points to post combustion capture as the most practical method, with chemical and physical absorption as the most likely techniques to do this (Anderson & Newell, 2003). However, whilst CO<sub>2</sub> capture by chemical absorption is favoured, the debate on the choice of the best solvent is still open.

Capture by amine scrubbing is probably the technology closest to commercial deployment. The benchmark solvent is aqueous MEA, as a result of its extensive use in gas sweetening processes in the last few decades (Yu, et al., 2012). However, whilst MEA has found favour on the grounds of its fast reaction kinetics and low price, it does suffer the drawback of requiring a high regeneration energy, in the form of low-pressure steam in the reboiler of the stripper, which is a barrier to its wide-scale use.

However, MEA is not the only option available. A wide range of amine solvents exist and more are being researched and developed, with the aim of creating energy efficient solvents. More specifically, the target has been to minimise the energy requirement in the reboiler, hence reducing steam consumption, which is the primary expense associated with amine-based carbon capture (Mofarahi, et al., 2008). Although many studies have investigated optimising solvents and their blends to reduce the energy requirement in the reboiler, few have investigated combining multiple factors associated with the capture process when determining the best

solvent for the process. Although reduction of energy requirement in the reboiler is critical, it is not the only relevant factor when selecting a solvent for consideration in a capture process.

As there are a number of factors that need to be taken into account in selecting a solvent for carbon capture, this study sets out to develop a performance indicator model for post-combustion carbon capture applications. The performance indicator will function as a rating scheme for solvents in a given process, where their performance can be ranked and compared with one another to determine the most efficient solvent for that specific process. A chemical absorption process, using some of the more prominent amines associated with carbon capture, was selected as the case study for the performance indicator development.

The objectives are as follows:

- Identify three possible industrial case studies that can be utilised for the development of the performance indicator and justify their selection.
- Identify relevant factors for assessing the performance of a solvent and justify their inclusion into, or rejection from, the indicator model.
- Develop an Aspen Plus® flow sheet for the modelling of the selected case studies from which the required results for the chosen indicator parameters can be extracted.
- Combine selected performance indicator factors into a single correlation and incorporate adjustable weighting factors to account for different levels of importance of selected indicator factors.

The correlation to rate the solvents will use the cost associated with each of the factors as the primary assessment method. The reason for this decision is two-fold: firstly, a monetary value can be placed on practically every consideration that is made when implementing the use of a solvent and; secondly, a major consideration with CCS is the economic viability of the various processes. As a result, a rating scheme based on a monetary background is considered to be an appropriate evaluation method.

Although the term ‘performance indicator’ has been used in literature to describe specific factors that are important when assessing the efficiency of a solvent in a carbon capture process, the concept of combining multiple factors to create a performance indicator rating scheme is novel. Whilst studies have investigated which solvents and blends have the lowest energy requirements or lowest capital investment, none have combined multiple factors to determine the best solvent for the entire capture process to the same extent as has this study.

Although every solvent has a combination of advantages and disadvantages, and determining the individual benefits of a solvent is important, when determining the most efficient solvent it is of more practical value to rank its performance based on the entire carbon capture process when determining the most efficient solvent for a system.

As a result of the expensive and time consuming nature of experimental work, simulations are a powerful, alternate means to rapidly assess various process flow sheets and solvents in a carbon capture process. Simulations can also be used to obtain a comprehensive analysis on the effects of operating parameters on target parameters in the process.

The motivation for developing the rating scheme was to create a simple correlation that could be used to evaluate the performance of a solvent in comparison with a benchmark solvent in order to provide guidance when choosing a new solvent for implementation in a CO<sub>2</sub> capture process.

## Chapter 2

### Background on Carbon Capture and Storage

#### 2.1 Overview of CO<sub>2</sub> capture systems

Carbon capture and storage (CCS) is a process involving the separation of CO<sub>2</sub> from industrial and energy related sources followed by transportation to a suitable storage site, where long term isolation from the atmosphere is achieved. It is a vital technology in attempting to keep the atmospheric CO<sub>2</sub> concentrations below 450 ppm and preventing the global temperature from rising by more than 2°C (Leonard, 2013). Although CCS is only a short term solution in the energy sector for the capture of CO<sub>2</sub>, due to the high energy costs associated with its implementation and the limited availability of fossil fuels, it allows for a smoother transition from the current carbon based society to one based on renewable energy sources.

With regards to capture, the main focus for implementation are large point source emitters, particularly fossil fuel fired power stations, in addition to oil, gas, cement and steel industries (Padurean, 2012). There are hundreds of millions of CO<sub>2</sub> emissions sources in the world. However, most of them are quite small and capture from these sources would be impractical, such as capture from a gas heater used in a household. On the other hand, the 2000 largest CO<sub>2</sub> point source emitters in the world constitute 40 percent of the global CO<sub>2</sub> emissions. This illustrates the potential of CCS in significantly reducing CO<sub>2</sub> emissions, since a relatively small number of CCS installations would be required to cut global CO<sub>2</sub> emissions by a large percentage. An example is the Sasol Secunda fuel plant in South Africa, which is the world's largest point source emitter, releasing over 57 million tons of CO<sub>2</sub> a year, which is more than the entire CO<sub>2</sub> emissions count of Norway (Zero Emission Resource Organization, 2014).

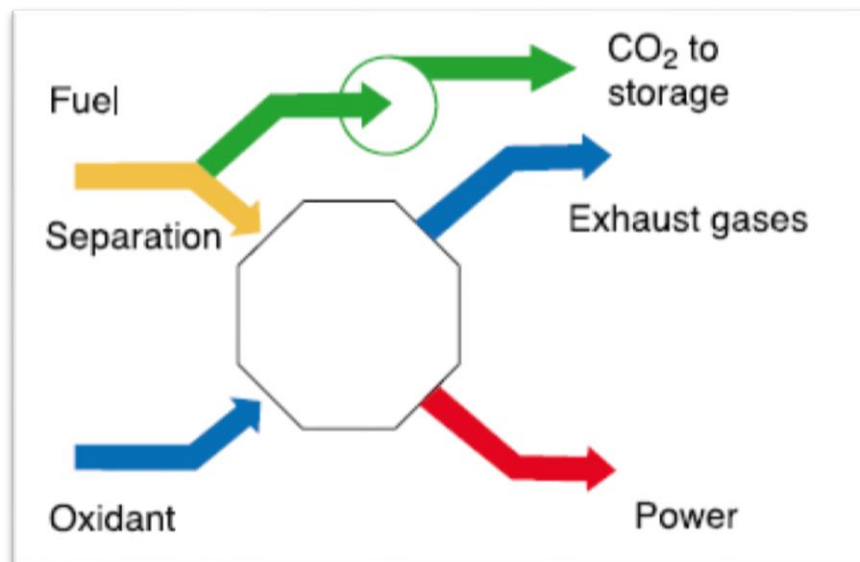
There are three types of carbon capture methods, which are categorised as follows (Kothandaraman, 2010):

- Pre-combustion capture
- Post-combustion capture
- Oxyfuel combustion

In this study, the performance indicator model for carbon capture applications will be based on post-combustion capture with chemical solvents. However, a brief background will be given below on all three capture methods to justify the relevance of developing a post-combustion capture CCS indicator model with amine solvents.

### 2.1.1 Pre-combustion capture

In pre-combustion capture, CO<sub>2</sub> emissions are reduced by preventing the production of carbon dioxide during combustion. By using a gasification or a steam reforming process, the fuel is converted into H<sub>2</sub> and CO<sub>2</sub> (Leonard, 2013).



**Figure 2-1: Schematic of pre-combustion capture. Extracted from (Metz, et al., 2005)**

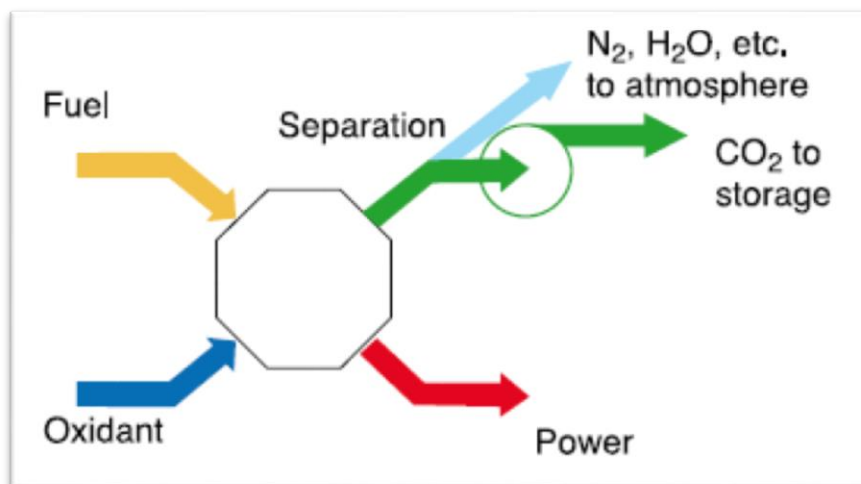
The first step of the process in pre-combustion decarbonisation is the conversion of the fuel into a synthesis gas. If the fuel is coal, this is achieved by a gasification process and if the fuel is natural gas, a steam reforming process is used. A water gas shift reaction then converts the synthesis gas into carbon dioxide and hydrogen. The resulting stream is at a high pressure and has a high CO<sub>2</sub> concentration. These conditions favour CO<sub>2</sub> capture for two reasons: firstly the high pressure results in a lower volume of gas to be treated, resulting in smaller equipment requirements and secondly, the high CO<sub>2</sub> partial pressure allows for the use of solvents that form weaker bonds with CO<sub>2</sub>, thus lowering the regeneration energy requirements (Can, 2002).

Typically, the  $\text{CO}_2$  and  $\text{H}_2$  would be separated by pressure swing absorption or physical absorption and the pure  $\text{CO}_2$  would thereafter be sent for compression and storage. The hydrogen produced can be valorised as a chemical or burned to produce electricity (Leonard, 2013).

Although pre-combustion capture is proven and shows promise for lower emissions and reduced water consumption, there is reluctance from the energy production sectors to utilise pre-combustion capture, since it cannot simply be retrofitted into existing technologies and would therefore involve replacing current systems. For this reason, pre-combustion capture is deemed to be a technology that could be utilised in the next generation of industrial expansion, but not with current processes (Graus, et al., 2008).

### 2.1.2 Post-combustion capture

Post-combustion capture is a downstream process that involves the capture of  $\text{CO}_2$  after the combustion of the fuel utilised in the plant. The flue gas  $\text{CO}_2$  concentration typically varies between 3-15%, depending on the type of fuel used, but can be as high as 33%, as is the case in a cement plant (Leonard, 2013) (Zero Emmissions Platform, 2013).



**Figure 2-2: Schematic of post-combustion capture. Extracted from (Metz, et al., 2005)**

The oxidant used is normally air, thus the flue gas is considerably diluted with nitrogen. One of the main disadvantages is that the flue gas is generally at or slightly above atmospheric

pressure, and so a large volume of gas needs to be treated, which results in large equipment requirements (Kothandaraman, 2010). The atmospheric pressure also means that significant compression is required before transport, which results in additional equipment and operating expenses (Leonard, 2013). The flue gas is discharged to the atmosphere once the CO<sub>2</sub> has been separated.

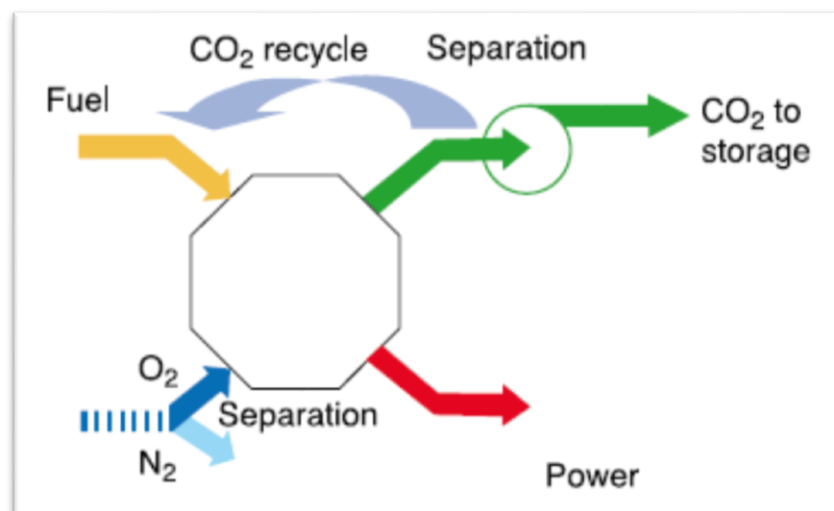
Post-combustion capture is the preferred means for capturing CO<sub>2</sub> in the commercial deployment of CCS technologies. Post-combustion technology is appropriate for both retrofit to existing installations, as well as for new developments. It can also be used as a retrofit for process related CO<sub>2</sub> emissions in industries such as the cement and steel industries. There is also substantial knowledge and experience available on scrubbing processes using amine-based solvents (Graus, et al., 2008).

Although chemical absorption is currently favoured for post-combustion CCS applications, other techniques such as physical absorption, adsorption, membrane separation and cryogenic separation are under research (Leonard, 2013). These do not form part of this study however.

### 2.1.3 Oxyfuel combustion capture

In oxyfuel combustion, pure oxygen is used as the oxidant rather than air, which eliminates the issue of nitrogen diluting the flue gas, as is the case in post-combustion capture. Dilution of the flue gas is problematic, since it is more difficult to capture CO<sub>2</sub> from a stream that has a low CO<sub>2</sub> concentration. However, the burning of fuel in oxygen can lead to temperatures as high as 3500°C. Temperature regulation is required to ensure the materials of construction can handle this high temperature. Recycling a portion of the exhaust gases is the method typically applied for temperature regulation (Kothandaraman, 2010).





**Figure 2-3: Schematic of oxyfuel combustion capture. Extracted from (Metz, et al., 2005)**

The primary flue gas components that result from oxyfuel combustion are CO<sub>2</sub> and H<sub>2</sub>O, but it may also contain oxidised forms of sulphur and nitrogen (SO<sub>x</sub> and NO<sub>x</sub>) depending on the type of fuel employed. The benefit of not having nitrogen in the oxidant is the reduced formation of NO<sub>x</sub>. However, if the fuel has large amounts of nitrogen bound within it, it may be necessary to remove the NO<sub>x</sub> prior to recycling, since it will be at a high concentration due to the absence of dilution by means of nitrogen (Kothandaraman, 2010).

After combustion, the flue gas is condensed to remove water and depending on the fuel type and content, will then contain 80-98% CO<sub>2</sub> (Kothandaraman, 2010). An additional benefit of this method is the potential to store SO<sub>x</sub> compounds with the CO<sub>2</sub>, thus eliminating the need for a desulphurisation unit. However, for this to be a viable option, complete dehydration of the flue gas needs to be attained in order to prevent corrosion and hydrate precipitation.

The main disadvantage of oxyfuel combustion is the high energy penalty that arises from the separation of oxygen from air. At present, the energy intensive process of cryogenic separation is employed to obtain an oxygen stream with a purity of 95% (Leonard, 2013). However, the additional cost associated with the air separation unit is counter balanced by the elimination of the need for an energy intensive CO<sub>2</sub> capture technique, as well as an increased boiler thermal efficiency due to the reduction in volume of inert N<sub>2</sub> gas.

Unfortunately, the use of oxyfuel combustion is restricted to use in new installations, since substantial redesign of the power generation turbines is required. Thus, retrofitting to existing plants is considered to be an economically unattractive option (D'Allesandro, et al., 2010). One of the key areas of research in oxyfuel combustion is determining ways in which to reduce the operating cost of the air separation unit, which would make this process more economically competitive.

A variant of oxyfuel combustion is chemical looping, where catalysed combustion with oxygen is performed. Although fuel combustion still utilises oxygen rather than air, it is not strictly an oxyfuel process since no air separation unit is required. Figure 2-4 depicts the process of chemical looping combustion. In the air reactor a metal is oxidised at temperatures between 700-900°C, depending on the type of metal used. The oxidised metal is then sent to the fuel reactor where it reacts with the carbon-based fuel at approximately 900 °C. Similar to conventional oxyfuel combustion, the main flue gas components are CO<sub>2</sub> and H<sub>2</sub>O, thus separation is still achieved by water condensation. The reaction in the air reactor is exothermic, with part of the heat being used for electricity generation and the remainder being recycled to the fuel reactor to act as the heat source for endothermic reaction in the fuel reactor (Leonard, 2013).

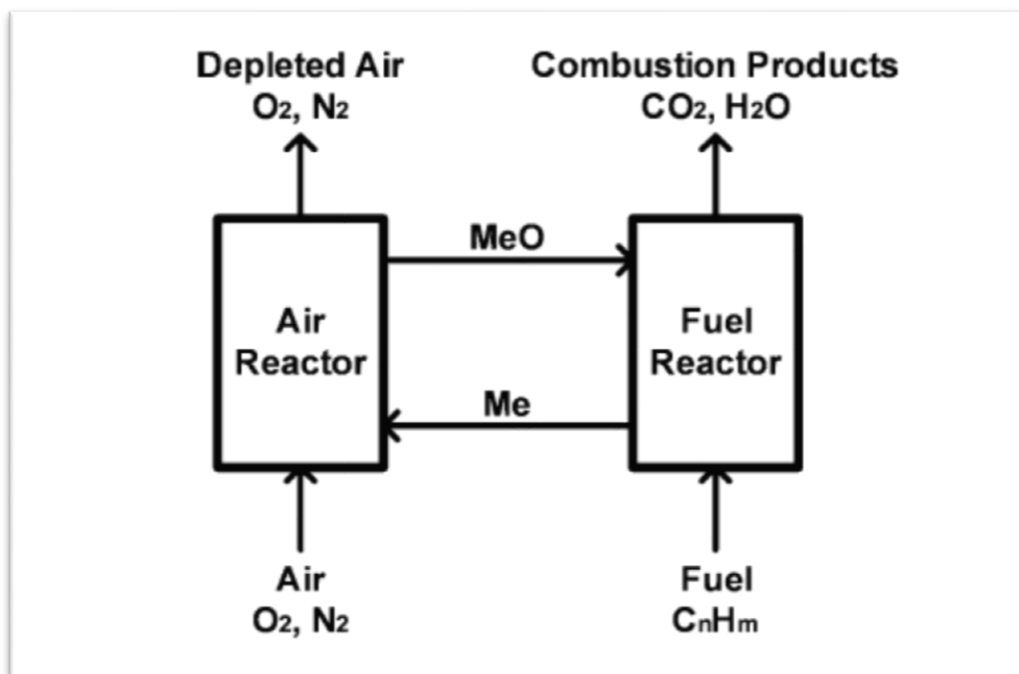


Figure 2-4: Schematic of chemical looping combustion (Kothandaraman, 2010)

In both cases of conventional oxyfuel combustion and chemical looping combustion, more research and development is required before commercial deployment is possible. Advancements in the technology are still required, since there is little commercial experience in fuel combustion in an environment rich in O<sub>2</sub>, CO<sub>2</sub> and steam (Graus, et al., 2008). In addition, as these processes are located within production process, neither process is of direct interest to this study, which is exclusively focused on post-combustion CCS.

## 2.2 Carbon dioxide storage and utilisation

The means of extraction of CO<sub>2</sub> is, however, only half the story. The CO<sub>2</sub> would then need to be prevented from entering the atmosphere. Although the original intention was to capture CO<sub>2</sub> for storage underground so that its effect as a greenhouse gas could be prevented, the utilisation of the CO<sub>2</sub> instead appears to be a more economically feasible alternative, since this will aid in offsetting the costs associated with carbon capture. However, in the near term, in the case of large-scale implementation of CCS, the vast amounts of CO<sub>2</sub> generated would exceed its demand and hence the majority of it would require storage (Leonard, 2013).

Storage is accomplished by the injection of CO<sub>2</sub> into underground geological formations, where over thousands of years the CO<sub>2</sub> dissolves and mineralises into carbonate. The geological structures have to satisfy three main characteristics in order to be suitable candidates for CO<sub>2</sub> storage, namely (Leonard, 2013):

1. The rocks capacity has to be sufficient. This factor is related not only to size but also to rock porosity.
2. The rock permeability has to allow for CO<sub>2</sub> injection.
3. The rock formation has to maintain containment of the injected CO<sub>2</sub>

Another consideration for storage is the temperature and pressure conditions of the storage location. The site would generally be chosen so that the CO<sub>2</sub> would exist in a supercritical or liquid form, which would reduce the spatial volume required to store a given mass of CO<sub>2</sub>. To achieve CO<sub>2</sub> storage in these preferred states, a depth of at least 800 metres would be required. The precise depth requirement would depend on factors such as the pressure profile of the rock formation and the surrounding temperature gradient (EASAC, 2013).

One of the foremost drawbacks to CCS is the expense of the technology. As a result, valorising CO<sub>2</sub> would be a more viable option to storage (Leonard, 2013). Approximately 80% of CO<sub>2</sub> currently captured for the purpose of utilisation is used for enhanced oil recovery, whilst the remainder is predominantly used in the chemical and food processing sectors (Anderson & Newell, 2003).

Some of the alternatives shown in Figure 2-5 do release CO<sub>2</sub> into the environment during their application, but they still contribute to the overall decrease of CO<sub>2</sub> emissions, since they continually immobilise new amounts of CO<sub>2</sub>. Due to the great variety of CO<sub>2</sub> reuse options, its utilisation, instead of storing it, offers a promising alternative and could lead to the development of new economic activities (Leonard, 2013).

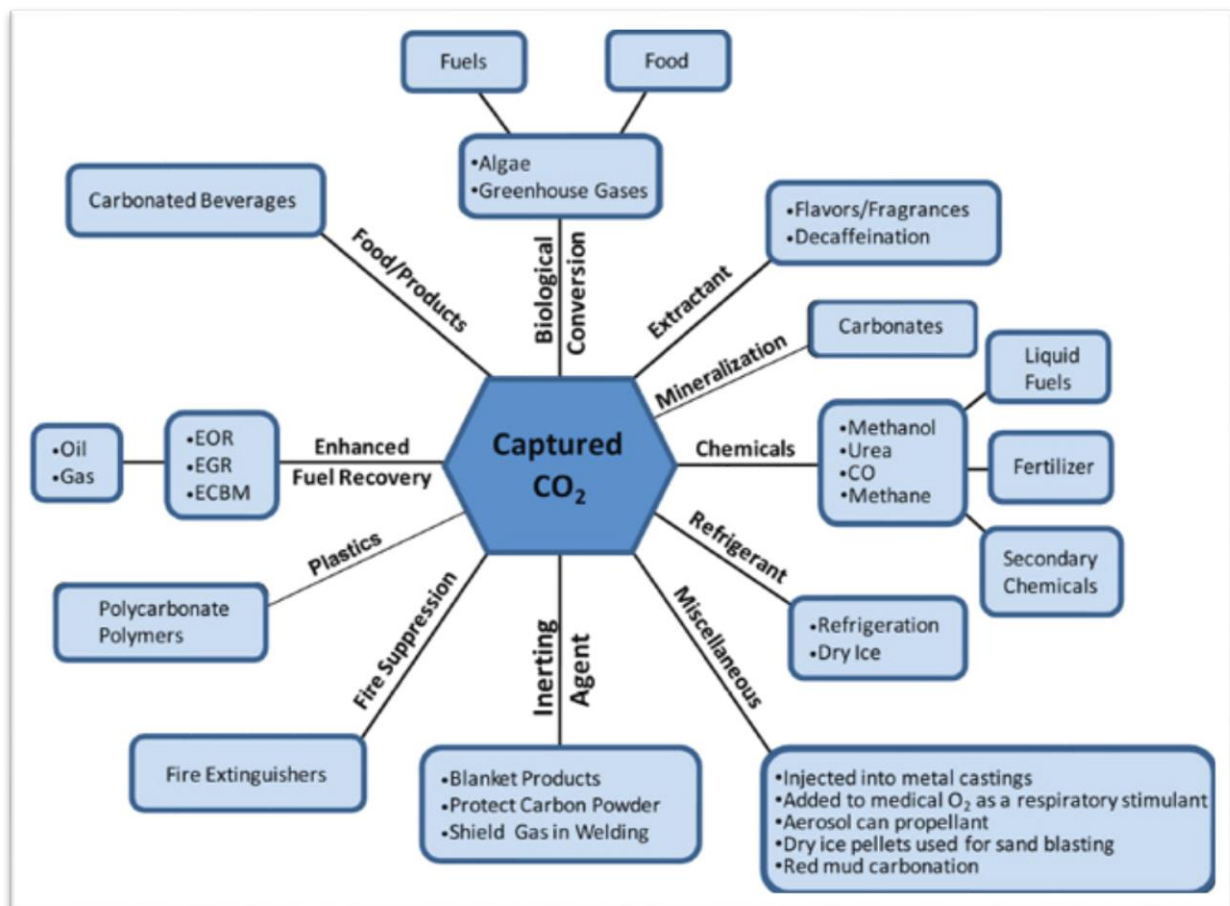


Figure 2-5: Potential alternative uses for captured CO<sub>2</sub> (NETL, 2014)

## 2.3 Carbon Dioxide Capture Techniques

Now that we have gained an overview on the types and purpose of CCS, the following section goes into more detail to describe some of the more conventional CO<sub>2</sub> capture techniques that have been used in industries in the past for gas sweetening (process for removal of CO<sub>2</sub> and H<sub>2</sub>S from gas streams) or quality control purposes. Traditional methods of absorption with chemical or physical solvents will be covered. However, some of the newer technologies, such as ionic liquids and gas hydrate are also explored. These techniques show potential to improve the energy efficiency of the carbon capture process. Although this study focuses on chemical absorption using amine based aqueous solvents, this background is required here in order to justify the exclusion of other capture techniques as they are not suited for post-combustion capture applications at present.

### 2.3.1 Chemical solvents

The performance indicator model was developed based on solvents and blends used in chemical absorption, since it is currently the most common technique for the post-combustion capture of CO<sub>2</sub>. It is the preferred method when the CO<sub>2</sub> partial pressure is low, a factor that is independent of the operating pressure. A chemical reaction between a chemical solvent and CO<sub>2</sub> occurs at low to moderate temperatures in an absorption unit; hence this method is also known as reactive absorption. The CO<sub>2</sub> is released by reversing the reaction in a stripper, which operates at an elevated temperature and pressure, approximately 120°C and 200 kPa respectively. The main drawback of chemical absorption is the high-energy requirement for solvent regeneration, which is in the form of steam usage in the stripper reboiler (Leonard, 2013).

When choosing a solvent, many of its properties need to be evaluated such as its reaction rate and loading capacity. A low absorption enthalpy is also critical if regeneration energy is to be minimised. Its vapour pressure should be low to limit evaporation losses and it needs to degrade into harmless products in case of leakage into the environment. It should not be toxic or corrosive and degradation during the capture process should be minimal. It also needs to be

cheap and commercially available in order for it to be an economically viable option (Leonard, 2013).

Aqueous amine solvents are at present the most popular choice. They can be primary, secondary or tertiary amines and are often alkanolamines (amines containing a hydroxyl group). Some of the more common amines used are (Merikoski, 2012):

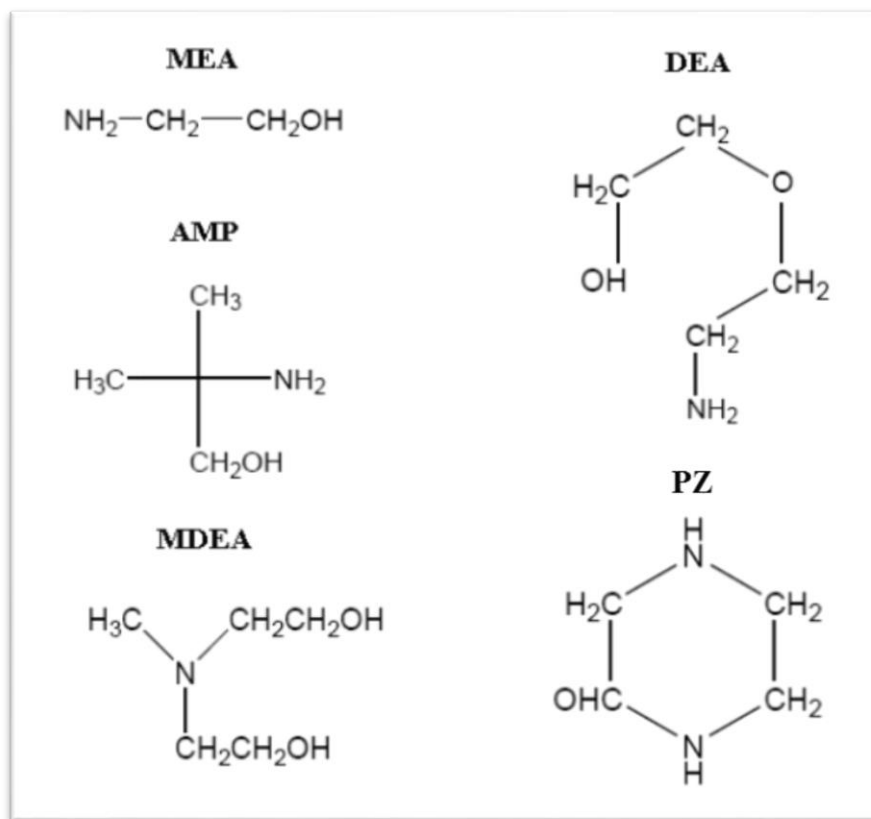
- Monoethanolamine (MEA)
- Diethanolamine (DEA)
- Methyldiethanolamine (MDEA)
- 2-amino-2-methylpropanol (AMP)
- Piperazine (PZ)
- Diglycol amine (DGA)
- Ethylenediamine (EDA)

In the past decade, alternatives to amine solvents have been investigated. Chilled ammonia and potassium carbonate have been the most widely studied. New generations of chemical solvents, such as amino acids and ionic liquids, have also been developed. Demixing solvents are a promising option, which take advantage of the phase separation between a CO<sub>2</sub> rich loaded amine and a CO<sub>2</sub> lean loaded amine. By separating the lean amine phase from the rich amine phase, a lower amine flow rate has to be processed in the stripper, which reduces the energy consumption in the reboiler (Leonard, 2013). However, in this study the main focus will be aqueous amine solvents: both single aqueous amine solvents and blends thereof.

Amines are a group of compounds derived from ammonia, where at least one of the hydrogen atoms has been replaced by a hydrocarbon chain, such as an alkyl group. Alkanolamines, which are amines with a hydroxyl group, have been identified as the specific amine group most suitable for post-combustion capture. The amino component is responsible for providing the required alkalinity in the water solution to allow for the absorption of the acidic gases, such as CO<sub>2</sub>, H<sub>2</sub>S and SO<sub>2</sub>. The hydroxyl component increases the molecules solubility in water and reduces its vapour pressure (Kohl & Nielsen, 1997). Amines can be divided into three groups: primary, secondary and tertiary amines, where primary amines are generally the most alkaline.

The alkanolamines monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and piperazine (PZ) are considered the most important amines for post combustion CO<sub>2</sub> capture as they have received the most attention in scientific research. Sterically hindered

amines, most prominently 2-amino-2-methyl-1-propanol (AMP), have also been investigated in the last decade for their potential to absorb CO<sub>2</sub> from flue gases. (Merikoski, 2012). Many studies also investigate the use of these five amines in conjunction with one another to combine and enhance desired properties.



**Figure 2-6: Chemical structure of most prominent amines to be used in carbon capture.**  
Adapted from (Kohl & Nielsen, 1997).

### 2.3.1.1 Monoethanolamine (MEA)

MEA, like most other primary amines, is a strong base and is completely miscible in water. Aqueous MEA solutions have been used for decades as a solvent to remove CO<sub>2</sub> and H<sub>2</sub>S from natural gas as well as specific synthesis gas streams. However, its use as a solvent is being replaced by more efficient systems, especially in the treatment of natural and synthetic gas at high pressure (Kohl & Nielsen, 1997). In high-pressure systems, the use of physical solvents represent the more efficient system.

MEA, despite advancements in other solvents, is still considered as the benchmark solvent for streams with low CO<sub>2</sub> and H<sub>2</sub>S concentrations, because of its favourable properties towards acid gas absorption (Lepaumier, et al., 2009d). Its low molecular weight allows for high solution capacity, even at moderate concentrations, and its high alkalinity results in rapid reaction rates with CO<sub>2</sub>. Its low price makes it particularly attractive as a solvent, since the economic viability of a solvent is just as important as any other favourable characteristics it may possess.

However, one of the drawbacks of MEA is its propensity to degrade over time. The compounds CO<sub>2</sub>, CO, SO<sub>x</sub>, NO<sub>x</sub> and O<sub>2</sub> are generally present in flue gas and they have the effect of enhancing the degradation of MEA. Although degradation is an issue with all amine solvents, MEA is especially vulnerable to oxidative degradation, more so than when compared to secondary and tertiary amines. Degradation increases the make-up solvent rate, as well as reclaimer and waste disposal costs.

When compared to other amines, MEA is far more corrosive, especially when the solvent acid gas loading is high and the amine concentrations surpass 20 wt. % (Kohl & Nielsen, 1997). Degradation products may also worsen the corrosion problem, but corrosion inhibitors can be employed to allow for MEA concentrations as high as 30 wt. %, but only if the solvent is utilised for the absorption of primarily CO<sub>2</sub> and minor amounts of H<sub>2</sub>S (Merikoski, 2012).

The high vapour pressure of MEA results in significant vaporisation losses. However, this issue can be overcome with the use of a wash water section in the absorption column to reduce MEA losses in the purified gas (Kohl & Nielsen, 1997). Another inherent disadvantage of MEA is its high heat of reaction with CO<sub>2</sub> when compared to other amine solvents, which implies a higher energy requirement for regeneration, which is in the form of low-pressure steam in the stripper. The reduction of the energy penalty associated with regeneration will be an important factor to consider in the synthesis and use of alternative amine solvents for CO<sub>2</sub> capture in the future (Chowdhury, et al., 2011).



### 2.3.1.2 Diethanolamine (DEA)

DEA is a secondary amine that is used for the treatment of refinery gases that contain appreciable amounts of COS and CS<sub>2</sub>, which are compounds that would degrade other amines rapidly (Kohl & Nielsen, 1997). However, flue gases do not typically contain these compounds. Thus, this benefit is not of much relevance in post-combustion CO<sub>2</sub> capture. The low vapour pressure of DEA results in much lower losses due to vaporisation and its heat of reaction is approximately 30% less than MEA, thus lowering the energy penalty associated with regeneration. The acid gas reaction products are also less corrosive than the products formed during absorption with MEA (Kohl & Nielsen, 1997).

The disadvantage of DEA is the degradation it undergoes in the presence of CO<sub>2</sub>, since it produces several corrosive degradation compounds. Another issue is that amine reclaim may require vacuum distillation to separate DEA and its degradation by-products. Although DEA on its own may not be a suitable candidate for treating gases with a high CO<sub>2</sub> content, it still has potential to be used as one of the solvents in a blend (Merikoski, 2012).

### 2.3.1.3 Methyldiethanolamine (MDEA)

MDEA is a tertiary amine that was originally used for selectively removing H<sub>2</sub>S in streams containing high concentrations of CO<sub>2</sub>. MDEA possesses a near instantaneous mass transfer rate with H<sub>2</sub>S, which results in a fast reaction rate whilst its mass transfer rate with CO<sub>2</sub> is slow and limited. This difference in mass transfer rates creates the selectivity towards H<sub>2</sub>S absorption (Pacheco & Rochelle, 1998). Although this feature is not of any particular benefit in CO<sub>2</sub> capture, MDEA still has the potential to be applied in CCS applications due to other advantageous features it possesses as a solvent.

MDEA is highly resistant to oxidative and thermal degradation when compared to other amines and has a very low vapour pressure, both of which contribute to low make-up solvent requirements as a result of lower degradation and vaporisation losses respectively. Both MDEA and its reaction products are practically non-corrosive compounds and thus MDEA can be used at concentration levels as high as 60 wt. %. It also has a low heat of reaction with CO<sub>2</sub> and H<sub>2</sub>S

and a low specific heat, which aids in reducing the regeneration energy penalty (Kohl & Nielsen, 1997).

The major disadvantage with MDEA is its slow CO<sub>2</sub> absorption rate. Thus, in order for it to be used in large scale CO<sub>2</sub> capture processes, its reaction rate needs to be enhanced so as to remain as a viable solvent. This is accomplished by blending other amines, such as MEA and PZ, into the aqueous solvent mixture, which has been found to increase the absorption rate without sacrificing the advantages that MDEA offers (Kohl & Nielsen, 1997).

#### 2.3.1.4-Amino-2-methyl-propanol (AMP)

AMP is a primary amine but differs from regular amines, since it is a sterically hindered amine. In terms of a structural definition, a sterically hindered amine is a primary amine in which the amino group is connected to a tertiary carbon atom or it may be a secondary amine that is connected to a secondary or tertiary carbon (Sartori & Savage, 1983).

Sterically hindered amines are classified as specialty amines and have been formulated in an attempt to overcome some of the shortfalls of primary, secondary and tertiary amines. They are able to achieve higher CO<sub>2</sub> loadings, since they react in a different way when compared to regular amines. Due to the formation of carbamates, which are less stable than the ones formed with regular amines, AMP has a lower heat of reaction with CO<sub>2</sub> and a lower regeneration temperature, which reduces the energy requirement in the stripper. Their CO<sub>2</sub> reaction products are also relatively non-corrosive, or at least less corrosive than MEA associated products (D'Allesandro, et al., 2010).

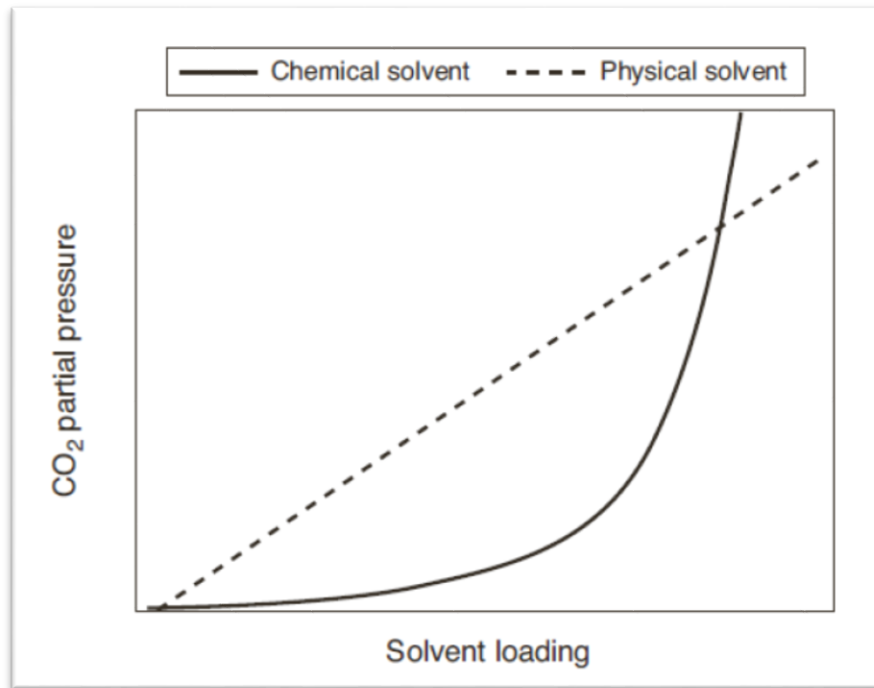
#### 2.3.1.5 Piperazine

PZ differs from the amines discussed previously in two ways. Firstly, it is not an alkanolamine, since it does not contain a hydroxyl group. Secondly, its structure consists of a six-membered ring. This structure, with the nitrogen atoms opposite one another, allows for higher loadings and a more rapid absorption rate. In comparison with MEA, PZ has an absorption rate approximately 15% higher (Ma'mun, et al., 2007).

Although PZ has not been used in the gas treatment industry, it is used as an activator for solvents where absorption rates require improvement, such as MDEA (Kohl & Nielsen, 1997). Unlike other amines where thermal degradation becomes an issue at 125°C, PZ is capable of withstanding 150°C without significant thermal degradation. This higher temperature limit results in reduced energy requirements during regeneration, since the column can be operated at higher pressures which favours the reverse reaction in the stripper. When compared to MEA, it has a higher resistance to oxidative degradation, a lower volatility and its CO<sub>2</sub> reaction products are non-corrosive. It can also be reclaimed by methods already in use in the gas treatment industry, such as distillation (Rochelle, et al., 2011).

### 2.3.2 Physical solvents

In physical absorption, CO<sub>2</sub> dissolves into the solvent rather than reacting with it. Henry's law governs the CO<sub>2</sub> loading capability of the solvent, which is thus proportional to the partial pressure of the CO<sub>2</sub>. This is not the case for chemical solvents, where loading can be high even at low CO<sub>2</sub> partial pressures. This difference between the two solvents can be depicted by Figure 2-7. For this reason, physical absorption is less relevant than chemical absorption when CO<sub>2</sub> partial pressure is low. It becomes the preferred technique when the system pressure is high or even when the CO<sub>2</sub> content is high whilst the system is at moderate pressure (35-40% CO<sub>2</sub> in a stream at 20 bar), since both these conditions create a high CO<sub>2</sub> partial pressure. Absorption occurs at high pressure and low temperature, whilst desorption occurs at low pressure and high temperature (Leonard, 2013).



**Figure 2-7: Comparison between chemical and physical absorption. Extracted from (Bailey & Feron, 2005)**

The following is a list of commercialised physical solvents along with their more recognised process names (Heintz, 2011):

- Methanol – Rectisol
- Polyethylene glycol dialkyl ethers – Selexol
- n-Methyl-2-pyrrolidone – Purisol
- Polypropylene carbonate – Fluor
- Tributyl phosphate – Ectasolvan

### 2.3.3 Blended solvents

Blended solvents are mixtures of like solvents, which are combined together with the intention of optimising the absorption process. Blending of solvents is particularly useful for amine solvents since primary, secondary and tertiary amines each have their pros and cons which can be resolved by mixing them. Primary amines, such as MEA, are known for their high

absorption rates but are very corrosive and thus have to be diluted with significant amounts of water to reduce the threat of corrosion. However, due to the high specific heat capacity of the water, the overall heat capacity of the solvent is increased, which makes the regeneration process more energy intensive. In order to counteract this problem tertiary amines, such as MDEA, are added to the solvent. This replaces a portion of the water component, thus lowering the heat capacity of the solvent. The solvents corrosiveness is also reduced since tertiary amines are less corrosive. Furthermore, the presence of tertiary amines allows for the solvent to absorb other pollutants such as H<sub>2</sub>S and SO<sub>2</sub>. This is just one example of how solvents are blended together to possess the benefits of each of its constituent solvents (Osman, 2010).

#### 2.3.4 Hybrid solvents

Hybrid solvents are mixtures of chemical and physical solvents. It is a method of bringing together the advantages of each of the solvent types whilst masking their disadvantages. An example is the mixture of MEA and methanol. The chemical part of the solvent (MEA) enhances the solubility of CO<sub>2</sub> in the solvent at low CO<sub>2</sub> partial pressures due to its rapid reaction rate with CO<sub>2</sub>. The physical part of the solvent (methanol) reduces the energy requirement during regeneration and maintains the ability to absorb CO<sub>2</sub> at high partial pressure (Sema, et al., 2013). In general, chemical solvents allow for rapid absorption rates and also have the ability to absorb CO<sub>2</sub> at low CO<sub>2</sub> partial pressures whilst physical solvents allow for high loading, low corrosiveness and low energy requirements for regeneration of the solvent (Osman, 2010).

#### 2.3.5 Emerging alternatives

There are a few alternate CO<sub>2</sub> capture technologies available that have shown promising results, when compared to conventional solvent absorption. Most are still in the developmental stages, whilst others are commercially used in other gas separation applications, but need to be adapted for the capture of CO<sub>2</sub> from flue gas.

Membranes are a promising CO<sub>2</sub> capture option, provided that the driving force for the separation is at a high enough level. Gas separation membranes require that the flue gas be fed

to the membrane at high pressure in order to achieve a high purity CO<sub>2</sub> stream. This is not feasible for post-combustion capture, since the flue gas is at atmospheric pressure, and the high cost associated with compression would make the process economically unattractive. Gas absorption membranes are a more favourable option, since they make use of a solvent to create the selectivity and driving force of the separation process. Typically amines would be the solvent of choice for a gas absorption membrane. The reliability and cost concerns associated with membranes are currently the main barriers to their implementation (Hassan, 2005).

Adsorption makes use of solid sorbents to perform a reversible separation of CO<sub>2</sub> from a gas mixture. Certain gases have higher affinities towards specific solid materials and it is these intermolecular forces that drives the separation. The adsorption process operates on a repeating cycle of adsorption followed by regeneration. There are three adsorption methods which are classified based on their regeneration method: pressure swing adsorption (PSA), temperature swing adsorption (TSA) and electric swing adsorption (ESA). PSA is the preferred technique since TSA has higher energy requirements and longer cycle times. ESA has the lowest energy requirement of the three, but it is not yet commercially available (Mondal, et al., 2012).

Ionic liquids are a novel class of compounds, which consist of an organic cation bonded to an inorganic/organic anion. It is possible to combine various compatible cations and anions with each other, thus ionic liquids can be tailor made for specific tasks. By combining various compatible counterparts, the characteristics of the ionic liquid can be tuned and the desired capture properties of the solvent can be enhanced (Mumford, et al., 2015).

Gas hydrates are crystalline structures consisting of water and gas and are formed under specific conditions of high pressure and low temperature. This capture method involves exposing the flue gas stream to water under high pressure, which results in the formation of hydrates whilst concurrently absorbing the CO<sub>2</sub> in the stream. The hydrate can then be separated from the rest of the mixture and through dissociation a stream of pure CO<sub>2</sub> is released (Mondal, et al., 2012).

## Chapter 3

### Potential Industries for Carbon Capture

The performance indicator model developed in this study is in the form of a scheme for the performance rating of amine solvents and their blends in a given post-combustion capture process. In Chapter Two it was highlighted why the particular method of chemical absorption was selected. In this section, the choice of industry for the three case studies are identified. In order to do this, it is important to first identify and explore the features of the main carbon emitting industries.

As was previously mentioned, research towards the application of CCS technologies has focused primarily on the power sector, since this is the primary contributor of global anthropogenic CO<sub>2</sub> emissions. At present, however, there are no large-scale capture instalments in the coal power generation sector (Nykvist, 2013). In addition, other industrial point source emitters also need to be addressed if the required CO<sub>2</sub> emissions abatement is to be realised.

The industrial sector is responsible for approximately 20% of global CO<sub>2</sub> emissions due to the combustion of fossil fuels to provide energy for their production processes (ENGO, 2011). Currently all operational large-scale CCS demonstrations are in the industrial sector and most of the promising CCS instalment options to be deployed in the near future are also in industrial applications (IEA, 2011).

One of the reasons the application of CCS in industries is favourable is that application in the power sector requires a large scale up of a technology to a level not yet commercially accomplished due to the large volumes of flue gas that requires treatment in power plants. This lack of experience leads to uncertainty in both performance and cost of the capture instalment (Razi, et al., 2013). Whilst scale up remains a challenge, the power sector is the main focus for carbon capture since it is the primary contributor of CO<sub>2</sub> emissions. Thus, industrial applications of CCS provide an initial approach that can be used to gain information on operations and expenditure. Furthermore, in multiple industries, CCS is the only option available, apart from improved energy efficiency, to achieve considerable reductions in CO<sub>2</sub>

emissions. Even once there has been a switch to renewable energy sources, certain industries will continue to emit process-related CO<sub>2</sub> unless these emissions are captured.

**Table 3-1: Global CO<sub>2</sub> emissions from large point source emitting more than 0.1 million tonnes of CO<sub>2</sub> per year (MtCO<sub>2</sub>/year) (IPCC, 2005)**

Industry	Number of Sources	Emissions
	Globally	(Mt CO <sub>2</sub> /year)
Power	4 942	10 539
Cement	1 175	932
Refineries	638	798
Iron and Steel	269	646
Petrochemical	470	379
Oil and Gas	Not available	50
Biomass	303	91
Other	90	33
<b>Total</b>	<b>7887</b>	<b>13 446</b>

### 3.1 Power Generation Industry

The generation of electricity from thermal power plants is the largest contributor of global anthropogenic CO<sub>2</sub> emissions. Thus, the fossil fuel energy generation sector has been the main target in research for carbon capture technology. There are three power generation systems that have been the focus for CCS implementation: pulverised coal (PC) plants, integrated gasification combined cycle (IGCC) plants and natural gas combined cycle (NGCC) plants (Kanniche, et al., 2010).

PC power plants are the oldest of the three power generation methods. The process of operation is a simple cycle that involves burning finely ground coal in boilers to heat water and generate high-pressure steam. This steam then passes through turbines, which rotate a generator to produce electricity. The steam is then cooled, condensed, and returned back to the boilers to begin the cycle again. The flue gas generated in the boilers is typically treated to remove SO<sub>2</sub> and NO<sub>x</sub> to meet environmental emission standards. The amount of cleaning required depends on the quality of the coal used as well as environmental regulations (Mirfendereski, 2008).



The low pressure and low concentration of CO<sub>2</sub> in the flue gas streams make post-combustion capture with amine based chemical solvents the preferred method of separation at present. The installation of a CO<sub>2</sub> capture plant is an end of the pipe retrofit option that does not require modifications to existing units or the process in the plant. The drawback of amine based chemical absorption is the high regeneration energy required, which is supplied in the form of low-pressure steam. There is also a high electricity demand from the CO<sub>2</sub> compression section of the plant and flue gas blower.

One of the issues with post-combustion capture is the CO<sub>2</sub> dilution that occurs due to the presence of nitrogen, which results in a larger volume of flue gas that has to be processed. In a coal-fired power plant, flue gas flow rates are so large that a train of three or four absorption and stripper columns in parallel would be required, at unit sizes currently in existence (Kothandaraman, 2010).

Therefore, oxyfuel combustion is a potential candidate for PC power plants. This would result in a flue gas stream of CO<sub>2</sub> and water, where the water vapour could be easily condensed to produce a relatively pure CO<sub>2</sub> stream ready for compression. However, the air separation unit required to produce the oxygen for combustion has a high electricity demand, which would lower the plant's energy efficiency (Mirfendereski, 2008).

In an NGCC facility, compressed air is used as an oxidant in a natural gas combustion vessel, which results in the production of high-pressure flue gas. This flue gas is then expanded through a series of gas turbines, where a generator produces electricity as a result of the mechanical working of the rotating turbines. Although the flue gas pressure is lost through this process, it still maintains a high temperature of around 500°C. This heat can be recovered and used to produce high-pressure steam, which can then be expanded through a series of steam turbines. The combination of gas and steam turbines not only increases the overall power output, but also improves the efficiency of the plant, since a larger percentage of the stored energy in the fuel is converted into useful energy.

Whilst all methods of capture are possible candidates for CO<sub>2</sub> abatement in an NGCC facility, they are not equally viable. Pre-combustion capture would involve methane gas reforming and conversion of CO to CO<sub>2</sub> before capture. However, implementing this as the chosen carbon capture process is believed to be more expensive than the other two methods and thus would probably only be economical in particular cases (Kanniche, et al., 2010).

Oxyfuel combustion is still in the early stages of development and thus is not considered to be a short-term solution. Post-combustion capture is therefore the best solution for CO<sub>2</sub> abatement in NGCC facilities at present, with absorption using amine-based solvents being the favoured technique due to the low partial pressure of CO<sub>2</sub> in the flue gas stream and the level of commercial development of the technology (Mirfendereski, 2008).

IGCC facilities, a relatively new type of power plant, combine coal gasification technology with gas turbine and steam turbine electricity generation technology. The improvement in efficiency from the use of a combined gas and steam turbine cycle counteracts the efficiency loss that results from the process of coal gasification. Furthermore, IGCC plants promise to have lower energy generation costs, reduced pollutant emissions and allow for easier capture of CO<sub>2</sub>.

However, the current capital costs and availability of IGCC technology make it no real contest to orthodox PC plants at present (Mirfendereski, 2008). In the IGCC process, a gasifier, operated under high temperatures and with limited oxygen, is used to convert coal into syngas, which is mostly a mixture of hydrogen and carbon monoxide. It is required that the syngas be cleaned of particulate matter and contaminants, predominantly sulphur, before it is subjected to a water gas shift reaction to convert the CO to CO<sub>2</sub> (Graus, et al., 2008). Thereafter the hydrogen stream is used as the fuel for a gas turbine in order to turn a generator to produce electricity. Furthermore, the heat from the high temperature exhaust gas is recovered to generate steam for a steam turbine to turn another electric generator and produce electricity (Mirfendereski, 2008).

The stream produced from the water gas shift reaction is under high pressure and has a high CO<sub>2</sub> concentration. These conditions make pre-combustion capture with a physical solvent the most suitable separation technique, which would produce a stream of CO<sub>2</sub> and a relatively pure stream of hydrogen (Kanniche, et al., 2010). CO<sub>2</sub> capture from IGCC plants also results in a smaller energy penalty and hence the plant efficiency is reduced by a lesser extent in comparison to a conventional PC plant. This is because CO<sub>2</sub> removal occurs from a stream rich in CO<sub>2</sub> rather than a dilute flue gas stream and the regeneration process is far less energy intensive (Graus, et al., 2008).

### 3.2 Cement Industry

CO<sub>2</sub> emissions arise from two specific areas in the cement production process. About 40% of emissions result from fuel combustion to provide heat for the production process, whilst the remaining 60% is from the calcination of limestone. The two potential capture methods in the cement industry are post-combustion and oxyfuel combustion technologies. Pre-combustion is not considered to be a viable option, since it will only result in the capture of CO<sub>2</sub> from energy production, leaving the CO<sub>2</sub> from the calcination process unaffected (Koring, et al., 2013).

Although retrofitting of post-combustion capture technologies to the cement industry is costly, it remains a promising option for the reason that post-combustion capture technologies do not typically require vast alteration to the manufacturing process already in place: more specifically, the clinker burning process (IEA, 2011).

As previously mentioned, the flue gas stream produced during cement production can have a CO<sub>2</sub> concentration of up to 33%, which is much higher than the CO<sub>2</sub> concentration of 14% from the flue gas stream in a PC power plant (EASAC, 2013). The conventional technique for CO<sub>2</sub> capture from this stream would be absorption with the use of an aqueous amine solvent due to its proven utility in other industrial sectors.

It is also possible to valorise the amine waste produced during the capture process. MEA for instance has a calorific value of approximately 22 MJ/kg, thus there is the prospect of using it as part of the fuel in the cement kiln (Barker, 2010). Due to the energy intensive process of solvent regeneration, cogeneration plant installations would have to accompany the CCS installation to meet the high-energy demands.

Membrane and adsorption processes are promising post-combustion alternatives due to their potential to reduce energy requirements when compared to absorption, but these techniques are still in the research and development phase (IEA, 2011).

It should be noted that post-combustion capture using amine-based absorption processes is only relevant to existing plants, which require retrofitting, in the cement industry. The high-energy requirements of solvent regeneration in post-combustion capture, point to the use of oxyfuel combustion due to its successful application in other high temperature processes. However, although oxyfuel combustion avoids the energy penalty associated with solvent regeneration

in post-combustion capture, it has the drawback of a high electricity demand during the process of oxygen separation from air. In addition, the process cannot be retrofitted.

At present, there are two proposals for capture with oxyfuel combustion (Barker, 2010):

- Partial capture: fuel is burned in the pre-calciner in an oxygen rich environment, where pure CO<sub>2</sub> is thereafter captured from a CO<sub>2</sub> rich stream.
- Total capture: fuel is burned in both the pre-calciner and rotary kiln in an oxygen rich environment, where pure CO<sub>2</sub> is thereafter captured from a CO<sub>2</sub> rich stream.

The high CO<sub>2</sub> concentrations in the streams produced in either of the cases above allows for less energy intensive capture methods to be used, such as vacuum pressure swing absorption (VPSA). Oxyfuel combustion cannot be retrofitted to existing cement plants, since it requires considerable modifications to the cement production process and equipment. Thus, oxyfuel combustion is restricted to new cement plant installations (Zero Emmissions Platform, 2013).

### 3.3 Refinery Industry

In a refinery, the CO<sub>2</sub> point sources are typically scattered throughout the plant from a variety of different unit operations. However, it is not practical to capture all the CO<sub>2</sub> from every source. Thus, to simplify the implementation of CCS in the refining sector, only the four primary CO<sub>2</sub> emitters in the plant are of interest: process heaters, the fluid catalytic cracker (FCC), the hydrogen production unit and utilities. Due to the diversity of these CO<sub>2</sub> producing processes, all three capture methods are potential candidates in the long term: pre-combustion capture from syngas, post-combustion capture from flue gas streams and oxyfuel combustion to produce flue gas streams with high CO<sub>2</sub> concentrations, to allow for easier separation. Although all methods are feasible, post-combustion capture is the preferred technique for the capture of CO<sub>2</sub>, in exiting refineries, in the near future (Brown, 2010).

In the past, hydrogen requirements in a refinery were met by the hydrogen produced as a by-product in the FCC and catalytic reformer. However, due to changes in fuel specification, the hydrogen supply from these units is now insufficient. Thus, to meet the demand, additional hydrogen is produced by natural gas steam reforming or by gasification of fuel oils and heavy residues, a process that is responsible for approximately 5-20% of CO<sub>2</sub> emissions in a refinery (Brown, 2010).

Both hydrogen production processes require that the impurities, which is primarily CO<sub>2</sub>, be removed from the gas stream to produce a pure hydrogen stream. This is undertaken by means of one of the following:

- Steam reforming: In the past, chemical absorbents, such as MDEA and potassium carbonate, were used for purification and resulted in high purity CO<sub>2</sub> streams. Nowadays, purification by pressure swing adsorption is favoured. It results in a high purity hydrogen stream, greater than 99.9%, and in lower concentration CO<sub>2</sub> streams with about 20-30% impurities. These impurities include hydrogen and methane, which make the stream suitable for recycling as fuel in the steam reforming furnace. If CCS is to be applied in this process, the use of chemical absorbents results in lower CO<sub>2</sub> capture cost, but this benefit has to be weighed against the use of the stream as a fuel in the reformer furnace (IEA, 2011).
- Gasification: Due to the high pressure involved in this process, typically 50-70 bar, physical absorbents rather than chemical absorbents are preferred. Under these conditions, physical absorbents have high CO<sub>2</sub> loadings, low regeneration energy requirements and produce a CO<sub>2</sub> stream free of water (Brown, 2010).

During FCC operation, which is a unit where heavy oils are broken down into lighter oils, carbon is deposited on the catalyst in the column, thus deactivating it. The catalyst regeneration process involves using air to oxidise the carbon, thus creating CO<sub>2</sub>. This regeneration procedure results in the FCC being responsible for 20-50% of the CO<sub>2</sub> emissions in a refinery (Brown, 2010).

In this instance, post-combustion capture with amine scrubbing is a retrofit option for CO<sub>2</sub> capture. Oxyfuel combustion technology is a promising alternative for CO<sub>2</sub> capture, since it would have lower operating costs, although initial investment costs would be high. It has been demonstrated that stable FCC operation can be achieved with oxy-firing. However, this has only been accomplished at pilot plant scale (IEA, 2011).

Process heaters, which can be responsible for 30-60% of CO<sub>2</sub> emissions in a refinery, can be retrofitted in the near future with post-combustion capture processes, such as absorption with amine-based solvents. However, this is made difficult by the wide distribution of process heaters throughout the refinery complex. One of the options is to duct all the flue gas streams to a central location, where CO<sub>2</sub> can be captured, but the feasibility of this is questionable due to the piping and spatial requirements for this alternative (IEA, 2011). Pre-combustion capture

could also be utilised by decarbonising the fuel gas in a central location within the refinery before distribution of the fuel to the various process heaters. However, in the long term, oxyfuel combustion in process heaters is believed to be the most economical solution for carbon capture, since lowering the production cost of oxygen is of particular interest in research at present (EASAC, 2013).

Steam and electricity are utilities that are required by various unit processes throughout the refinery, the production of which is responsible for 20-50% of the CO<sub>2</sub> emissions in the plant. Steam is produced in boilers with cogeneration of power. Short-term carbon capture plans for utility units involves retrofitting of post-combustion capture with amine technology, which has been developed for the power generation sector. In the future, the use of an integrated gasification combined cycle (IGCC) is a promising alternative, since not only can the hydrogen be used for the production of steam and in turn electricity, but also for meeting the refineries hydrogen demand (Brown, 2010). The additional benefit of combining the utility and hydrogen facilities is that it centralises the source of the CO<sub>2</sub> emissions, thus making capture easier.

### 3.4 Iron and Steel Industry

Power production, iron ore reduction, coke ovens and sinter plants are the primary CO<sub>2</sub> contributors in the iron and steel sector. There are three routes by which steel is produced: in an integrated steel mill (ISM), in an electric arc furnace (EAF) and in a direct reduced iron (DRI) process (Birat, 2010).

An ISM is a series of interconnected plants, where CO<sub>2</sub> is emitted from ten or more sources within the plant, most of which are stacks. However, the blast furnace is the single largest source of CO<sub>2</sub> during the steel production process, accounting for approximately 70% of the CO<sub>2</sub> emissions.

Carbon capture from the ISM furnace represents the best means to significantly reduce these emissions, since technological advances have resulted in blast furnaces that operate only 5% away from thermodynamic equilibrium. Thus, further energy efficiency improvements are unlikely to produce a considerable reduction in CO<sub>2</sub> emissions from the blast furnace (Birat, 2010).

The top gas from the ISM blast furnace typically consists of 25% CO<sub>2</sub> and 25% CO, whilst the rest is nitrogen. Thus, it is possible to retrofit the blast furnace with post-combustion capture technologies, such as amine scrubbing, to capture CO<sub>2</sub> from the furnace top gas. Post-combustion capture has the advantage of requiring no modification to the production process or the furnace itself. Oxyfuel blast furnaces are also an option, but this is probably more suitable for new installations rather than for modifying existing processes and equipment (IEA, 2011).

The DRI process for steel production uses natural gas as a reducing agent to convert iron ore to iron. During the process, the natural gas is converted to carbon monoxide and hydrogen. The DRI process already employs carbon capture as a means to improve flue gas quality. Pre-combustion capture, using PSA, VPSA or chemical absorption, is the most suitable method for CO<sub>2</sub> capture. The DRI process is therefore not relevant to this study, which is focussed on post-combustion capture.

The EAF route uses secondary raw materials, which is basically recycled steel or scrap iron, to produce steel. This process mostly requires energy in the form of electricity, coal and oxygen. Out of the three routes this is the least carbon intensive, with most of the emissions resulting from power production, which can be captured either with post-combustion or oxyfuel combustion technology as discussed previously (Birat, 2010).

Advanced smelting technologies offer alternatives to the conventional blast furnace method to reduce iron ore. Current research associated with this technology involves determining the most energy efficient way to capture CO<sub>2</sub> from the gas recycling system:

- The Finex process is an advancement on the blast furnace and is more energy efficient. During normal operation a portion of the CO<sub>2</sub> in the recirculation gas is removed, which at present is simply vented. However, there is potential to modify this process so that all the CO<sub>2</sub> can be captured without reducing the energy efficiency of the process (IEA, 2011).
- The Hlsarna process produces liquid iron from coal and iron ore by combining two types of technologies: smelting and cyclone furnace conversion. By utilising oxygen instead of air, it results in an overhead gas from the furnace with a high CO<sub>2</sub> concentration and no nitrogen. The preferred capture techniques for this process would be PSA and VPSA, which have the potential to capture about 80% of the CO<sub>2</sub> produced during the process (IEA, 2011).

Although post-combustion capture can be applied in steel mills, it is a very challenging task, both economically and technically due to the various CO<sub>2</sub> sources in the mill and the multiple stacks (EASAC, 2013). CO<sub>2</sub> capture from recycling top gas from the blast furnace is an achievable short-term option, since it is a simple retrofit alternative.

The potential of CCS in the iron and steel sector is particularly promising in the case of the new production processes. However, more research and development is required for these processes in order to ascertain the optimal CO<sub>2</sub> capture method (IEA, 2011).

### 3.5 Petrochemical Industry

The petrochemical industry is a diverse sector with an assorted range of processes, most of which involve the conversion of fossil fuel based raw materials, such as natural gas, ethane and naphtha. The products from the industry can be classified into three categories, namely petrochemicals (e.g. ethylene and propylene), basic inorganics (e.g. ammonia and chlorine) and polymers (e.g. polyethylene and polypropylene). These serve as the constituents for conversion into final products, such as, fertilisers, plastics and rubbers. CCS is only a viable option for some of these industries, due to the relatively high cost associated with capturing small volumes of CO<sub>2</sub>. At present, the feasible CO<sub>2</sub> capture options are in the ammonia production process and steam cracking in the petrochemical industry (Zero Emmissions Platform, 2013).

The principal process in the petrochemical industry is the conversion of saturated hydrocarbons into olefins by steam cracking. Superheated steam is used for the cracking process. The steam is generated by means of the combustion of fossil fuels. It is this process that is responsible for the majority of the CO<sub>2</sub> emissions in the petrochemical industry (Zero Emmissions Platform, 2013). Since CO<sub>2</sub> emissions are combustion related and not process related, all CO<sub>2</sub> capture methods are potential options: pre-combustion, post-combustion and oxyfuel combustion.

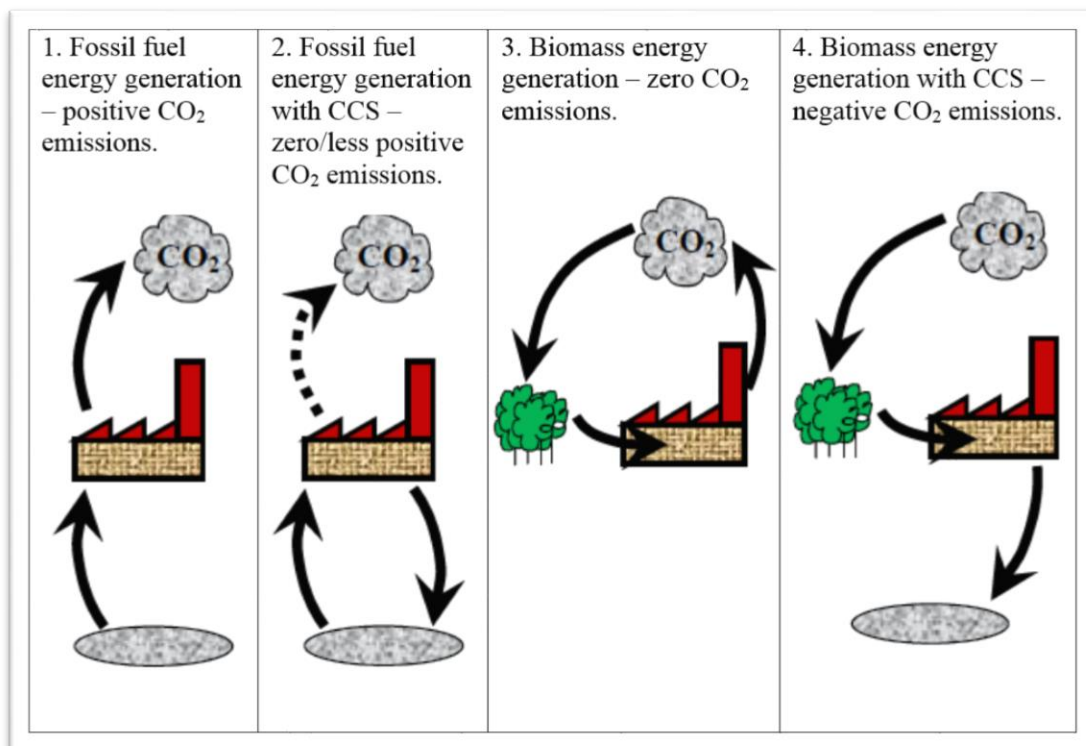
The production of ammonia, 80% of which is used for fertiliser production, is responsible for considerable CO<sub>2</sub> emissions in the petrochemical industry. Ammonia is produced by combining hydrogen with nitrogen. The nitrogen is separated from air, whilst the hydrogen is most commonly produced by means of the steam reforming of methane. It is the hydrogen production aspect of the process that is the primary source of CO<sub>2</sub> emissions in ammonia production, accounting for approximately 70% of the CO<sub>2</sub> released to the atmosphere.



CO<sub>2</sub> removal is already part of the production process and is generally accomplished by chemical absorption with amine-based solvents, which at present is simply vented. Thus, the only retrofit required in the ammonia production industry is a CO<sub>2</sub> compression instalment. CO<sub>2</sub> emissions generated from fuel combustion for steam generation is not an economically attractive option due to the relatively small size of the steam generation facility in the ammonia industry (Zero Emmissions Platform, 2013).

### 3.6 Biomass Industry

The biomass sector is diverse and encompasses multiple industries, where a raw biomass feedstock is converted into a product. The two biggest industries in this sector are the pulp and paper and biofuel industries. An interesting feature of the biomass industry is the concept that negative CO<sub>2</sub> emissions can be achieved. This concept is illustrated in Figure 3-1.



**Figure 3-1: The concept of negative CO<sub>2</sub> emissions. Adapted from (Gough & Upham, 2010)**

At present, the pulp and paper industry is the largest consumer of biomass and also produces the most CO<sub>2</sub> emissions of all the industries in the biomass sector. There are two pulping techniques used in the industry: chemical and mechanical pulping. The chosen method is dependent on the grade of paper that is to be produced. Pulping is the process by which the lignin in the wood is degraded to release the cellulose fibres, which is the constituent required to make paper.

Only chemical pulping is considered eligible for CCS, since the relatively small amounts of CO<sub>2</sub> produced in mechanical pulping is regarded as economically unfeasible for capture. Black liquor is an aqueous solution that is produced during chemical pulping and is composed of lignin, hemicellulose and pulping chemicals. Black liquor is used as fuel in recovery boilers to generate steam for the process as well to recover the pulping chemicals.

There is potential to capture the CO<sub>2</sub> from the boilers used in chemical pulping, thus resulting in a carbon negative cycle for that specific pulp and paper mill. The relatively low CO<sub>2</sub> content of 13-14% makes the retrofitting of a post-combustion capture installation with chemical absorption the preferred technique for CO<sub>2</sub> abatement. A potential alternative use for black liquor is gasification, which is presently in the research and development phase. Gasification of black liquor will allow for the production of biofuels, which is a more profitable approach rather than the generation of steam and electricity in the mill (Carbo, 2011).

Combining CCS with synthetic fuels from sustainable biomass sources is an attractive option due to the process producing by-product streams with high CO<sub>2</sub> concentrations. Biomass is generally converted into biofuels in one of two ways: biological processing or gasification. Biological processing involves the bio-chemical conversion of biomass feedstock into a gas or liquid fuel. The most common method used to accomplish this is fermentation aided by micro-organisms. The resulting products are liquid ethanol and gaseous CO<sub>2</sub>, which does not require any additional separation equipment due to a phase difference being present. Biomass gasification, also known as thermo-chemical conversion, uses pyrolysis to generate gaseous products and char. This process is carried out at high temperatures, in the region of 600-1000°C. Either air or oxygen is used as an oxidant to achieve these temperatures (Carbo, 2011).

There are multiple processes already in existence for conversion of biomass to biofuels by means of gasification. These processes along with the CO<sub>2</sub> concentration of the capture stream are shown in Table 3-2. The CO<sub>2</sub> separation technique employed would typically be those that are used for pre-combustion capture applications.

**Table 3-2: CO<sub>2</sub> compositions in capture streams for biofuel processes.**

<b>Product</b>	<b>CO<sub>2</sub> concentration in capture stream (mol %)</b>
<b>Ethanol (bio-chemical)</b>	15-35
<b>Fischer-Tropsch liquids (thermo-chemical)</b>	50
<b>Substitute natural gas (thermo-chemical)</b>	40-45
<b>Bio-dimethyl ether (thermo-chemical)</b>	50
<b>Hydrogen (thermo-chemical)</b>	90

### 3.6 Selected case studies

This study sets out to develop a performance indicator model for the evaluation of CO<sub>2</sub> absorption capture techniques using aqueous amine solvents and blends thereof. The use of amines is of particular interest in applications where the CO<sub>2</sub> partial pressure in the stream to be treated is low. Therefore, this eliminates investigating CO<sub>2</sub> capture applications involving pre-combustion and oxyfuel combustion capture. Here, alternative techniques could be employed to cater for the high pressure and high CO<sub>2</sub> concentrations present in these systems. These would typically be preferable to the energy intensive process of capture by amine absorption.

Three case studies were chosen, in order to develop criteria for the performance indicator under varied process operating parameters. In terms of equipment requirements and the process flow scheme, the amine-based CO<sub>2</sub> capture plant would only have minor variations between different instalments, most of which are related to how the capture plant would be integrated with the production plant.

The main influence on performance in amine-based capture plants is the nature of the flue gas to be treated, and primarily, the concentration of CO<sub>2</sub>. Thus, when choosing a case study, the main consideration was a variance in the CO<sub>2</sub> concentration, which would produce considerably different simulation results.

Since the power generation sector is the primary candidate for CCS technologies, two of the cases were selected from this sector, namely PC and NGCC power plant flue gas, whilst the third case chosen was the cement industry. In a NGCC power plant, the flue gas has a CO<sub>2</sub>

concentration of approximately 4 % by volume, which is the lowest of the three cases selected. In most industries, capture from such a lean CO<sub>2</sub> stream would be economically unfeasible, but this is counter-acted by the large flow rate of gas to be treated. This results in a large overall volume of CO<sub>2</sub>, making CO<sub>2</sub> capture from NGCC power plants an economic viability. PC power plant flue gas has a CO<sub>2</sub> concentration of around 12 % by volume.

In many industries, CO<sub>2</sub> emissions arise from a combination of heat, and power plant installations that provide the utility requirements for the plant. Coal and natural gas are typical fuels employed for these instalments and thus the CO<sub>2</sub> concentration in the flue gas stream is similar to that present in PC and NGCC power plants. Thus, the CO<sub>2</sub> source of a cement plant was selected as the final case.

The flue gas from a cement plant has a CO<sub>2</sub> concentration of approximately 22 % by volume, which is considerably higher than the case studies involving power plants as well as other process-related sources that are eligible for post-combustion capture with amine based solvents. Table 3-3 shows the specific flue gas parameters of each case that were used in the Aspen simulations developed.

**Table 3-3: Flue gas parameters for selected case studies.**

	<b>PC power plant<sup>[1]</sup></b>	<b>NGCC power plant<sup>[2]</sup></b>	<b>Cement plant<sup>[3]</sup></b>
<b>Flow rate (tonne/hr)</b>	2516.330	2610.000	252.711
<b>Temperature (°C)</b>	125	105	160
<b>Pressure (bar)</b>	1.01325	1.01325	1.01325
<b>Composition (mole fraction)</b>			
<b>Nitrogen (N<sub>2</sub>)</b>	0.7347	0.7480	0.6806
<b>Oxygen (O<sub>2</sub>)</b>	0.0551	0.1282	0.0234
<b>Water vapour (H<sub>2</sub>O)</b>	0.0797	0.0768	0.0723
<b>Carbon dioxide (CO<sub>2</sub>)</b>	0.1201	0.0383	0.2236
<b>Hydrochloric acid (HCl)</b>	$3.306 \times 10^{-5}$	0	0
<b>Sulphur dioxide (SO<sub>2</sub>)</b>	$1.255 \times 10^{-3}$	$4.444 \times 10^{-8}$	0
<b>Sulphur trioxide (SO<sub>3</sub>)</b>	$5.063 \times 10^{-6}$	0	0
<b>Nitric oxide (NO)</b>	$3.026 \times 10^{-4}$	0	0
<b>Nitrogen dioxide (NO<sub>2</sub>)</b>	$1.593 \times 10^{-5}$	$1.238 \times 10^{-6}$	0
<b>Argon (Ar)</b>	0.0088	0.0088	0

<sup>[1]</sup> (Khalil & Gerbino, 2007), <sup>[2]</sup> (HTC, 2007), <sup>[3]</sup> (Hassan, 2005)

## Chapter 4

### Aspen Modelling

In Chapter Three, three case studies were selected from industry on the basis of the properties of the flue gas to be treated, more specifically the CO<sub>2</sub> concentration, as this was identified as the main variation in conditions between plants. These case studies were then simulated on Aspen Plus to develop the model under varied process operating parameters. In order to accomplish this accurately, the use of thermodynamic models is required.

This section describes the thermodynamic models used in the Aspen Plus simulation and justifies their selection as the chosen method. The reasoning behind the chosen sub-models are also explored. Finally, this section contains the units considered in the Aspen flow sheet, as well as the reason for their inclusion and the assumptions regarding their operation.

#### 4.1 Thermodynamic modelling

In a simulation selected from Aspen Plus, studies involving simulation work, predictions of component properties, and how they interact with each other, are made, which is accomplished by means of thermodynamic models. Two of the more flexible equation of state property methods that Aspen Plus offers are the Peng Robinson and Soave Redlich Kwong equations of state. These equations are suitable to apply for mixtures of polar and non-polar compounds and light gases. They are capable of dealing with high pressures and high temperatures, as well as with mixtures close to their critical point (Ibrahim, et al., 2015).

The Peng Robinson and Soave Redlich Kwong equations of state would typically be used for systems with acid gases and physical acid gas absorption processes (Diamantonis, et al., 2013). However, in chemical absorption, the reaction that takes place is typically an acid-base reaction, thus an electrolyte property method is required to describe the system.

The *amine* property method built into Aspen would typically be a candidate for carbon capture processes, however, it is only compatible with four amines: MEA, DEA, DIPA and DGA. The

Electrolyte Non-Random Two Liquid (E-NRTL) model is the most versatile for use on electrolytes, and it is recommended for chemical acid gas absorption. It is capable of dealing with mixed solvents as well as aqueous ones and can handle concentrations ranging from very low to very high (Song & Chen, 2009).

#### 4.1.1 Electrolyte Non-Random Two Liquid model

The E-NRTL model is consistent with NRTL-RK model in Aspen, since the molecular interactions are determined in an identical manner. Thus, the binary interaction parameters for the E-NRTL model are obtained from the data bank for the NRTL-RK model.

Chen was the first to propose the E-NRTL model, which was later extended by Chen and Mock (Kothandaraman, 2010). It is used to model the excess Gibbs energy of electrolytic systems and assumes that the excess Gibbs free energy can be described by the sum of two contributions (Haghtalab, et al., 2011). The first contribution is the short-range interactions between all species in the system, which consists of ion-ion, molecule-molecule and ion-molecule interactions. The second contribution is due to the long-range electrostatic interactions between ions (Kothandaraman, 2010). The E-NRTL model is based upon two assumptions, namely (Haghtalab, et al., 2011):

- Local neutrality: it is assumed that the distribution of anions and cations surrounding a central molecule is such that the net local ionic charge is zero.
- Like ion repulsion: it is assumed that the local composition of anions around anions and cations around cations is zero due to the large repulsive forces between like ions.

The expression to describe the excess Gibbs free energy for the E-NRTL model is:

$$g^E = g^{E,S.R.} + g^{E,L.R.} \quad (4-1)$$

Where:

$g^E$  is the molar excess gibbs free energy

$g^{E,S.R.}$  is the short range molar excess gibbs free energy

$g^{E,L.R.}$  is the long range molar excess gibbs free energy

#### 4.1.1.1 Short range interactions

The short-range contribution to the total excess Gibbs free energy for the E-NRTL model is based on the regular NRTL model. For a multicomponent mixture, it can be expressed as:

$$g^{E,S.R.} = RT \sum_i \sum_j x_i x_j \lambda_{ij} (\tau_{ij} - 1) \quad (4-2)$$

And:

$$\tau_{ij} = \frac{\beta_{ij}}{\sum_{k=1}^n x_k \beta_{kj}} \quad (4-3)$$

$$\beta_{ij} = \exp\left(-\alpha_{ij} \frac{g_{ij} - g_{jj}}{RT}\right) \quad (4-4)$$

Where:

R is the universal gas constant

T is the absolute temperature

$x_i$  is the mole fraction of species i

$x_j$  is the mole fraction of species j

$\lambda_{ij}$  is the binary adjustable energy interaction parameter

$\tau_{ij}$  is the non-random factor

$\beta$  is the Boltzmann factor

$\alpha_{ij}$  is the nonrandomness

$g_{ij}$  is the Gibbs interaction energy parameter



### 4.1.1.2 Long range interactions

The long-range constituent of the E-NRTL model contains a further two terms, which can be expressed as:

$$g^{E,L.R.} = g^{E,PDH} + g^{E,Born} \quad (4-5)$$

Where:

$g^{E,PDH}$  is the Pitzer-Debye-Huckel component of the long range molar excess gibbs free energy

$g^{E,L.R.}$  is the Born component of the long range molar excess gibbs free energy

The first term of equation 4-5 is the Pitzer-Debye-Huckel expression. It is the term responsible for modelling the long-range interaction forces which contribute to the total excess Gibbs free energy (Kothandaraman, 2010). It can be expressed by the following equation:

$$g^{E,PDH} = -RT \left( \sum_k x_k \right) \left( \frac{1000}{M_s} \right)^{0.5} \left( \frac{4A_\phi I_x}{a_o} \right) \ln(1 + a_o I_x^{0.5}) \quad (4-6)$$

Where:

$x_k$  is the liquid phase mole fraction

$M_s$  is the solvent molecular weight

$A_\phi$  is the Debye-Huckel parameter

$I_x$  is the ionic strength

$a_o$  is the closest approach parameter

The Debye-Huckel and ionic strength parameters are described further by the following expressions:

$$A_\phi = \frac{1}{3} \left( \frac{2\pi N_o \rho}{1000} \right)^{0.5} \left( \frac{e^2}{D_w k_b T} \right)^{1.5} \quad (4-7)$$

$$I_x = \frac{1}{2} \sum_k x_k z_k^2 \quad (4-8)$$

Where:

$N_o$  is Avogadro's number

$\rho$  is the solvent density

$e$  is the charge of an electron

$D_w$  is the dielectric constant for water

$k_B$  is the Boltzmann constant

$z_k$  is the charge

The second term of equation 4-5 is the Born expression. The ideal solute state in water is the reference state for ionic species in the E-NRTL model. However, in this study the reference state for ionic species is the ideal dilute state of electrolyte in mixed solvent. The Born expression is a means to correct for this (Kothandaraman, 2010). It can be defined as:

$$g^{E,Born} = RT \left( \frac{e^2}{2k_b T} \right) \left( \frac{1}{D_s} - \frac{1}{D_w} \right) \left( \sum_k \frac{x_k z_k^2}{r_k} \right) \times 10^{-2} \quad (4-9)$$

Where:

$D_s$  is the dielectric constant of the mixed solvent

$r_k$  is the Born radius

#### 4.1.2 Soave Redlich Kwong equation of state

The Soave Redlich Kwong (SRK) equation of state (EOS) possesses a slight alteration from the initial Redlich Kwong (RK) EOS and was introduced in 1972. In 1955, Pitzer had developed the concept of an acentric factor ( $\omega$ ), which was created with the purpose of more accurately describing fluid properties. Up to that point, all modifications to the van der Waals

EOS had focused on an attraction parameter, which was assumed to be dependent on temperature only. However, Soave proposed that it was a function of both temperature and Pitzer's acentric factor. This implied that the attraction parameter was a function of the shape of the molecule, since the acentric factor is a measure of the configuration and sphericity of the molecule (Adewumi, 2014).

$$\alpha = \alpha(T, \omega)$$

Where:

$\alpha$  is the attractive parameter

$\omega$  is the acentric factor

The SRK EOS, like all cubic EOS, is explicit in pressure and can be described by the following expression:

$$P = \frac{RT}{v_m - b} - \frac{\alpha a}{v_m(v_m + b)}$$

Where:

P is the pressure

$v_m$  is the molar volume

And:

$$\alpha = [1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1 - \sqrt{T_r})]^2$$

$$a = 0.427480 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.086640 \frac{RT_c}{P_c}$$

Where:

$T_r$  is the reduced temperature

$T_c$  is the critical temperature

$P_c$  is the critical pressure

For mixtures, Soave proposed the use of a binary interaction parameter,  $k_{ij}$ . This modified the mixing rules as shown by equations 4-10, 4-11 and 4-12:

$$(\alpha\alpha)_m = \sum \sum y_i y_j (\alpha\alpha)_{ij} \quad (4-10)$$

$$(\alpha\alpha)_{ij} = \sqrt{(\alpha\alpha)_i (\alpha\alpha)_j (1 - k_{ij})} \quad (4-11)$$

$$b_m = \sum y_i b_i \quad (4-12)$$

Although the factor  $k_{ij}$  has no scientifically based derivation to justify its inclusion, it is now regarded as a means to tweak equations of state in order to improve their fit with experimental data and can be thought of as a measure of interaction between unlike molecules. Determining its value is based on the regression of experimental data from binary systems:  $k_{ij}$  results from the value that gives the selected equation of state the best match with experimental data (Adewumi, 2014).

#### 4.1.3 Soave Redlich Kwong Boston Mathias equation of state

The Soave Redlich Kwong Boston Mathias (SRK-BM) EOS is a model utilised for systems at temperatures higher than the critical temperature of the mixture. It is necessary for the modelling of the compression sections in the Aspen flows sheet, particularly in the CO<sub>2</sub> compression section where conditions are in the supercritical phase (Kothandaraman, 2010). The necessity for this adaptation is because the accuracy of cubic equations of state primarily depend on the model used to describe the alpha function,  $\alpha(T)$ . The Soave Redlich Kwong Twu model is another adaptation capable of predicting pure compound and mixture thermodynamic properties in the supercritical range. Both the Boston Mathias and Twu adaptations deliver satisfactory performance at pressures above 50 bar. However, below this pressure the accuracy of the Twu model decreases significantly, with a deviation of approximately 33% below

experimental enthalpy literature results (Neau, et al., 2009). Thus, the Boston Mathias adaptation was selected since it provides satisfactory accuracy through a wider pressure range.

The SRK-BM EOS contains a modified alpha function to describe mixtures in this condition, which can be expressed as follows:

$$\alpha_i(T) = \left( \exp \left( c_i (1 - T_{r,i}) \right) \right)^2 \quad (4-13)$$

And:

$$d_i = 1 + \frac{0.48508 + 1.55171\omega_i - 0.15613\omega_i^2}{2} \quad (4-14)$$

$$c_i = 1 - \frac{1}{d_i} \quad (4-15)$$

## 4.2 Development of the Aspen Plus flow sheet

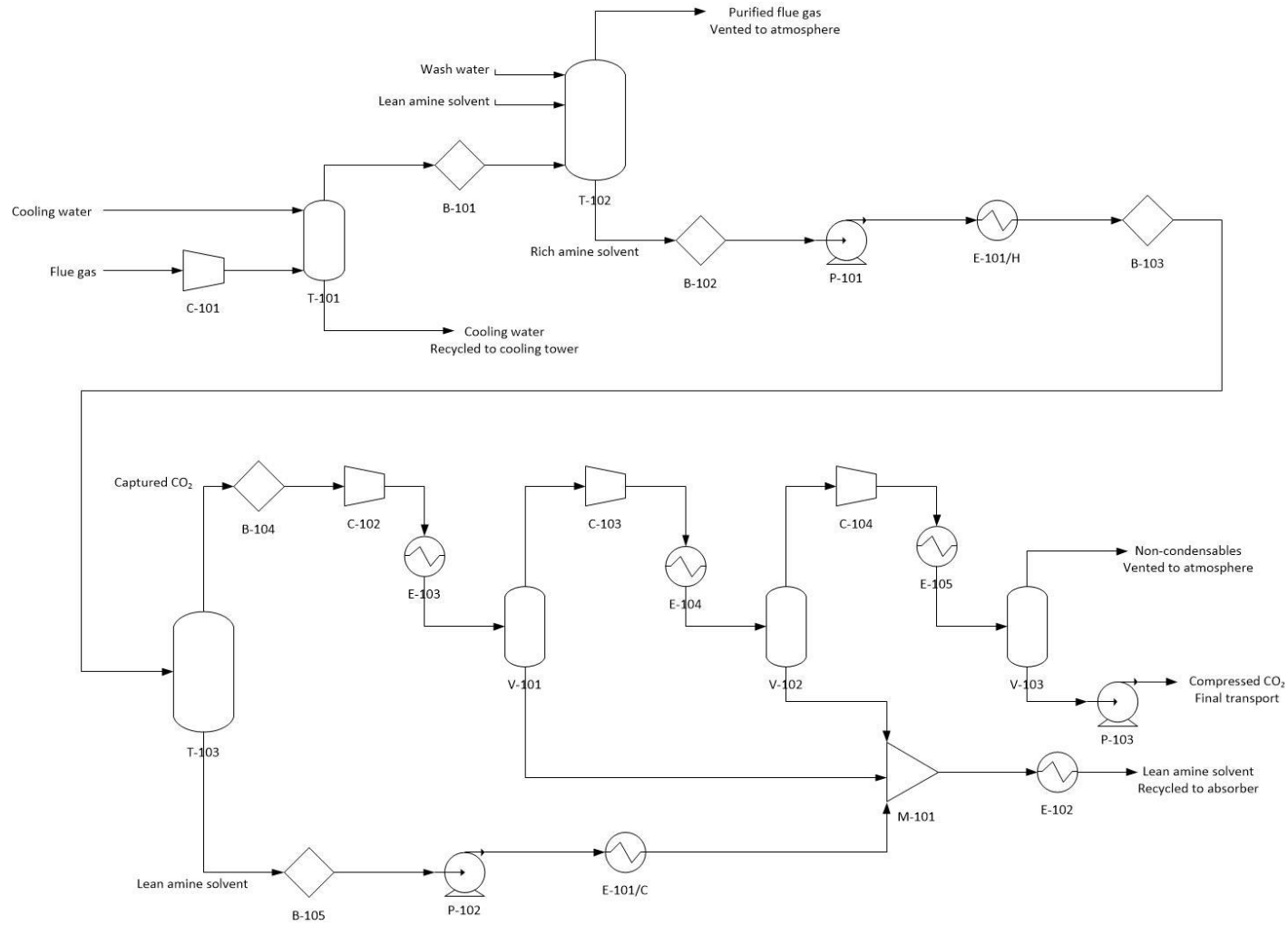
As was previously mentioned, the overall process flow sheet in a post-combustion carbon capture application with chemical absorption would be relatively similar between applications. Variations to the process would arise only from the way the carbon capture plant is integrated with the main plant. A brief overview of the carbon capture process will be provided, prior to proceeding to the more detailed operational parameters of the individual units. A process flow diagram of the carbon capture process is presented in Figure 4-1 before divulging into the details of the various unit operations.

Flue gas is typically supplied from the power plant at atmospheric pressure and a temperature of 100 - 150°C. The flue gas passes through a blower to slightly elevate its pressure to overcome pressure drops in the system. It is also cooled to 40 - 50°C before being fed into the absorber. The absorber is a packed column, where absorption takes place at a pressure slightly above atmosphere, approximately 1.05 bar, and at a temperature of approximately 35-55°C. The flue gas and lean aqueous amine solvent flow countercurrent within the column, with the CO<sub>2</sub> in the flue gas reacting with the amine solvent to form intermediary compounds. The purified flue gas exits the top of the absorber and is vented to atmosphere. The use of a wash

water column can be employed to recover entrained amine solvent from the flue gas prior to venting (Padurean, et al., 2011).

The CO<sub>2</sub> rich solvent from the absorber is then pumped and preheated to approximately 110°C, using the hot lean solvent from the bottom of the stripper, prior to being fed to the stripper. Here, solvent regeneration occurs at both an elevated temperature and pressure, typically at 100 - 120°C and 2 bar respectively. The energy required to regenerate the solvent is supplied by low-pressure steam. The overhead gas is cooled in a condenser to recover the amine and water vapour, with the CO<sub>2</sub> remaining in a gaseous state. The hot lean amine solvent from the bottom of the stripper is then cooled and recycled to the beginning of the process (Padurean, et al., 2011). A slipstream of the hot lean amine solvent is passed through a reclaimer to remove any degraded amine.

The captured CO<sub>2</sub> is fed to the compression section of the plant. Multistage compression to 80 bar is used, with interstage cooling to prevent overheating of the compressor and interstage separators to remove any water that may have condensed (Padurean, et al., 2011). At this point, the captured CO<sub>2</sub> is a liquid, since it is in a supercritical state. Thus, the liquid CO<sub>2</sub> stream can then be pumped to the final transport pressure of 110 bar



**Figure 4-1: Process flow diagram of carbon capture process utilised in this study.**

**Table 4-1: Description of symbols used in the process flow diagram.**

<b>Symbol</b>	<b>Description</b>
<b>B-101</b>	Aspen block multiplier function
<b>B-102</b>	Aspen block multiplier function
<b>B-103</b>	Aspen block multiplier function
<b>B-104</b>	Aspen block multiplier function
<b>B-105</b>	Aspen block multiplier function
<b>C-101</b>	Blower
<b>C-102</b>	1 <sup>st</sup> Stage compressor
<b>C-103</b>	2 <sup>nd</sup> Stage compressor
<b>C-104</b>	3 <sup>rd</sup> Stage compressor
<b>E-101/C</b>	Lean amine cross exchange heater
<b>E-101/H</b>	Rich amine cross exchange cooler
<b>E-102</b>	Rich amine cooler
<b>E-103</b>	1 <sup>st</sup> Stage intercooler
<b>E-104</b>	2 <sup>nd</sup> Stage intercooler
<b>E-105</b>	3 <sup>rd</sup> Stage intercooler
<b>M-101</b>	Mixer
<b>P-101</b>	Rich amine pump
<b>P-102</b>	Lean amine pump
<b>P-103</b>	CO <sub>2</sub> pump
<b>T-101</b>	Direct contact cooler
<b>T-102</b>	Absorber
<b>T-103</b>	Stripper
<b>V-101</b>	1 <sup>st</sup> Stage separator
<b>V-102</b>	2 <sup>nd</sup> Stage separator
<b>V-103</b>	3 <sup>rd</sup> Stage separator



### 4.2.1 Sub-models

The Aspen Plus simulation engine has two options for simulating the CO<sub>2</sub> capture process in the absorption and stripping section of the flow sheet: RadFrac and Ratefrac. The RadFrac model is equilibrium based and assumes thermodynamic equilibrium is achieved when performing calculations. This eliminates the need for column specifications such as size and packing, and usually incorporates efficiency factors to improve the accuracy of predictions (Mudhasakul, et al., 2013). The RateFrac model is an extension of the RadFrac model and takes into account heat and mass transfer effects during the separation process. It assumes that thermodynamic equilibrium is only achieved at the gas-liquid interface, making this model the more accurate in describing the CO<sub>2</sub> absorption and stripping process (Zhang & Guo, 2013).

However, the increased level of accuracy in the RateFrac model does come at a cost: a difficulty in achieving convergence during simulations. The difficulty in achieving convergence is enhanced by the ionic nature of the system and the presence of kinetic reactions (Mudhasakul, et al., 2013). In order to model the process as a closed loop process, highly accurate initial estimates of tear streams would be required in order to prevent divergence during simulation calculations, which is often difficult and time consuming. Furthermore, even with accurate initial estimates, a large number of iterations are still required to converge the tear streams, due to the large flow rates in the system (Alie, et al., 2005).

RateFrac uses a two-film model when performing heat and mass transfer calculations. There are number of film discretisation options, namely (Kothandaraman, 2010):

- No film – Aspen Plus performs an equilibrium calculation since it assumes there is no film resistance.
- Film – Aspen Plus performs diffusion resistance calculations across the film but assumes no reactions occur in the film.
- Filmrxn – Aspen Plus performs diffusion resistance and reaction calculations across the film. An adjustable, user specified, reaction conditioning factor is used to calculate the film reaction rate. This factor is used for calculating the temperatures and concentrations to be used in the evaluation of the film reaction rate. The factor can be varied between 0 and 1, where 0 represents the interphase conditions and 1 represents the bulk conditions.

- Discrxn – Aspen Plus discretises the film into multiple segments and calculates the concentrations of the relevant species at each of these segments so that an accurate concentration profile through the film is calculated. This is the most robust of the film discretisation options and is necessary when the reactions that occur across the film are rapid. The number and the location of discretisation points within the film are user specified. This feature of user specification is important in systems where rapid reactions occur, since additional discretisation points are required close to the interphase.

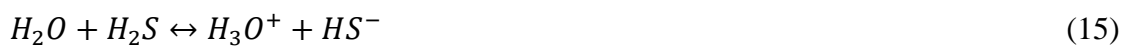
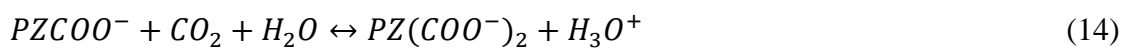
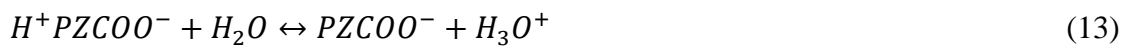
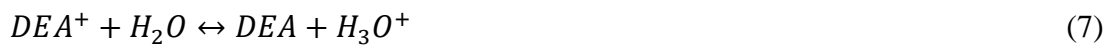
In order to avoid convergence complications, the Aspen Plus flow sheet was modelled as an open loop process. However, it was ensured that the parameters of the lean solvent into the absorber and out of stripper, were consistent. This was accomplished by using the design specification (*Design Spec*) function to match the CO<sub>2</sub> recovery rate in the absorber to the CO<sub>2</sub> release rate in the stripper. This ensures that the amount of CO<sub>2</sub> in the lean solvent before and after the capture process is equal, which theoretically creates a closed loop.

Make-up water and amine requirements, which would usually be incorporated in the flow sheet closed loop process, are catered for manually by taking into account the difference in component flow rate of the lean solvent entering and leaving the process. The lean/rich amine heat exchanger also needs to be split in this flow sheet arrangement and it was ensured that the duties of the heating and cooling components of these heat exchangers matched. Although this method is tedious, since there is a constant need to manually adjust parameters to ensure consistency in results, it does avoid the difficulty experienced with process convergence, from which the system suffers. It is the easiest method to ensure convergence is achieved during simulations (Han, et al., 2011). A similar approach was adopted by Kothandaraman, 2010, to allow for easier convergence and perform multiple runs quickly in her simulation based CO<sub>2</sub> absorption studies with MEA.

#### 4.2.2 System chemistry and kinetics of amines

In the capture process, amines react with CO<sub>2</sub> to form intermediary compounds in the absorber followed by reversal of the reaction in the stripper to release the CO<sub>2</sub>. Since this procedure is a reactive one, the Aspen Plus simulation requires information regarding kinetics and chemical

equilibrium of the system to accurately simulate the process. The following reactions were the ones that were taken into consideration for the amine chemical absorption process:



The kinetic reaction and equilibrium constant equations used in Aspen Plus to describe the above reactions are expressed respectively as follows:

$$r = kT^n \exp\left(\frac{-E_a}{RT}\right) \quad (4-16)$$

$$\ln(k_{eq}) = A + \frac{B}{T} + C \ln(T) + DT \quad (4-17)$$

The kinetic and equilibrium constants to be used in the above two equations are given in Table 4-2 and Table 4-3. It should be noted that reactions 3-16 are taken as equilibrium reactions since they are assumed to occur instantaneously due to the reaction being one that just involves proton transfer between reacting species (Mudhasakul, et al., 2013).

**Table 4-2: Values of kinetic reaction constants in amine systems.**

Reaction	K	n	E <sub>a</sub> (J/kmol)
1 <sup>[1]</sup>	4.3152 x 10 <sup>13</sup>	0.0	5.54709 x 10 <sup>7</sup>
2 <sup>[1]</sup>	3.7486 x 10 <sup>14</sup>	0.0	1.05807 x 10 <sup>8</sup>

<sup>[1]</sup> (Pellegrini, et al., 2010)

**Table 4-3: Values of temperature dependant parameters for equilibrium constants in amine systems.**

Reaction	A	B	C	D
3 <sup>[1]</sup>	132.899	-13445.9	-22.4773	0.0
4 <sup>[1]</sup>	216.049	-12431.7	-35.4819	0.0
5 <sup>[1]</sup>	-3.038325	-7008.357	0.0	-0.00313489
6 <sup>[1]</sup>	-0.52135	-2545.53	0.0	0.0
7 <sup>[2]</sup>	-13.3373	-4218.708	0.0	0.00987175
8 <sup>[2]</sup>	16.5026	-4068.76	-1.5027	0.0
9 <sup>[3]</sup>	-3.68672	-6754.686	0.0	0.0
10 <sup>[2]</sup>	-9.4165	-4234.98	0.0	0.0
11 <sup>[3]</sup>	-62.28	-2564	6.787	0.0
12 <sup>[3]</sup>	466.497	1614.5	-97.54	0.2471
13 <sup>[3]</sup>	6.822	-6066.9	-2.29	0.0036
14 <sup>[3]</sup>	-11.563	1769.4	-1.467	0.0024
15 <sup>[1]</sup>	214.582	-12995.4	-33.5471	0.0
16 <sup>[1]</sup>	-9.742	-8585.47	0.0	0.0

<sup>[1]</sup> (Pellegrini, et al., 2010), <sup>[2]</sup> (Borhani, et al., 2015), <sup>[3]</sup> (Haghtalab, et al., 2014)

### 4.2.3 Units considered in Aspen

The final set of criteria that was required for the development of the model was the design of the carbon capture process. As a result, a summary of the equipment and operational design effects of an optimal is presented in the sections that follow. Details of the design parameters used for the units are also provided where applicable.

#### 4.2.3.1 Inlet gas blower

Although the use of a gas blower is uncharacteristic in a carbon capture application, owing to the large volume of gas being processed, it is required, since flue gases would typically be supplied to the carbon capture section of the plant at atmospheric pressure. Whilst increasing the pressure of the flue gas increases the CO<sub>2</sub> partial pressure, and hence the rate of absorption in the absorber, this is at the expense of a higher blower power requirement. Due to this energy penalty, the increase in pressure would generally be to just overcome the pressure drop that occurs through the direct contact cooler and the absorber packing (Fisher, et al., 2007). However, it is possible to optimise the blower pressure in order to balance the competing factors of a higher energy penalty and an improved absorption rate.

With regard to compressors in the system, there exists two options for the method in which the compressor operates. The compressor drivers can either be operated by steam or electricity, both of which would typically be provided from the power plant. In the case of a power plant, if it is taken that the net power output from the plant is constant, then it is necessary to increase boiler capacity to cope with the demand of steam in the CO<sub>2</sub> capture section of the plant. If it is assumed that heat input to the power plant is constant, then the net power output from the plant has to decrease. Since carbon capture is to be a retrofit technology, at least in the early stages of implementation, the second option was chosen and hence electric drivers were used in all compressors (Fisher, et al., 2007).

In this study, the blower was set to deliver the flue gas at 1.1 bar. This increase was sufficient to overcome the pressure drop through the direct contact cooler and the absorber column. Isentropic compression was assumed for the unit, with an isentropic efficiency of 0.75 assumed (Smith, et al., 2005). The unit is represented by unit C-101 in Figure 4-1.

#### 4.2.3.2 Direct contact cooler

A direct contact cooler (DCC) is used to cool the flue gas from the power plant, which is typically supplied at 100-150°C (Padurean, et al., 2011). This method utilises less cooling water than an indirect contact cooler would, since it employs latent heat rather than sensible heat to cool the flue gas. A DCC also has the advantage of rapid cooling of flue gases, simple condensate removal and all critical parts being protected from the heat effects of the flue gas (Martin, 1955). Furthermore, in comparison, indirect contact coolers have higher capital costs, higher pressure drops and higher operating costs (Direct Contact LLC, 2011). The lower pressure drop is particularly beneficial in this application, since the inlet gas blower is required to overcome the pressure drop in the flue gas cooling system and absorber. Thus, a lower pressure drop through these units allows for the blower to operate at a reduced load.

The use of a DCC does have the major disadvantage of carrying contaminants, especially oxygen, into the flue gas. Although oxygen is already present in the flue gas, an increase in its concentration would have the effect of increasing oxidative degradation of the amine absorbents (Martin, 1955). Caustic is added to the cooling water to maintain the pH at a specific level so that absorption of SO<sub>2</sub> is favoured over CO<sub>2</sub> absorption in the DCC (Fisher, et al., 2007).

The DCC is modelled in Aspen Plus as a RadFrac column, where the condenser and reboiler have been removed. The cooling water and flue gas flow countercurrent within the column. The desired temperature for the flue gas to be cooled to was 45°C, which was accomplished with cooling tower water at 35°C. The unit is represented by unit T-101 in Figure 4-1.

#### 4.2.3.3 Absorber

The aqueous amine solvent contacts the flue gas in the absorber and removes the CO<sub>2</sub>. Due to the large flow rates of flue gas from a power plant, the flow needs to be divided into multiple trains. This allows for the use of absorption and stripper columns with diameters that are found in commercial units presently, which range in size to up to 13 metres (Kothandaraman, 2010). However a diameter of 15 metres is thought to be feasible in order to minimise the number of trains required (Steenefeldt, et al., 2006). The absorber is a packed, vertical column with a

wash water section at the top of the unit. The purpose of the wash water section is to reclaim any amine that would have otherwise been discharged to the atmosphere with the purified flue gas, which reduces the cost of required make-up amine solvent. The use of packing rather than trays is preferred since packing has a lower pressure drop, increased gas-contacting efficiency, allows for higher gas flow rates and a lower chance of foaming (Fisher, et al., 2007). The specifications of the absorber column used in this study are presented in Table 4-4.

**Table 4-4: Absorber column design specifications.**

<b>Column Model</b>	Rate-based
<b>Stage 1 pressure (bar)</b>	1.05
<b>Number of sections</b>	2
<b>Number of stages</b>	22
<b>Section 1 number of stages</b>	2
<b>Section 2 number of stages</b>	20
<b>Column packed height (m)</b>	22
<b>Section 1 packed height (m)</b>	2
<b>Section 2 packed height (m)</b>	20
<b>Column Diameter (m)</b>	13
<b>Packing type</b>	Flexipac
<b>Packing size</b>	1Y
<b>Condenser</b>	None
<b>Reboiler</b>	None

In the absorption column, the film discretisation option of *Discrxn* was selected for the liquid film to account for the rapid reaction rates that occur across the film. The use of this model is recommended for systems where CO<sub>2</sub> is absorbed by aqueous amine solvents (Kucka, et al., 2003). The *Film* option was selected for the vapour film, since no reactions occur across the vapour film. The *Film* option still allows for mass transfer resistance to be calculated (Kothandaraman, 2010). The discretisation points specified in the liquid film are shown in Table 4-5. The term ratio in the table refers to the non-dimensional distance from the vapour side in the liquid film.

**Table 4-5: Discretisation points specified in the liquid film.**

Point	Ratio
1	0.001
2	0.005
3	0.01
4	0.05
5	0.1
6	0.15
7	0.2
8	0.3

The *Design Spec* function was utilised to ensure that 80% of the CO<sub>2</sub> in the flue gas was captured. The solvent flow rate into the absorber was the parameter varied to achieve this capture rate. The unit is represented by unit T-102 in Figure 4-1.

#### 4.2.3.4 Rich and lean amine pump

A pump is required after the absorber to elevate the pressure of the solvent to overcome the pressure drop in the rich/lean amine heat exchanger, pressure drops in the line (including that required to elevate the solvent to the feed point of the stripper) 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 corrosion problems occurring in the heat exchanger, control valves and subsequent piping systems (Fisher, et al., 2005). A lean amine pump is required after the stripper for similar reasons as given above for the recycle of lean amine solvent to the absorber.

In this study, the delivery pressure of the pump is set at 5 bar to overcome the pressure drop through the heat exchanger and account for any line losses that may occur in being fed to the stripper. Although acid gas breakout would not be simulated in the heat exchanger, the 5 bar set point was chosen with this in mind for applications in reality. A pump efficiency of 0.7 was assumed (Smith, et al., 2005). These units are represented by unit P-101 and P-102 in Figure 4-1.



#### 4.2.3.5 Rich/lean heat exchanger and lean amine cooler

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 elevated pressure to prevent acid gas breakout, which prevents corrosion of the heat exchanger and down-stream piping and equipment. 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. Since only about 65% of the available heat from the hot lean mine is transferred to the rich amine stream, a cooler is required in the recycle loop for the lean amine stream to return it to the absorber operating temperature of 40-50°C (Fisher, et al., 2005).

Since the process is modelled as an open loop process, two heat exchangers are required to act as the cross exchanger between the rich amine stream and the hot lean amine stream. The heat balance for the operation of these solvent heat exchangers is accomplished as follows:

- The rich amine solvent from the absorber is heated in a pre-heater to 110°C.
- The regenerated lean amine solvent from the stripper is cooled in a cooler. The cooling duty for this unit is specified to be the duty calculated in the preheater above.
- The lean amine passes through a secondary cooler with a set point of 45 °C.

The unit is represented by unit E-101/H and E-101/C in Figure 4-1 to represent the heating and cooling unit operations respectively.

#### 4.2.3.6 Stripper

The stripper is responsible for releasing the captured CO<sub>2</sub> from the rich amine solution. By utilising steam stripping, the reactions in the absorber are reversed with the heat provided by the reboiler (Fisher, et al., 2007).

**Table 4-6: Stripper column design specifications.**

<b>Column Model</b>	Rate-based
<b>Stage 1 pressure (bar)</b>	2
<b>Number of sections</b>	1
<b>Number of stages</b>	22
<b>Column packed height (m)</b>	17
<b>Column Diameter (m)</b>	13
<b>Packing type</b>	Flexipac
<b>Packing size</b>	1Y
<b>Condenser</b>	Partial
<b>Reboiler</b>	Kettle

In a closed loop process, the CO<sub>2</sub> loading of the solvent entering the absorber should be identical to the CO<sub>2</sub> loading of the solvent leaving the stripper. In this study, an open loop process was utilised, thus a consistent mass balance has to be obtained manually. Since an 80% CO<sub>2</sub> capture rate was set in the absorber, the mass of CO<sub>2</sub> captured is constant in each case study. The *Design Spec* function was utilised to set the CO<sub>2</sub> mass flow rate in the overhead gas of the absorber at the amount that was captured in the absorber. The boilup rate in the stripper reboiler was the parameter varied to achieve the specified CO<sub>2</sub> vent rate from the stripper. The unit is represented by unit T-103 in Figure 4-1.

#### 4.2.3.7 CO<sub>2</sub> compression train

The captured CO<sub>2</sub> from the stripper is compressed to 80 bar in a train of multi-stage compressors. Electric drivers were assumed for the compressors for the same reasons as the inlet gas blower. Under these supercritical conditions, CO<sub>2</sub> forms a dense liquid-like phase. Interstage coolers are used between compressors to cool the CO<sub>2</sub> to temperatures of 5-40°C. There is no specific temperature requirement, but rather it is based on the temperature of the available cooling water, as this is the preferred medium for cooling (Fisher, et al., 2007).

Downstream of each interstage cooler, separators are required to separate condensed liquids from the gas before further compression. The condensed liquid is mostly water, which can be recycled back into the amine solvent loop, thus reducing the required make-up water rate. After the compression train, the CO<sub>2</sub> is pressurised further to 110 bar by a multi-stage centrifugal pump, which represents the pressure recommended for pipeline transport (Fisher, et al., 2007).

In this study, a series of three compressors were utilised in pressurising the captured CO<sub>2</sub> to 80 MPa, which is represented by units C-102, C-103 and C-104 in Figure 4-1. The discharge pressures of each compressor were set at 4.3, 18.6 and 80 bar respectively. These delivery pressures were based on maintaining the pressure ratio of each compressor constant. Isentropic compression was assumed for each unit, with an efficiency of 0.75 assumed (Smith, et al., 2005). After each compressor, the stream is cooled to 40°C with cooling tower water, which is represented by units E-103, E-104 and E-105 in Figure 4-1. The stream then proceeds to a separator to remove any condensate, prior to entering the next compression stage. The separation operation is represented by units V-101, V-102 and V-103 in Figure 4-1. In the final separator, the captured CO<sub>2</sub> exists as a liquid. Thus, any non-condensable gases are vented to atmosphere, whilst the CO<sub>2</sub> is pumped to its final delivery pressure of 110 bar for transport, which is represented by P-103 in Figure 4-1.

#### 4.2.4 Reclaimer

The reclaimer has been excluded from the flow sheet due to the complexity of the amine degradation process. The complexity arises as a result of limited kinetic data on amine degradation mechanisms and thus cannot be modelled accurately within Aspen Plus. The method by which degradation is accounted for and the how the reclaimer is incorporated in this study will be elaborated upon in Chapter Five.

#### 4.2.5 Aspen flow sheet

Due to the multiple trains of absorber and stripper columns that are required in the power plant case studies, the block multiplication function on Aspen Plus is utilised to act as the method by which the streams would be split and recombined in the process. In the case of the cement plant, only a single train is required. Thus, the multiplication block is simply set to a value of one so that it has no effect on the stream flow rates. The required solvent flow rate in the absorber and energy requirements in the stripper, are multiplied by the number of trains in the system externally to ensure the total resource requirement of the process is determined during solvent evaluation.

## Chapter 5

### Performance Indicator Factors

The use of amine-based solvents for carbon capture is a process that has a high-energy penalty. This is mostly associated with the steam required for the regeneration of the circulating solvent. Many studies have focused on minimising this factor, since steam requirements can account for as much as two-thirds of the operation cost, as is the case in a MEA based capture process (Khalil & Gerbino, 2007). Other studies have investigated optimising capital cost to determine the most feasible solvent for carbon capture. However, there are multiple additional factors that should be taken into account when assessing the overall performance of a solvent. Nevertheless, no work has been found in literature that looks at combining multiple factors at once into a single comprehensive model to determine the most cost effective solvent for carbon capture. As a result, the model developed in this study is novel.

This section begins by describing the additional factors that can be taken into consideration when assessing solvent performance. Thereafter, the model developed to calculate the rating for a given solvent is presented.

#### 5.1 Amine degradation

During the capture process, degradation of the amine solvents takes place. There are three unique forms of amine degradation and they occur in three different stages of the CO<sub>2</sub> capture process (Shao & Stangeland, 2009):

- Oxidative degradation – predominantly occurs in the absorber.
- Thermal degradation – predominantly occurs in the stripper.
- Atmospheric degradation – degradation of escaped amines that occurs in the atmosphere.

There are multiple degradation products that are formed in the CO<sub>2</sub> capture process in each of the three degradation types. The type of degradation is only one factor that influences the

degradation products formed. The type of amine and the time spent in the capture process also play a role in affecting the amount and nature of the degradation products formed (Shao & Stangeland, 2009).

### 5.1.1 Oxidative degradation

Flue gas from a power plant will generally contain unreacted oxygen from the combustion process and even traces of metal ions. The presence of these components results in the amine solvent being subjected to oxidative degradation. The absorber is the main point at which oxidative degradation occurs, since the oxygen concentration is highest at this point of the capture process. It is suspected to occur mostly in the liquid hold-up at the bottom of the absorber as a result of the dissolved oxygen in the solution. The typical degradation products are oxidised forms of the amine solvents, such as organic acids, ammonia and oxidants. The main issue with this form of degradation is that it results in increased amine losses, increased amine waste and a reduced capture capacity of the system (Shao & Stangeland, 2009).

Initially the amines react with the metal ions, namely  $\text{Cu}^+$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , to form oxide radicals. In an environment without dissolved oxygen, further reaction with metal ions or alternative oxidants results in the formation of imines from the radicals. If dissolved oxygen is present, the oxide radical will react with oxygen to form peroxide radical. These peroxide radicals then react with amines to form hydrogen peroxide and imines. The final degradation products are formed when the imines undergo further processes such as oxidative fragmentation and hydrolysis (Shao & Stangeland, 2009).

### 5.1.2 Thermal degradation

The reactions of amines with  $\text{CO}_2$  results in the formation of soluble carbonate salts. Although this reaction is reversible, the conditions in the stripper allows the carbonate salts to further react with amines to produce thermal degradation products. The amines will also be subject to a hydrolysis process to form the final degradation products (Shao & Stangeland, 2009).

The high CO<sub>2</sub> concentration and temperature in the stripper present an ideal condition for amine thermal degradation. The high temperature causes the chemical bonds of the amines to be broken, which allows for the increased reaction rate with CO<sub>2</sub> to form the various thermal degradation products. As with oxidative degradation in the absorber, the degradation products are formed mostly in the bottom of the column as well as the reboiler and the effect of the degraded amine is the same as mentioned previously (increased amine loss etc.). Temperature and pressure influence the rate of thermal degradation, where an increase in either of these factors results in increased degradation and thus increased amine loss. The concentration of the amine and the CO<sub>2</sub> loading also have a pronounced effect on the rate of thermal degradation. The CO<sub>2</sub> loading has a first order effect on the degradation rate, whilst the amine concentration has an effect that is greater than a first order effect (Shao & Stangeland, 2009).

### 5.1.3 Atmospheric degradation

Once in the atmosphere, amines go through a series of chemical and physical processes such as absorption, adsorption, degradation and photolysis. In comparison with oxidative and thermal degradation, there is a far wider range of degradation products created by atmospheric degradation. The effects of atmospheric degradation have no impact on the performance of the carbon capture plant, since the amines are no longer part of the system, hence it is not included in the indicator model. However, atmospheric degradation still remains an important aspect to study for health and environmental concerns (Shao & Stangeland, 2009).

Research on amine degradation has focused mainly on oxidative and thermal degradation, but in recent times, valuable information has been obtained on atmospheric degradation reaction mechanisms and products. A brief overview of the reaction mechanisms and the main products for the more prominent amines follows (Shao & Stangeland, 2009):

- MEA: hydrogen subtracted from the carbon atoms in MEA by hydroxide radicals usually results in the formation of 2-hydroxy-acetamide and formamide. Peroxyacetyl-nitrates and other amides are also formed but to a lesser extent. Hydrogen subtracted from the amino group in MEA results in the formation of different amides, nitrosamine and nitramines.

- AMP: hydrogen subtraction from any of the carbon atoms results in acetamide and other amides as degradation products. Hydrogen subtraction from the amino group results in the formation of various nitrosamines and nitramines.
- MDEA: hydrogen subtraction from the carbon atoms results in the production of amides and polyacrylonitrile-like molecules. Nitrosamines and nitramines are produced from amino based radicals
- PZ: the major atmospheric degradation products from PZ are 2-piperazinone and amides. Nitrosamine and nitramines are also formed from the degradation of PZ.

#### 5.1.4 Modelling of amine degradation

In a CO<sub>2</sub> capture plant there are multiple factors that play different roles in contributing to the degradation of the amine solvent. Furthermore, there is an array of different operating temperatures, pressures and concentrations of degradative inducing components in the different sections of the process. These variable operating conditions make understanding the reaction mechanisms and formation of degradation products difficult to accomplish (Vevelstad, et al., 2013). In literature degradation kinetics are rare, with MEA being one of the better-researched amines due to its important role in amine scrubbing in gas sweetening processes. Even though MEA degradation is the most prominent in literature, there are still significant gaps in the research, since most studies have focused on determining the overall degradation rate of MEA rather than the degradation of MEA into the various degradation products, due to the vast number of compounds that are produced. Kinetic data on kinetics for the degradation of other amines included in this study, if not absent, are rare. Taking both of these factors into account, it is difficult to model the degradation of amines in the CO<sub>2</sub> capture process, since the compounds that are formed as well as the kinetics of the reactions are not well explored. Furthermore, including degradation kinetics into the Aspen flow sheet would enhance the convergence issues that the system is already susceptible to. For these reasons, a general degradation model was adopted, where calculations for the amount of amine degraded were performed outside of the Aspen Plus flow sheet to account for the makeup stream required.

The degradation rates were obtained from batch degradation studies of amines. Although this approach is not entirely accurate in terms of describing the levels of degradation that would occur in full-scale industrialised installations, it aids in determining the amount of amine



degraded. This approach provides a useful model to ascertain the relative amount of amine degraded since the stability classification of amines between the laboratory studies and full-scale applications would remain consistent (Lepaumier, et al., 2009a). Understanding and information required for describing the complexity of amine degradation will increase in the future, as CO<sub>2</sub> capture using amines enters the market. Thus, the possibility does exist to include more precise degradation models should this be an issue of paramount importance in future studies.

The degradation rates used in the indicator model were expressed as a percentage of the total amine in the circulating solvent that will degrade per hour. Both thermal and oxidative degradation were taken into account and values obtained from literature were for amine degradation in the presence of O<sub>2</sub>, as is the case in the absorber, and in the presence of CO<sub>2</sub>, as is the case with the loaded solvent in the absorber, stripper and other auxiliary equipment in the process. Lepaumier, et al., 2009, performed two separate batch degradation studies: one for oxidative degradation and one for thermal degradation. The oxidative degradation study was performed with temperatures and O<sub>2</sub> partial pressures higher than that typically found in industrial applications. This was done to reduce the length of the experiment to 15 days, since amine degradation is a slow process. The thermal degradation study was performed with CO<sub>2</sub> partial pressures higher than that typically found in industrial applications, however, the temperature was within the expected range. Like the oxidative degradation study, this was done to reduce the length of the experiment to 15 days. The amines of interest in this work were part of both these oxidative and thermal degradation studies found in literature. Since the conditions used in the literature study were altered to reduce experimental time, it was important to use only these two literature studies when establishing degradation rates to be used in this work. This was done to maintain the relative degradation rates between amines, which is the most important aspect in maximising the accuracy of the degradation model used, since ultimately the performance indicator model ranks the amines relative to one another. Wang & Jens, 2012, presented results on the relative degradation rates of the amines of interest in this study. Although the values in their study was not utilised in the degradation model itself, it was used as a means to quantify the uncertainty in the values used which was incorporated into the sensitivity analysis undertaken.

**Table 5-1: Degradation rates expressed as a percentage of total amine degraded in circulating solvent per hour.**

<b>Amine</b>	<b>O<sub>2</sub> Induced Thermal Degradation<sup>[1]</sup></b>	<b>O<sub>2</sub> Induced Oxidative Degradation<sup>[1]</sup></b>	<b>CO<sub>2</sub> Induced Thermal Degradation<sup>[2]</sup></b>	<b>CO<sub>2</sub> Induced Oxidative Degradation<sup>[2]</sup></b>
<b>MEA</b>	4.842 X 10 <sup>-3</sup>	3.894 X 10 <sup>-2</sup>	5.124 X 10 <sup>-3</sup>	3.129 X 10 <sup>-2</sup>
<b>DEA</b>	6.917 X 10 <sup>-5</sup>	2.407 X 10 <sup>-2</sup>	1.830 X 10 <sup>-4</sup>	6.112 X 10 <sup>-2</sup>
<b>MDEA</b>	1.508 X 10 <sup>-2</sup>	5.838 X 10 <sup>-2</sup>	1.555 X 10 <sup>-2</sup>	1.169 X 10 <sup>-1</sup>
<b>AMP</b>	2.234 X 10 <sup>-2</sup>	6.128 X 10 <sup>-2</sup>	2.251 X 10 <sup>-2</sup>	2.589 X 10 <sup>-1</sup>

Data adapted from literature sources <sup>[1]</sup> (Lepaumier, et al., 2009b) <sup>[2]</sup> (Lepaumier, et al., 2009c)

## 5.2 Corrosion

Corrosion is probably of the biggest operational issues when using aqueous alkanolamine solutions. It can adversely affect the economic feasibility of the plant by causing unexpected downtime, equipment damage and can create a potential injury hazard. Corrosion can also limit the plant's operation limits, since higher amine concentrations increase the risk of corrosion. This is a disadvantage because higher amine concentrations reduce the large energy penalty associated with solvent regeneration, due to the reduced water content in the circulating solvent (Veawab, et al., 2001). Capital costs are reduced due to higher amine concentrations, since circulating solvent flow rates are lower resulting in smaller equipment sizes (Folger, 2013). Although the use of amines are not corrosive, it is the reaction products of amines with CO<sub>2</sub> as well as their degradation products that are hazardous.

To counter-act these issues, the use of corrosion inhibitors would generally be employed with the use of amine solvents. Sodium metavanadate and copper carbonate are two of the more prominent compounds that are being investigated as corrosion inhibitors for carbon capture applications. Current and more established corrosion inhibitors, such as arsenic and antimony, are toxic to both the environment and humans. (Soosaiprakasam & Veawab, 2009).

## 5.3 Energy consumption

In a carbon capture plant, the main energy consumers can be grouped into three categories:

- Electrical power consumption
- Steam usage
- Water usage

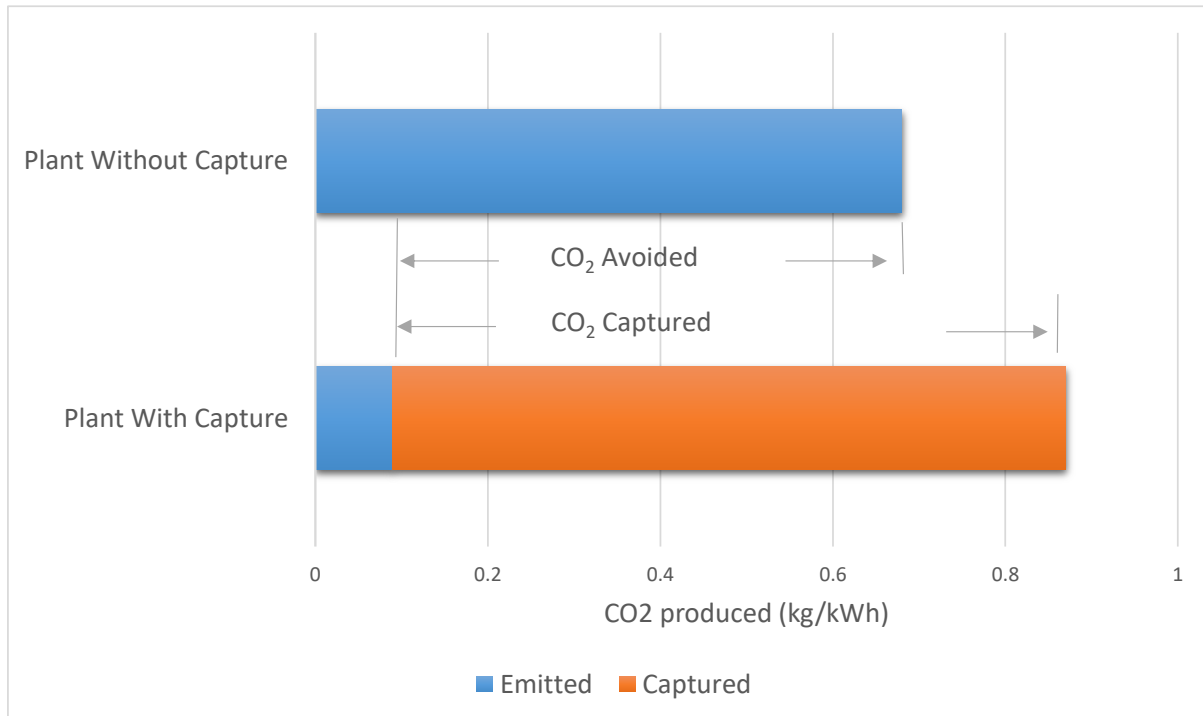
### 5.3.1 Electrical power consumption

The main consumer of electrical power in a carbon capture instalment are the compressors, namely the flue gas blower and the CO<sub>2</sub> compression train. Auxiliaries, such as pumps, also consume power, but to a far lesser extent than the compressors in the process.

In the case of a power plant, the electricity required for these units would typically be drawn from the power plant grid. It is also possible to supply the capture plant with an auxiliary heat and power plant. By adopting this approach, it maintains the electricity generation output of the power plant and this facility could even be used to increase the amount of electricity delivered to the grid if the need arises. Another benefit of this approach is that there is almost no need to modify the current power plant instalment to accommodate the capture plant. Integrating the power plant and capture plant does make deploying the capture plant more complex and costly. However, the benefit of this approach is that a higher thermal efficiency can be realised, resulting in a reduced CO<sub>2</sub> capture cost (Alie, 2004).

Drawing electricity from the grid would have the effect of reducing the net power output from the power plant. This in turn lowers the plant efficiency, since the efficiency of a plant is based on the percentage of the total energy content of the fuel that is converted into electricity. Due to the reduced electricity output of the plant because of the capture process, more fuel has to be combusted in order to meet the demand. For this reason, it is useful to base the cost of capture on CO<sub>2</sub> avoided rather than CO<sub>2</sub> captured, since in the effort to capture CO<sub>2</sub> more CO<sub>2</sub> is created through combustion in order to provide energy for the capture process. The effect of this is a reduction in the thermal efficiency of the power plant. The extent of the reduction is dependent on the type of fuel and process used and would therefore vary between applications.

The concept of CO<sub>2</sub> avoided versus CO<sub>2</sub> captured is illustrated in Figure 5-2, the reference being a PC power plant in the values presented.



**Figure 5-1: Illustration of the concept of CO<sub>2</sub> avoided versus CO<sub>2</sub> captured (Herzog, 1999).**

### 5.3.2 Steam usage

The steam usage in carbon capture section of the plant is confined to the reboiler for regeneration of the amine solvent, since it was assumed the compressors utilised electricity generated by the plant. From simulations, the duty required for the reboiler to regenerate the amine solvent to the necessary condition is known. This heating duty needs to be converted to steam usage in order for its cost to be evaluated. A basic model was used to accomplish this rather than designing the reboiler in each simulation. Although the latter would be a more accurate way of determining steam requirements, it was omitted in order to allow for faster simulation run times. The equation used to determine the amount of steam required to generate the required duty in the reboiler is:

$$\dot{m}_s = \frac{\dot{Q}_{heat}}{H_v} \quad (5-1)$$

Where:

$\dot{m}_s$  is the flow rate of steam required

$\dot{Q}_{heat}$  is the duty of the reboiler

$H_v$  is the vaporisation enthalpy of low-pressure steam

The only decision that needs to be made with regard to this model was the steam pressure since this affects the amount of energy it can provide as well as the cost of the steam. Typically, the pressure is decided by determining the pressure at which the steam shall condense at a temperature that is 10°C above the contents of the reboiler. This corresponds to steam at a pressure of 3.5 bar since the reboiler is typically restricted to an operating temperature of 125°C in order to limit thermal degradation of the amine solvent. It was also assumed that not all of the steam condenses in the reboiler. The amount remaining was taken as 2.5% of the initial flow into the reboiler.

### 5.3.3 Water usage

There are multiple sections where water is used as a cooling medium in the carbon capture process. These include the:

- Direct contact cooler.
- Stripper condenser.
- CO<sub>2</sub> compression train intercoolers.
- Lean amine solvent cooler.

For the direct contact cooler, the amount of water required as a cooling medium can be obtained from the stream results in the Aspen Plus simulation. As with the reboiler, a simple energy balance model was utilised to determine the amount of cooling water required to achieve the cooling duty in the remaining indirect contact heat exchangers. Cooling water was assumed to be supplied from cooling towers at 30°C and was allowed to be heated to a maximum of 45°C. The equation used to determine the amount of cooling water required is:

$$\dot{m}_{cw} = \frac{\dot{Q}_{cool}}{Cp_{cw}\Delta T} \quad (5-2)$$

Where:

$\dot{m}_{cw}$  is the flow rate of cooling water required

$\dot{Q}_{cool}$  is the duty of the cooler

$Cp_{cw}$  is the specific heat of water

$\Delta T$  is the change in temperature of the cooling water

The usage of cooling water extends beyond just the necessary amount to achieve a cooling duty, since there are make-up water requirements. Cooling water is normally part of a cycle involving a cooling tower, where cooling water is continuously recycled between the process units and the cooling tower. This loop is not a closed one as there are water losses brought about by evaporation, blowdown and purging. Evaporation losses are part of the operating principle of cooling towers, however, this loss still adds to make-up water requirements. Blowdown losses, which are also known as windage or drift losses, are a result of the natural or induced draft created in the cooling tower, which results in losses that can be synonymous with spillage. Water in the loop is also continuously drawn-off in order to prevent continuous increase in the concentration of dissolved minerals in the cooling water loop in order to maintain optimum operating efficiency (Cavano, 2008). The equations to determine the required make-up water rate are: (Tecumseh Group, 2006):

$$M = E + B + P \quad (5-3)$$

$$E = \frac{C\Delta TCp_{cw}}{H_v} \quad (5-4)$$

$$Cycles = \frac{M}{P+B} = \frac{M}{M-E} = 1 + \frac{E}{P+B} \quad (5-5)$$

$$B = fC \quad (5-6)$$

Where:

M is the make-up water rate

E is the evaporation rate

B is the blowdown rate

P is the purge rate

C is the total cooling water circulation rate

f is a constant: 0.003 – 0.01 for natural draft cooling tower

0.001 – 0.003 for induced draft cooling tower

0.0001 for cooling towers with blowdown drift eliminators

The term cycles, more commonly known as cycles of concentration, refers to the ratio of the concentration of a soluble salt in the circulating cooling water to the concentration in the make-up cooling water. The choice of soluble salt to use as an indicator is arbitrary, but chlorides are the usual preference. It is a term for describing the number of times that dissolved minerals are allowed to accumulate in the circulating cooling water. In the refinery industry, this ratio is usually set between three and seven, but in large power plants, the cycles of concentration value can be even higher than this (Tecumseh Group, 2006). A greater number of cycles reduces the cost for make-up water and chemicals in the cooling water loop. However, at the same time, a higher number of cycles results in an increased chance for corrosion and mineral deposition to occur (Cavano, 2008).

## 5.4 Costing

For carbon capture applications, MEA is one of the cheaper options as a solvent, with an approximate price of €1450 per ton (ICIS, 2014). DEA has a price of approximately 1.2 times higher than MEA (Merikoski, 2012). In the absence of the commodity price of MDEA, AMP and PZ, the price supplied by chemical companies was used as a means to establish an estimate for these amines. Data from the chemical companies Alfa Aesar and Sigma Aldrich indicate

that MDEA is in the region of 40-50% more expensive than MEA. AMP is significantly more expensive than MEA, since it is somewhat more difficult to synthesize as well as produce than the other amines. Data from Spectrum Chemicals indicated that AMP is approximately 4 times the price of MEA. Sigma Aldrich prices also show that AMP is more expensive, but no valid conclusion about the difference in price could be made since product purities did not match. The cost of PZ is assumed to be 2-4 times more expensive than MEA (Merikoski, 2012). The expense of make-up solvent was considered as a factor in the performance indicator, however, the initial purchase of solvent was excluded.

The prices given in this section are not entirely accurate in terms of the price they may be sold at by the supplier to the industry, since this expense would typically be negotiated between the two parties and would be based on factors such as quantity purchased and future deals. However, they do provide a means by which the cost relationship between various amines can be established, thus allowing for the economical evaluation of the solvents to be accomplished.

**Table 5-2: Estimated amine commodity prices. Based on the conversion 1€=14.63 ZAR, July 2015.**

<b>Amine</b>	<b>Price (€/ton)</b>	<b>Price (R/ton)</b>
<b>MEA</b>	1 450.00	21 213.50
<b>DEA</b>	1 740.00	25 456.00
<b>AMP</b>	5 800.00	84 854.00
<b>MDEA</b>	2 100.00	30 723.00
<b>PZ</b>	4 350.00	63 640.50

The cost of utilities is also an important aspect to be considered in the performance indicator model. In the use of aqueous MEA, it is estimated about two-thirds of the operating cost in the carbon capture section of the plant is due to steam requirements for solvent regeneration (Khalil & Gerbino, 2007). Hence, minimising this is of paramount importance to ensure a solvent is economically viable for the plant. The circulation of cooling tower water also has associated costs due to pumping requirements and cooling tower operation. Make-up for the cooling water in circulation also has to be taken into account due to the continual losses that occur in the system. The values in column 3 of Table 5.3 was determined from the average of the prices presented in column 2. The variance in the values found in literature act as the uncertainty that was incorporated into the sensitivity analysis on the rating model.



**Table 5-3: Estimated utility prices. Based on the conversion 1£= 18.31 ZAR, July 2015.**

Utility	Price (£/ton)	Price (R/ton)
Low pressure steam	6.50 <sup>[1]</sup> , 7.00 <sup>[2]</sup>	123.60
Cooling tower water	0.025 <sup>[1]</sup> , 0.015 <sup>[2]</sup>	0.37
Make-up water	0.50 <sup>[1]</sup> , 0.6 <sup>[2]</sup>	10.08

<sup>[1]</sup> (Pitt, 2003), <sup>[2]</sup> (Coulson & Richardson, 2005)

## 5.5 Amine reclaim and disposal

Degradation of amine solvents is an inevitability. The flue gas to be processed from the combustion of carbonaceous fuels will always contain trace amounts of NO<sub>x</sub>, SO<sub>2</sub> and fly ash, even though a gas treating unit would be present upstream of the carbon capture section of the plant which would be responsible for removing these elements. The flue gas may also contain residual amounts of NH<sub>3</sub>, limestone and gypsum from upstream gas treatment processes (Rochelle, et al., 2011). All of these impurities will result in degradation and corrosion products being formed, which would accumulate in the circulating solvent.

Thus, it is necessary to separate these products from the usable amine in the solvent circulation loop in order to maintain solvent capacity, reduce degradation, maintain energy performance, control corrosion and avoid foaming (Rochelle, et al., 2011). The reclaimer is the unit responsible for removing sludge and high boiling point degradation products from the recyclable amine. A portion of the solvent in circulation would be re-routed to pass through a reclaimer unit, typically 0.5-3% of the total solvent flow. There are multiple methods for solvent reclaim, but thermal reclaim is usually favoured due to the reliability and simplicity of the operation and due to it already being commercially used in the gas treating industry presently. The method chosen for reclaim also depends on the amine in circulation. MEA is reclaimed under atmospheric conditions with the use of low pressure steam, whilst less volatile amines, such as MDEA, generally employ vacuum distillation for reclaim of the solvent (Fisher, et al., 2007). However, due to the variety of degradation products generated complexity of degradation mechanisms explained previously, it is not possible to simulate the reclamation process. Therefore, it was assumed that the costs associated with reclaim is equivalent for all amines, where it is only dependant on the calculated amount of degradation products generated

during the CO<sub>2</sub> capture process. The overall cost for treatment and disposal are combined, since these factors depend on the quantity of the amine to be processed.

**Table 5-4: Costs associated with reclaim, treatment and disposal of amine solvent.**

**Based on the conversion 1\$= 12.57 ZAR, July 2015.**

Operation	Cost (\$/ton)	Cost (R/ton)
Reclaim	850 <sup>[1]</sup>	10 684.50
Treatment and disposal	250 <sup>[2]</sup>	3 142.50

<sup>[1]</sup> (Merikoski, 2012), <sup>[2]</sup> (Sexton, 2013)

## 5.6 Carbon taxes

Carbon taxes are a form of pollution tax, which are levies placed on the amount of CO<sub>2</sub> that is released into the environment by the industrial facility. They act as a means to provide an indirect financial incentive for plants to reduce their emissions, as this would result in a reduced financial liability on the company. Some nations have already implemented carbon tax as part of their environmental policies, due to the impending threat of climate change. Many other nations are set to accept this enactment as well, South Africa being one of them (Glazewski, et al., 2012).

The effect of having a carbon tax levied on the process is included in the performance indicator model. In this study, the capture rate is set at 80%, which is achieved by varying the solvent flow rate and stripper boil up rate to achieve this target. Hence, the carbon tax would be the same for all the amine blends investigated in a particular case study and it would not have a unique effect on the rating scheme. However, it is an important aspect to include, since in practice certain amines and their blends would be capable of absorbing more CO<sub>2</sub> per ton of solvent. Thus, for a given flow rate or stripper boil up ratio, the carbon tax levied on the process would vary for different blends if this approach rather than a set capture rate were adopted.

Carbon taxes, similar to the price of resources, differ vastly from nation to nation. Table 5-5 shows the variation in this tax rate for various countries. The values quoted are converted into South African Rands as well in order to conveniently compare the tax rates. For this study, the carbon tax rate that is to be implemented in South Africa in 2016 was used.

**Table 5-5: Carbon tax rates per ton of CO<sub>2</sub> emitted in various countries. Based on the conversion 1\$= 12.57 ZAR, July 2015 and 1€=14.63 ZAR, July 2015.**

<b>Country</b>	<b>Tax rate (Price/ton of CO<sub>2</sub>)</b>	<b>Tax rate (ZAR/ton of CO<sub>2</sub>)</b>
<b>Chile</b>	USD 5 <sup>[1]</sup>	62.85
<b>Denmark</b>	USD 31 <sup>[1]</sup>	389.67
<b>Finland</b>	EUR 35 <sup>[1]</sup>	512.05
<b>France</b>	EUR 7 <sup>[1]</sup>	102.41
<b>Iceland</b>	USD 10 <sup>[1]</sup>	125.70
<b>Ireland</b>	EUR 20 <sup>[1]</sup>	292.60
<b>Japan</b>	USD 2 <sup>[1]</sup>	25.14
<b>South Africa</b>	ZAR 120 <sup>[1]</sup>	120
<b>Sweden</b>	USD 168 <sup>[1]</sup>	2 111.76
<b>Switzerland</b>	USD 68 <sup>[1]</sup>	854.76
<b>United Kingdom</b>	USD 15.75 <sup>[1]</sup>	197.98

<sup>[1]</sup> (The World Bank, 2014)

## 5.7 Capital

Post-combustion capture with amine solvents is ultimately a retrofit technology for plants already in operation. Therefore, it is possible that these sites will have limited space available for the installation of a carbon capture plant. Thus, there is the potential for the size of equipment required by the carbon capture plant to be limited by this restriction. It is also acknowledged that the annual operating cost of the plant would significantly outweigh the annual capital costs of the plant (Alie, et al., 2005). Hence, only factors associated with the operational expense of the plant are considered as it is of more interest in improving the overall economic viability of the installation. Furthermore, inclusion of the capital cost when assessing solvent performance would excessively increase the complexity of the model as this would involve undertaking a life cycle assessment of the plant to determine the effectiveness of implementing the equipment in question. This was deemed to be of little value considering that operating costs would overshadow the initial capital investment in the life span of the plant and would have a minimal influence when comparing various solvents.

## 5.8 Fuel type and cost

The cost of the carbonaceous fuels used can be an influential factor, since the process of capturing CO<sub>2</sub> is an energy intensive one. In the process of capturing CO<sub>2</sub> from flue gas, more fuel has to be utilised by the plant to meet the required energy demands of the capture process. Fuel cost is typically very sensitive to the different locations around the world and often varies from nation to nation, which can fluctuate drastically over time depending on the market (IEA, 2004). The type of fuel affects the economics of the carbon capture process, since different grades of coal and gas have varying costs and result in streams with differing flue gas compositions. The effect of fuel cost was not incorporated directly into the model. Since steam usage was taken into account in the model by converting the steam requirement into an operation expense, the effect of fuel price would be reflected by variance in the cost of steam.

## 5.9 Flue gas pre-treatment and post-treatment

SO<sub>2</sub>, NO<sub>x</sub> and particulate matter are components that need to be removed prior to the subjection of the flue gas to the CO<sub>2</sub> capture process due to the operational problems they can cause. The amount of these components created is dependent on the fuel source and the levels of these impurities would vary across different sites (Spigarelli & Kawatra, 2013). The reaction between SO<sub>2</sub> and NO<sub>x</sub>, and the amine solvent results in the formation of heat stable salts, thus lowering the active amine component of the solvent. Furthermore, the resulting particulate matter can cause clogging in the absorption tower packing thus hindering the reaction, increasing the pressure drop and increasing foaming. Post-treatment of the flue gas is also required in order to remove any entrained amine in the flue gas. This is usually accomplished by a wash water column or a wash water section in the absorption column (Cousins, et al., 2011). The level of pre-treatment and post-treatment would be site specific and would be set based on minimising the operational expense of the plant by balancing the costs associated with solvent make-up and installing and operating additional systems for removal of impurities (Spigarelli & Kawatra, 2013).

Although pre-treatment is a vital component of the capture process, the effect of its operations on the performance of the capture plant are not taken into consideration. This is because pre-

treatment does not have a unique solvent specific effect and is required for all amines to reduce the amount of solvent degradation. Pre-treatment processes to remove  $\text{SO}_2$  and  $\text{NO}_x$  are already in place at several plants in order for the flue gas to meet environmental regulations prior to release into the atmosphere. Furthermore, in the  $\text{NO}_x$  component, generally only 10% is  $\text{NO}_2$ , which is the compound responsible for the degradation of amine into heat stable salts. The remaining 90% is  $\text{NO}$ , which has no negative effect on the amine solvent, hence it is likely that simply removing the resulting degradation products would be a cheaper alternative than installing measures to limit the  $\text{NO}_x$  content (Rameshni, 2009). Thus, the pre-treatment process is not a new requirement if amine based post-combustion capture technology is retrofitted to the plant although slight tuning of the removal rates may have to be accomplished where this equipment is already present in order to limit the  $\text{SO}_2$  and  $\text{NO}_x$  induced degradation on the circulating amine solvent.

### 5.10 Dehydration of captured $\text{CO}_2$

The dehydration of the captured  $\text{CO}_2$  stream was not considered in the developed Aspen Plus simulation or as part of the performance indicator. This is based on two reasons, the first one being the dehydration process occurs at the end of the capture process. Thus, the solvent selected would have negligible influence on the water removal system. Although the dehydration system would have a parasitic effect on the energy usage in the plant, the energy load utilised would not be solvent specific. The energy penalty and chemical consumption would be linked to the overall  $\text{CO}_2$  capture rate specified and would not have a unique effect on the performance indicator. Secondly, dehydration requirements are mostly related to the final use of the  $\text{CO}_2$ . For use in local enhanced oil recovery (EOR) or storage in local geologic sites, dehydration would not be required. However, if the  $\text{CO}_2$  were to be transported long distances in pipelines, dehydration would be essential to minimise the risk of corrosion (Fisher, et al., 2005). Triethylene glycol is generally the solvent that would be employed in the dehydration process when this procedure is required (Molina & Bouallou, 2013).

### 5.11 Health and environmental effects

The amines considered for carbon capture applications are regarded as hazardous, albeit at different levels depending on the specific amine selected. Since amines are basic and can form strong alkaline solutions, they can cause irritation and sensitisation in the case of human exposure but amines in their original form are non-mutagenic (Lag, et al., 2011). However, in terms of environmental effects, amines are known to be toxic to land and aquatic organisms and have the potential to cause acidification and eutrophication in aquatic environments if released in high concentrations. The main threat amines pose are the degradation products that are formed once they have been released into the environment. Whilst most of the products will not have any adverse health effects, there are a few compounds that of particular concern. The most hazardous of these degradation products is nitrosamines as they are carcinogenic, can contaminate potable water and can negatively affect aquatic organisms (Shao & Stangeland, 2009). A range of nitramines are also produced from degradation reactions, some of which are known to be carcinogenic. Like nitrosamines, they are toxic in an aquatic environment, albeit to a lesser extent (SEPA, 2013).

Although the degradation of amines into products is challenging to determine accurately, amines can be ranked in terms of their potential to cause adverse health and environmental impacts. Firstly, secondary amines have the highest chance of nitrosamine formation followed by tertiary amines and then primary amines. Secondly, amine solvents that have lower vapour pressures are generally safer than solvents with high vapour pressure. Finally, the more stable the amine, the safer it is, since there is a lower risk for the formation of degradation products (Thong, et al., 2012). If these guidelines are abided, the risk of adverse health and environmental impacts of the amines in this study can be ranked as follows:

PZ > AMP > MEA > MDEA > DEA

The health and environmental impact of amines were not taken to be a factor to be included in the performance indicator. This is due to the complexity of the degradation mechanisms, which makes predicting the formation of the concerning degradation products difficult. This makes any discernible difference in health and environmental impact between amines on the performance indicator superficial. Furthermore, the adverse health and environmental impacts of the amines investigated for use in carbon capture are controllable and are not of appreciable

concern in terms of limiting their deployment in CCS applications. Thus, any advantages between amines in this regard would be negligible (Shao & Stangeland, 2009).

## 5.12 Required inputs and rating determination

A summary of the various inputs required to evaluate the rating of a solvent is provided in this section. Inputs can be classified as either *user defined inputs* or *result inputs*. The user-defined inputs would vary from user to user, since these include operation parameters that would vary from site to site as well as resource prices, which fluctuate continuously. The *result inputs* refers to the results obtained from the simulation used to evaluate solvent performance. By entering these variables into the performance model, outputs in the form of costing of the various factors are generated. The equations developed to determine the rating value of each solvent is also shown. A demonstration of calculating the rating value of a solvent is presented in Appendix A in the form of sample calculations.

### 5.12.1 Variable: user defined inputs

- Prices:
  - Amines
  - Water
  - Cooling tower water (CTW) operation
  - Steam
  - Corrosion inhibitors
  - Amine reclaim
  - Amine disposal
  - Carbon tax rate
- Cooling tower operation specifics:
  - Temperature range
  - Purge
  - Blowdown
  - Cycles of concentration

- Steam operation specifics:
  - Pressure
  - Condensation percentage in reboiler
- Power plant specifics:
  - Regular output
  - Efficiency
- Degradation rates
- Reclaimer operating specifics:
  - Slip stream fraction
  - Amine recovery fraction
  - Water recovery fraction
- Weighting factors

#### 5.12.2 Simulation inputs

- Capture rate percentage
- Flow rate of solvent into the system
- Flow rate of amine component:
  - Into the absorber
  - Out of the stripper
  - Vented from the absorber
  - Compressed
- Flow rate of water component:
  - Into the absorber
  - Out of the stripper
  - Vented from the absorber
  - Compressed
- Wash water flow rate
- DCC water flow rate
- Utility Usage
- Total cooler duty



- Total heating duty
- Baseline – simply the above mentioned specifics for the chosen benchmark case (MEA 30 wt. % solution used in this study).

### 5.12.3 Outputs

- Make-up amine cost
- Corrosion inhibitor cost
- CTW cost
- Make-up water cost
- Steam cost
- Reclaimer cost
- Disposal costs
- Carbon tax cost
- Plant efficiency drop
- Total cost of CO<sub>2</sub> captured
- Total cost of CO<sub>2</sub> avoided
- Rating

### 5.12.4 Rating determination

The following set of equations were used to calculate the rating value for each solvent in this study. The equations have not been combined into one distinct formula, but are instead represented as a summation of the contributing effects when determining the rating. This approach of showing equations allows for the addition of other factors to be easily incorporated into the model in future work.

$$C_{T,j,captured} = \sum C_{i,j} \quad (5-7)$$

$$C_{T,i,j,avoided} = C_{T,i,j,captured} \times \frac{\varepsilon_{OP}}{\varepsilon_j} \quad (5-8)$$

$$x_{i,j} = \frac{C_{i,j,avoided}}{C_{T,i,j,avoided}} \quad (5-9)$$

$$x_{n,i,j} = \frac{w_i \times x_{i,j}}{\sum w_i \times x_{i,j}} \quad (5-10)$$

$$Rating (R) = \sum x_{i,j} \times \frac{C_{i,b,avoided}}{C_{i,j,avoided}} \quad (5-11)$$

Where:

- C – refers to cost
- T – refers to total
- j – refers to the various cases, eg. 30 wt. % MEA at 0.18 loading, 15wt. % MEA/15 wt. % AMP etc.
- i – refers to input, eg. make-up amine, steam cost etc.
- $\varepsilon$  – refers to plant efficiency
- OP – refers to original plant
- x – refers to percentage of input variable contributing to total cost – eg. make-up amine being 15% of total cost etc.
- n – refers to a normalised value
- w – refers to the weighting factor
- R – refers to rating
- b – refers to benchmark case

The rating calculation procedure is applied to all the solvents of interest in a given application. Since there are various parameters that can affect the performance of a solvent, it is possible to end up with multiple ratings for a single solvent based on operational parameters. These operational parameters can include factors such as the solvent lean loading, absorber pressure,

stripper pressure and the CO<sub>2</sub> capture rate to name a few. However, in this study, only solvent lean loading was varied when determining the rating value for each solvent. The lean loading that produces the highest rating value becomes the representative rating value for that specific solvent when comparing it to the ratings of other solvents. An additional use of the performance indicator model, apart from solvent comparison, is that it can be utilised for optimising process parameters by determining which set of conditions produces the highest rating value for a given solvent in a carbon capture process.

The concept of placing the performance of solvents alongside one another was previously accomplished by Padurean et al.,2011. However, only energy consumption was utilised in making the comparison between solvents, whilst this study seeks to incorporate further influential factors. Furthermore, the various energy consumptions were simply stacked upon one another to determine the most energy efficient solvent for the process, which does not incorporate the cost aspect of the carbon capture process. This study aims to include the cost in the analysis, since minimising the cost of capture would be the primary focus in all applications of carbon capture.

The details of the method by which the rating model is developed and interpreted for a range of solvents shall be elaborated further in Chapter 6. A full detailed explanation of the calculation procedure by which the rating value for each solvent is determined is presented in the form of sample calculations in Appendix A.

# Chapter 6

## Results and Discussion

This section provides an analysis of the results achieved in this work. It begins by introducing the literature study that was used as the comparison for this study, and the regression of the data set to determine the weighting factors used in equation the 5-10 presented in Chapter 5. It then proceeds to describe the results achieved in the three case studies, namely the PC power plant, NGCC power plant, and cement plant.

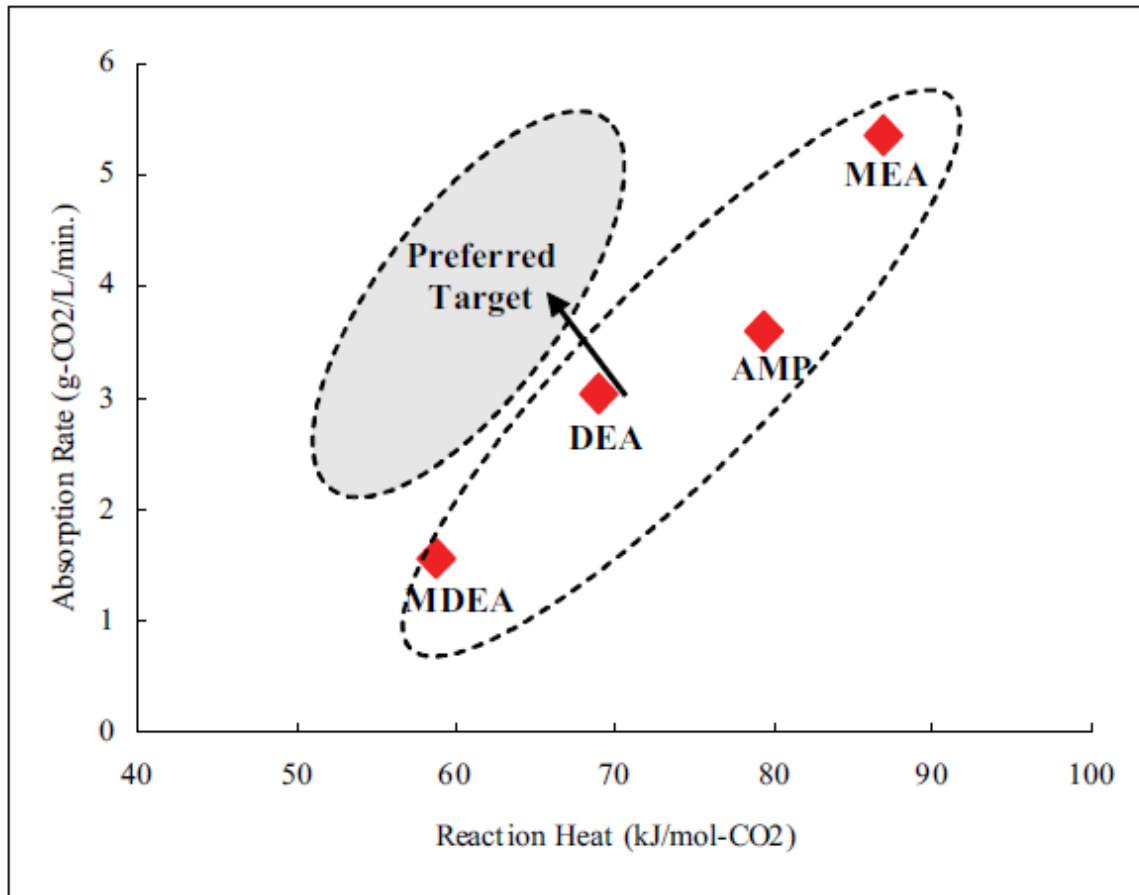
### 6.1 Literature chosen for comparison

Padurean et al., 2011, performed a multi criterial analysis of amines and their blends to determine the most efficient solvent for carbon capture. The solvents investigated in the literature study included MEA, DEA, AMP and MDEA. The study focused primarily on energy consumption during the carbon capture process, in order to assess which blend was the most efficient at capturing CO<sub>2</sub>, using mega joules/kg CO<sub>2</sub> captured as the method of evaluation. The energy sources included in the analysis included heating and cooling units in the process, as well as electrical energy consumption from operations such as pumping and compression. The literature study included the use of a CO<sub>2</sub> drying section in the capture process, which is absent from this study. However, the effect of this on the results obtained in this study was assumed to be minimal, since the CO<sub>2</sub> drying section, as well as the CO<sub>2</sub> compression section, are not solvent specific processes. These processes are primarily influenced by the volume of CO<sub>2</sub> fed into these sections, and not by the specific solvent utilised in the CO<sub>2</sub> capture process.

Since the literature expressed results in the form of a specific energy consumption, these were converted into a rating via the equations developed in this study, where specific energy consumption replaced the use of costs. This conversion to a rating value did not make use of any unique weighting factors. For the literature case, a 30 wt. % MEA solution was used as the benchmark solvent as well.

The literature results serve as a mean by which the adjustable weighting factors in the performance indicator model are regressed for. Although the number of factors taken into account in the rating scheme in this study exceed that of the literature investigation, energy expenses make up a predominant proportion of the total cost of carbon capture, approximately 60-80% depending on the amine. Thus, it was established that these two studies could be compared with some degree of confidence. It should be noted that the regression could be performed against any literature results. At present, the investigation completed by Padurean et al., 2011, represents the only study found in terms of assessing several solvents based on multiple factors simultaneously, hence it is used in this study.

Figure 6-1 shows the relationship between heat of reaction and absorption rate of CO<sub>2</sub> for the amines of interest in this study. A trend can be clearly established from this graph that the higher the heat of reaction, the higher the absorption rate. A higher heat of reaction results in a higher energy requirement for regeneration of a given amount of solvent, i.e. a higher specific regeneration energy. A higher absorption rate results in a lower solvent recirculation rate for a given flue gas flow rate at a specified CO<sub>2</sub> capture rate. This implies that MEA will have the highest specific energy requirement for solvent regeneration and the lowest L/G ratio (solvent flow rate/flue gas flow rate), whilst the converse is true for MDEA. These two factors have to be looked at together, since the total regeneration energy requirement of a system is based on both the specific energy requirement and the solvent recirculation rate. The main goal of blending solvents is to reduce the total regeneration energy requirement. This is accomplished by creating a blend that has properties in the “preferred target” area of Figure 6-1.



**Figure 6-1: The trade-off between absorption rate and reaction heat (Chowdhury, et al., 2011).**

Table 6-1 presents the results that were achieved by Padurean et al, 2011. Unlike the work accomplished in this study, the CO<sub>2</sub> capture rate was not fixed to a specific value in the literature study. As previously mentioned, only the energy consumption involved in the capture process for each solvent was recorded, namely the heating duties, cooling duties, and electrical power consumption.

**Table 6-1: Specific energy consumption for various amines and their blends (Padurean, et al., 2011).**

<b>Solvent (wt.% amine)</b>	<b>Capture rate (% CO<sub>2</sub>)</b>	<b>Cooling (MJ/kg CO<sub>2</sub>)</b>	<b>Heating (MJ/kg CO<sub>2</sub>)</b>	<b>Power (MJ/kg CO<sub>2</sub>)</b>
<b>30 MEA</b>	90.315	297.808	291.615	0.169
<b>30 DEA</b>	93.4	310.781	292.906	0.274
<b>50 MDEA</b>	89.306	344.301	336.17	0.467
<b>30 AMP</b>	93.815	268.904	242.878	0.171
<b>10 MEA + 20 DEA</b>	90.082	323.264	313.421	0.275
<b>20 MEA + 10 DEA</b>	95.837	372.544	346.303	0.275
<b>10 MEA + 20 AMP</b>	90.508	289.767	260.583	0.169
<b>20 MEA + 10 AMP</b>	96.241	292.454	266.798	0.167
<b>10 DEA + 20 AMP</b>	91.115	262.282	234.103	0.184
<b>20 DEA + 10 AMP</b>	95.397	324.215	302.275	0.28
<b>10 MDEA + 20 AMP</b>	95.841	297.999	268.5	0.263
<b>20 MDEA + 10 AMP</b>	90.555	282.312	250.768	0.269
<b>10 MDEA + 20 MEA</b>	92.575	309.519	280.267	0.212
<b>20 MDEA + 10 MEA</b>	90.402	340.167	310.614	0.304
<b>20 MDEA + 10 DEA</b>	91.398	323.11	293.612	0.33
<b>10 MDEA + 20 DEA</b>	95.847	301.89	269.42	0.281

The results presented in Table 6-1 were converted to a rating value, in order to allow for easier comparison with the results achieved in this work. This was accomplished by using equations 5-7 to 5-11 presented in Chapter 5, where cost in these equations was replaced with energy consumptions. CO<sub>2</sub> capture rates in the literature study were not consistent for all the solvents investigated. This was accounted for in the rating model by treating the capture rate as an efficiency and dividing the rating values obtained by the CO<sub>2</sub> capture rate achieved by each solvent. The resultant rating values that will be used as the comparison for the results achieved in this study are illustrated in Figure 6-2.



**Figure 6-2: Ratings of various amines and their blends from Padurean et al.,2011.**

In relation to Figure 6-2, it is observed that 30 wt. % AMP considerably out performs the MEA benchmark, due to its lower heat of reaction. This results in a lower regeneration energy requirement. However, this is not the case for 30 wt. % DEA and 50 wt. % MDEA, even though they have lower reaction heats than MEA and AMP. Whilst the specific regeneration energy of DEA and MDEA is lower, their absorption rates are also lower, which results in a higher required solvent recirculation rate to meet the CO<sub>2</sub> capture target. This recirculation rate is high enough to offset the benefit of a lower specific regeneration energy, such that the total regeneration energy requirements for 50 wt. % MDEA becomes higher than that of 30 wt. % MEA, whilst 30 wt. % DEA performs only marginally better than 30 wt. % MEA.

Figure 6-2 shows that the blends of DEA/MEA have a lower rating value than either of its single amine solvent counterparts. Whilst DEA reduces the specific regeneration energy in the blend, it decreases the absorption rate, and hence increases the required solvent recirculation rate to an extent where the overall energy requirement of the system becomes higher. On the contrary, blends of MEA/AMP performed better than their individual amine counterparts. AMP, like DEA, would lower the specific regeneration energy requirement, but it maintains the absorption rate of the solvent better than DEA, hence the required solvent recirculation rate



remains low enough to achieve a reduced overall energy requirement. In the blend of AMP/DEA, the specific regeneration energy remains low enough to offset the higher solvent recirculation rate and achieve a lower overall energy consumption. A similar explanation can be applied to the blend of AMP/MDEA. For the blend of MEA/MDEA and DEA/MDEA, it is observed that when MDEA is the minor component, the overall energy requirement of the system is lower than the benchmark due to the reduction in the specific regeneration energy that MDEA creates. However, once MDEA becomes the major component in these blends, the higher solvent recirculation rates once again offset the benefit of a low specific regeneration energy and increase the overall energy consumption.

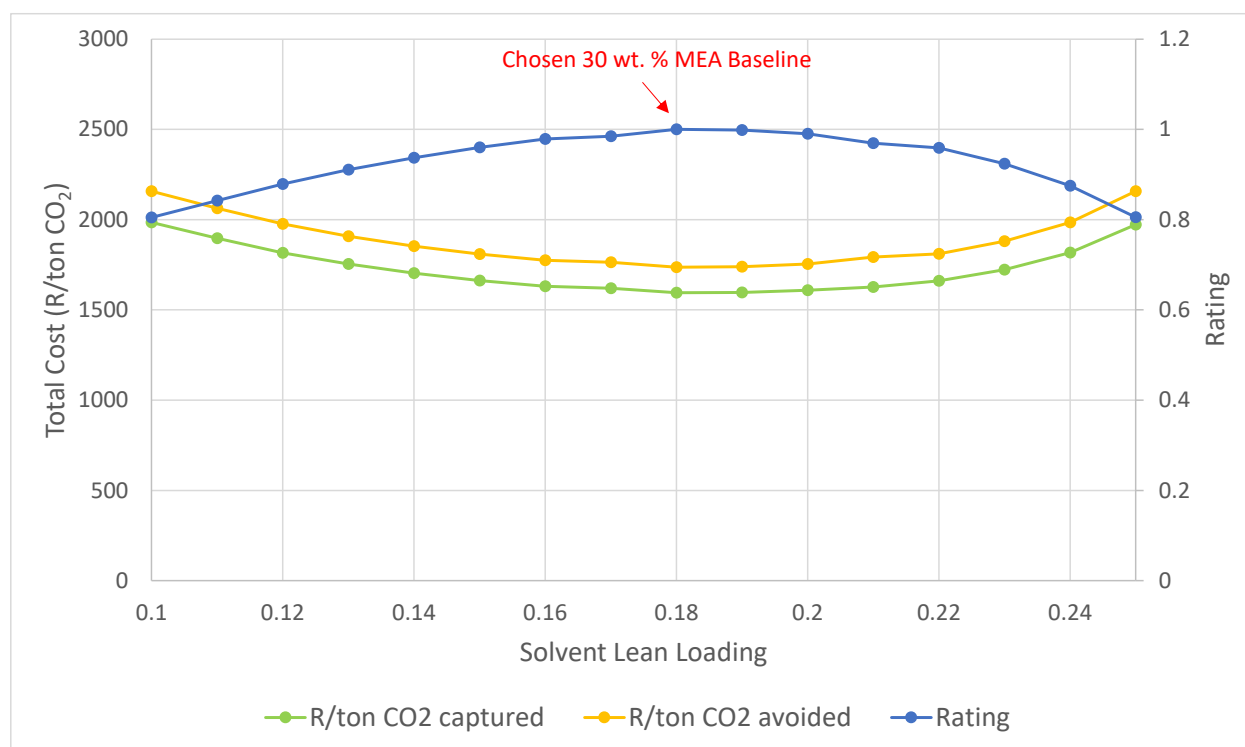
Although Figure 6-2 shows that there are multiple blends that obtained higher rating values than the MEA benchmark, Padurean et al. concluded that 30 wt. % MEA and 30 wt. % AMP, along with their blends, give the best results as solvents in the carbon capture process. The literature study did not provide an explicit reason for discounting blends that had comparably higher ratings than the benchmark, although a highly probable reason for this can be provided. In the literature study, column diameters were not present under the specifications section. This would imply that column diameter was a variable in the study that was adjusted during each simulation to accommodate the desired capture rates for each solvent. With size limitations in mind, it may have been concluded that MEA/AMP blends were the optimal solvents for CO<sub>2</sub> capture.

## 6.2 Determining the operating point.

This section describes the procedure followed to obtain the rating value for each of the amine solvents investigated. Since the loading of the solvent plays a critical part in the absorption characteristics of the solvent, it is important to determine the optimum operating point for each solvent. This process is explained for the 30 wt. % MEA solvent used in the PC power plant case study.

The optimum operating conditions for the 30 wt. % MEA system is the point at which the individual costs combine to form the lowest overall CO<sub>2</sub> capture cost. This is performed by performing simulations over a wide range of operable lean loadings. This point also becomes the benchmark operating point for the specific case study of interest, since 30 wt. % MEA is

taken as the benchmark solvent. In the coal power plant case study, the optimal operating condition occurs at a lean loading of 0.18 for a 30 wt. % MEA solvent. The loading of the solvent refers to the ratio of all the CO<sub>2</sub> containing species in a solvent to all the amine containing species in a solvent on a molar basis. The term lean loading simply refers to the point in the system where the loading is the lowest, which is typically the stream that enters the absorber. The process of determining the optimum operating point is graphically illustrated in Figure 6-3.

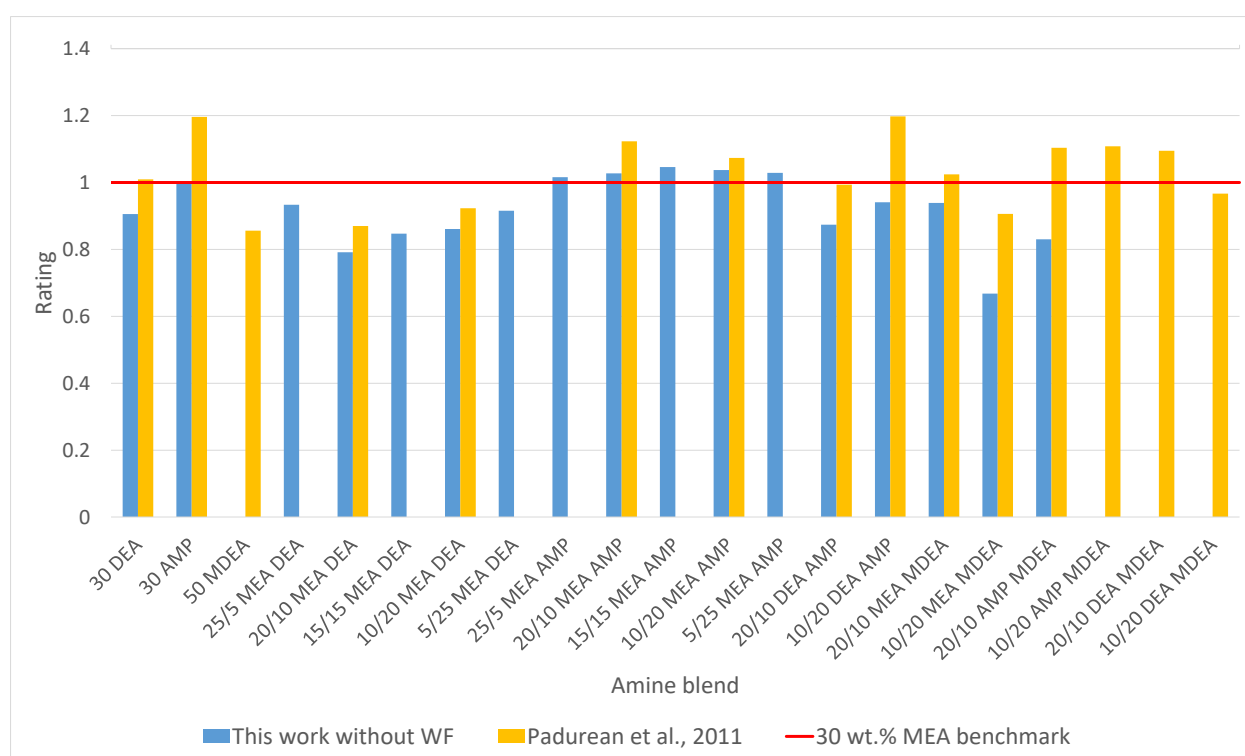


**Figure 6-3: Illustration of determining the optimal operating point for each solvent investigated.**

When the rating formulas are applied to the benchmark operating point, it results in a rating of one. Thus, when the rating calculation are completed for other amines and their blends, any rating below one will show an inferior performance, whilst a rating above one will show a superior performance, as compared to the benchmark case. The process that was used to determine the optimum operating point for the benchmark case was also carried out for each of the other amines and their blends, in order to ascertain the point that produces the best rating value. This result, and its individual factor parameters, then becomes the representative case for that specific amine blend.

### 6.3 Results achieved for the PC power plant (without weighting factors)

It was observed that the rating values of the amines in this study were lower than of its literature counterparts. However, similarities in the general trend of amine performance relative to one another can be observed, as shown in Figure 6-4. This disparity in the absolute rating values between the two studies can be explained by the fact that the literature study only took into account the energy considerations of the system when evaluating the amines and their blends. The individual contributions of each of the considered factors to the overall rating is tabulated in Tables B-1 to B-3 in Appendix B.



**Figure 6-4: Rating of various amines and their blends without the weighting factor (WF) in a PC power plant.**

For instance, the ratings of 30 wt. % AMP and 30 wt. % DEA in this study are considerably lower than that of the literature rating values, since the current work takes into account the required amine make-up rate. DEA has the highest degradation rate, whilst AMP has the highest vent rate of the amines considered in this study. This results in these two amines having high make up requirements, in comparison to MEA. Since both these amines are more expensive than MEA (DEA 1.2 times more expensive than MEA whilst AMP is 4 times the

price of MEA), by taking into account the cost of implementing these amines in a carbon capture process, it reduces their rating considerably when compared to the literature study, due to the cost associated with make-up amine requirements. This explanation also holds true for the blends of DEA and AMP, which can also be seen to have considerably lower ratings than their literature counterparts. The difference between the two studies is smaller for blends containing MEA, since incorporating MEA into the blend reduces the make-up requirements of DEA and AMP, hence reducing the disparity in rating values that arises from high solvent make-up expenses. For the blends containing MDEA, the rating values in this study are once more lower than literature. Although MDEA lowers the solvent regeneration energy requirement per ton of solvent, it increases the required solvent flow rate of the system to achieve a given CO<sub>2</sub> capture rate, due to its much slower absorption rate, to a point where the overall energy requirement of the system is higher. Higher recirculation rates also result in higher make-up requirements, due to increased amounts of degraded and vented solvent.

It can be seen that there are a few solvent blends that are absent from the graph for comparison with the literature study, more specifically the ones containing MDEA, namely 50 wt. % MDEA, 10 wt. % AMP/20 wt. % MDEA, 20 wt. % DEA/10 wt. % MDEA and 10 wt. % DEA/20 wt. % MDEA. The reason for their exclusion is that the recirculation rates required for these blends to meet the specified CO<sub>2</sub> capture rate was higher than that which could be supported by the column sizes used in this study. The column sizes in this study were limited to 13 metres, as this is considered to be the largest feasible size that can be implemented in carbon capture applications (Kothandaraman, 2010). Hence, these blends could not be evaluated without the addition of another absorber and stripper train in the process, which would then not allow for fair comparison between all the amine systems, and their blends. Among the blends investigated, MEA/AMP blends were the only solvents that outperformed the MEA benchmark.

Referring to the results produced by Padurean et al., 2011, it was concluded in the literature study that the amines MEA and AMP, along with their blends, produced the most promising results, even though other amine combinations yielded comparable rating values. As previously explained, this was probably due to size limitations being considered. Although no specific mention of this is made in the literature study, it remains a highly plausible explanation considering the results achieved in this study.

## 6.4 PC power plant results achieved with weighting factors

The necessity of introducing an adjustable parameter is due to the performance indicator model being developed on a monetary basis. Whilst this basis was convenient, since a cost could be attached to all factors considered, it does leave the model susceptible to changes in price of commodities over time, as well as differences in price from nation to nation. The concept of introducing a weighting factor is to create a set of adjustable parameters that can be used to improve the accuracy of the performance indicator model to take into account these aforementioned variations. Its purpose is synonymous with that of adjustable parameters used in thermodynamic models.

When the initial regression for the weighting factor was performed without bounds, it was found that the weighting factors for some factors became near zero values, which essentially removed them from the model. The reason for this is that the literature study only took energy considerations into account. Thus, when performing the regression, the solution that optimised the objective function was one where energy was predominantly favoured by the weighting factor. As a result of this, bounds on the weighting factor were imposed in order to ensure that the regression would not eliminate, or exaggerate, the effect of any of the factors included. The range imposed on each weighting factor was 0.25 – 2. However, this range can be redefined should it be deemed necessary.

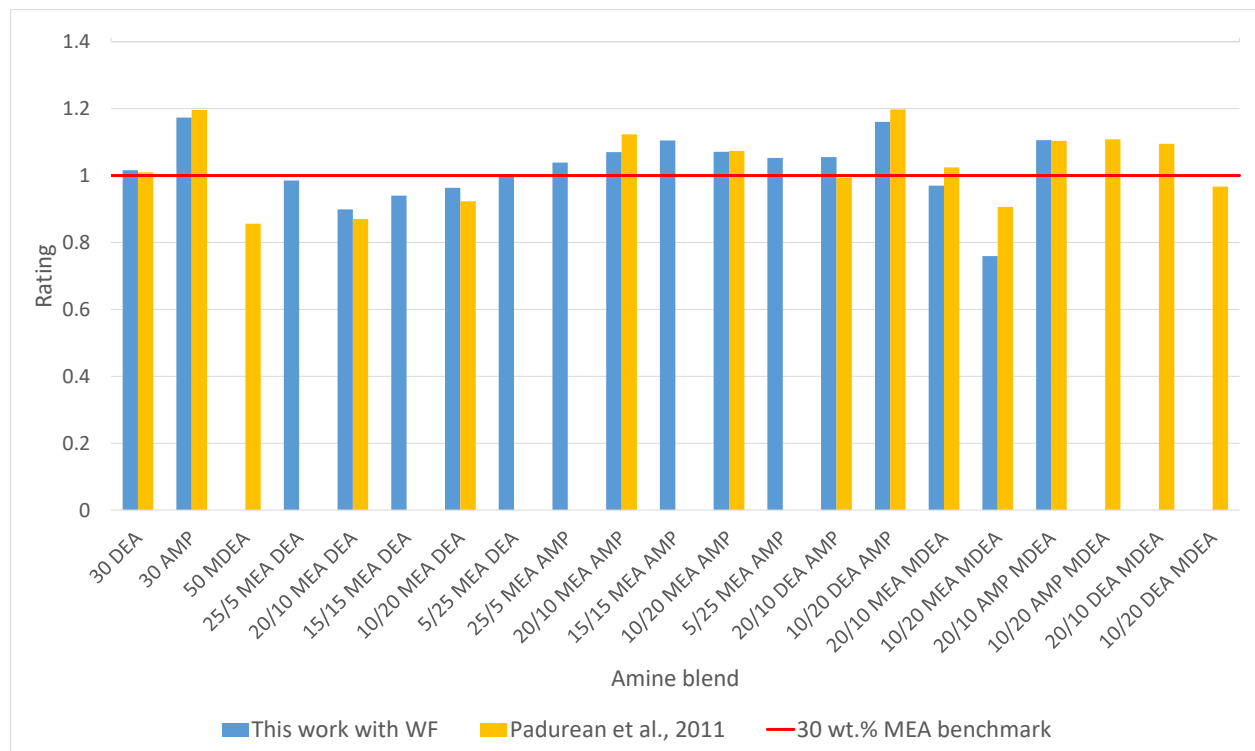
Figure 6-5 was constructed with the use of the weighting factors, the values of which were regressed for against the adapted literature data by minimising the following objective function:

$$OF = \sum (R_{tw} - R_l)^2 \quad (6-1)$$

Where:

$R_{tw}$  refers to the rating value achieved in this study.

$R_l$  refers to the rating value adapted from literature.



**Figure 6-5: Rating of various amines and their blends with the weighting factor in a PC power plant.**

It can be observed in Figure 6-5 that the agreement between the rating values achieved in this work and the literature ratings was greatly improved upon the inclusion of the regressed weighting factors, whilst still maintaining the general trends observed in the results achieved without the weighting factors. This justifies the ability of the weighting factor in being used as a tool to emulate results more accurately. The individual contributions of each of the considered factors to the overall rating is tabulated in Tables B-10 to B-12 in Appendix B.

The regressed weighting factor values for each of the parameters of interest in this study is presented in Table 6-2. It is observed that for many of the factors that the regressed values tend towards the limits imposed, except for steam and amine cost. These two factors have the most predominant influence on the rating model. Therefore, influencing these factors has the greatest effect on the ratings achieved. Furthermore, the results were regressed against a literature study that only took into account the energy considerations of the system. Thus, the fine-tuning that would be provided by the weighting factors on the remaining parameters to improve the correlation with literature could not occur, since the impact of these more minor influences were not captured in the literature study.

The error in the Table 6-2 refers to the standard error obtained between the results achieved in this study and literature. It can be observed that upon regression of the weighting factors, the error improves by 87.3%.

**Table 6-2: Original and regressed weighting factor values for PC power plant case study.**

<b>Factor</b>	<b>Original</b>	<b>Regressed</b>
<b>Amine</b>	1	0.484
<b>Corrosion Inhibitor</b>	1	2
<b>Cooling Tower Water Cost</b>	1	0.25
<b>Makeup Water Cost</b>	1	0.25
<b>Steam Cost</b>	1	0.911
<b>Reclaimer Cost</b>	1	0.25
<b>Amine Disposal Cost</b>	1	0.25
<b>CO<sub>2</sub> Taxes</b>	1	2
<b>Error</b>	0.281	0.036

## 6.5 Sensitivity analysis

A sensitivity analysis was undertaken in order to measure the extent of the deviation on the rating values presented in this study. This was accomplished by varying the user-defined inputs to quantify the effect on the rating scheme obtained.

For factors where a price had to be specified, the standard deviation of a sample of various prices for that resource was determined and used as the uncertainty in price for that specific commodity. A similar process was adopted for determining the uncertainty in the degradation rates used in this study. For user-defined inputs, such as cooling water operating ranges, the lower and upper limits of these factors would typically be user defined specifications as well, which would then represent the uncertainty factor applied to these parameters. By combining all the uncertainties in a manner that lead to an increase in rating values and all the uncertainties in a manner that leads to a decrease in rating values, the respective upper and lower limits on the rating results achieved in this study were determined. The individual deviation results for each of the blends investigated is presented in Table 6-3.

**Table 6-3: Sensitivity analysis on performance ratings for PC power plant based results.**

<b>Solvent (wt. %)</b>	<b>Rating</b>	<b>+ Error</b>	<b>- Error</b>
<b>30 DEA</b>	1.0160	0.9471	1.1022
<b>30 AMP</b>	1.1731	1.1168	1.2393
<b>25/5 MEA DEA</b>	0.9853	0.9810	0.9901
<b>20/10 MEA DEA</b>	0.8987	0.8703	0.9307
<b>15/15 MEA DEA</b>	0.9398	0.9080	0.9765
<b>10/20 MEA DEA</b>	0.9634	0.9236	1.0104
<b>5/25 MEA DEA</b>	1.0030	0.9454	1.0732
<b>25/5 MEA AMP</b>	1.0385	1.0345	1.0430
<b>20/10 MEA AMP</b>	1.0703	1.0624	1.0790
<b>15/15 MEA AMP</b>	1.1047	1.0936	1.1173
<b>10/20 MEA AMP</b>	1.0712	1.0361	1.1109
<b>5/25 MEA AMP</b>	1.0526	1.0044	1.1084
<b>20/10 DEA AMP</b>	1.0549	0.9935	1.1301
<b>10/20 DEA AMP</b>	1.1603	1.1020	1.2303
<b>20/10 MEA MDEA</b>	0.9699	0.9633	0.9759
<b>10/20 MEA MDEA</b>	0.7591	0.7461	0.7714
<b>20/10 AMP MDEA</b>	1.1059	1.0528	1.1658
<b>Standard error</b>		<b>0.0225</b>	<b>0.0277</b>
<b>Average of + and -</b>		<b>0.0251</b>	

The average deviation is plotted in the form of error bars on the rating value in Figure 6-6, instead of using the unique values presented in the Table 6-3 above. As with all models, the error would vary depending on the band that the model is operating within. Thus, it will always have a unique value for each blend investigated. However, it is critical that the overall error of the model be within reasonable limits, in order to have a higher degree of confidence in the accuracy of the rating values achieved for the various solvents.

From Figure 6-6 below, it can be seen that the 2.51% error does not cause significant alterations to the results achieved. It can be observed that the bottom error bars on the MEA/AMP blends remain above the benchmark, which supports prior conclusions of this blend as the optimal carbon capture solvent for this case study.





**Figure 6-6: Sensitivity analysis on performance ratings for PC power plant based results.**

## 6.6 Result for the NGCC and cement plant case studies without weighting factors

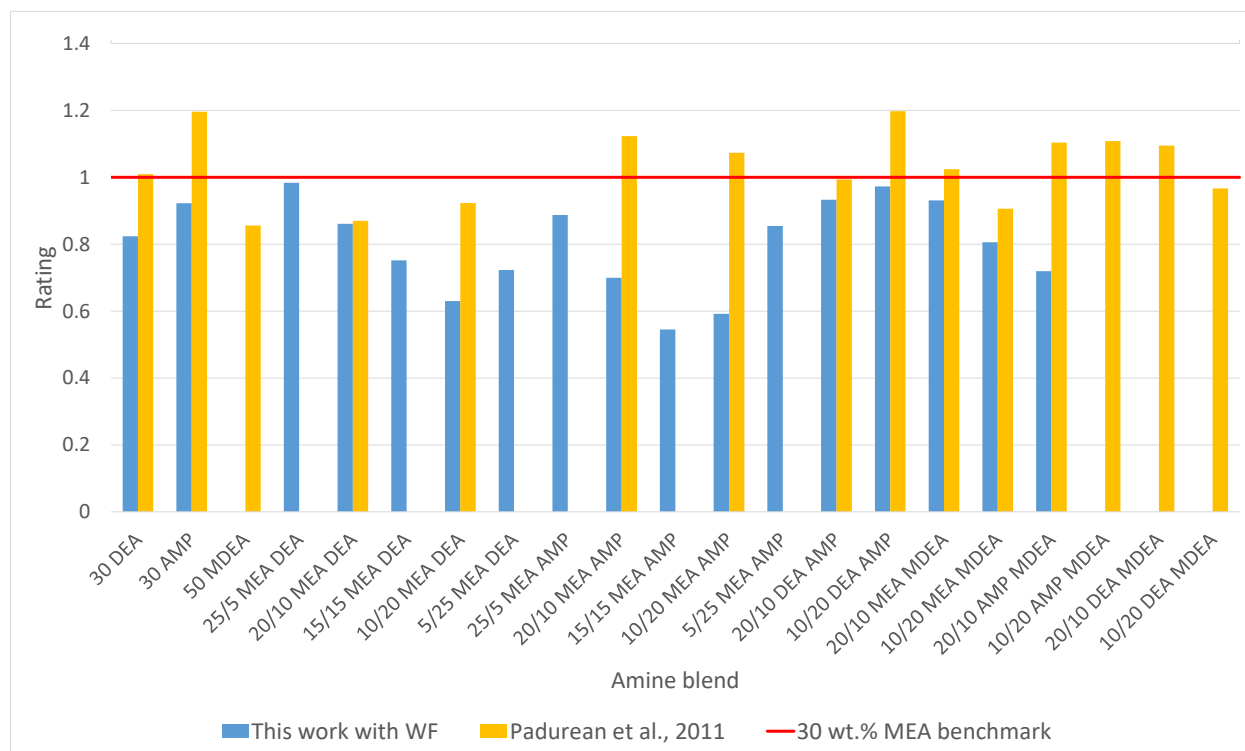
The work presented by Padurean et al., 2011, represented the only source of literature found that performed a multi criterial analysis of amine solvent blends. Unfortunately, the literature study only conducted the investigation based on simulations using a flue gas with comparable properties to the flue gas used in the PC power plant.

Very few studies in literature have been accomplished to create simulation-based models for carbon capture using flue gas from NGCC power plants and cement plants. These two cases are rare in comparison with PC power plants and they have been completed using only individual amines to create the simulation model. No multi criterial studies were identified, where solvent comparisons were undertaken using NGCC and cement plant case studies. Thus, it is not possible to conduct an evaluation between the results achieved for the NGCC and cement plant cases in this study and the respective literature investigations in a similar manner as previously completed for the PC power plant case study.

Although there are no literature results to confirm the validity of the amine ratings attained for the NGCC and cement plant cases, the agreement of results achieved between the PC power plant case study and the work by Padurean et al., 2011, serves as a justification for the techniques utilised and results obtained in this study. On this basis, an analysis of the performance ratings achieved for these two case studies was performed. However, it was not possible to introduce weighting factors into the model. The literature ratings adapted from the results of Padurean et al., 2011, as previously used in the PC power plant case study, are plotted alongside the ratings developed in this study for the NGCC and cement plant case studies. Although the literature results refer to a PC power plant application, they are used here for illustrative purposes to demonstrate the difference in performance ratings achieved from a change in the properties of the flue gas. This seeks to emphasise the pros and cons each amine will have in each application. In the two remaining case studies, it can be seen once more that rating values are absent for certain blends. This is due to the size limitations imposed on the columns in this study, which prevents some solvents from being evaluated due to their high solvent recirculation rates. This explanation was elaborated on previously in section 5.3 for the PC power plant case study, which also applies in these case studies.

In the NGCC power plant case study, the individual amine solvents of 30 wt. % DEA, and 30 wt. % AMP are both seen to perform worse than the benchmark case. The lower CO<sub>2</sub> concentration in the NGCC power plant case study hindered these amines, since their slower reaction rate resulted in high solvent recirculation rates, which offset the benefit of their lower specific regeneration energy requirements. It can be observed that for both the MEA/DEA and MEA/AMP blends that the performance rating decreases to values below both of their individual amine counterparts. Whilst the MEA component in each of these blends will aid in reducing the required solvent recirculation rate, it simultaneously increases the specific regeneration energy requirement to levels whereby the total energy requirement of the system is higher. An opposing result is witnessed for the blends of DEA/AMP, where the rating of the blend is higher than the individual amine constituents. However, its performance rating still remains below that of the benchmark, and is thus of no interest. The individual contributions

of each of the considered factors to the overall rating is tabulated in Tables B-4 to B-6 in Appendix B.



**Figure 6-7: Rating of various amines and their blends without the weighting factor in NGCC power plant case study vs ratings in a PC power plant by Padurean et al., 2011.**

In the cement plant case study, the results as plotted in Figure 6-8 indicate that 30 wt. % DEA has a comparable rating with the benchmark, whilst 30 wt. % AMP exceeds the performance of the benchmark. The higher CO<sub>2</sub> concentration in the flue gas from the cement plant aids in increasing the reaction rate of DEA and AMP with CO<sub>2</sub>. The higher reaction rate assists in lowering the required solvent recirculation rate. However, only in the case of AMP is the flow rate reduced significantly enough to benefit from the lower specific regeneration energy requirement that these two solvents possess. Thus, the total regeneration energy requirement for AMP remains below that of the benchmark, whilst DEA has a requirement comparable with that of the benchmark, which results in only AMP having a rating value considerably higher than that of the benchmark.

For blends of MEA/DEA, it can be observed that combining these two amines produces solvents that have performance ratings slightly higher than the individual constituent amines. This occurs in the blend because MEA reduces the required solvent recirculation rate, whilst

DEA lowers the specific regeneration energy, in such a way that on each occasion the overall energy consumption is lower than that of its individual counterparts, hence resulting in marginally higher performance ratings. This result follows the trends observed in blends of MEA/AMP in the PC power plant case study.

In blends of MEA/AMP, it can be witnessed that the rating value increases as the weight percentage of AMP in the blend increases. This indicates that the addition of MEA to AMP does not enhance the properties of the solvent, but also does not subtract from it to such an extent that the performance ratings dropped to values below both of its individual constituents. A similar result is observed for blends of DEA/AMP.

In all cases of addition of MDEA to the system, it can be seen that the blend either has a rating lower than that of the benchmark, or is absent due to the extent by which MDEA increases the solvent recirculation rate. This results either in a higher required energy for the system, or in prevention of an evaluation due to violation of the constraints in the column size. The individual contributions of each of the considered factors to the overall rating is tabulated in Tables B-7 to B-9 in Appendix B.



**Figure 6-8: Rating of various amines and their blends without the weighting factor in cement plant case study vs ratings in a PC power plant by Padurean et al.,2011.**

### 6.7 Results for the NGCC and cement plant case studies with weighting factors

Although no multi criterial analysis study based on NGCC power plants and cement plants was found in literature, the weighting factor of these two remaining case studies were still regressed for against the PC power plant based results found in the work of Padurean et al.,2011. This was accomplished to assess the capability extent of the weighting factors in adjusting results to better match literature when the literature used is of the incorrect type.

For the NGCC power plant case study, a 26.1% improvement in the error is obtained upon application of the regressed weighting factors, whilst the improvement in error for the cement plant case study was only 0.2%. Both of these improvements are vastly inferior to that of the 87.3% that was obtained in the PC power plant case study. The failure of the weighting factors to significantly improve the error is further compounded by the fact that the original error in these systems was far higher than the PC power plant. Although this higher error was expected,

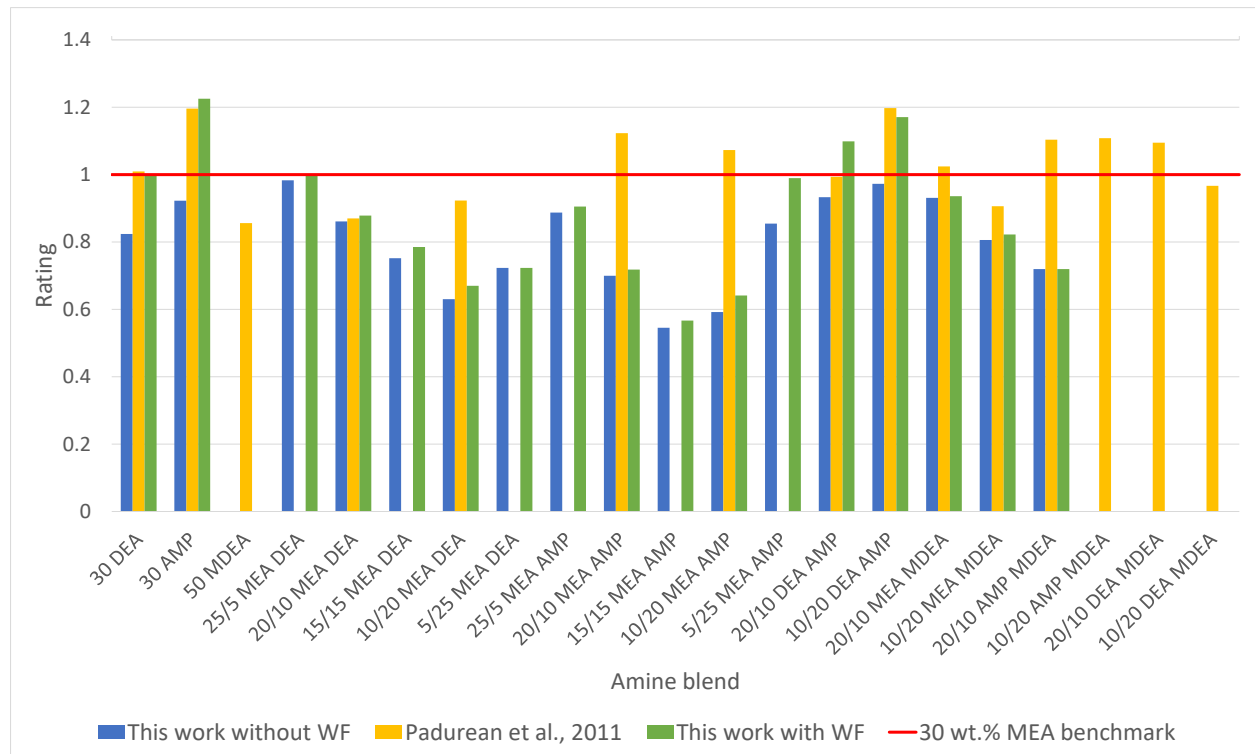
due to the inappropriate literature data set, a higher error creates a greater opportunity for improvement, which the weighting factors were unable to accomplish in these two case studies.

In reference to Figure 6-9, inclusion of the weighting factors significantly changed the performance ratings of only DEA and AMP, and their associated blends, whilst the effect on the remaining blends was marginal. In Figure 6-10, it was observed that incorporating weighting factors into the model had minimal effect on the performance rating across all blends, which would be expected considering only a 0.2% improvement in error was achieved. The individual contributions of each of the considered factors to the overall rating is tabulated in Tables B-13 to B-15 in Appendix B and Tables B-16 to B-18 in Appendix B for the NGCC and cement plant case studies respectively.

The combination of the above results establish the weighting factors as tuning parameters, whose use is limited to only tweaking the performance ratings obtained in order to better correlate the ratings achieved against the desired data set and is not capable of altering the results achieved in its entirety. This result is analogous with that of adjustable parameters in thermodynamic models, where the regression of parameters against literature results can only create an accurate system model if the correct thermodynamic model is used.

**Table 6-4: Original and regressed weighting factor values for the NGCC power plant case study.**

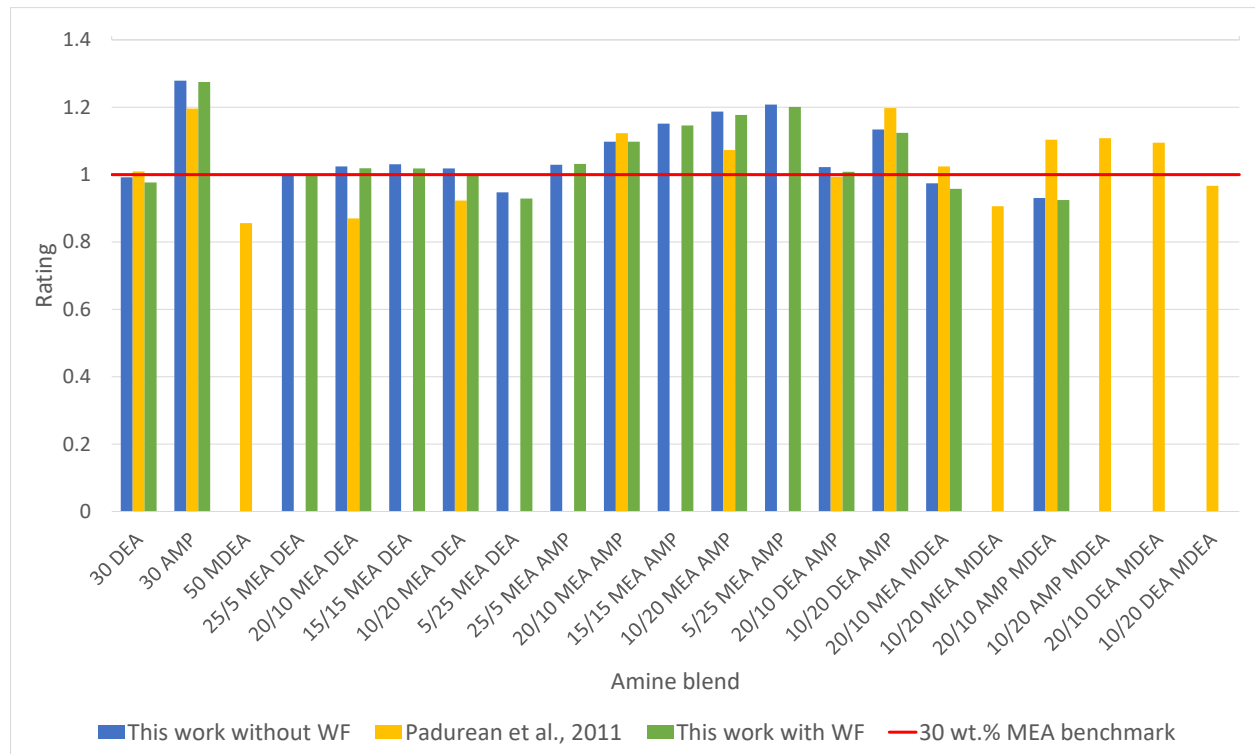
<b>Factor</b>	<b>Original</b>	<b>Regressed</b>
<b>Amine</b>	1	0.905
<b>Corrosion Inhibitor</b>	1	2
<b>CTW Cost</b>	1	0.25
<b>Makeup Water Cost</b>	1	2
<b>Steam Cost</b>	1	1.089
<b>Reclaimer Cost</b>	1	0.25
<b>Amine Disposal Cost</b>	1	0.25
<b>CO<sub>2</sub> Taxes</b>	1	2
<b>Error</b>	0.801	0.592



**Figure 6-9: Rating of various amines and their blends with the original and regressed weighting factors in the NGCC power plant case study vs ratings in a PC power plant by Padurean et al.,2011.**

**Table 6-5: Original and regressed weighting factor values for the cement plant case study.**

Factor	Original	Regressed
Amine	1	0.521
Corrosion Inhibitor	1	2
CTW Cost	1	0.25
Makeup Water Cost	1	0.25
Steam Cost	1	0.402
Reclaimer Cost	1	0.25
Amine Disposal Cost	1	0.25
CO <sub>2</sub> Taxes	1	2
Error	0.913	0.911

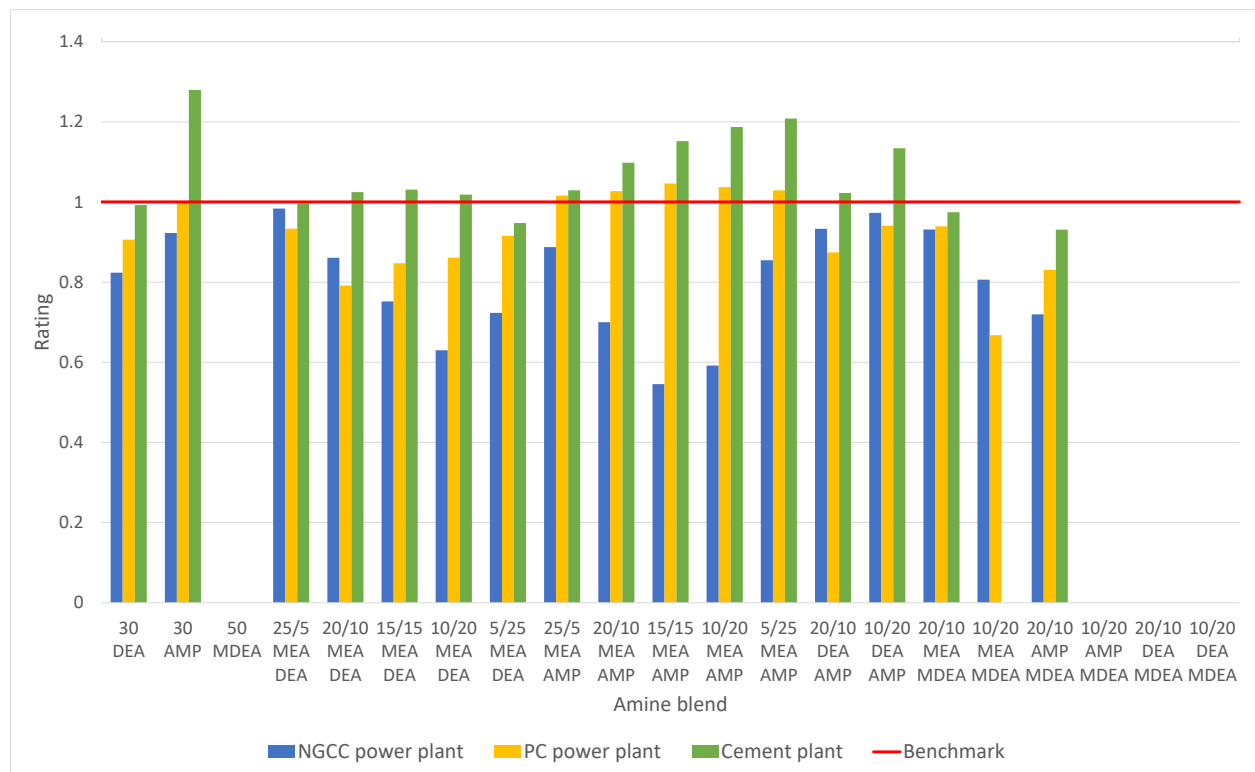


**Figure 6-10: Rating of various amines and their blends with the original and regressed weighting factors in the cement plant case study vs ratings in a PC power plant by Padurean et al.,2011.**

## 6.8 Summary of all case studies

A summary of the results achieved in this study showing the performance ratings for the amine solvents investigated and their blends in the various case studies is presented in Figure 6-11. This information assists in assessing the advantages and disadvantages each solvent delivers based on the application. The case studies have been arranged in an ascending order, based on the CO<sub>2</sub> concentration of the flue gas used in the study. It should be noted that the results for the PC power plant presented in Figure 6-11 do not incorporate the weighting factor in order to allow for a fair comparison between case studies.





**Figure 6-11: Rating of various amines and their blends without the weighting factor in all case studies.**

The benchmark in Figure 6-11 still refers to the 30 wt. % MEA solution used in each case study. Only a single line is required to represent the benchmark across all case studies, since in each case the value of the benchmark rating is one. It can be observed that the performance of 30 wt. % DEA and 30 wt. % AMP, increases significantly as the CO<sub>2</sub> concentration in the flue gas becomes richer. This result can be explained based on the reaction kinetics of the system. Since the reaction rate of CO<sub>2</sub> with DEA and AMP is slower than that of MEA, an increase in CO<sub>2</sub> would typically assist the performance of these two amines. Furthermore, the capture rate has been set at 80% across all case studies for all blends in order to minimise the addition of unnecessary variables in the investigation. This infers that the CO<sub>2</sub> content of the flue gas leaving the absorber in the cement plant would be higher than that of the PC power plant, which would in turn be higher than that of the NGCC power plant. This would imply that the reaction rate is better maintained in the cement plant case study, since the flue gas CO<sub>2</sub> concentration remains relatively high even in the final stages of the absorption column. The benefit of a higher reaction rate is that it reduces the required solvent recirculation rate, which is vital if the overall energy consumption of the system is to remain low. However, as CO<sub>2</sub> concentration increases,

so will the L/G ratio of the system, since more amine will be required to capture the larger CO<sub>2</sub> volume. The overall energy consumption of the system is derived from the specific regeneration energy and the solvent recirculation rate. Thus, a critical flow rate exists, where the solvent recirculation must remain under in order for solvents containing DEA and AMP to benefit from their lower specific regeneration energies and achieve a lower overall energy consumption than the benchmark.

Since DEA has a lower reaction rate with CO<sub>2</sub> than MEA and AMP, it will always have the highest L/G ratio in each case study. DEA also has the highest degradation rate. Thus, the combination of a high recirculation rate and a high degradation rate would result in the make-up requirements of DEA to be the largest. The reclaimer model in the study bases the cost added to the CO<sub>2</sub> capture operation solely on the tonnage of solvent treated. Therefore, a higher solvent recirculation rate results in a higher slipstream flow rate to the reclaimer and thus higher reclamation expenses. Furthermore, the high degradation rate of DEA would result in higher disposal costs when compared to other amine systems, since this factor is also based on the tonnage of solvent disposed. The concept of the critical flow rate expressed previously also has to take into account these costs mentioned above, since they escalate as solvent recirculation rate increases and has the potential to offset the benefit of a lower system energy consumption. In comparison with the benchmark, it may have been possible that 30 wt. % DEA possesses a lower energy consumption. However, by taking the three factors mentioned above into consideration, it results in a performance rating that is below the benchmark.

Similar to DEA, AMP will also be susceptible to the performance deterioration as a result of higher flow rates through the reclaimer as CO<sub>2</sub> content increases. Although AMP has the lowest degradation rates of the amines investigated, which would contribute to it having a low make-up requirement and lower disposal expenses, the cost of the make-up amine will always be the highest when compared to other amines, since its price is substantially higher than both MEA and DEA. Despite these drawbacks, the performance rating of 30 wt. % AMP improves considerably as CO<sub>2</sub> concentration increases. It is highly probable that the energy consumption of the system was below that of the benchmark in all case studies, but by factoring the other costs in, it reduced the rating to below the benchmark in all studies except the cement plant. This result, along with that of 30 wt. % DEA, highlights the importance of a multi criterial performance indicator, where multiple aspects of a solvent are evaluated in order to determine the most cost effective one.

For blends of MEA/DEA, it can be observed that in the power plant case studies, the performance rating of the blends are lower than the individual ratings of the single amine counterparts. The MEA component of MEA/DEA blends contributes to reducing the L/G ratio across all the case studies and thus assists in minimising the disadvantages associated with a high solvent recirculation rate, which were previously discussed in the DEA system. However, it also increases the specific regeneration energy, thus resulting in the lower solvent recirculation rate to still be above the critical flow rate of the system. Only in the case of the cement plant does the blend improve upon the performance of the individual amine constituents. This is due to the high CO<sub>2</sub> concentration in cement plant flue gas, which assists in increasing the reaction rate of the blended amine solvent with CO<sub>2</sub>, thus overcoming the drawbacks that arise with this amine combination due to high solvent recirculation rates.

For blends of MEA/AMP, different trends can be noted for each of the three case studies. In the NGCC power plant case study, the blends of MEA/AMP achieved performance ratings considerably lower than the values of the single amine counterparts. The reaction rate of AMP with CO<sub>2</sub> is slower than that of MEA and the addition of it to a system with a low CO<sub>2</sub> concentration results in the flow rate to be increased substantially. This higher flow rate, coupled with the high specific regeneration energy that MEA brings to the blend, results in a solvent that has a substantially greater regeneration energy requirement, hence resulting in the inferior ratings. In the PC power plant, combining these two amines resulted in enhanced performance ratings. The higher CO<sub>2</sub> concentration in this case study allowed for the addition of AMP to the system, which maintained the reaction at a sufficient rate such that the benefit of the reduced specific regeneration energy could be realised, since the flow rate remained below the critical value of the system. In the cement plant case study, it is noticed that as the AMP composition in the blend increases, the performance rating increases, which infers that MEA does not enhance the performance of the blend. Although MEA would reduce the solvent recirculation rate, the benefit of this reduction is not evident due to the offset created by the considerably higher regeneration energy requirement of the blend. The high CO<sub>2</sub> concentration in this case study removes the reaction rate as the limiting factor in AMP achieving high performance ratings, thus 30 wt. % AMP has the highest performance rating for the cement plant case study.

Similar to 30wt. % AMP, blends of DEA/AMP produced different trends in each of the case studies. In the NGCC power plant, the ratings of the blends were higher than that of the individual constituents, which implies that the blends managed to get closer to the critical flow

rate, but were unable to reduce below it and achieve a better rating than the benchmark. The opposite result was achieved for the PC power plant case study, where the blend shifted further away from the critical flow rate value, resulting in lower performance ratings than the individual constituent amines. In the cement plant, the ratings increased as AMP concentration in the blend increased, resulting in the benchmark being outperformed. However, the rating of 30 wt. % AMP was still higher than the ratings achieved by blends of DEA and AMP, which leaves this result in being of not much interest at present.

It can be observed for all case studies that blends containing MDEA do not have performance ratings that are comparable to the benchmark. In many cases, blends with MDEA cannot be evaluated due to the flow rate constraints of the system, which were imposed by the column size limits set. Although MDEA possessed a desirable low specific regeneration energy, its slow reaction rate with CO<sub>2</sub> was the major drawback as it resulted in the solvent having very high solvent recirculation rates. The amines added to MDEA serve as activators to induce faster reaction rates. Unfortunately, none of the other amines investigated were able to act as an adequate activator for systems containing MDEA. However, this does not imply that MDEA does not have potential as a carbon capture solvent. Although the amines investigated in this study did not have the required activator properties, literature shows that blends of MDEA with a PZ activator have been successfully used as solvents for CO<sub>2</sub> capture (Samanta & Bandyopadhyay, 2011).

## Chapter 7

### Conclusions

- A performance indicator model was successfully developed for carbon capture applications using aqueous amine solvents and blends as the capture technique, where the number and variety of factors considered exceeded that found in present literature.
- Above the typical energy considerations when selecting an amine solvent for carbon capture, the performance between amines and their blends was quantified by make-up requirements for water and amines, amine degradation, corrosion inhibitors, amine reclamation, amine disposal and carbon tax.
- The model was developed based on a monetary principle of cost of CO<sub>2</sub> avoided, since the cost associated with the considered factors is easily quantified and understood.
- In order to develop the model under a wide array of flue gas parameters, three case studies with significantly different CO<sub>2</sub> concentrations were selected: a PC power plant, a NGCC power plant, and a cement plant where the benchmark in all cases was a 30wt. % MEA aqueous solution.
- The rating of a solvent is effectively dependant on two characteristics: regeneration energy, and solvent recirculation rate. A higher regeneration energy typically occurs for solvents with faster reaction rates, which in turn reduces the required recirculation rate. In terms of performance ratings, these two effects are contrasting, since both a high regeneration energy and high solvent recirculation result in a high capture cost. Thus, a critical recirculation rate exists for each blend, which the solvent flow rate must remain below in order to benefit from the reduction in the regeneration energy cost, which may result in a higher performance rating than the benchmark.
- For the NGCC power plant case study, the benchmark solvent of 30 wt. % MEA attained the highest performance rating, due to the low CO<sub>2</sub> concentration which favoured the faster reaction kinetics of CO<sub>2</sub> with MEA. The low CO<sub>2</sub> concentration hindered the other amines investigated due to their high solvent recirculation rates, which increased above the critical flow rate.

- For the PC power plant case study, blends of MEA/AMP attained the highest performance rating, since the higher reaction rate of MEA assisted in minimising the required solvent recirculation rate, whilst the AMP component reduced the specific regeneration energy. Thus, the solvent flow rates for these blends were able to stay below the critical flow rate of the solvent, and allowed them to achieve higher performance ratings than the benchmark.
- For the cement plant cases study, AMP attained the highest performance rating, due to the high CO<sub>2</sub> concentration, which enhanced the reaction rate of AMP with CO<sub>2</sub>. This allowed the solvent recirculation rate to below the critical flow rate, and enabled the solvent to fully benefit from its lower regeneration energy.
- A sensitivity analysis incorporating uncertainty in resource price, uncertainty in values obtained from literature, and changes to the required input user parameters showed an error of 0.025 existed in the performance rating values obtained in this study, which did not significantly alter the results obtained and trends observed.
- The weighting factors in the PC power plant were successfully regressed for against a multi criterial literature study, which reduced the standard error between the results achieved in this study and literature from 0.289 to 0.036. This represented an 87.6% improvement, which proved the ability of the weighting factor to improve the accuracy of the rating values achieved.
- Since there is a lack of a similar analysis for the NGCC and cement plants, the weighting factors were regressed for against the PC power plant literature data. The respective reductions in error were only 26.1% and 0.2%, which demonstrated the weighting factor only has the capability of a tuning parameter, and cannot completely alter the ratings obtained from the model.

## Chapter 8

### Recommendations and Future Work

The model in this study took into account more factors when assessing the performance between a range of solvents and their blends than any study previously accomplished in literature. However, there is opportunity to add further parameters to the system, and improve upon the accuracy of the current considered parameters.

The most prominent addition in terms of factors to consider would be to take into account the required equipment costs for the system. In this study, the effect of varying equipment sizes between differing solvent blends was neglected due to the complexity it would add to running the Aspen Plus simulation, since it would require that column dimensions be constantly changed and optimised manually for each run. The potential exists to automate the procedure via an Aspen Plus user interface that will perform these changes automatically, thus allowing for the addition of capital cost to the model. The code produced to perform this automation could initially focus solely on column diameter, and vary this parameter based on the calculated diameter from Aspen. This would be a useful addition to the model, since the current study assumes a constant column diameter across all blends in each case study. Furthermore, this would be a simple first addition, which could lead to further, more complex considerations, such as pump and heat exchanger sizing. At first glance, the inclusion of pumps and heat exchangers may seem to be an aspect that would have little influence between solvents. However, the various blends operate through a wide range of solvent recirculation rates, which is ultimately the determining factor when it comes to the sizing of these units. The combination of taking into account absorber dimensions, stripper dimensions, pump sizing and heat exchanger sizing could potentially lead to substantial differences between solvents and their blends, especially if space constraints are imposed.

In this study, solvent blends comprising of only two constituent amines were considered in order to limit the number of permutations that exist with regards to the solvent blend compositions to be investigated. The reason for limiting the number of blends to be investigated was that the process of assessing blends was a procedure that had to be accomplished manually on Aspen Plus. Furthermore, the compositions used followed that which was found in the

literature study, since the purpose of this investigation was to develop a performance indicator model. Therefore, it did not warrant doing additional blends until the validity of the model was proven against literature. Thus, solvent compositions were fixed to round numbers, i.e. 20% MEA/10% AMP or 15% MEA/15% DEA. Whilst this approach was adequate for determining prominent solvents for carbon capture in each case study, it did not allow for the optimum composition of each blend to be determined. Future work could involve developing an Aspen Plus user interface that will allow for the running of the simulations to be done automatically. The code developed could use the performance indicator model as an objective function, where the program shall investigate multiple amine blends with various compositions to determine the blend with the highest rating in a specific case study.

This study was limited to the four prominent carbon capture amines of MEA, DEA, AMP and MDEA. Future work could involve the addition of more amines to the system. Investigating performance ratings with the addition of new amines to the system would be a simple endeavour provided that the user interface to automate the running of the simulations is accomplished. The user interface could also be developed to create a true recycle stream in the system rather than the artificial one modelled in this study, where make-up water and amine would be added directly to the flow sheet instead of calculating it manually.

As literature around the topic of carbon capture with amine solvents expands, the potential to increase the accuracy of the performance indicator model increases. These improvements would mostly be centred on the degradation aspects of amines, which at present is not well researched. A better understanding of amine degradation and the amine reclamation process will allow for the effect of these two factors to be better estimated in the model by incorporating the simulation of these two parameters in the Aspen Plus simulation.

The concept of a performance indicator model is not restricted to carbon capture applications with amine solvents. The model developed in this study can be easily adapted to any solvent absorption process, and used to quantify the difference in performance between existing options and determine the optimum alternative.



## Chapter 9

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## Appendix A

### Sample Calculations

This section serves to illustrate the method by which the rating value of a solvent is determined. This is demonstrated for the benchmark operating point of 30 wt. % MEA. In order to execute the calculations, two types of inputs are required: the variable user defined operating parameters and the user inputs from the simulation results, as was previously explained in section 5.12. The required parameters along with the values used in this section are as follows:

Variable user defined inputs:

- Amine price : MEA – R21,213.50/ton
- Make-up water price : R10.08/ton
- Cooling tower water price : R0.37/ton
- Steam price : R123.60/ton
- Corrosion inhibitor price : R3784.40/ton
- Amine reclaim cost : R10,684.50/ton
- Amine disposal cost : R3142.50/ton
- Carbon tax rate : R120.00/ton
- Amine degradation rates : MEA – 0.2059%/hour
- Cooling tower water operating temperatures : 35 - 50°C
- Cooling tower water heat capacity : 4.181 kJ/kg.K
- Cooling tower water vaporisation enthalpy : 2260 kJ/kg
- Cooling tower windage loss fraction : 0.002
- Cooling tower cycles of concentration : 5
- Steam pressure and vaporisation enthalpy : 2147.35 kJ/kg at 3.5 bar
- Steam condensed fraction : 0.975
- Amine reclaim slipstream fraction : 0.005
- Amine reclaim loss fraction : 0.05
- Water reclaim loss fraction : 0.9

- Generated power plant output : 500 MW
- Power plant efficiency : 43%

Required user inputs:

- Capture rate : 80%
- L/G ratio : 2.826 (mass based)
- Flue gas temperature : 45.7°C
- Lean amine temperature : 45°C
- CO<sub>2</sub> flow rate : 450.345 tons/hr
- Lean amine flow rate in to absorber : 2072.966 tons/hr
- Lean amine flow rate out of stripper : 2071.642 tons/hr
- Amine vent rate from absorber : 0.054 tons/hr
- Lean solvent flow rate out of stripper : 6922.64 tons/hr
- Lean water flow rate into absorber : 4832.541 tons/hr
- Lean water flow rate out of stripper : 4577.204 tons/hr
- Water vent rate from absorber : 333.097 tons/hr
- Required utility duty : 40.879 MW
- Required cooling duty : 1202.188 MW
- Required heating duty : 1301.497 MW
- Wash water flow rate : 39.988 tons/hr
- Water direct contact cooler flow rate : 2500 tons/hr

Required cooling water flow rate through coolers in system

$$\dot{Q}_{cool} = \dot{m}_{CW} C_p \Delta T$$

$$1202188 = \dot{m}_{CW} \times 4.181 \times (50 - 35)$$

$$\dot{m}_{CW} = 16169.066 \text{ kg/s} = 69008.639 \text{ tons/hr}$$

Total cooling tower water circulation rate:

$$\dot{m}_{CTW} = \dot{m}_{DCC} + \dot{m}_{CW}$$

$$\dot{m}_{CTW} = 2500 + 69008.639$$

$$\dot{m}_{CTW} = 71508.639 \text{ tons/hr}$$

Water losses in cooling tower due to evaporation:

$$E = \frac{C\Delta T C p_{cw}}{H_v}$$

$$E = \frac{71508.639 \times 4.181 \times (50 - 35)}{2260}$$

$$E = 1984.365 \text{ tons/hr}$$

Water losses due to blow down:

$$B = fC$$

$$B = 0.002 \times 71508.639$$

$$B = 143.017 \text{ tons/hr}$$

Water loss due to purging:

$$\text{Cycles} = 1 + \frac{E}{P + B}$$

$$5 = 1 + \frac{1984.365}{P + 143.017}$$

$$P = 353.074 \text{ tons/hr}$$

Required steam flow with steam condensation fraction incorporated:

$$\dot{m}_{steam} = \frac{\dot{Q}_{heat}}{0.975 H_v}$$

$$\dot{m}_{steam} = \frac{1301497}{0.975 \times 2147.35}$$

$$\dot{m}_{steam} = 621.64 \text{ kg/s} = 2237.887 \text{ tons/hr}$$

Solvent reclaimer flow:

$$\dot{m}_{reclaimer-solvent} = 0.005 \times 6922.64$$

$$\dot{m}_{reclaimer-solvent} = 34.613 \text{ tons/hr}$$

Reclaimer MEA flow:

$$\dot{m}_{reclaimer-MEA} = 0.005 \times 2071.642$$

$$\dot{m}_{reclaimer-MEA} = 10.358 \text{ tons/hr}$$

Reclaimer water flow:

$$\dot{m}_{reclaimer-water} = 0.005 \times 4577.204$$

$$\dot{m}_{reclaimer-water} = 22.886 \text{ tons/hr}$$

Degraded amine loss:

$$\dot{m}_{degraded-MEA} = \tau_{MEA} \dot{m}_{absorber-MEA}$$

$$\dot{m}_{degraded-MEA} = 2072.986 \times 0.00173$$

$$\dot{m}_{degraded-MEA} = 3.593 \text{ tons/hr}$$

Reclaimer amine loss:

$$\dot{m}_{reclaimer-MEA-loss} = 0.05 \times \dot{m}_{reclaimer-amine}$$

$$\dot{m}_{reclaimer-MEA-loss} = 0.05 \times 10.358$$

$$\dot{m}_{reclaimer-MEA-loss} = 0.338$$

Reclaimer water loss:

$$\dot{m}_{reclaimer-water-loss} = 0.9 \times \dot{m}_{r-water}$$

$$\dot{m}_{reclaimer-water-loss} = 0.9 \times 22.886$$

$$\dot{m}_{reclaimer-water-loss} = 20.597 \text{ tons/hr}$$



Coal plant potential output:

$$\varepsilon_{old} = \frac{MW_{out}}{MW_{in}}$$

$$0.43 = \frac{500}{MW_{in}}$$

$$MW_{in} = 1162.79 \text{ MW}$$

New plant efficiency:

$$\varepsilon_{new} = \frac{MW_{out} - MW_{CCS-utilities}}{MW_{in}}$$

$$\varepsilon_{new} = \frac{500 - 40.879}{1162.79}$$

$$\varepsilon_{new} = 0.395$$

Make up amine cost:

$$C_{MEA} = \dot{m}_{MEA-lost} P_{MEA}$$

$$C_{MEA} = (\dot{m}_{reclaimer-MEA} + \dot{m}_{degraded-MEA} + \dot{m}_{vented-MEA}) \times P_{MEA}$$

$$C_{MEA} = (0.054 + 3.592 + 0.338) \times 18937$$

$$C_{MEA} = R84\,735.63/\text{hour}$$

Corrosion inhibitor cost (assumed to be included as part of the make up amine):

$$C_{Inhibitor} = x_{Inhibitor} \dot{m}_{MEA-lost} P_{Inhibitor}$$

$$C_{Inhibitor} = x_{Inhibitor} \times (\dot{m}_{reclaimer-MEA} + \dot{m}_{degraded-MEA} + \dot{m}_{vented-MEA}) \times P_{Inhibitor}$$

$$C_{Inhibitor} = 0.0005 * (0.054 + 3.592 + 0.338) \times 3787.40$$

$$C_{Inhibitor} = R75.64/\text{hour}$$

Cooling tower water circulation cost:

$$C_{CTW} = \dot{m}_{CTW} P_{CTW}$$

$$C_{CTW} = 71508.639 \times 0.37$$

$$C_{CTW} = R26\ 458.20/\text{hour}$$

Make up water cost:

$$C_{Water} = \dot{m}_{Water-lost} P_{Water}$$

$$C_{Water} = (\dot{m}_{vented-water} + \dot{m}_{reclaimer-water} + E + B + P) \times P_{Water}$$

$$C_{Water} = (333.097 + 20.597 + 1984.647 + 143.017 + 353.074) \times 10.08$$

$$C_{Water} = R24\ 838.31/\text{hour}$$

Steam cost:

$$C_{Steam} = \dot{m}_{Steam} P_{Steam}$$

$$C_{Steam} = 2237.887 \times 123.60$$

$$C_{Steam} = R276\ 602.83/\text{hour}$$

Reclaimer cost:

$$C_{Reclaimer} = \dot{m}_{Reclaimer} P_{Reclaimer}$$

$$C_{Reclaimer} = 34.6132 \times 10684.50$$

$$C_{Reclaimer} = R369\ 824.74 / \text{hour}$$

Disposal cost:

$$C_{Disposal} = \dot{m}_{Reclaimer} P_{Disposal}$$

$$C_{Disposal} = (\dot{m}_{reclaimer-water-loss} + \dot{m}_{reclaimer-MEA-loss} + \dot{m}_{Degraded-MEA}) \times P_{Disposal}$$

$$C_{Disposal} = (3.592 + 0.338 + 20.597) \times 3142.50$$

$$C_{Disposal} = R77\,076.10/\text{hour}$$

CO<sub>2</sub> taxes:

$$C_{CO_2-tax} = \dot{m}_{CO_2-released} P_{CO_2-tax}$$

$$C_{CO_2-tax} = (\dot{m}_{CO_2-in} \times (1 - f_{capture\ rate})) \times P_{CO_2-tax}$$

$$C_{CO_2-tax} = (450.345 \times (1 - 0.8)) \times 120$$

$$C_{CO_2-tax} = R10\,808.28/\text{hour}$$

Total cost of CO<sub>2</sub> capture:

$$C_{CO_2-capture-total} = \sum C_i$$

$$C_{CO_2-capture-total}$$

$$= 84\,735.63 + 75.64 + 26\,458.20 + 24\,838.31 + 276\,602.83$$

$$+ 369\,824.74 + 77\,076.10 + 10\,808.28$$

$$C_{CO_2-capture-total} = R870\,419.73$$

Cost of CO<sub>2</sub> capture per ton:

$$C_{CO_2-capture} = \frac{C_{CO_2-capture-total}}{\dot{m}_{CO_2-captured}}$$

$$C_{CO_2-capture} = \frac{C_{CO_2-capture-total}}{f_{capture\ rate} \times \dot{m}_{CO_2-in}}$$

$$C_{CO_2-capture} = \frac{870\,419.73}{0.8 \times 450.345}$$

$$C_{CO_2-capture} = R2\,415.98/\text{ton } CO_2$$

The cost calculations completed above represents the cost of CO<sub>2</sub> capture based on each of the individual factor costs. However, in order to obtain a truer representation of solvent performance, the cost of CO<sub>2</sub> avoided has to be determined. The procedure for converting the cost of CO<sub>2</sub> capture into a cost of CO<sub>2</sub> avoided is illustrated only for the total CO<sub>2</sub> capture cost. However, this calculation is also applied to all individual factor costs determined in this section, the results of which are summarised in Table C-1 below.

$$C_{CO_2-avoided} = \frac{C_{CO_2-capture} \varepsilon_{old}}{\varepsilon_{new}}$$

$$C_{CO_2-avoided} = \frac{2\,415.98 \times 0.43}{0.395}$$

$$C_{CO_2-avoided} = R2\,630.05 \text{ ton } CO_2$$

**Table A-1: Cost of CO<sub>2</sub> captured and avoided for benchmark operating point.**

<b>Factor</b>	<b>Cost of CO<sub>2</sub> captured (R/hour)</b>	<b>Cost of CO<sub>2</sub> avoided (R/hour)</b>
<b>Make up amine</b>	84 735.63	92 243.85
<b>Corrosion inhibitor</b>	75.64	82.34
<b>CTW</b>	26 458.20	28 802.60
<b>Make up water</b>	24 838.63	27 039.52
<b>Steam</b>	276 602.83	301 111.94
<b>Amine reclaim</b>	369 824.74	402 594.02
<b>Amine disposal</b>	77 076.10	83 905.62
<b>CO<sub>2</sub> taxes</b>	10 808.28	11 765.98
<b>Total cost</b>	870 419.73	947 545.53

To determine the rating value, the relevant weighting factors have to be applied to each of the individual cost influences considered in the model. Initially a weighting factor of 1 had to be used for all the rated factors since these values could not be regressed for as yet.

Since performing the calculations with only the benchmark operating point will result in a value of 1, the results of the simulation for MEA operating at a lean loading of 0.25 is used. The calculation procedure to determine the individual factor costs is not repeated here as it follows the same steps outlined previously for the benchmark operating point. A summary of the results that will be used in the following calculation are shown below. Only the cost of CO<sub>2</sub> avoided is used when determining the rating value.

**Table A-2: Cost of CO<sub>2</sub> captured and avoided for pseudo operating point.**

<b>Factor</b>	<b>Cost of CO<sub>2</sub> captured (R/hour)</b>	<b>Cost of CO<sub>2</sub> avoided (R/hour)</b>
<b>Make up amine</b>	57 528.84	65 252.99
<b>Corrosion inhibitor</b>	131.71	144.03
<b>CTW</b>	33 250.78	36 361.74
<b>Make up water</b>	27 323.61	29 880.02
<b>Steam</b>	272 126.24	297 586.56
<b>Amine reclaim</b>	641 482.23	701 499.74
<b>Amine disposal</b>	134 613.57	147 208.11
<b>CO<sub>2</sub> taxes</b>	10 808.28	11 819.51
<b>Total cost</b>	1 251 442.948	1 368 528.798

Firstly the fraction by which each factor contributes to the overall cost for the benchmark operating point has to be determined. This has to be repeated for the pseudo operating point as well. This is illustrated for one factor with the results of the remaining factors presented in Table C-3.

$$f_{make\ up-amine} = \frac{C_{make\ up-amine}}{C_{total}}$$

$$f_{make\ up-amine} = \frac{92\ 243.85}{947\ 545.53}$$

$$f_{make\ up-amine} = 0.0973$$

**Table A-3: Factor contribution for benchmark and pseudo operating point.**

<b>Factor</b>	<b>Benchmark fraction</b>	<b>Point of interest fraction</b>
<b>Make up amine</b>	0.0973	0.1031
<b>Corrosion inhibitor</b>	$8.690 \times 10^{-5}$	$1.031 \times 10^{-5}$
<b>CTW</b>	0.0304	0.0260
<b>Make up water</b>	0.0285	0.0214
<b>Steam</b>	0.3178	0.2130
<b>Amine reclaim</b>	0.4249	0.5021
<b>Amine disposal</b>	0.0885	0.1054
<b>CO<sub>2</sub> taxes</b>	0.0124	0.0085

The contribution to the rating factor for each of the parameters considered is then determined. This is illustrated for one factor with the results of the remaining factors presented in Table C-4. The rating value for the pseudo operating point is simply determined from the sum of the individual contributions.

$$R_{make\ up-amine} = f_{make\ up-amine} \frac{C_{make\ up-amine,b}}{C_{make\ up-amine,j}}$$

$$R_{make\ up-amine} = 0.1031 \times \frac{92\ 243.85}{65\ 252.99}$$

$$R_{make\ up-amine} = 0.1457$$

**Table A-4: Rating values for pseudo operating point.**

<b>Factor</b>	<b>Rating</b>
<b>Make up amine</b>	0.1457
<b>Corrosion inhibitor</b>	$5.894 \times 10^{-6}$
<b>CTW</b>	0.0206
<b>Make up water</b>	0.0194
<b>Steam</b>	0.2155
<b>Amine reclaim</b>	0.2882
<b>Amine disposal</b>	0.0601
<b>CO<sub>2</sub> taxes</b>	0.0085
<b>Total rating</b>	0.758

## Appendix B

## Results

Table B-1: Coal power plant rating results without weighting factors.

	30 DEA	30 AMP	50 MDEA	25/5 MEA DEA	20/10 MEA DEA	15/15 MEA DEA	10/20 MEA DEA
<b>Make up amine</b>	0.074	0.082	N/A	0.076	0.065	0.069	0.070
<b>Corrosion inhibitor</b>	0.000	0.000	N/A	0.000	0.000	0.000	0.000
<b>CTW</b>	0.038	0.042	N/A	0.039	0.033	0.035	0.036
<b>Make up water</b>	0.032	0.035	N/A	0.033	0.028	0.030	0.030
<b>Steam</b>	0.337	0.373	N/A	0.348	0.295	0.316	0.321
<b>Amine reclaim</b>	0.342	0.378	N/A	0.352	0.299	0.320	0.325
<b>Amine disposal</b>	0.072	0.080	N/A	0.074	0.063	0.068	0.069
<b>CO<sub>2</sub> taxes</b>	0.011	0.012	N/A	0.011	0.009	0.010	0.010
<b>Total rating</b>	0.906	1.001	N/A	0.933	0.791	0.847	0.861

**Table B-2: Coal power plant rating results without weighting factors.**

	<b>5/25</b>	<b>25/5</b>	<b>20/10</b>	<b>15/15</b>	<b>10/20</b>	<b>5/25</b>	<b>20/10</b>
	<b>MEA DEA</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>DEA AMP</b>
<b>Make up amine</b>	0.075	0.083	0.084	0.085	0.085	0.084	0.071
<b>Corrosion inhibitor</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>CTW</b>	0.038	0.042	0.043	0.044	0.043	0.043	0.037
<b>Make up water</b>	0.032	0.036	0.036	0.037	0.037	0.036	0.031
<b>Steam</b>	0.341	0.378	0.383	0.390	0.386	0.383	0.326
<b>Amine reclaim</b>	0.345	0.383	0.387	0.395	0.391	0.388	0.330
<b>Amine disposal</b>	0.073	0.081	0.082	0.083	0.083	0.082	0.070
<b>CO<sub>2</sub> taxes</b>	0.011	0.012	0.012	0.012	0.012	0.012	0.010
<b>Total rating</b>	0.915	1.016	1.027	1.046	1.037	1.029	0.874



**Table B-3: Coal power plant rating results without weighting factors.**

	10/20	20/10	10/20	20/10	10/20	20/10	10/20
	DEA AMP	MEA MDEA	MEA MDEA	AMP MDEA	AMP MDEA	DEA MDEA	DEA MDEA
<b>Make up amine</b>	0.077	0.077	0.054	0.068	N/A	N/A	N/A
<b>Corrosion inhibitor</b>	0.000	0.000	0.000	0.000	N/A	N/A	N/A
<b>CTW</b>	0.039	0.039	0.028	0.035	N/A	N/A	N/A
<b>Make up water</b>	0.033	0.033	0.024	0.029	N/A	N/A	N/A
<b>Steam</b>	0.351	0.350	0.249	0.309	N/A	N/A	N/A
<b>Amine reclaim</b>	0.355	0.354	0.252	0.313	N/A	N/A	N/A
<b>Amine disposal</b>	0.075	0.075	0.053	0.066	N/A	N/A	N/A
<b>CO<sub>2</sub> taxes</b>	0.011	0.011	0.008	0.010	N/A	N/A	N/A
<b>Total rating</b>	0.941	0.939	0.668	0.830	N/A	N/A	N/A

**Table B-4: NGCC power plant rating results without weighting factors.**

	<b>30 DEA</b>	<b>30 AMP</b>	<b>50 MDEA</b>	<b>25/5 MEA DEA</b>	<b>20/10 MEA DEA</b>	<b>15/15 MEA DEA</b>	<b>10/20 MEA DEA</b>
<b>Make up amine</b>	0.079	0.089	N/A	0.095	0.083	0.072	0.061
<b>Corrosion inhibitor</b>	0.000	0.000	N/A	0.000	0.000	0.000	0.000
<b>CTW</b>	0.012	0.014	N/A	0.015	0.013	0.011	0.009
<b>Make up water</b>	0.080	0.089	N/A	0.095	0.083	0.073	0.061
<b>Steam</b>	0.592	0.663	N/A	0.706	0.618	0.540	0.453
<b>Amine reclaim</b>	0.042	0.047	N/A	0.050	0.044	0.038	0.032
<b>Amine disposal</b>	0.009	0.010	N/A	0.011	0.009	0.008	0.007
<b>CO<sub>2</sub> taxes</b>	0.010	0.012	N/A	0.012	0.011	0.009	0.008
<b>Total rating</b>	0.824	0.923	N/A	0.984	0.862	0.752	0.631

**Table B-5: NGCC power plant rating results without weighting factors.**

	<b>5/25</b>	<b>25/5</b>	<b>20/10</b>	<b>15/15</b>	<b>10/20</b>	<b>5/25</b>	<b>20/10</b>
	<b>MEA DEA</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>DEA AMP</b>
<b>Make up amine</b>	0.069	0.085	0.067	0.052	0.057	0.082	0.090
<b>Corrosion inhibitor</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>CTW</b>	0.011	0.013	0.010	0.008	0.009	0.013	0.014
<b>Make up water</b>	0.070	0.086	0.068	0.053	0.057	0.083	0.090
<b>Steam</b>	0.519	0.638	0.503	0.392	0.425	0.614	0.670
<b>Amine reclaim</b>	0.037	0.045	0.036	0.028	0.030	0.044	0.048
<b>Amine disposal</b>	0.008	0.010	0.008	0.006	0.006	0.009	0.010
<b>CO<sub>2</sub> taxes</b>	0.009	0.011	0.009	0.007	0.007	0.011	0.012
<b>Total rating</b>	0.724	0.888	0.700	0.546	0.592	0.855	0.934

**Table B-6: NGCC power plant rating results without weighting factors.**

	10/20	20/10	10/20	20/10	10/20	20/10	10/20
	DEA AMP	MEA MDEA	MEA MDEA	AMP MDEA	AMP MDEA	DEA MDEA	DEA MDEA
<b>Make up amine</b>	0.093	0.089	0.077	0.080	N/A	N/A	N/A
<b>Corrosion inhibitor</b>	0.000	0.000	0.000	0.000	N/A	N/A	N/A
<b>CTW</b>	0.014	0.014	0.012	0.022	N/A	N/A	N/A
<b>Make up water</b>	0.094	0.090	0.078	0.019	N/A	N/A	N/A
<b>Steam</b>	0.699	0.669	0.579	0.259	N/A	N/A	N/A
<b>Amine reclaim</b>	0.050	0.048	0.041	0.234	N/A	N/A	N/A
<b>Amine disposal</b>	0.011	0.010	0.009	0.049	N/A	N/A	N/A
<b>CO<sub>2</sub> taxes</b>	0.012	0.012	0.010	0.032	N/A	N/A	N/A
<b>Total rating</b>	0.974	0.932	0.807	0.697	N/A	N/A	N/A

**Table B-7: Cement plant rating results without weighting factors.**

	<b>30 DEA</b>	<b>30 AMP</b>	<b>50 MDEA</b>	<b>25/5 MEA DEA</b>	<b>20/10 MEA DEA</b>	<b>15/15 MEA DEA</b>	<b>10/20 MEA DEA</b>
<b>Make up amine</b>	0.143	0.184	N/A	0.143	0.147	0.148	0.146
<b>Corrosion inhibitor</b>	0.000	0.001	N/A	0.000	0.000	0.000	0.000
<b>CTW</b>	0.022	0.028	N/A	0.022	0.023	0.023	0.022
<b>Make up water</b>	0.019	0.025	N/A	0.019	0.020	0.020	0.020
<b>Steam</b>	0.371	0.478	N/A	0.372	0.382	0.385	0.380
<b>Amine reclaim</b>	0.293	0.377	N/A	0.294	0.302	0.304	0.300
<b>Amine disposal</b>	0.061	0.079	N/A	0.061	0.063	0.064	0.063
<b>CO<sub>2</sub> taxes</b>	0.084	0.108	N/A	0.084	0.086	0.087	0.086
<b>Total rating</b>	0.992	1.279	N/A	0.997	1.024	1.031	1.018

**Table B-8: Cement plant rating results without weighting factors.**

	<b>5/25</b>	<b>25/5</b>	<b>20/10</b>	<b>15/15</b>	<b>10/20</b>	<b>5/25</b>	<b>20/10</b>
	<b>MEA DEA</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>DEA AMP</b>
<b>Make up amine</b>	0.136	0.148	0.158	0.166	0.171	0.174	0.147
<b>Corrosion inhibitor</b>	0.000	0.000	0.001	0.001	0.001	0.001	0.000
<b>CTW</b>	0.021	0.023	0.024	0.025	0.026	0.027	0.022
<b>Make up water</b>	0.018	0.020	0.021	0.022	0.023	0.024	0.020
<b>Steam</b>	0.354	0.384	0.410	0.430	0.443	0.451	0.382
<b>Amine reclaim</b>	0.279	0.303	0.324	0.340	0.350	0.356	0.301
<b>Amine disposal</b>	0.058	0.063	0.068	0.071	0.073	0.075	0.063
<b>CO<sub>2</sub> taxes</b>	0.080	0.087	0.093	0.097	0.100	0.102	0.086
<b>Total rating</b>	0.948	1.029	1.098	1.152	1.187	1.208	1.023

**Table B-9: Cement plant rating results without weighting factors.**

	10/20	20/10	10/20	20/10	10/20	20/10	10/20
	DEA AMP	MEA MDEA	MEA MDEA	AMP MDEA	AMP MDEA	DEA MDEA	DEA MDEA
<b>Make up amine</b>	0.163	0.140	N/A	0.134	N/A	N/A	N/A
<b>Corrosion inhibitor</b>	0.001	0.000	N/A	0.000	N/A	N/A	N/A
<b>CTW</b>	0.025	0.021	N/A	0.020	N/A	N/A	N/A
<b>Make up water</b>	0.022	0.019	N/A	0.018	N/A	N/A	N/A
<b>Steam</b>	0.423	0.364	N/A	0.348	N/A	N/A	N/A
<b>Amine reclaim</b>	0.334	0.287	N/A	0.274	N/A	N/A	N/A
<b>Amine disposal</b>	0.070	0.060	N/A	0.057	N/A	N/A	N/A
<b>CO<sub>2</sub> taxes</b>	0.096	0.082	N/A	0.079	N/A	N/A	N/A
<b>Total rating</b>	1.134	0.974	N/A	0.931	N/A	N/A	N/A

**Table B-10: Coal power plant rating results with weighting factors.**

	<b>30 DEA</b>	<b>30 AMP</b>	<b>50 MDEA</b>	<b>25/5 MEA DEA</b>	<b>20/10 MEA DEA</b>	<b>15/15 MEA DEA</b>	<b>10/20 MEA DEA</b>
<b>Make up amine</b>	0.075	0.086	N/A	0.073	0.066	0.069	0.071
<b>Corrosion inhibitor</b>	0.000	0.000	N/A	0.000	0.000	0.000	0.000
<b>CTW</b>	0.020	0.023	N/A	0.019	0.018	0.018	0.019
<b>Make up water</b>	0.017	0.019	N/A	0.016	0.015	0.015	0.016
<b>Steam</b>	0.644	0.743	N/A	0.624	0.569	0.595	0.610
<b>Amine reclaim</b>	0.179	0.206	N/A	0.173	0.158	0.165	0.169
<b>Amine disposal</b>	0.038	0.044	N/A	0.037	0.033	0.035	0.036
<b>CO<sub>2</sub> taxes</b>	0.044	0.051	N/A	0.043	0.039	0.041	0.042
<b>Total rating</b>	1.016	1.173	N/A	0.985	0.899	0.940	0.963



**Table B-11: Coal power plant rating results with weighting factors.**

	<b>5/25</b>	<b>25/5</b>	<b>20/10</b>	<b>15/15</b>	<b>10/20</b>	<b>5/25</b>	<b>20/10</b>
	<b>MEA DEA</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>DEA AMP</b>
<b>Make up amine</b>	0.074	0.076	0.079	0.081	0.079	0.077	0.078
<b>Corrosion inhibitor</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>CTW</b>	0.020	0.020	0.021	0.022	0.021	0.021	0.021
<b>Make up water</b>	0.017	0.017	0.018	0.018	0.018	0.017	0.017
<b>Steam</b>	0.635	0.658	0.678	0.700	0.679	0.667	0.668
<b>Amine reclaim</b>	0.176	0.183	0.188	0.194	0.188	0.185	0.186
<b>Amine disposal</b>	0.037	0.039	0.040	0.041	0.040	0.039	0.039
<b>CO<sub>2</sub> taxes</b>	0.044	0.045	0.047	0.048	0.047	0.046	0.046
<b>Total rating</b>	1.003	1.039	1.070	1.105	1.071	1.053	1.055

**Table B-12: Coal power plant rating results with weighting factors.**

	10/20	20/10	10/20	20/10	10/20	20/10	10/20
	DEA AMP	MEA MDEA	MEA MDEA	AMP MDEA	AMP MDEA	DEA MDEA	DEA MDEA
<b>Make up amine</b>	0.085	0.071	0.056	0.081	N/A	N/A	N/A
<b>Corrosion inhibitor</b>	0.000	0.000	0.000	0.000	N/A	N/A	N/A
<b>CTW</b>	0.023	0.019	0.015	0.022	N/A	N/A	N/A
<b>Make up water</b>	0.019	0.016	0.013	0.018	N/A	N/A	N/A
<b>Steam</b>	0.735	0.614	0.481	0.700	N/A	N/A	N/A
<b>Amine reclaim</b>	0.204	0.171	0.134	0.195	N/A	N/A	N/A
<b>Amine disposal</b>	0.043	0.036	0.028	0.041	N/A	N/A	N/A
<b>CO<sub>2</sub> taxes</b>	0.051	0.042	0.033	0.048	N/A	N/A	N/A
<b>Total rating</b>	1.160	0.970	0.759	1.106	N/A	N/A	N/A

**Table B-13: NGCC power plant rating results with weighting factors.**

	<b>30 DEA</b>	<b>30 AMP</b>	<b>50 MDEA</b>	<b>25/5 MEA DEA</b>	<b>20/10 MEA DEA</b>	<b>15/15 MEA DEA</b>	<b>10/20 MEA DEA</b>
<b>Make up amine</b>	0.055	0.068	N/A	0.055	0.049	0.044	0.037
<b>Corrosion inhibitor</b>	0.000	0.000	N/A	0.000	0.000	0.000	0.000
<b>CTW</b>	0.019	0.023	N/A	0.019	0.017	0.015	0.013
<b>Make up water</b>	0.124	0.151	N/A	0.124	0.108	0.097	0.083
<b>Steam</b>	0.708	0.867	N/A	0.708	0.621	0.555	0.474
<b>Amine reclaim</b>	0.065	0.080	N/A	0.065	0.057	0.051	0.044
<b>Amine disposal</b>	0.014	0.017	N/A	0.014	0.012	0.011	0.009
<b>CO<sub>2</sub> taxes</b>	0.016	0.020	N/A	0.016	0.014	0.013	0.011
<b>Total rating</b>	1.001	1.226	N/A	1.001	0.878	0.785	0.670

**Table B-14: NGCC power plant rating results with weighting factors.**

	<b>5/25</b>	<b>25/5</b>	<b>20/10</b>	<b>15/15</b>	<b>10/20</b>	<b>5/25</b>	<b>20/10</b>
	<b>MEA DEA</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>DEA AMP</b>
<b>Make up amine</b>	0.040	0.050	0.040	0.031	0.036	0.055	0.061
<b>Corrosion inhibitor</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>CTW</b>	0.014	0.017	0.014	0.011	0.012	0.019	0.021
<b>Make up water</b>	0.089	0.112	0.089	0.070	0.079	0.122	0.136
<b>Steam</b>	0.511	0.640	0.508	0.401	0.453	0.700	0.777
<b>Amine reclaim</b>	0.047	0.059	0.047	0.037	0.042	0.064	0.071
<b>Amine disposal</b>	0.010	0.012	0.010	0.008	0.009	0.014	0.015
<b>CO<sub>2</sub> taxes</b>	0.012	0.015	0.012	0.009	0.010	0.016	0.018
<b>Total rating</b>	0.723	0.905	0.718	0.567	0.641	0.990	1.099

**Table B-15: NGCC power plant rating results with weighting factors.**

	10/20	20/10	10/20	20/10	10/20	20/10	10/20
	DEA AMP	MEA MDEA	MEA MDEA	AMP MDEA	AMP MDEA	DEA MDEA	DEA MDEA
<b>Make up amine</b>	0.065	0.052	0.046	0.077	N/A	N/A	N/A
<b>Corrosion inhibitor</b>	0.000	0.000	0.000	0.000	N/A	N/A	N/A
<b>CTW</b>	0.022	0.018	0.016	0.015	N/A	N/A	N/A
<b>Make up water</b>	0.145	0.116	0.102	0.013	N/A	N/A	N/A
<b>Steam</b>	0.828	0.662	0.582	0.355	N/A	N/A	N/A
<b>Amine reclaim</b>	0.076	0.061	0.053	0.175	N/A	N/A	N/A
<b>Amine disposal</b>	0.016	0.013	0.011	0.037	N/A	N/A	N/A
<b>CO<sub>2</sub> taxes</b>	0.019	0.015	0.013	0.048	N/A	N/A	N/A
<b>Total rating</b>	1.171	0.936	0.822	0.719	N/A	N/A	N/A

**Table B-16: Cement plant rating results with weighting factors.**

	<b>30 DEA</b>	<b>30 AMP</b>	<b>50 MDEA</b>	<b>25/5 MEA DEA</b>	<b>20/10 MEA DEA</b>	<b>15/15 MEA DEA</b>	<b>10/20 MEA DEA</b>
<b>Make up amine</b>	0.138	0.180	N/A	0.141	0.144	0.144	0.142
<b>Corrosion inhibitor</b>	0.001	0.001	N/A	0.001	0.001	0.001	0.001
<b>CTW</b>	0.023	0.030	N/A	0.023	0.024	0.024	0.023
<b>Make up water</b>	0.020	0.026	N/A	0.021	0.021	0.021	0.021
<b>Steam</b>	0.338	0.442	N/A	0.346	0.353	0.353	0.347
<b>Amine reclaim</b>	0.306	0.399	N/A	0.313	0.319	0.319	0.313
<b>Amine disposal</b>	0.064	0.083	N/A	0.065	0.067	0.067	0.065
<b>CO<sub>2</sub> taxes</b>	0.087	0.114	N/A	0.090	0.091	0.091	0.090
<b>Total rating</b>	0.977	1.275	N/A	1.000	1.019	1.018	1.001

**Table B-17: Cement plant rating results with weighting factors.**

	<b>5/25</b>	<b>25/5</b>	<b>20/10</b>	<b>15/15</b>	<b>10/20</b>	<b>5/25</b>	<b>20/10</b>
	<b>MEA DEA</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>MEA AMP</b>	<b>DEA AMP</b>
<b>Make up amine</b>	0.131	0.146	0.155	0.162	0.166	0.170	0.143
<b>Corrosion inhibitor</b>	0.001	0.001	0.001	0.001	0.001	0.001	0.001
<b>CTW</b>	0.022	0.024	0.026	0.027	0.027	0.028	0.024
<b>Make up water</b>	0.019	0.021	0.023	0.024	0.024	0.025	0.021
<b>Steam</b>	0.322	0.357	0.380	0.397	0.408	0.416	0.349
<b>Amine reclaim</b>	0.291	0.323	0.343	0.359	0.368	0.376	0.315
<b>Amine disposal</b>	0.061	0.068	0.072	0.075	0.077	0.079	0.066
<b>CO<sub>2</sub> taxes</b>	0.083	0.092	0.098	0.103	0.105	0.108	0.090
<b>Total rating</b>	0.929	1.032	1.098	1.146	1.177	1.201	1.008

**Table B-18: Cement plant rating results with weighting factors.**

	10/20	20/10	10/20	20/10	10/20	20/10	10/20
	DEA AMP	MEA MDEA	MEA MDEA	AMP MDEA	AMP MDEA	DEA MDEA	DEA MDEA
<b>Make up amine</b>	0.159	0.135	N/A	0.131	N/A	N/A	N/A
<b>Corrosion inhibitor</b>	0.001	0.001	N/A	0.001	N/A	N/A	N/A
<b>CTW</b>	0.026	0.022	N/A	0.022	N/A	N/A	N/A
<b>Make up water</b>	0.023	0.020	N/A	0.019	N/A	N/A	N/A
<b>Steam</b>	0.389	0.332	N/A	0.320	N/A	N/A	N/A
<b>Amine reclaim</b>	0.352	0.300	N/A	0.289	N/A	N/A	N/A
<b>Amine disposal</b>	0.074	0.063	N/A	0.060	N/A	N/A	N/A
<b>CO<sub>2</sub> taxes</b>	0.101	0.086	N/A	0.083	N/A	N/A	N/A
<b>Total rating</b>	1.124	0.958	N/A	0.925	N/A	N/A	N/A