

CRANFIELD UNIVERSITY



EBUWA IYORE OSAGIE

**MODELLING AND EVALUATION OF 2-AMINO-2-METHYL-1-
PROPANOL (AMP) BASED PROCESS FOR CO₂ CAPTURE FROM
NATURAL GAS-FIRED POWER PLANT**

SCHOOL OF WATER, ENERGY AND ENVIRONMENT
Ph.D. in Energy and Power

Ph.D. Thesis

Academic Year: 2017 – 2018

Primary Supervisor: Professor Vasilije Manovic,

Associate supervisor: Dr. Dawid Hanak

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ABSTRACT

It is widely accepted that emissions of CO₂, which is a major greenhouse gas, are the primary cause of climate change. This has led to the development of carbon capture and storage (CCS) technologies in which CO₂ is captured from large-scale point sources such as power plants. However, retrofits of carbon capture plants result in high-efficiency penalties, which have been reported to fall in the range of 7–12% points in the case of post-combustion capture (PCC) from natural gas combined cycle (NGCC) power plants. Therefore, a reduction of these efficiency losses is a high priority in order to deploy CCS at a large scale. At the moment, chemical solvent scrubbing using amines, such as monoethanolamine (MEA), is considered as the most mature option for CO₂ capture from fossil fuel-fired power plants. However, due to high heat requirements for solvent regeneration, the use of substitute solvents has been considered. This thesis investigates the capture of CO₂ from the flue gas of a NGCC power plant using 2-amino-2-methyl-1-propanol (AMP) solvent, the aim of which was to identify and evaluate opportunities for improvement. The methodology adopted in achieving the set objectives is subdivided into three sections. Firstly, a rate-based model for AMP pilot-scale PCC plant was developed with default parameters in Aspen Plus®, validated with published experimental data, and scaled up to commercial scale. Afterwards, the AMP-based plant was retrofitted into the 474 MWe NGCC power plant model, and an economic analysis was performed with the MEA-based PCC plant used as a benchmark. Lastly, the AMP-based CO₂ capture plant with solvent storage was retrofitted into the NGCC. A thermodynamic assessment revealed that the AMP-based process resulted in 25.6% lower reboiler duty, compared to that of the MEA-based process. Regardless of the superior thermodynamic performance, the economic performance of the AMP-based process was shown to be better than that of the MEA-based process only for make-up rates below 0.03% of total flowrate in the system. Furthermore, results revealed that the process with solvent storage was found to increase the profit by approximately 1% compared to that without solvent storage. Hence, this thesis showed that the use of AMP as a solvent in chemical solvent scrubbing is a good option, but may not be the most feasible option from the economic standpoint.

Keywords: Post-combustion capture, 2-Amino-2-Methyl-1-Propanol, Natural gas combined cycle, Modelling and simulation, Solvent storage, Economic analysis.

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TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS.....	ii
LIST OF FIGURES.....	vii
LIST OF TABLES	x
LIST OF ABBREVIATIONS	xii
LIST OF SYMBOLS	xiv
Superscripts	xv
1 INTRODUCTION.....	1
1.1 Research Background	1
1.1.1 Climate Change and CO ₂ Emission	1
1.1.2 Reconciling the Problem of Climate Change.....	3
1.2 Carbon Capture and Storage (CCS)	5
1.3 Combined Cycles Power Plants.....	5
1.3.1 Integrated Gasification Combined Cycle (IGCC)	6
1.3.2 Biomass Gasification Combined Cycle (BGCC).....	7
1.3.3 Natural Gas Combined Cycle (NGCC)	8
1.4 Major CO ₂ Capture Approaches	10
1.4.1 Post-Combustion Capture	10
1.4.2 Pre-Combustion Capture.....	11
1.4.3 Oxy-Fuel Combustion.....	11
1.5 Technology readiness level	12
1.6 Gas Treating Processes	14
1.6.1 Absorption	14
1.6.2 Physical Absorption.....	14
1.6.3 Chemical Absorption	14
1.7 Alkanolamines in Gas Treating	14
1.7.1 MEA	15
1.7.2 Diethanolamine (DEA).....	16
1.7.3 Methyldiethanolamine (MDEA).....	16
1.7.4 Sterically Hindered Amines	16
1.8 Motivation	17
1.9 Scope of Study	19
1.10 Aim and Objectives	20
1.11 Thesis Structure.....	21
2 LITERATURE REVIEW	22
2.1 Chemistry of CO ₂ Reaction with Aqueous Alkanolamines.....	22
2.1.1 Mechanism of CO ₂ Reaction with Aqueous Alkanolamines	23
2.1.2 Zwitterion Mechanism	23
2.1.3 AMP Solvent	25
2.1.4 Advantages of AMP over MEA.....	27
2.2 AMP-Based CO ₂ Post-Combustion Capture Process	32

2.2.1 Process Description	32
2.3 Degradation Studies	34
2.3.1 Thermal Degradation.....	35
2.3.2 Oxidative Degradation.....	35
2.4 AMP Degradation Chemistry	36
2.4.1 Mechanism for the Degradation Products	36
- Formation of Acetone	36
- Formation of 4, 4-Dimethyl-2-Oxazolidinone	37
- Formation of 2, 4-Lutidine	38
2.5 AMP-Based Process for CO ₂ Capture Plant from NGCC Power Plant ...	39
2.6 Solvent Storage System	40
2.7 Different Flowsheeting Configurations	42
2.7.1 Split Flow Configuration	42
2.7.2 Intercooling Configuration	43
2.7.3 Lean Amine Flash Configuration	44
2.7.4 Rich Split Configuration.....	45
2.7.5 Vapour Recompression.....	46
2.8 Research Gaps.....	47
3 PROCESS SIMULATION	51
3.1 Introduction	51
3.2 Methods/Approaches Available for Modelling and Simulation of Amine-Based Process for CO ₂ Capture from NGCC Power Plant.....	52
3.3 Aspen-Plus Rate Based Modelling	52
3.4 Gas-Liquid Phase Equilibria.....	55
3.5 Fugacity and Fugacity Coefficient.....	55
3.5.1 Activity and Activity Coefficient.....	55
3.6 Rigorous Vapour-Liquid-Equilibrium (VLE) Models for CO ₂ -Amines- H ₂ O Systems	56
3.6.1 Models for the Fugacity Coefficient	56
3.6.2 Models for the Activity Coefficient	57
- Electrolyte-NRTL Model (e-NRTL)	57
4 AMP-Based Capture Plant Modelling and Simulation	59
4.1 Introduction	59
4.2 Model Description	60
4.3 Model Validation	62
4.3.1 Absorber Model Validation	63
4.3.2 Stripper Model Validation	67
4.4 Scale-Up of the Capture Plant Model.....	70
4.4.1 Considerations	70
4.4.2 Procedure for Scale-Up.....	70
4.5 Process Analysis of Capture Plant.....	73
4.5.1 Sensitivity Analysis.....	73
4.6 Conclusion	78
5 INTEGRATION STUDIES	79

5.1 Introduction	79
5.2 Power Plant Modelling	80
5.3 CO ₂ Compression Train	81
5.4 Process Integration with amine-based solvents	83
5.4.1 Integration of the AMP-Based Process into the NGCC Power Plant.....	83
5.4.2 Thermodynamic Performance Analysis.....	84
5.5 Solvent Storage Tanks Description.....	90
5.5.1 Process Integration with Solvent Storage.....	91
5.6 Integration with Solvent Storage Tanks	94
5.7 Conclusions	95
6 ECONOMIC ANALYSIS	96
6.1 Introduction	96
6.2 Measures of Costs	97
6.2.1 Cost of electricity (COE).....	97
6.2.2 Cost of capture (COC).....	98
6.2.3 Total cost (TC)	98
6.2.4 Levelized cost of electricity (LCOE)	98
6.2.5 CO ₂ avoidance cost.....	99
6.3 Considerations.....	99
6.3.1 Estimation of Cost for Solvent Storage.....	101
6.4 Economic Performance Assessment of the NGCC Power Plant Retrofit with the AMP-Based and MEA-based Capture Plants.....	105
6.5 Sensitivity Analysis	107
6.5.1 Variation of Fuel Cost.....	107
6.5.2 Variation of Capacity Factor	108
6.5.3 Variation of Make-Up Flowrate	109
6.6 Economic Performance of the NGCC Power Plant Retrofit with the AMP-Based Capture Plant and Solvent Storage	110
6.7 Sensitivity Studies.....	113
6.7.1 Variation of Price Change Difference	113
6.7.2 Variation of Carbon Tax	114
6.7.3 Payback period	116
6.8 Conclusion	117
7 CONCLUSION and RECOMMENDATION.....	118
7.1 Conclusions	118
7.2 Linkage of Projects Objectives.....	120
7.3 Recommendations for Future Work	123
REFERENCES.....	125
Appendix A NGCC Power Plant Validation	146
Appendix B Capture Plant Design and Operating Conditions	147
Appendix C Integration Calculations.....	152
Appendix D Publications and Conferences.....	156

LIST OF FIGURES

Figure 1-1: CO ₂ concentration in the atmosphere (a), and temperature (b), as a function of the year (CO ₂ .earth, 2018; National Oceanic and Atmospheric Administration, 2016).....	2
Figure 1-2: Global greenhouse gas emission.....	3
Figure 1-3: Anticipated contributions of various technology options to worldwide CO ₂ emissions decrease (IEA, 2015).....	4
Figure 1-4: Integrated gasification combined cycle power plant (Buchanan et al., 2000)	6
Figure 1-5: Biomass gasification combined cycle system (Zafar, 2018).....	7
Figure 1-6: Natural gas combined cycle power plant (Siemens, 2012)	9
Figure 1-7: Various options for fossil-fuel based power generation systems (Rao & Rubin, 2002).....	9
Figure 1-8: CO ₂ capture technical options (Global CCS Institute, 2011)	11
Figure 1-9: Different alkanolamines (Kohl & Nielsen, 1997).....	15
Figure 1-10: Structures of sterically hindered amines (Kohl & Nielsen, 1997).....	15
Figure 1-11: Post-combustion research gaps (IEAGHG, 2013; Shi et al., 2014).....	19
Figure 2-1: Loading capacity (Anthony, 2006).....	27
Figure 2-2: Regeneration efficiencies of different alkanolamines at a concentration of 1.0kmol/m ³ , regeneration temperature of 383k (Zhang et al., 2008)	28
Figure 2-3: Heat of reaction of amines (Anthony, 2006).....	29
Figure 2-4: Degradation rates of different amines (Wang & Jens, 2012)	29
Figure 2-5: Thermal degradation of AMP (Wang & Jens, 2012).....	30
Figure 2-6: Environmental impacts of CO ₂ absorbents (Hassim and Ali, 2009).....	31
Figure 2-7: Absorption rates of different amines (Chowdhury et al., 2011)	32
Figure 2-8: Basic flowsheet for an amine-based CO ₂ capture process (Global CCS Institute, 2012b).....	33
Figure 2-9: Scheme for oxidative degradation of AMP with O ₂ (Wang & Jens, 2012)	36
Figure 2-10: Scheme for degradation of AMP with CO ₂ (Wang & Jens, 2012)	37
Figure 2-11: Scheme for degradation for 2, 4-Lutidine (Wang & Jens, 2012)	38
Figure 2-12: Solvent storage process flowsheet (Chalmers and Gibbins, 2007).....	41
Figure 2-13: Split-flow process configuration (Cousins et al., 2011)	43

Figure 2-14: Intercooled absorber configuration (Cousins et al., 2011).....	44
Figure 2-15: Lean amine flash process configuration (Ahn et al., 2013).	45
Figure 2-16: Rich split modification (Cousins et al., 2011)	46
Figure 2-17: Vapour recompression process flowsheet (Cousins et al., 2011).	47
Figure 3-1: Approaches for modelling reactive absorption processes (Kenig et al., 2001)	53
Figure 3-2: Two film theory approach (Richardson et al., 2007).....	54
Figure 4-1: Process flowsheet of the AMP-based pilot plant for CO ₂ capture (Dash et al., 2014)	60
Figure 4-2: Liquid phase temperature profiles in the absorber	65
Figure 4-3: Liquid phase temperature profiles in the stripper	68
Figure 4-4: Generalized pressure drop correlation chart (Sinnott and Towler, 2013; Perry & Green, 2008)	72
Figure 4-5: Effect of solvent concentration and lean loading on reboiler duty	74
Figure 4-6: Effect of solvent concentration on circulation rate	76
Figure 4-7: Effect of stripper pressure on reboiler duty and reboiler temperature for AMP solvent	77
Figure 5-1: Process flow diagram of the five-stage CCU model for the AMP-based process.....	82
Figure 5-2: Aspen Plus process flowsheet of the NGCC power plant retrofitted with AMP-based process and CO ₂ compression unit.....	88
Figure 5-3: Parasitic load distribution for NGCC retrofit with MEA-based process...	89
Figure 5-4: Parasitic load distribution for NGCC retrofit with the AMP-based process	89
Figure 5-5: Aspen Plus process flowsheet of the integrated NGCC power plant, AMP-based capture plant, CO ₂ compression unit (CCU) and solvent storage tanks.....	93
Figure 6-1: Flowchart of economic analysis framework (Aspen Technology, 2010)	101
Figure 6-2: Variation of time against electricity spot price (EPEX SPOT, 2017).....	103
Figure 6-3: Distribution of LCOE by cost component	106
Figure 6-4: Effect of fuel cost on LCOE	107
Figure 6-5: Effect of capacity factor on LCOE	108
Figure 6-6: Effect of make-up rate on LCOE	110

Figure 6-7: Economic evaluation of the NGCC power plant with AMP-based plant and solvent storage; (a) Comparison of short-run profit, (b) daily revenue distribution	113
Figure 6-8: Effect of peak price differential on the short-run profit.....	114
Figure 6-9: Effect of carbon tax on the short-run profit.....	115
Figure 7-1: Linkage of project objectives.....	122
Figure B-1: Effect of packing height against temperature.....	147
Figure B-2: Temperature profile for case 34.....	149
Figure B-3: Temperature profile for case 1.....	150
Figure B-4: Temperature profile for case 33.....	150
Figure B-5: Temperature profile results for case 1	151
Figure B-6: Temperature profile results for case 33	151
Figure B-7: Temperature profile results for case 34	152

LIST OF TABLES

Table 1-1: Summary of CO ₂ capture technologies (Global CCS Institute, 2012b) ...	13
Table 1-2: Summary of CO ₂ capture technologies (Florin & Fennell, 2010; Oko et al., 2017; IEAGHG, 2015)	13
Table 2-1: A review of different studies on the modelling with packed columns using AMP solvent for CO ₂ capture technology	50
Table 4-1: Coefficients of equilibrium constants	62
Table 4-2: Power law expressions constants	62
Table 4-3: Design data of the pilot plant (Gabrielsen et al., 2007)	62
Table 4-4: Input parameters for validation of absorber model (Gabrielsen et al., 2007)	63
Table 4-5: Comparison of model predictions with experimental data (Gabrielsen et al., 2007) for the absorber.....	63
Table 4-6: Comparison of model predictions with experimental data (Gabrielsen et al., 2007) for the temperature profiles in the absorber	66
Table 4-7: Input parameters for validation of stripper model (Gabrielsen et al., 2007)	67
Table 4-8: Comparison of model predictions with experimental data for the stripper (Gabrielsen et al., 2007).....	67
Table 4-9: Comparison of model predictions with experimental data for the temperature profiles in the stripper (Gabrielsen et al., 2007)	69
Table 4-10: Flue gas composition (NETL, 2010).....	70
Table 4-11: Operating conditions for the full-scale AMP-based process model in Aspen Plus (Aspen Tech, 2008b; Lawal et al., 2010; Agbonghae et al., 2014) .	71
Table 4-12: AMP-based process full-scale plant preliminary design parameters in Aspen Plus	73
Table 4-13: MEA-based process full-scale plant preliminary design with Aspen Plus	78
Table 5-1: NGCC design specifications (NETL, 2010)	81
Table 5-2: Compression train design data.....	82
Table 5-3: Energy performance of the AMP-based and MEA-based process retrofits	85
Table 5-4: Aspen Plus AMP PCC large-scale PCC plant with solvent storage specification and operations	91
Table 5-5: Results for solvent storage system	94

Table 5-6: Results for integration with solvent storage.....	94
Table 6-1: Economic analysis assumptions and cost inputs	102
Table 6-2: Economic analysis for AMP-based and MEA-based processes.....	105
Table 6-3: Economic performance indicators	111
Table 6-4: Results for payback period	116
Table A-1: Aspen Plus NGCC power plant model with capture stream data (NETL, 2010)	146
Table A-2: Validation of the Aspen Plus NGCC power plant model	146
Table B-1: Comparison of different packing materials.....	148
Table B-2: Validation of aqueous MEA plant model against the pilot plant data by Notz et al. (2012).....	149

LIST OF ABBREVIATIONS

AMP	2-Amino-2-Methyl-1-Propanol
APEA	Aspen Process Economic Analyser
BGCC	Biomass Gasification Combined Cycle
CCGT	Combined Cycles Gas Turbine
CCS	Carbon Capture and Storage
CCU	CO ₂ Compression Unit
COC	Cost of Capture
COS	Carbonyl sulphide
CS ₂	Carbon disulfide
DCC	Direct Contact Cooler
DEA	Diethanolamine
DGA	Diglycolamine
DOE	Department of Energy
ELECNRTL	Electrolyte-Non-Random-Two-Liquid
EJ	Exajoule
EOS	Equation of State
EPEX	European Power Exchange
FCF	Fixed Charge Factor
GCCSI	Global Carbon Capture and Storage Institute
GHG	Greenhouse Gas
HP	High Pressure
HRSG	Heat Recovery Steam Generator
IEA	International Energy Agency
IEAGHG	International Energy Agency Greenhouse Gas
IGCC	Integrated Gasification Combined Cycle
IP	Intermediate Pressure
IPCC	Intergovernmental Panel on Climate Change
LCOE	Levelised Cost of Electricity
LHV	Lower Heating Value
LP	Low Pressure
LR	Long Range electrostatic interactions
MDEA	Methyl diethanolamine
MEA	Monoethanolamine
NETL	National Energy Technology Laboratory
NGCC	Natural Gas Combined Cycle
NOAA	National Oceanic and Atmospheric Administration
NRTL	Non-Random Two Liquid
O&M	Operation and Maintenance
PCC	Post-Combustion Capture

PDH	Pitzer-Debye-Huckel
PZ	Piperazine
R&D	Research and Development
RK	Redlich-Kwong
SR	Short Range electrostatic interactions
SRK	Soave-Redlich-Kwong
SRMC	Short-Run Marginal Cost
SRP	Short-Run Profit
TEA	Triethanolamine
UNIQUAC	Universal Quasi-Chemical

LIST OF SYMBOLS

Symbol	Description	SI Unit
A	Heat transfer area	m^2
C	Concentration	Mol dm^{-3}
C_o	Capacity factor	-
C_p	Specific heat capacity	$\text{J kg}^{-1}\text{K}^{-1}$
A, B, C, D	Constant parameters in the equation relating equilibrium constant to temperature	-
D	Diameter	m
D	Discount factor	-
F_g	Fugacity of species i in gas phase	Nm^{-2} (Pa)
f_i	Fugacity of species i	Nm^{-2} (Pa)
f_i^{id}	Fugacity of species i in an ideal solution	Nm^{-2} (Pa)
F_l	Fugacity of species i in liquid phase	Nm^{-2} (Pa)
F_p	Packing factor	m^{-1}
G	Gas flowrate	Kg s^{-1}
G^E	Excess molar Gibbs energy of a mixture	J mol^{-1}
$G^{E,LR}$	Long-range contribution to the excess Gibbs energy	J mol^{-1}
$G^{E,SR}$	Short-range contribution to the excess Gibbs energy	J mol^{-1}
h_c	Convective heat transfer coefficient	$\text{J sec}^{-1}\text{m}^{-2}\text{K}^{-1}$
H_i	Henry's constant of species i	Nm^{-2} (Pa)
k	Rate of cooling constant	-
K	Thermal conductivity	$\text{J sec}^{-1}\text{m}^{-1}\text{K}^{-1}$
k^0	Pre-exponential factor	-
K_{eq}	Equilibrium constant	-
L	Length	m
L	Liquid flowrate	Kg s^{-1}
m	mass	kg
N_u	Nusselt number	-
P	Pressure	bar
P_r	Prandtl number	-
Q	Heat transfer	J
r	Rate constant	$\text{Mol dm}^{-3}\text{s}^{-1}$

R	Gas constant	$\text{J mol}^{-1}\text{K}^{-1}$
R	Rating of the plant	MW
R_e	Reynolds number	-
t	Time	secs
T_a	Ambient temperature	K
U	Plant utilisation	hours/yr
U_s	Superficial velocity	m s^{-1}
V	Velocity	m s^{-1}
V	Volume	m^3
V_i	Molar volume of species i	$\text{m}^3 \text{kmol}^{-1}$
X	Flow parameter	-
X_i	Mole fraction of species i in solution	-
Y	Analysis period	Years
$n_{j \neq i}$	Number of moles of all species, excluding the i th species, present in a given system	mol
ρ_g	Density of the gas	Kg m^{-3}
ρ_l	Density of liquid	Kg m^{-3}
μ	Kinematic viscosity	$\text{m}^2 \text{s}^{-1}$
γ_i	Activity coefficient of species i	-
$\emptyset_i$	Fugacity coefficient of species i	-

Superscripts

Symbol	Description
a	Reaction order
E	Excess property
N	Number of components in the reaction
sat	Saturated condition
v_i	Vapour phase condition stoichiometric number of species i
∞	Infinite dilution reference state
id	Ideal solution condition
l	Liquid or liquid phase
Y	Analysis period

Subscripts

Symbol	Description
i, j	Species in the gas and/or liquid phase(s)
∞	Infinite dilution reference state
t	Stages for the compressor
m	Mass holdup

1 INTRODUCTION

1.1 Research Background

1.1.1 Climate Change and CO₂ Emission

Anthropogenic CO₂ emissions have risen tremendously over the past 150 years; this has led to a significant increase of CO₂ level in the atmosphere (Figure 1-1a) and an increase in average global temperatures as shown in Figure 1-1(b) (Global CCS Institute, 2011a). The Intergovernmental Panel on Climate Change (IPCC) has shown that climate change and the anthropogenic CO₂ emissions are associated with energy production and consumption (IPCC, 2014a). This has led to the approval of the commitment to maintain global average temperature rise to 2 °C (IEA, 2013a) because this temperature rise is steady and most likely to maintain the atmospheric CO₂ equivalent concentration levels up to 430-480 ppm by 2050 (IPCC, 2014b).

There are so many consequences of climate change on the environment such as accelerated sea level rise, a continuous rise in temperature, intense heat waves etc. The concentration of global-scale trace-gas existing in the 1750s is governed by assumptions which have less dependence on human activities such as the burning of fossil fuels, increment of agriculture, etc. (IPCC, 2013). Based on global greenhouse gas emission data as shown in Figure 1-2, the IPCC suggested that energy supply is the major contributor/emitter of greenhouse gases (IPCC, 2014a).

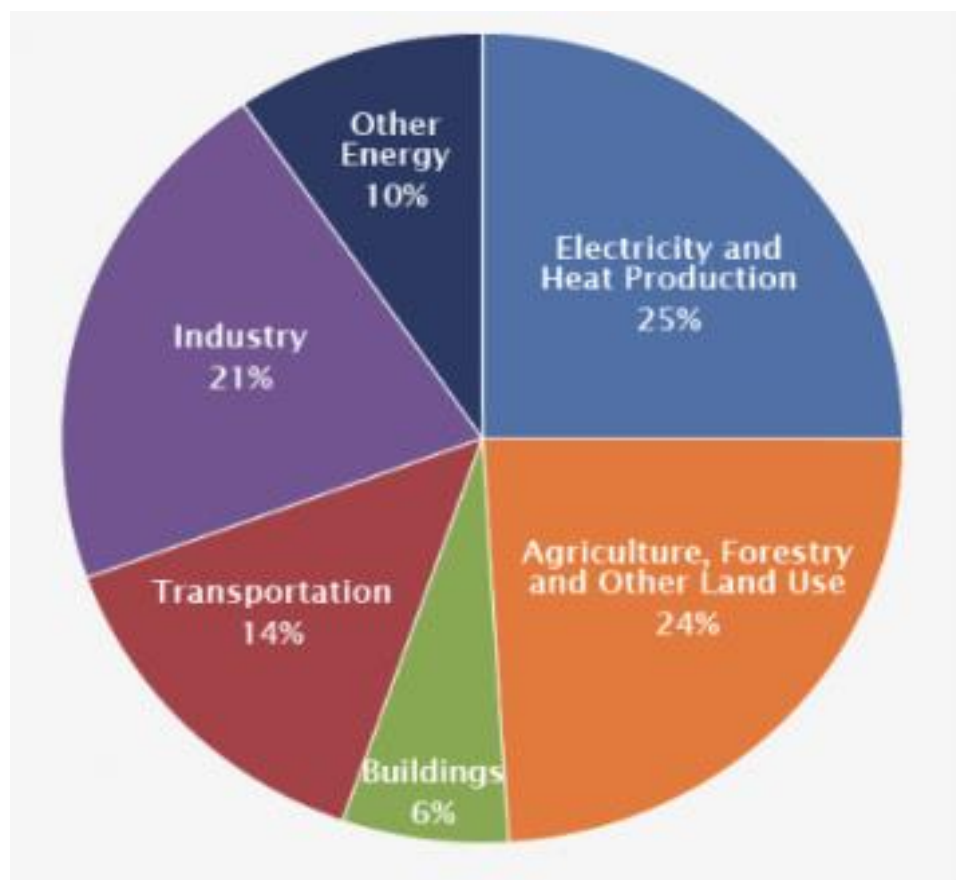


Figure 1-2: Global greenhouse gas emission

source (IPCC, 2014a)

1.1.2 Reconciling the Problem of Climate Change

A major challenge to the environment is the emission of greenhouse gases such as CO₂. Therefore, CO₂ emission reduction is important, and one of the means of overcoming this problem is via CO₂ capture. However, the cost involved in commercial scale capture plant is a major setback (Rubin et al., 2007).

Studies (Global CCS Institute, 2011a; IEA, 2010) suggest that CO₂ emissions from energy-related sources can be addressed through a portfolio of technologies.

- i. Reducing energy consumption by means of an effective energy conversion or utilisation
- ii. Switching to less carbon-intensive fuels (e.g. from coal to gas)
- iii. Increasing the use of renewable energy sources or nuclear energy
- iv. Sequestering CO₂ by enhancing biological absorption capacity in forests and soils
- v. Capturing and storing CO₂

It is also very likely that reduction in the energy consumption by way of the enhancement of less-energy intensive economic activities will have a high impact in the reduction of CO₂ emission in the short term (up to 2020). It is important to mention that between 2025 and 2030, CCS is expected to play a rapidly expanding role alongside the deployment of renewables. However, in accordance with the energy emission scenarios developed by International Energy Agency (IEA) as shown in Figure 1-3, CCS is relied upon to contribute around 13% to a worldwide CO₂ emission decrease by 2050 (IEA, 2015).

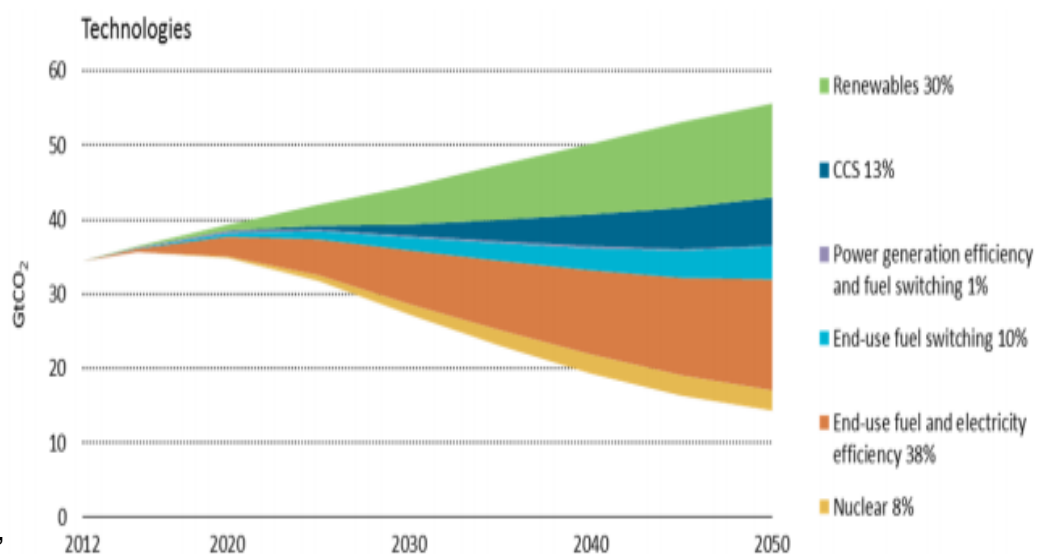


Figure 1-3: Anticipated contributions of various technology options to worldwide CO₂ emissions decrease (IEA, 2015)

1.2 Carbon Capture and Storage (CCS)

Carbon capture and storage (CCS) is the capturing of CO₂ from large industrial plants such as power stations that use fossil fuels (gas, coal, and crude oil) or other carboniferous fuels like biomass. The captured CO₂ is transported to a secure deposit spot and discharged in deep rock formations, or oceans at great depth, for permanent and secured storage (Global CCS Institute, 2011b).

The main restriction for deploying large-scale CO₂ capture systems is the cost associated with capture, which increases the cost of electricity, transport (safe route for pipelines) and storage (suitability of storage site and liability). This increase in cost arises when the capture plant is integrated into the power plant, leading to a reduction in power output. The addition of capture reduces the net power output for a fixed input energy. The reduction in net power output is because of the steam requirements needed for stripping of CO₂, which leads to an energy penalty and increases the cost of electricity (Aroonwilas & Veawab, 2007). Also, the equipment such as pumps, and the energy required for CO₂ compression etc. used in the amine process also utilises electricity. Therefore, efforts are required to ensure minimal energy penalty of the capture plant and its integration into the power plant. There are several means of reducing the energy penalty; these are the use of new or improved solvents, better heat integration, different flow sheeting configurations, etc. (Lucquiaud and Gibbins, 2009; Cousins et al., 2011).

1.3 Combined Cycles Power Plants

The use of combined cycles in the last decades brought about higher thermal efficiency and increased power generation when compared to simple cycles alone (Soares, 2007). Combination of multiple thermodynamic cycles (such as Brayton and Rankine cycles) to generate power refers to the combined cycle. In the power generation systems, integration of the Brayton cycle (top cycle) and Rankine cycle (bottom cycle), gives the combined cycle plant. The heat recovery steam generator (HRSG) is used to capture heat from the Brayton cycle to produce steam for the Rankine cycle, after which steam is expanded to increase the amount of electricity generated (NETL, 2010). Thus, these combined cycles bring about the recovery of waste heat from the HRSG. A typical gas turbine open cycle can produce up to 33% electricity, but by using combined cycle gas turbine (CCGT) with natural gas, a net

efficiency of about 55-60% LHV range can be achieved (Franco & Russo, 2002; Siemens, 2012; Franco, 2010).

1.3.1 Integrated Gasification Combined Cycle (IGCC)

Presently, efficiency of about 50% are expected with advanced integration of coal gasification combined cycle, and approximately 43% of global CO₂ emissions by the consumption of fossil fuels, result from the use of coal-fired power stations (IEA, 2011).

A standard integrated gasification combined cycle (IGCC) is a technology where solid fuel such as coal is gasified to obtain syngas, which involves using a shift reactor. The shift reactor ensures conversion of most of the CO in the syngas into CO₂ gas (Chiesa & Consonni, 1999) as shown in Figure 1-4.

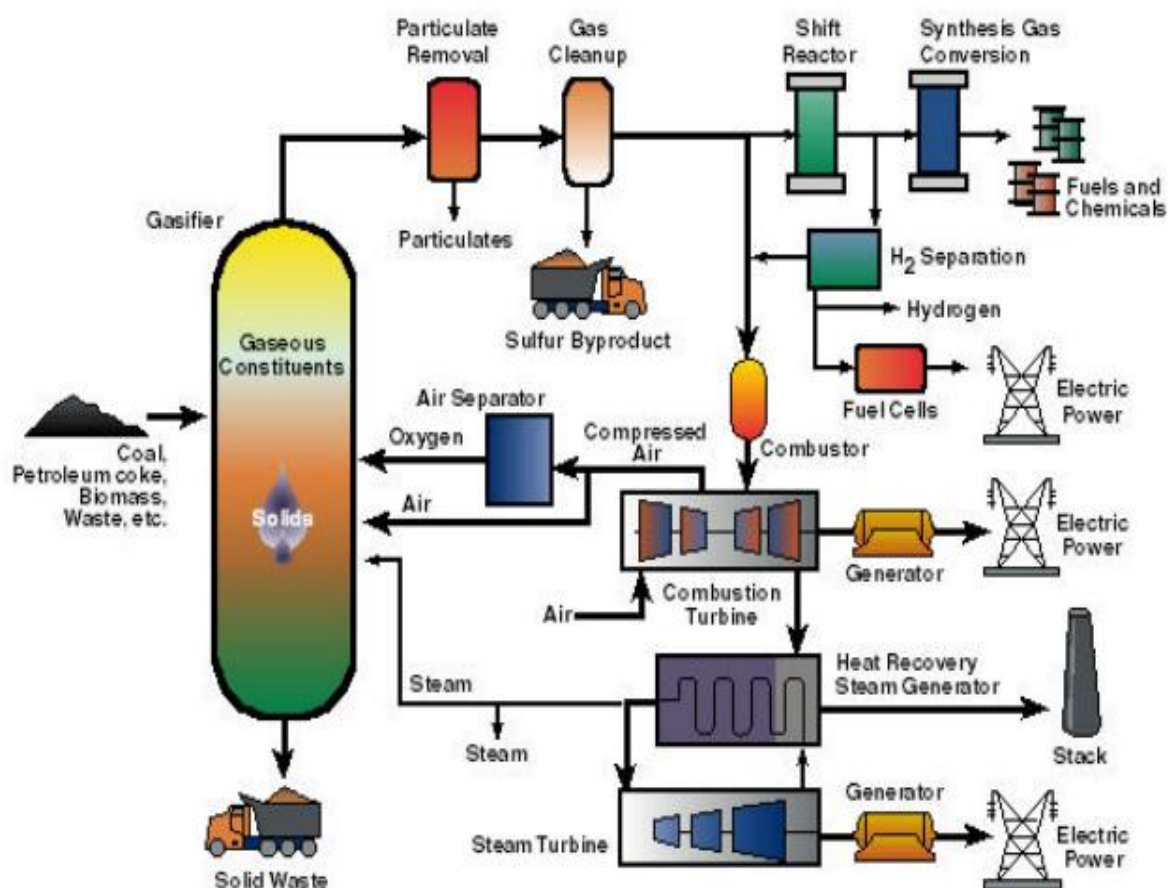


Figure 1-4: Integrated gasification combined cycle power plant (Buchanan et al., 2000)

1.3.2 Biomass Gasification Combined Cycle (BGCC)

The European Commission has high expectations for biomass and can be seen as a fuel with lots of potentials and a sustainable resource (IEA Bioenergy, 2010). The potential of biomass to produce a minimum of 50-75% of the total energy required in Europe is high (Ernsting, 2015). Past years confirms that biomass gasification is a very reliable means of converting fuels mostly solids into gaseous energy carriers. This has led to activities worldwide to focus on several technologies for the combination of heat and power production, which aims at demonstrating the economic possibilities to mark the hazards related to these techniques (Klimantos et al., 2009). Production of electricity from biomass usually involves two main options; these are combustion and gasification.

The primary challenge with biomass gasification is an effective gas cleaning (Ernsting, 2015). Also, an additional risk is associated with biomass technology, since wood dust is highly explosive, the health and safety risks associated with plants involving large quantities of woodchips poses a challenge (Ernsting, 2015). Figure 1-5 shows a typical biomass gasification system.

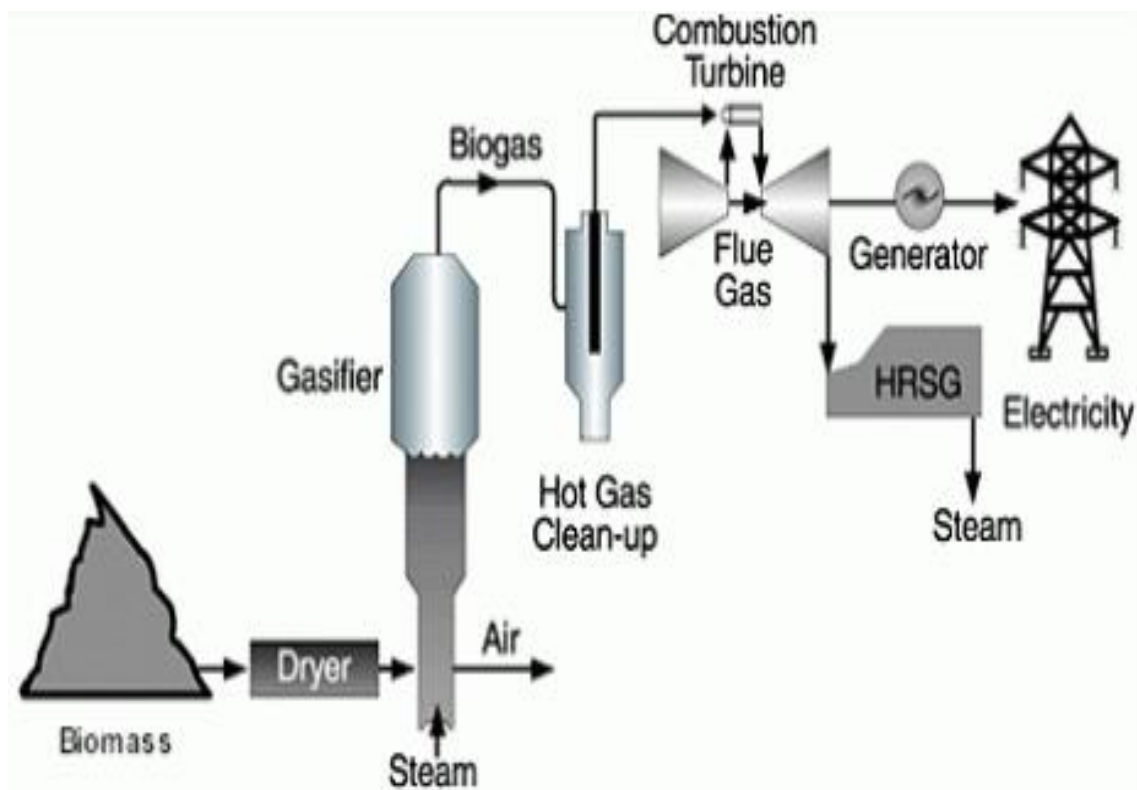


Figure 1-5: Biomass gasification combined cycle system (Zafar, 2018)

1.3.3 Natural Gas Combined Cycle (NGCC)

The natural gas power plant is among the power plant that emits a lower amount of CO₂ emissions compared to coal, oil, or biomass-fired power plant for power generation and has an efficiency of up to 55-60% (Siemens, 2012). Natural gas fuel has a greater advantage compared to coal. This is because of its low carbon intensity, and the emissions produced from natural gas is 50% lower than that of coal (EIA, 2012). Other advantages of natural gas power plants over coal include; higher operating flexibility, lower investment cost, and relatively short construction time. Therefore, in power generation systems, natural gas power plants will continuously be used to generate electricity and reduce the carbon emissions in CCS technology (NETL, 2010).

The natural gas combined cycle (NGCC) power plant as described in Figure 1-6 generates electricity from natural gas combustion and energy is extracted from the exhaust flue gases. Also, heat captured from the heat from the exhaust gases is used to produce steam, which in turn spins a generator to produce electricity. In the USA, from 2010 to 2020, the capacity of the NGCC power plant is expected to increase by 16 GW, and this will increase the generation of electricity from natural gas (EIA, 2012). Also, it is projected that by 2020, the efficiency of the CCGT will increase up to 65% (Rennings et al., 2009). Furthermore, natural gas is figured to be the quickest developing essential fossil fuel energy source worldwide, with an average growth of 2.0% every year and ascending to 161 EJ utilisation in 2025 (IEAGHG, 2006). The share of natural gas used to generate electricity worldwide is projected to increase from 25% of primary energy in 2004 to 31% in 2030 (IEAGHG, 2006).

Therefore, the possibility of using NGCC power plants for the capture of CO₂ with amines is a feasible option for short to medium term plan in reducing atmospheric CO₂ emissions from large point sources. New sources for natural gas have been identified (shale gas), which will account for 49% of the U.S.A total gas production in 2035 (EIA, 2012), because of this, natural gas has a high prospect for great improvement. The various options for the fossil-fuel based power generation systems are shown in Figure 1-7.

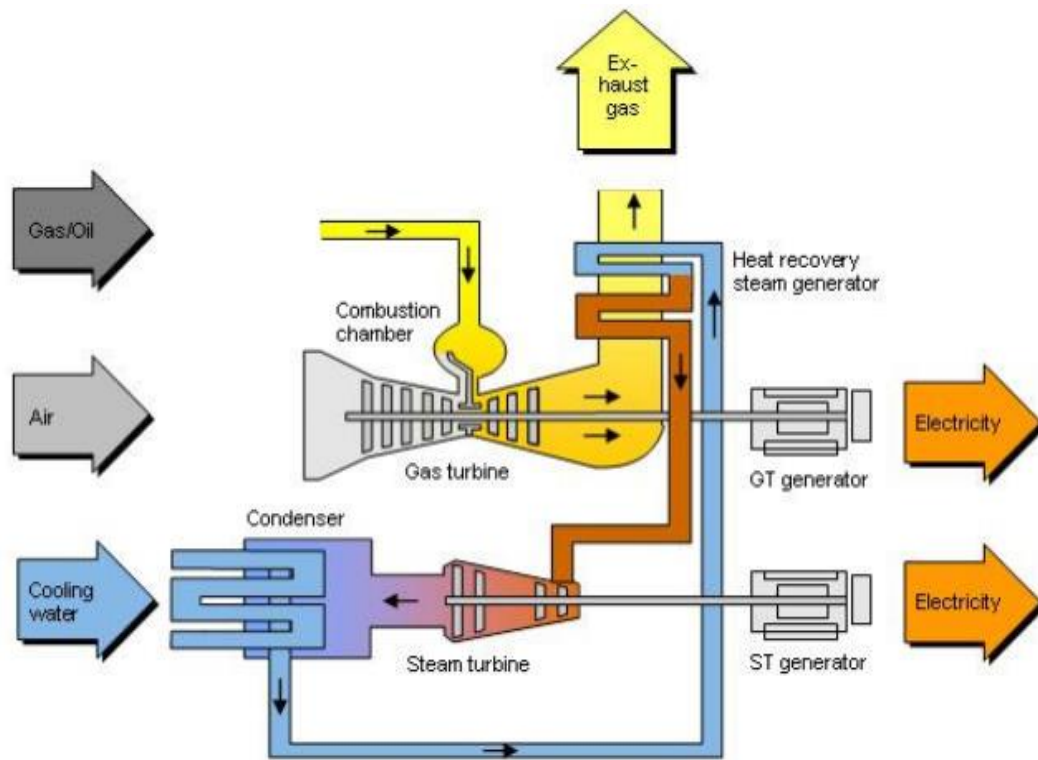


Figure 1-6: Natural gas combined cycle power plant (Siemens, 2012)

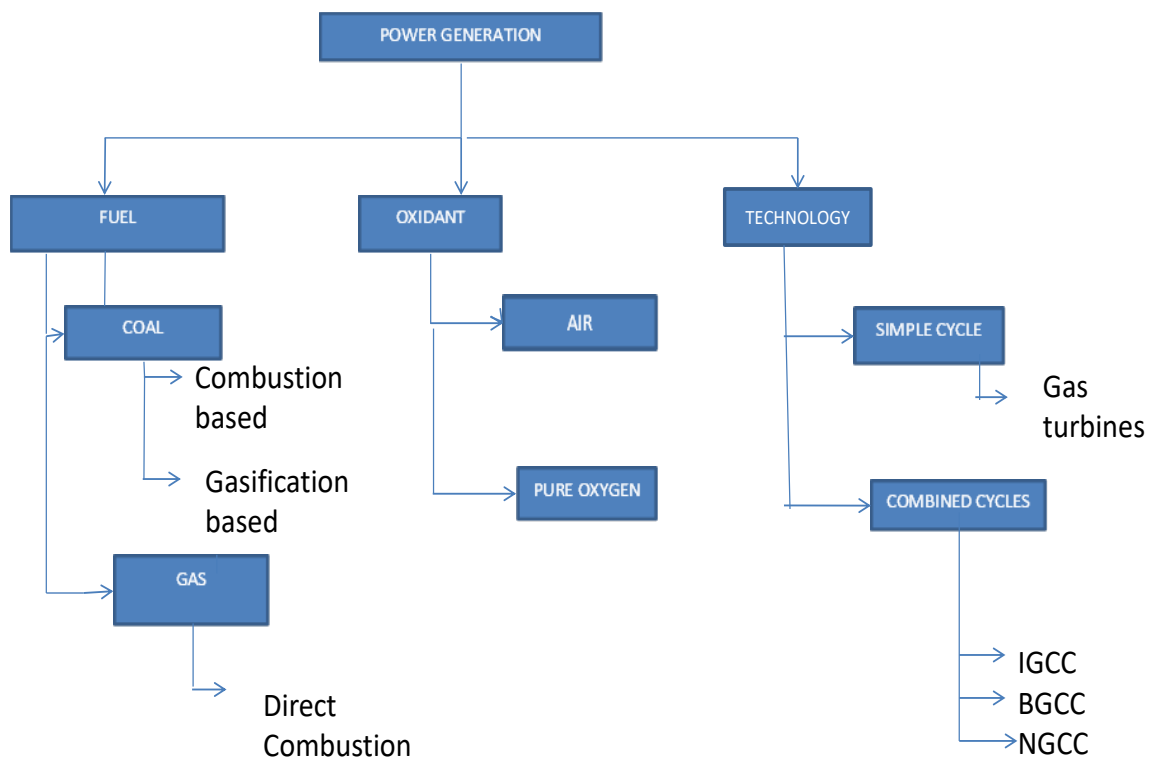


Figure 1-7: Various options for fossil-fuel based power generation systems (Rao & Rubin, 2002)

1.4 Major CO₂ Capture Approaches

The three major approaches for capturing CO₂ from power gas stations are (Florin and Fennell, 2010):

- Post-combustion
- Pre-combustion
- Oxy-fuel combustion

1.4.1 Post-Combustion Capture

Post-combustion capture (PCC) involves the absorption of CO₂ from flue gases emanating from large point CO₂ sources such as NGCC, cement plant, refinery etc. The combustion of fuel takes place, after which the CO₂ is captured. Chemical absorption is considered as the best choice for PCC, the reason being that the partial pressure of CO₂ in the flue gas which is sent to the stack is very low (Descamps et al., 2008). This capture process has advantages of being able to be retrofitted to an existing power plant (Wang et al., 2011). Also, this capture is energy intensive and represents about 75-80% of the total cost of CCS (Davison, 2007).

PCC technology, which has been used for over 50 years, has been employed mostly with primary alkanolamines using chemical absorption process (IPCC, 2007). The absorption involves the reaction of CO₂ with an amine to form carbamates (Khan et al., 2015). The carbamate formation accompanied with a high heat of formation leads to a significant energy penalty for solvent regeneration. The process also results in the reduction of efficiencies and increment in the cost of electricity. This is because of solvent sensitivity to chemical degradation, which comes from by-products such as sulphur oxides (SO_x) and nitrogen oxides (NO_x), and these products are usually present in the flue gas stream. Hence, pre-treatment such as flue gas desulphurisation to treat SO_x is carried out prior to entering the CO₂ capture plant. While to control the NO_x, a high-efficiency burner or selective catalytic reduction equipment is incorporated in the system (NETL, 2010).

Ways of improving PCC pose a major concern. As a result of this, the use of other amine-based solvents, which substitutes MEA having lower energy requirements for regeneration and degradation rates and solvent with better reaction kinetics, are the major priorities in future (Global CCS Institute, 2012b).

1.4.2 Pre-Combustion Capture

Pre-combustion capture can be used in coal gasification. The fuel is reacted first with air or oxygen to produce syngas, which contains CO, and H₂. The product reacts with steam in a shift gas reactor to produce CO₂ and H₂. After which, CO₂ is captured from the high-pressure gas mixture. The hydrogen is then used to generate electricity and heat (IEA, 2008). Physical absorption for a pre-combustion process is favoured by a high CO₂ partial pressure (Descamps et al., 2008). This capture is best employed in the IGCC plants in which coal is gasified under high temperatures and pressure. The solvent mostly used is rectisol or selexol, which are commercially available (Global CCS Institute, 2012a).

1.4.3 Oxy-Fuel Combustion

Oxy-fuel combustion is a process involving the use of pure oxygen for combustion instead of air as the primary oxidant. This leads to the production of flue gas that comprises CO₂ and H₂O. The partial recycling of flue gas into the combustion chamber controls the combustion temperature. This is because of the fuel combustion in pure oxygen. The separation of CO₂ from the flue gas stream then commences by the condensation of the water vapour (Davison, 2007). The various capture options are presented in Figure 1-8.

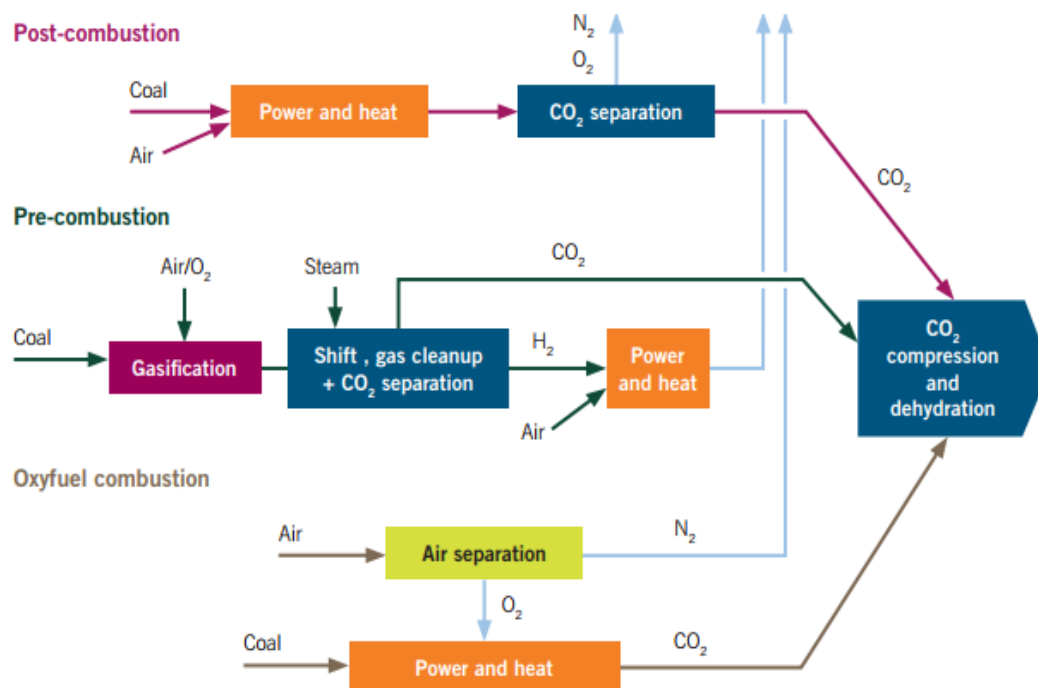


Figure 1-8: CO₂ capture technical options (Global CCS Institute, 2011)

Using NGCC with the solvent-based PCC has the following advantages over pre-combustion and oxy-fuel capture;

- PCC is the best option for natural gas-fired power plants because it is considered the most mature technology (IEA, 2013a). Hence, oxy-combustion and the pre-combustion approaches are rarely used for gas plants in the power industry (Global CCS Institute, 2014).
- It is considered the most flexible since the operation of the power plant is unaffected by shutting down the capture plant. The other capture options are extensively integrated into the power plant, which implies that, the failure of the capture plant at any point in time can lead to the shutdown of the entire plant (Global CCS Institute, 2014).
- Regarding cost, oxy-fuel offers the lowest because the need for any form of complexity is minimal. Hence, it does not require any extra solvent for separation, but high-level temperature materials and designs are required, while the complexity of pre-combustion lies with the chemical processes needed for gasification, which leads to high capital investment (Global CCS Institute, 2013).
- For Oxy-fuel combustion, the cycles are different from those in the NGCC because of the combustion system employed for oxy-fuel (Global CCS Institute, 2013). Thus, the different cycles may require a full re-design when taking into consideration the properties (transport) of CO₂, which comprises novel technologies and methodologies; this is very costly with high efforts required (Richards et al., 2012). This disadvantage poses a major setback for existing oxy-fuel systems.

1.5 Technology readiness level

Technology readiness level (TRL) is a system of ranking technology readiness using a scale of 1 to 9 as given in Table 1-1. Thus, the CCS technology using solvent absorption for CO₂ capture reaches TRL-9, as shown in Table 1-2.

Table 1-1: Technology readiness level (Global CCS Institute, 2012b)

TRL	Activity
1	Basic principles observed and initial concept
2	Formulation of application
3	Experimental proof of concept tests and component level
4	System validation in a laboratory environment
5	Subsystem validation in a relevant environment
6	Fully integrated pilot plant tested in a relevant environment
7	Subscale demonstration, fully functional prototype
8	Commercial demonstration, full-scaled deployment in final form
9	Actual commercial service in operational environment (CCS technology)

Table 1-2: Summary of CO₂ capture technologies (Florin & Fennell, 2010; Oko et al., 2017; IEAGHG, 2015)

Technology	Challenges
Solvent scrubbing with chemical solvents (TRL= 7-9)	High energy requirements (up to 4 GJ/tCO ₂), problems from corrosion, and degradation, huge sizes of equipment are needed
Ionic liquids (TRL= 2-3)	Extremely costly, complex process of manufacturing
Membrane separation technology (TRL=4-6)	Expensive materials, long period of time reliability issues with contaminants vulnerability, demonstration of commercial-scale pressure/vacuum equipment
Sorbent enhanced reforming using carbonate looping (TRL= 4-6)	The drop-off in CO ₂ capture capacity of sorbents, complex level of integration
Chemical-looping-combustion using solid metal-oxygen carriers (TRL=4)	Degradation of oxygen carriers during long-term cycling, usually relevant with the use of feedstock for coal or biomass
Oxy-fuel boiler with O ₂ separation from N ₂ by cryogenic air separation (TRL=4-6)	Very expensive and energy-intensive air-separation, temperature moderation when fuel is combusted in concentrated CO ₂

1.6 Gas Treating Processes

- I. Absorption into a liquid
- II. Adsorption on a solid
- III. Membranes
- IV. Chemical conversion to another compound
- V. Cryogenic separation

1.6.1 Absorption

Absorption involves the use of a solvent to dissolve CO₂ present in the flue gas. It is based on the reaction of a weak acid; CO₂ and a weak base, during which a water-soluble salt is formed (Vaidya & Kenig, 2007). Absorbing/regenerating with solvents such as alkanolamines is an effective method for eliminating acid gases (CO₂ and H₂S) from natural gas, oil refineries, and the production of ammonia and synthesis (Savage, 1980).

1.6.2 Physical Absorption

Physical absorption refers to a class of absorption processes, which use physical solvents such as selexol for separation. Physical absorption is most appropriate for gas mixtures having a high pressure and a high composition of the gas to be absorbed (Kohl & Nielsen, 1997).

1.6.3 Chemical Absorption

Chemical absorption is considered the most mature technology to be implemented in the mid-term for already existing power plants and new ones. However, it is regarded as an energy-intensive process because of the relatively large amount of energy required for the amine regeneration, which is the major drawback of this alternative (Manassaldi et al., 2014).

1.7 Alkanolamines in Gas Treating

Alkanolamines comprise the primary amines such as monoethanolamine (MEA), secondary amines, such as diethanolamine (DEA) and tertiary amines; an example is the methyl diethanolamine (MDEA). These amines are classified according to the number of organic groups attached to the alkaline nitrogen, and they also differ on the type of mechanism in which they react with CO₂, their reaction products and heat

of reaction (Morrison and Boyd, 1992). The structures for the unhindered and hindered amines are presented in Figure 1-9 and Figure 1-10 respectively.

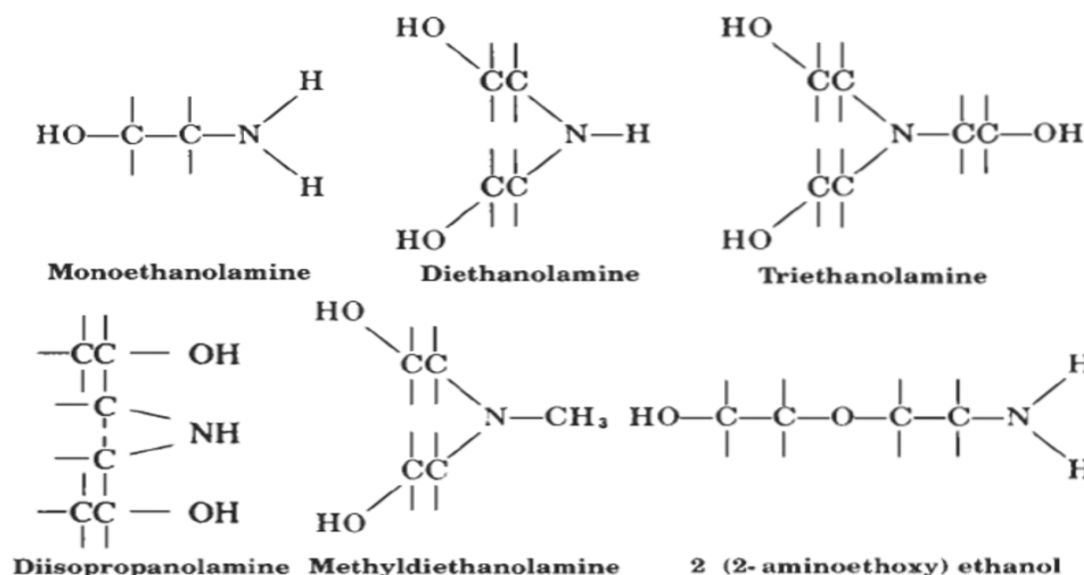


Figure 1-9: Different alkanolamines (Kohl & Nielsen, 1997)

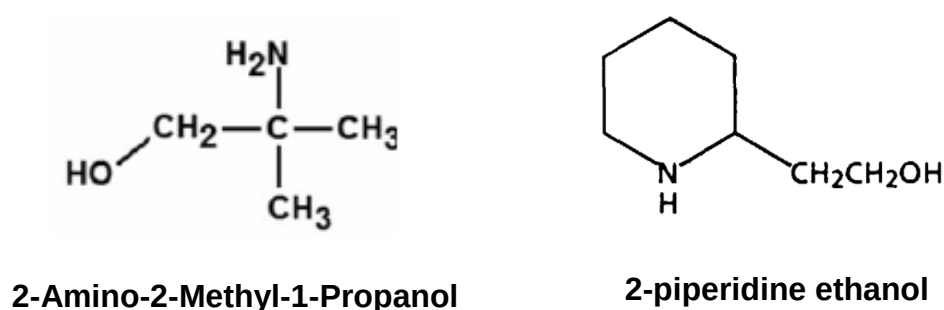


Figure 1-10: Structures of sterically hindered amines (Kohl & Nielsen, 1997)

1.7.1 Monoethanolamine (MEA)

This is a primary amine, which is known as the state-of-art solvent for gas streams, and some of the advantages for using the solvent are: the ease with which it can be reclaimed from contaminated solutions, its cheapness, and its high alkalinity. MEA is subject to oxidative and thermal degradation (Lepaumier et al., 2009b), this is a disadvantage. It is considered as a first choice in designing amine process for capture plants and has a very strong reactivity to CO₂ (Freguia, 2003). The main

benefits of using MEA is its high CO₂ reactivity, but it has a great disadvantage which is its high heat of reaction with CO₂, and this leads to a high energy requirement for regeneration in MEA systems (McCann et al., 2008; Kohl & Nielsen, 1997).

1.7.2 Diethanolamine (DEA)

This is a secondary amine, used for treating refinery gases which contains significant percentages of carbonyl sulphide (COS) and carbon disulphide (CS₂) in addition to H₂S and CO₂ (Kohl & Nielsen, 1997). For the treatment of gas streams containing COS and CS₂, most secondary amines like the DEA are proven to be better choices because their reactivity with COS and CS₂ is low compared with the primary amines. One of the disadvantages of DEA is that it undergoes many irreversible reactions with CO₂, forming products that are corrosive and can be degraded. Thus, this limits DEA to be considered as the optimum choice for the treatment of gases (Kohl & Nielsen, 1997).

1.7.3 Methyldiethanolamine (MDEA)

This is a tertiary amine widely utilised in the gas treating units and can be applied as a potential gas-sweetening agent, most especially for the selective removal of H₂S from gas streams in the presence of CO₂ (Frazier and Kohl, 1950). MDEA is likewise considered as an essential non-selective solvent for the huge elimination of CO₂ from gas streams, which is as a result of its low heating demands, huge capacity, wonderful stability, and other beneficial qualities. Also, due to its low vapour pressure, this amine can be applied in concentrations, which permit up to 60 wt% in aqueous solution without significant evaporation losses (Kohl & Nielsen, 1997). Furthermore, MDEA has a high resistant to thermal and chemical degradation, and it is non-corrosive. The principal disadvantage lies in the rate of reaction with CO₂ which is very low (Zhang & Chen, 2011).

1.7.4 Sterically Hindered Amines

Sterically hindered amine groups are referred to as primary amines because, in their structure, the amino group is linked to a tertiary carbon atom, they are also considered as secondary amines in which the amino group is linked to a secondary or tertiary carbon atom (Satori and Savage, 1987). These amines mostly use steric

hindrance in controlling the CO₂ and amine reactions (Kohl & Nielsen, 1997; Sartori et al., 1987). Typical examples of sterically hindered amines used in commercial gas treating include 2-amino-2-methyl-1-propanol (AMP), 2-piperidine ethanol (PE), AMPD (2-amino-2-methyl-1,3-propanediol), AMPA (2-amino-2-methyl propionic acid) etc. (White et al., 2003; Sartori et al., 1987). Figure 1-10 above shows the structural formulas of AMP and PE.

Research and development has directed all efforts in the improvement of PCC technologies (Department of Energy, 2010). One of the technologies is the use of improved solvents that have the potentials of improving CO₂ loading, reducing the energy requirement for regeneration and lastly, higher resistance to solvent degradation, compared to the MEA solvent (Department of Energy, 2015). The use of the improved solvents aim at a step forward progress in the phenomenon of a lower cost PCC technologies (Steenefeldt et al., 1995). A major reaction of interest between CO₂ and amines is the formation of a carbamate, which is likely to play some roles in the absorption of CO₂ (Khan et al., 2015).

1.8 Motivation

IEA predicted that global CO₂ emissions from the combustion of fuel will continue to grow unabated reaching about 35.4 GtCO₂ by 2035 (IEA, 2013b). Also, the IEA statistics shows that fossil fuels (coal, crude oil, and natural gas) account for approximately 80% of global energy production and consumption, and the fossil fuels are expected to remain the dominant sources of energy until 2050 (IEA, 2012). While the wide-scale deployment of renewable forms of energy (hydro, wind, biofuel etc.) is the anticipated long-term solution for climate change, our society will remain "fossil-fuelled" in short to medium term. Thus, the deployment of CCS is very important since fossil fuel will remain dominant in the global energy mix (IEA, 2009).

The global demand for natural gas use in power generation is expected to increase by about 85% from 2005 to 2030 (IEA, 2013a). Recent studies have shown that CO₂ can be captured and sequestered from natural gas-fired plants with a significant reduction in greenhouse gas emission (NETL, 2010; Lozza et al., 2009). CCS remains an available option for a reduction in CO₂ emissions. This implies that CCS has an important role to play in the sustainable energy development, and the continuous use of natural gas for electricity generation would substantially increase

CO₂ emissions (IEA, 2012). However, so many issues have to be addressed in order for CCS technologies to be implemented at a commercial scale. One of the challenges that hinders CCS from large-scale deployment in the power sector is the high capital and operating cost, which affects the cost of electricity. However, without CCS, it is estimated that the cost of reducing CO₂ emissions will increase by 40% (GCCSI, 2017). Therefore, CCS would not only help to protect the climate but also be an added-value to the fossil-fuel power plant fleet in future (IEA, 2013a).

Three main capture approaches commonly used to capture CO₂ in the power sector; include PCC (Saskpower, 2018), pre-combustion (NRG, 2018) and oxyfuel combustion capture (Vattenfall, 2006). The PCC approach contributes the most to CO₂ emission reduction from the fossil fuel power plant (Pfaff et al., 2010). The high energy penalty that is incurred when a PCC unit is added as an end-of-pipe retrofit to an existing power plant or as an integral part of a newly built power plant (MacDowell et al., 2010) is the key motivation to this study. To date, a high-efficiency penalty of PCC is far from being resolved. Therefore, studies on the solvent-based technology which employs the PCC approach are needed to reduce the energy penalty, capital and operating costs (Global CCS Institute, 2011; IEA, 2009). This is necessary to make PCC competitive with other technological options (i.e. pre-combustion and oxyfuel) and also as options for mitigating CO₂ emissions (e.g. renewables, and nuclear) (Global CCS Institute, 2011).

The MEA solvent, which is regarded as the benchmark solvent for CO₂ removal has been used in the early stage commercial-scale PCC plants (Pfaff et al., 2010). This MEA has several challenges, such as the high-energy requirement for regeneration, low resistance to degradation, high corrosion rates, and low absorption capacity. This leads to a significant energy penalty, which affects the performance of the power plant integrated with the capture plant. Because of this, improved solvents are proposed to help overcome the challenges of the MEA solvent. Thus, the use of sterically hindered amines, such as the AMP solvent is investigated in this research. This solvent has advantages which include lower energy requirement for regeneration, better resistance to solvent degradation, lower corrosion rates, and higher absorption capacity compared to that of the MEA solvent (Zhang et al., 2008; Wang & Jens, 2012; Anthony, 2006).

1.9 Scope of Study

CCS consists of three major areas: carbon capture, transportation, and storage. This study is focussed on the CO₂ capture at NGCC power plant. As stated in section 1.4, the solvent-based PCC technology is of high interest due to its TRL, which is 9. A highlight of different research directions within PCC is presented in Figure 1-11.

This research is focussed on the improvement of existing process design. This involves the PCC technology and the chemical absorption with aqueous alkanolamines. The sterically hindered amine (AMP) has been explored in this work due to its better characteristics compared to that of the unhindered amine (MEA). Furthermore, literature has confirmed that adding solvent storage brings about flexibility and could increase profit for the capture plant using MEA solvent (IEAGHG, 2012). Therefore, this study assesses the suitability of solvent storage in AMP application in order to improve the PCC process with AMP solvent. Thus, this research work is limited to analysis of process design involving solvent storage, and the use of more efficient operating conditions for the AMP-based process. The operating conditions include a higher temperature and pressure, a higher concentration and higher loadings as compared to that of the MEA-based process that will bring about savings in energy requirements, lead to a reduction of cost and increase the profit for the PCC technology.

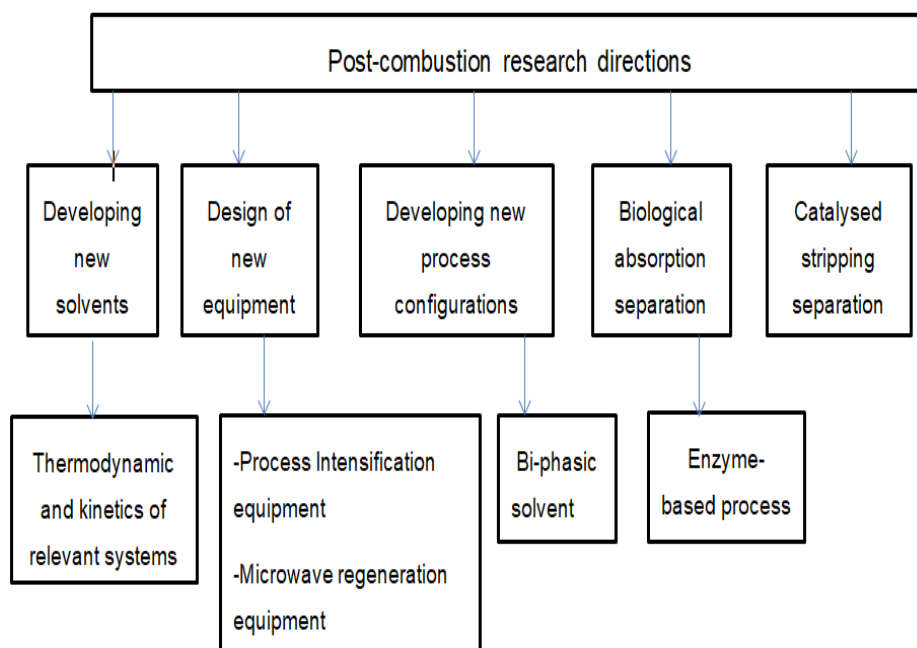


Figure 1-11: Post-combustion research gaps (IEAGHG, 2013; Shi et al., 2014)

1.10 Aim and Objectives

The aim of this study is to identify and evaluate opportunities for improving the AMP-based PCC plant performance and operation.

The objectives are as follows:

- I. Comprehensive review of relevant literature
- II. To develop the NGCC power plant model and validate with literature data
- III. To develop, validate and compare the AMP-based and MEA-based post-combustion CO₂ capture plant models
- IV. To quantify the impact of using MEA and AMP solvents on the performance of the PCC plant model retrofit to a NGCC power plant model
- V. To integrate the NGCC power plant model with the AMP-based capture plant model with compression train and solvent storage tanks
- VI. To perform economic analysis on the integrated processes

1.11 Thesis Structure

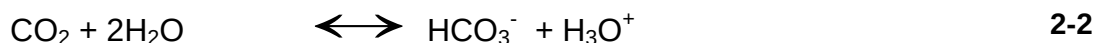
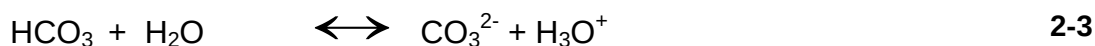
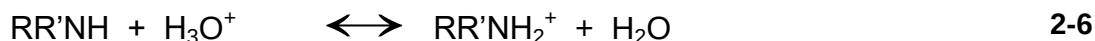
This thesis comprises seven chapters. The aim and objectives of the study are given in section 1.10. In **Chapter 2**, a general literature review is presented. This entails a review of gas purification processes and the properties of different amine solvents. Comparisons of different properties of these amines and absorption reaction mechanism are discussed. Furthermore, the advantages of AMP solvent over the MEA solvent are highlighted. In addition, studies on modelling and simulation using AMP solvent for the PCC technology are presented. **Chapter 3** describes the methodology employed in the modelling and simulation of the AMP-based and the MEA-based capture plant processes. In **Chapter 4**, the modelling and simulation of the AMP-based capture plant are presented. Also, the AMP-based capture plant built at pilot scale is validated with experimental data from the literature and scaled up to handle flue gas from a NGCC power plant. Afterwards, sensitivity analysis is carried out to identify the near-optimal operating conditions for the AMP-based process. While in **Chapter 5**, integration studies are presented therein. The AMP-based capture plant model is retrofitted into the NGCC power plant model, and the MEA-based process is used as a benchmark. The MEA process model is also validated with experimental data from the literature. The comparison of the thermodynamic and economic performances between the MEA and AMP-based plant models are made. Furthermore, the NGCC power plant model retrofitted with the AMP-based capture plant model and with solvent storage is also presented in **Chapter 5**. Thus, the thermodynamic performances of the processes with and without solvent storage are presented therein. In **Chapter 6**, the economic performances of the AMP-based and MEA-based processes and sensitivity studies for the AMP-based process (such as the effect of make-up flowrate on cost etc.) are presented. Furthermore; the economic analysis of the NGCC power plant retrofit with the AMP-based capture plant and with solvent storage is performed. This is compared to that of the process without solvent storage. More importantly, a sensitivity study is conducted to show the impact of carbon tax on the retrofit process with solvent storage. Finally, the conclusions drawn from this work and recommendations for future research work are provided in **Chapter 7**.

2 LITERATURE REVIEW

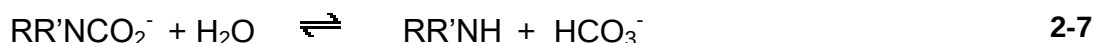
This Chapter is a review of the CO₂ absorption in aqueous solutions of alkanolamines, the use of amine solvents to capture CO₂ from power generation systems, the advantages of other solvents over the widely used MEA solvent and ways of improving the amine-based capture process.

2.1 Chemistry of CO₂ Reaction with Aqueous Alkanolamines

The chemical reactions that take place when alkanolamines absorb CO₂ from a gas stream may be represented as follows (Kohl & Nielsen, 1997; Austgen et al., 1989; Liu et al., 1999; Aboudheir et al., 2003):



Where RR'NH in Equations (2-5) and (2-6) represents a primary amine (R'=H), or a secondary amine (R' ≠ H). Base 'B' in Equation (2-5) can be H₂O or OH, or a combination of bases present in the system (Vaidya & Kenig, 2007; Mahajani & Joshi, 1988). RR'NCOO⁻ and RR'NH₂⁺ are carbamate and protonated amine respectively. Equations (2-1) and (2-6), describe water ionization and amine protonation respectively. On the other hand, Equation (2-2) represents the direct reaction of CO₂ with water, and it is a very slow reaction when compared with Equation (2-5), which represents carbamate formation (Vaidya & Kenig, 2007). A study by Sharma (1965) has reported that steric effects reduce the stability of carbamates formed by sterically hindered amines. Thus, a second very important reaction that contributes to the overall reaction is the reversion of carbamate to bicarbonate by means of hydrolysis reaction (Bosch et al., 1990).



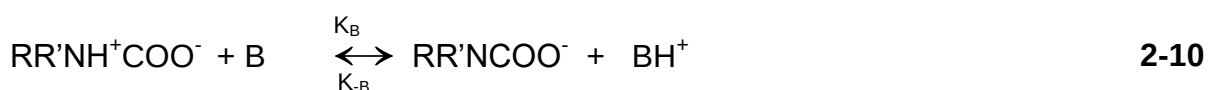
Equation (2-7) is hydrolysis reaction, while Equation (2-8) is a reversion to bicarbonate

2.1.1 Mechanism of CO₂ Reaction with Aqueous Alkanolamines

The reaction of CO₂ with primary and secondary amines as portrayed by Equations (2-5) and (2-6) above is explained using a two-step zwitterion mechanism which was originally proposed by Caplow (1968). While the reaction of CO₂ with tertiary amines is typically depicted by the base-catalysed hydration of CO₂, as proposed by Donaldson and Nguyen (1980).

2.1.2 Zwitterion Mechanism

The two-step zwitterion mechanism recommends that CO₂ reacts reversibly with a primary or secondary amine in the initial step to form an unstable zwitterion, as given in Equation (2-9) (Blauwhoff et al., 1984). The unstable zwitterion may invert back to the actual CO₂ and amine from which it was formed, or it will get deprotonated by a base (or bases) introduced in the system to form carbamate in the second step as shown in Equation (2-10) (Danckwerts, 1979; Glasscock et al., 1991).



Again, the base (B) in Equation (2-10) can be H₂O and OH⁻, or a combination of bases present in the system. It is seen that the combination of Equations (2-9) and (2-10) will give Equation (2-5). Also, it is important to highlight that the zwitterion mechanism is mostly used for describing the reaction of CO₂ with primary and secondary amines in both aqueous and non-aqueous solutions, as presented in the literature (Vaidya & Kenig, 2007; Mahajani & Joshi, 1988; Danckwerts, 1979).

Sterically hindered amines have been seen to be of high interest. This is because, they show capacity, and absorption rate advantages over the unhindered amines for CO₂ removal from gases by absorption in aqueous amines (Satori and Savage,

1983). Also, because reaction rate is reduced by steric hindrance, producing less stable amines, hindered amines undergo hydrolysis forming bicarbonates while releasing the free amines (Satori et al., 1987), as shown in Equations (2-7) and (2-8). This free amine reacts with CO₂ resulting in a higher loading (Sartori & Savage, 1987). Therefore, these sterically hindered amines, have the tendency of forming weak carbamate salts, resulting in both higher carrying capacities for CO₂ in terms of the number of moles of CO₂ absorbed per mole of amine (Sartori & Savage, 1987). They also have a lower enthalpy of regeneration regarding the amount of energy required per unit mass of CO₂ regenerated (MacDowell et al., 2010).

In analysing new solvents based on theoretical capacity, sterically hindered amines (such as AMP), have been seen to have a higher absorption capacity and a lower regeneration heat when compared to un-hindered amines (such as MEA) (Gabrielsen et al., 2007; Aroonwilas & Veawab, 2004; Abu-Zahra et al., 2013). This is because of the high tendency of MEA to form strong or stable carbamates. The degree of hydrolysis of the carbamate formed to bicarbonate depends on the chemical stability of the carbamate, which is influenced by factors such as the molecular structure (Singh, 2011).

Studies have shown that the amine reaction stoichiometry with CO₂ and the bulkiness of the substituent (the presence of the methyl compound 'R') attached to the amino group has a great impact on the carbamate stability (Sartori & Savage, 1987). Thus, the presence of a methyl compound implies a low tendency to form stable carbamates; this is observed with sterically hindered amines, because of the unstable carbamates formed, bicarbonates ions are present in larger quantities than the carbamates ions (Kundu et al., 2003; Satori et al., 1987).

Reactions that take place in the absorption of CO₂ with amine solution



Equation (2-11) is the reaction for un-hindered amine, and it shows that no 'methyl compound' is attached to the NH₂ group. When the reaction occurs, stable carbamates will be formed. The reaction (Equation 2-11) shows a ratio of 2:1, i.e. 2 moles of amine per mole of CO₂, implying that half a mole of CO₂ will be absorbed

per mole of amine (Satori et al., 1987). Equation (2-12) is the reaction for the hindered amine, which shows the presence of a methyl compound attached to the NH_2 group. The reaction (Equation 2-12) occurs, forming unstable carbamates. The reaction shows a ratio of 1:1, meaning that one mole of CO_2 will be absorbed per mole of amine (Satori et al., 1987).

For desorption, the reverse of these reactions occurs, i.e. both reactions move from right to left. When this occurs, the reaction (Equation 2-11) will not go to completion because of the stable carbamates already formed. Thus, 1 mole of amine will need to be desorbed per half a mole of CO_2 . While the reaction (Equation 2-12), will go to completion, because of its unstable carbamates initially formed, which implies that, 1 mole of amine will be desorbed per mole of CO_2 . This shows that the number of CO_2 absorbed and desorbed (i.e. the capacity) for the hindered amines are higher than the un-hindered amine (Satori et al., 1987).

2.1.3 AMP Solvent

Recently, AMP is among the most viable sterically hindered amines for natural gas processing and solvent-based PCC. This is because it is a readily available monoamine, which makes its processing easier since there is only one reactive amino group to consider. Also, AMP is the hindered form of MEA, and it is also one of the least production cost amine of the sterically hindered amines (MacDowell et al., 2010; Chakraborty et al., 1986).

AMP has lower heat of regeneration than that of MEA, and it exhibits enhanced chemical and thermal stability with degradation rates of close to half of those observed for MEA. Furthermore, MEA has loadings up to about 0.5 $\text{molCO}_2/\text{mol}$ MEA due to the stable carbamates formed as shown in Equation (2-11), while AMP has low carbamate stability make loadings up to one i.e. 1 $\text{molCO}_2/\text{molAMP}$ feasible, as shown in Equation (2-12). AMP with its excellent absorption capacity induces less corrosion than MEA (Tontiwachwuthikul et al., 1995). Corrosion is a major operational problem in the conventional CO_2 absorption plant. This is because, corrosion results in a decrease in CO_2 capture efficiency and increase in operational cost (Supap et al., 2006). The only drawback of the AMP solution is its low reaction rate with CO_2 when compared with conventional amines (MEA and DEA). Thus, as rate constant decreases, steric hindrance increases. Therefore, rate constant

increases only with non-bulky substituents (Sartori et al., 1987; Steeneveldt et al., 2006; Chakma, 1995; Khan et al., 2015; Ciftja et al., 2013; Afkhamipour & Mofarahi, 2013; Aronu et al., 2009; Gabrielsen et al., 2007; Alatiqi et al., 1994; Abu-Zahra et al., 2013). Available solvents include: MEA, DEA, Triethanolamine (TEA), MDEA, AMP, Diglycolamine (DGA), ammonia as chemical solvents; and lastly Rectisol and Selexol as physical solvents. However, the major alkanolamines absorbents in industrial processes are the MEA, DEA, AMP, MDEA (Kim et al., 2011).

MEA is still the preferred choice, with the fact that an established technology supports the chemical absorption process. It also has a very strong reactivity to CO₂, this is because of the fast reaction providing capacity for CO₂, and hence, enhancing absorption rates (Freguia, 2003). MEA is relatively cheap compared to DEA and MDEA, but some of its great disadvantages are:

- i. the high heat of reaction with CO₂ which resulting in high energy requirement for regeneration in MEA system
- ii. Operational problems such as solvent degradation and corrosion

The use of substitute absorbents and operation is highly significant to overcome these problems. In this research, AMP is considered as an absorbent to help overcome the aforementioned disadvantages of using MEA. However, for this technology to be widely adopted to reduce greenhouse CO₂ gas emissions, overcoming operational challenges in the absorption plant such as amine degradation is vital.

AMP is preferred to the other conventional amines such as DEA and MDEA because of its benefits as stated previously. DEA requires higher energy to regenerate solvent, higher absorption capacity (lower loading) and is prone to more degradation than that of AMP. While for MDEA, in the absorption of CO₂, as previously stated, its mechanism of formation is very different when compared to primary and secondary amines, such that there is no direct reaction with CO₂. Instead, they serve as a base in aqueous solutions form which they catalyse the hydration of CO₂ forming bicarbonates and a protonated amine. See Equation (2-13).



Because MDEA lacks the presence of the N–H bond needed to form the carbamate ion, they are considered as the most severely hindered amines. Hence, they have slower kinetics (low rate constant) and lower CO₂ absorption rate than that of AMP (MacDowell et al., 2010; Aronu et al., 2009).

2.1.4 Advantages of AMP over MEA

❖ Loading capacity (higher CO₂ loading)

AMP possesses a steric character that reduces the stability of the formed carbamate, after carbamate hydrolysis (the formation of bicarbonate) and the release of free amines for continued reaction with CO₂. Hence, AMP enhances CO₂ equilibrium loading capacity up to one (1) as shown in Figure 2-1.

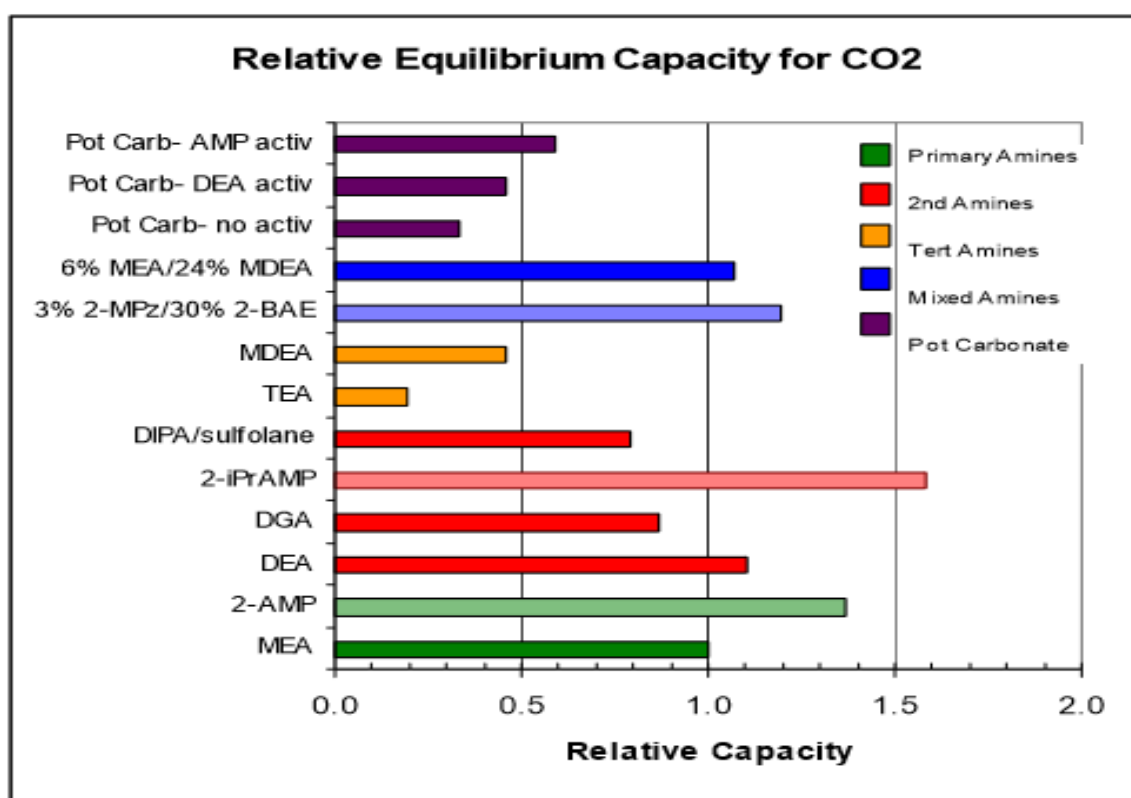


Figure 2-1: Comparison of loading capacity of different solvents (Anthony, 2006)

❖ **Lower regeneration energy and heat of absorption**

The regeneration efficiency for each amine is presented in Figure 2-2. AMP has the highest performance of 98.3%, while MEA has the lowest regeneration efficiency of 88.3%. The second cycle has similar performance with AMP having the highest regeneration efficiency at 97.8% compared to the other amine solvents.

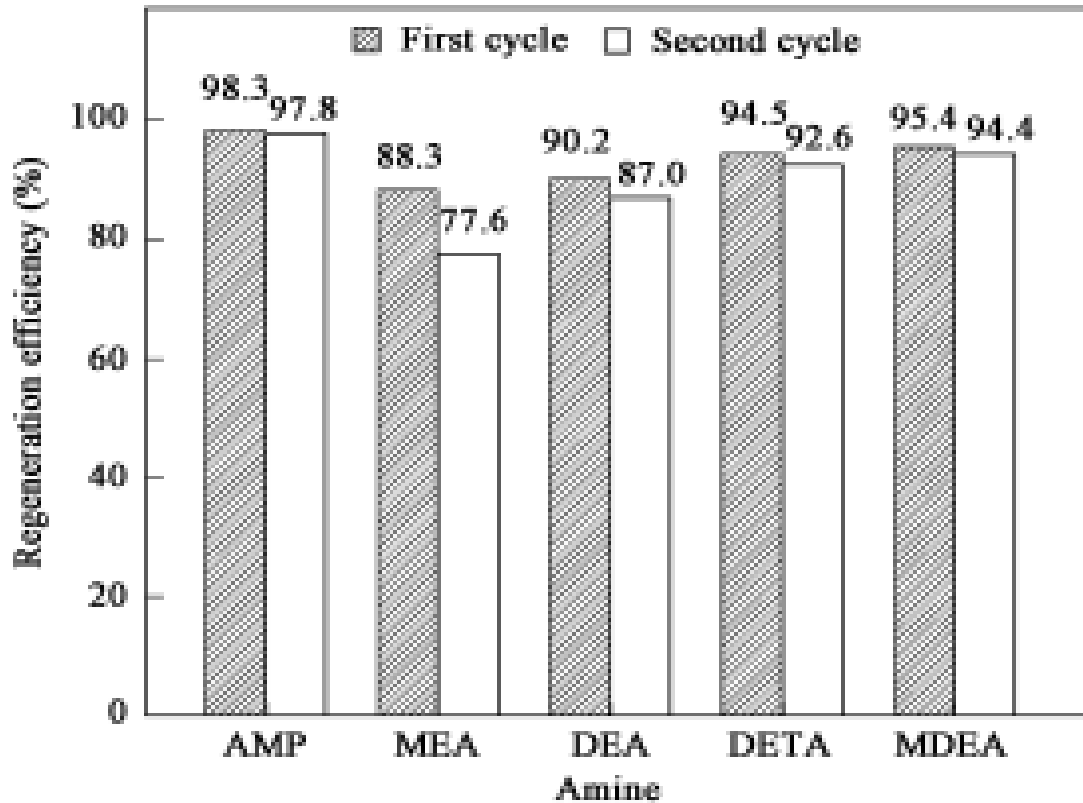


Figure 2-2: Regeneration efficiencies of different alkanolamines at a concentration of 1.0kmol/m^3 , regeneration temperature of 383k (Zhang et al., 2008)

Thus, as a result of the lower heat of reaction for the AMP compared to that of the MEA as shown in Figure 2-3, the energy required to regenerate AMP solvent is lower than that of MEA solvent (Kim & Svendsen, 2007) as observed in Figure 2-2 above.

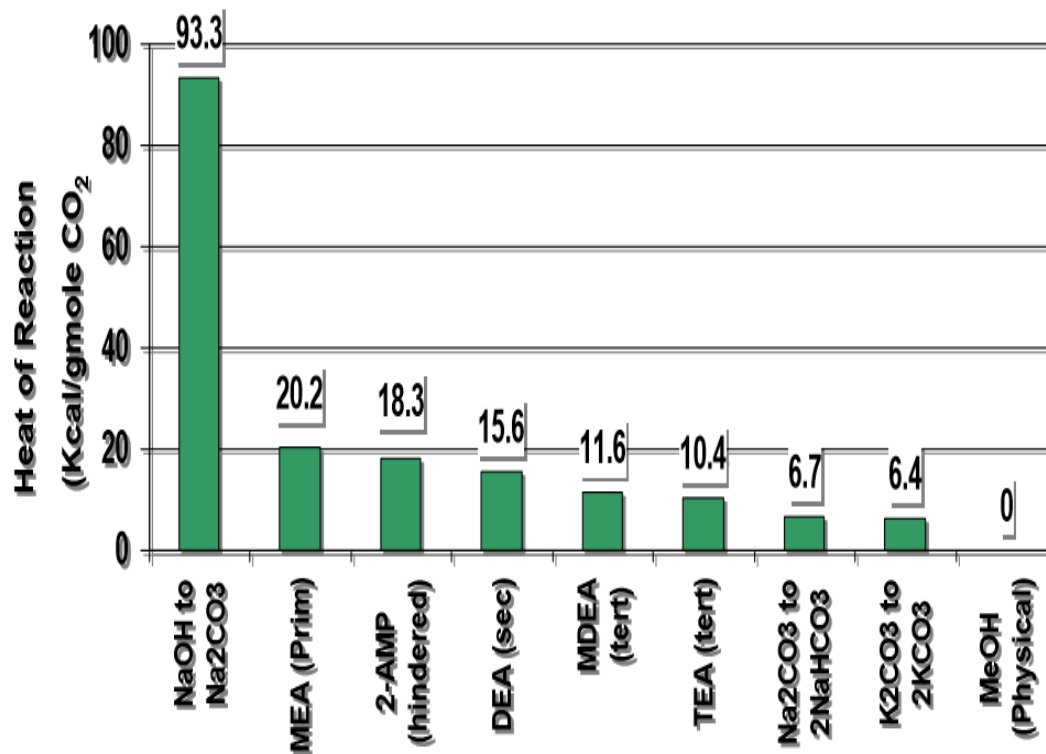


Figure 2-3: Heat of reaction of amines (Anthony, 2006)

❖ Higher degradation resistance

As shown in Figures 2-4 & 2-5, the degradation rates over time cycles for AMP is about half that for MEA, this proves better thermal and chemical stability.

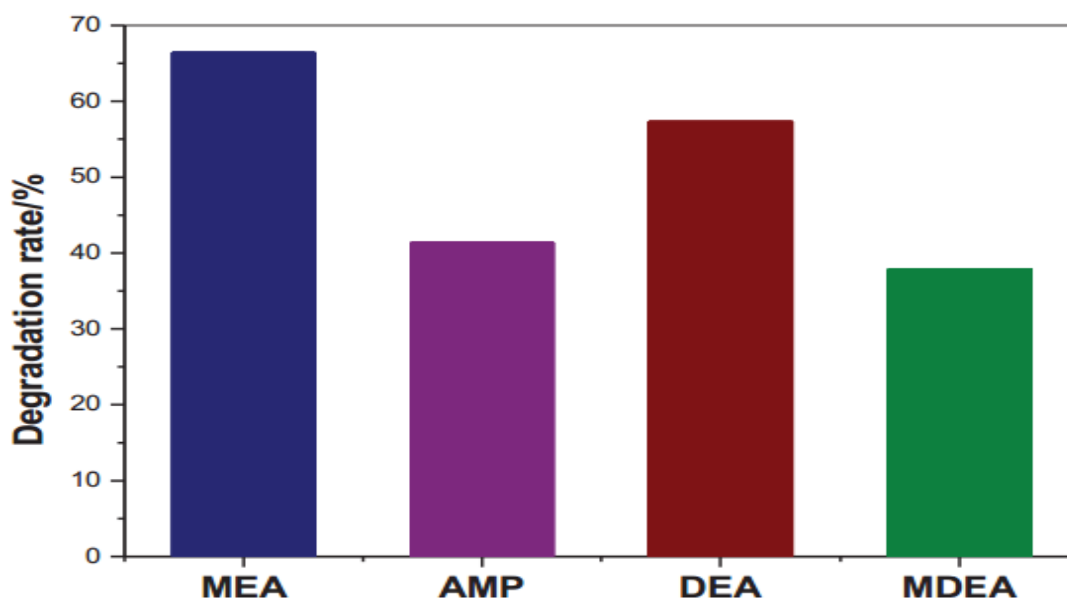


Figure 2-4: Degradation rates of different amines (Wang & Jens, 2012)

❖ Lower corrosion capacity

Corrosion is dependent on the chemical nature of the compound. AMP solvent is less corrosive than MEA (operates at higher concentrations), this is because MEA reacts more quickly having higher pH values (Singh, 2011). Also, AMP can be operated at temperatures up to 140 °C, unlike MEA, which cannot operate beyond 120 °C (Wang & Jens, 2012) as shown in Figure 2-5.

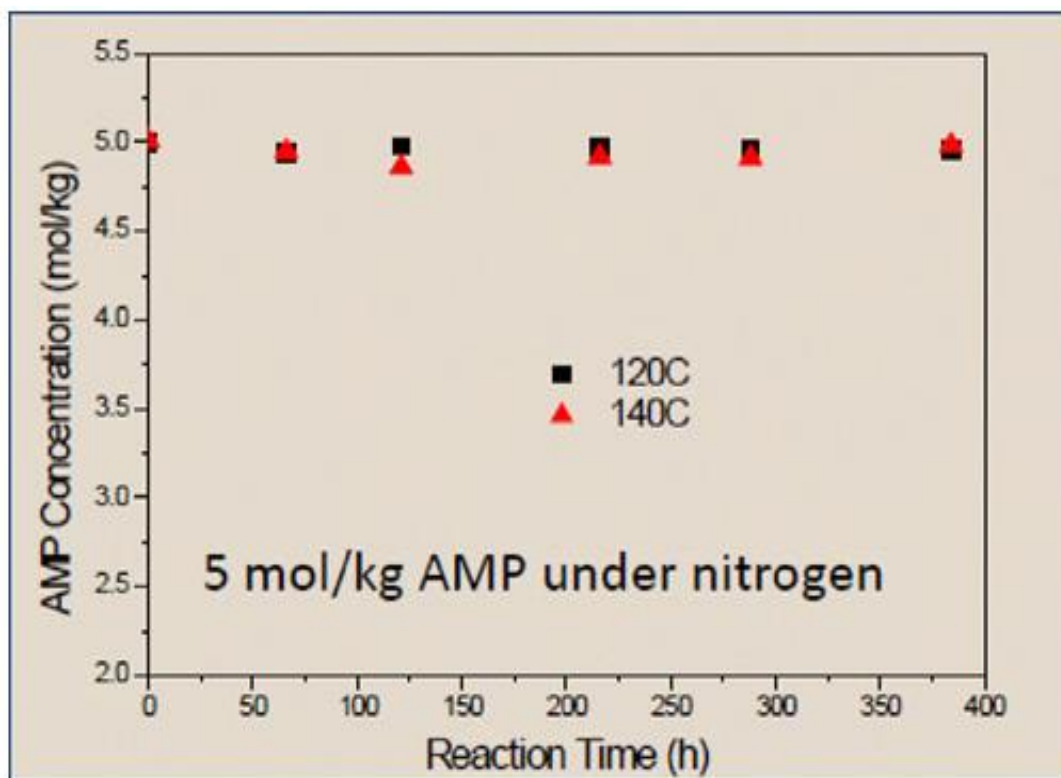


Figure 2-5: Thermal degradation of AMP (Wang & Jens, 2012)

❖ Environmental impact assessments

Environmental impact is a very important consideration for evaluating environmental sustainability in chemical process industries. Thus, sustainable development is a central objective for meeting the needs of the present without compromising the ability of future generation to meet their own need (Hassim & Ali, 2009). Based on chemical and physical properties, environmental and health impact can be evaluated. The environmental and health impact assessment criteria include volatility, chronic toxicity, and terrestrial toxicity (Hassim & Ali, 2009). Figure 2-6 shows different chemical solvents (y-axis) and their index values (x-axis), which are normalized to the same magnitude, the range of 0-10. Thus, a high rank indicates a

large potential hazard, while the lower the rank, the better the absorbent based on environmental and health index. As shown in Figure 2-6, AMP poses a lower potential hazard from environmental and health risk aspects, than that of MEA.

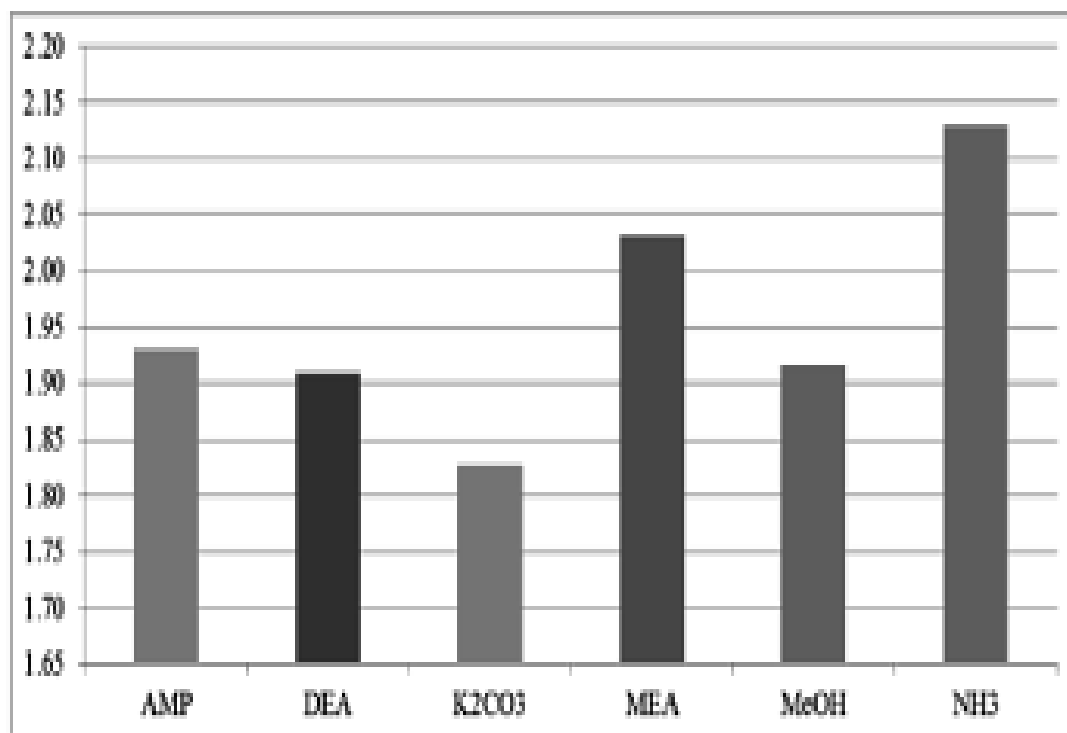


Figure 2-6: Environmental impacts of CO₂ absorbents (Hassim and Ali, 2009)

❖ Low absorption rate

The draw-back of AMP solvent is its low absorption rate when compared with MEA (Gabrielsen et al., 2007; Chowdhury et al., 2011), this is clearly seen in Figure 2-7. Thus, slower kinetics for AMP compared to that of MEA leads to poor mass transfer performance for AMP. A reason for this performance is the viscosity, which slows down the mass transfer, and this is almost five times higher for AMP compared to that of the MEA (Singh, 2011).

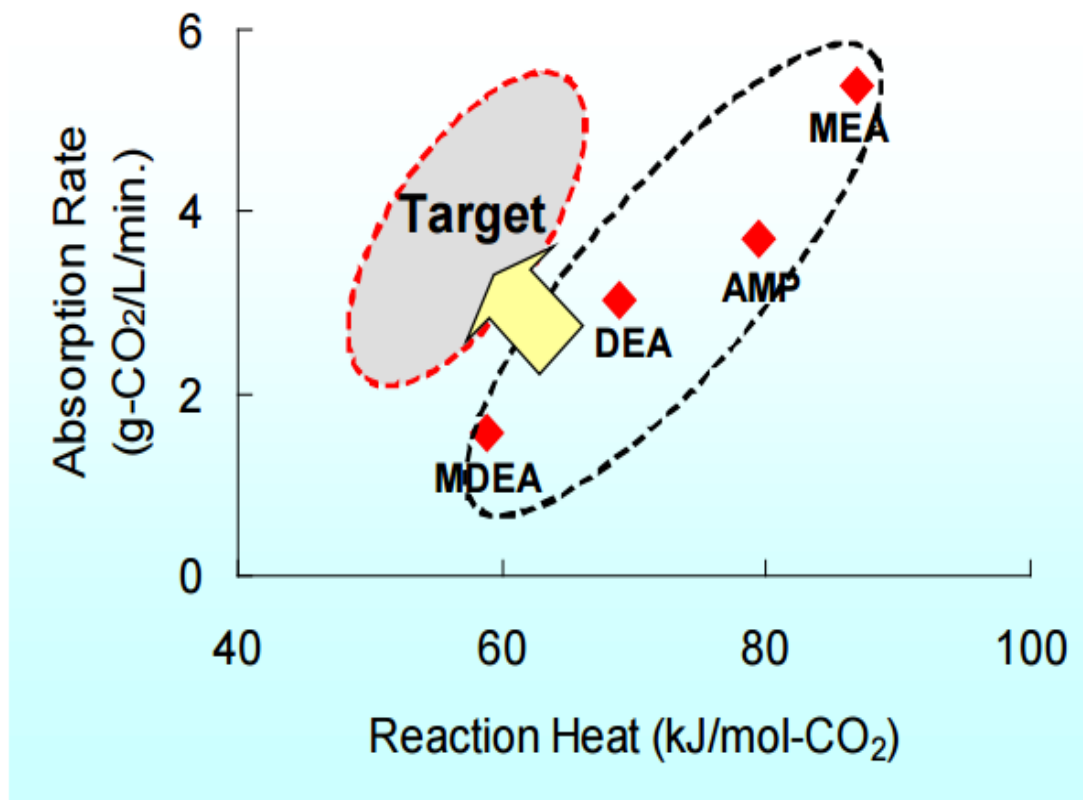


Figure 2-7: Absorption rates of different amines (Chowdhury et al., 2011)

2.2 AMP-Based CO₂ Post-Combustion Capture Process

2.2.1 Process Description

Figure 2-8 is a screenshot of the flowsheet of the AMP-based capture process. It consists of two columns; absorber and stripper. These columns are used in absorbing and desorbing CO₂. The aim of the absorber is to capture CO₂ while the stripper is to regenerate the solvent (Freguia, 2003).

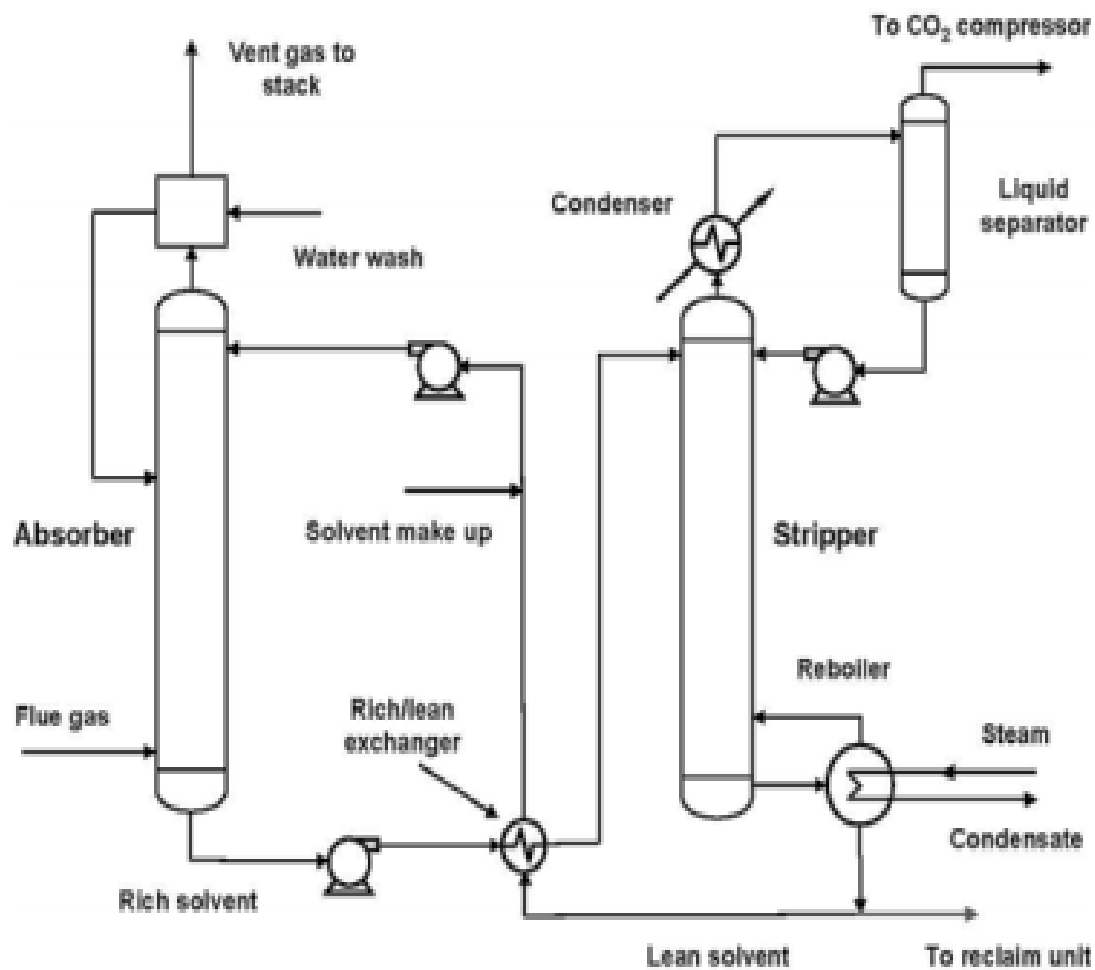


Figure 2-8: Basic flowsheet for an amine-based CO₂ capture process (Global CCS Institute, 2012b)

Flue gas with 3-4 mole% CO₂ (Amann and Bouallou, 2009) coming from the natural gas power plant, operating at a temperature of 40 °C (Davis, 2009), reacts in a countercurrent pathway with the amine solution (about 30-40 wt %) to capture 90% CO₂ in the absorber. The absorber operates at a pressure 1.2 bar, to enable the gas stream to overcome the column's pressure drop. After the reaction, a rich solvent (high CO₂ loading, between 0.5-1.0 molCO₂/molAMP) (Gabrielsen et al., 2007) exiting the absorber is fed to a stripper for regeneration, and the lean solvent (low CO₂ loading, between 0.1-0.2 molCO₂/molAMP) (Freguia, 2003) is recycled back into the system. The gas coming from the top of the absorber is often washed in a water wash section to minimize solvent losses because of mechanical entrainment and evaporation, and then, the gas is discharged into the atmosphere. In the stripper, CO₂ is separated from the solvent by the upward flow of steam, which is

generated in a reboiler at the bottom of the column. The energy, which is provided by utility steam, is used to vaporize the liquid at the bottom of the stripper, and the temperature at the bottom of the stripper is kept below 140 °C to avoid the thermal degradation of AMP (Wang and Jens, 2012). The steam produced drives mass transfer from the liquid phase to the gaseous phase. At the top of the stripper, the product comprises of the CO₂ mixture, steam, and little amount of amine, which is partially condensed in a condenser, and a part or all of the condensed liquid is returned to the top of the stripper as reflux. The uncondensed stream, which contains more CO₂ (up to 95%), is sent for compression, transportation, and sequestration. Solvent degradation is caused by the presence of SO_x and NO_x gases in the flue gas, which forms heat stable salts with an amine. This can be eliminated by using a desulphurisation unit for sulphur oxides (SO_x) and an electrostatic precipitator for nitro oxides (NO_x) (NETL, 2010).

2.3 Degradation Studies

Studies have shown that the degradation of amines is a major problem, and the amine solvents are considered to pose a relatively high emissions risk during the chemical absorption process (CSIRO, 2012). This degradation occurs through irreversible side reactions with CO₂ and other components in the flue gas forming degradation products (Strazisar et al., 2003). The degradation products then react with amines to form heat stable salts, which accumulate in the system over time. The problems associated with degradation include decreased plant equipment life, foaming, corrosion, high solvent viscosity, and acid gas removal capacity (Wang & Jens, 2012; Quanzhen Huang, 2015).

MEA is the benchmark solvent for solvent-based carbon capture process. This solvent removes about 70-90% of CO₂ from commercial power stations (IPCC, 2005). However, as a result of the high removal rates, the MEA poses many environmental and economic impacts due to its degradation products. This is because the degradation of MEA results in a solvent loss, which requires the replacement of 2.2 kg of MEA per tonne of CO₂ captured (Strazisar et al., 2003). Thus, amine loss and the cost of reclaiming degraded are important sources of the operational cost. Researchers have shown interest in characterising and quantifying atmospheric emissions of amines and their degradation products based on

experimental operations. With MEA absorption technology, solvent degradation contributes about 10% of the overall CO₂ capture cost (Fredriksen & Jens, 2013; Vega et al., 2014; Quanzhen Huang, 2015). During the process of CO₂ removal from a power plant flue gas stream, two types of degradation occur:

(1) Thermal degradation: this is caused by heat (mainly at temperatures below 200 °C) (Davis, 2009).

(2) Oxidative degradation: this is activated by oxygen (based on radical reactions, it is catalysed by metal ions, results in oxidized fragments of the solvent) (Bedell, 2009).

2.3.1 Thermal Degradation

Thermal degradation occurs mostly in a stripper (regenerator) due to the presence of high temperatures (above 120 °C and 140 °C for MEA and AMP respectively) during the CO₂ stripping process. At these high temperatures, enhanced solvent losses occur. This is because of the kinetic rates of degradation reactions increases. Thus, the concentration of the amine solution and CO₂ loading highly affects the rates of thermal degradation. Thermal degradation involves the degradation of its carbamate form. For MEA solvent, the main cause of thermal degradation is the carbamate polymerisation under high temperature, leading to oxazolidinone formation. While for AMP, the presence of steric hindrance prevents the oxazolidinone ring opening into an addition product. Thus, the thermal degradation of AMP is less compared with MEA (Davis, 2009; Vega et al., 2014; Lepaumier et al., 2009). However, thermal degradation is only affected by high temperatures in flue gas applications; it is not a major problem, so it is less studied (Tielin, 2012).

2.3.2 Oxidative Degradation

Oxidative degradation mainly occurs in the absorber. It involves the reaction of 3-5% oxygen concentration in the flue gas with the amine solution (Vega et al., 2014). Oxidative degradation rates of amines are dependent on temperature, dissolved oxygen, a solution of CO₂ and the concentration of impurities such as SO_x present in the flue gas (Lepaumier et al., 2009a). Oxidative degradation is a very important issue because of the impact on the environment, which is a result of solvent losses. It also affects the process economics (solvent make-up cost), which is about 10%

the total cost of capture (Rao and Rubin, 2002), and can lead to a decrease in equipment life due to corrosion. Thus, oxidative degradation is an unavoidable concern in the PCC technology, and the concentration of oxygen in flue gas is higher for natural gas-fired power plants than for pulverized coal-fired plants (IEAGHG, 2006).

2.4 AMP Degradation Chemistry

2.4.1 Mechanism for the Degradation Products

Reaction mechanisms and reaction pathways give useful information about the oxidative degradation phenomena present in the absorption chemistry of O_2 in amine solvents. Two mechanisms are likely to occur; electron abstraction and hydrogen abstraction. The mechanism involved in the initial step in the formation of these AMP degradation products is the hydrogen abstraction (Wang & Jens, 2012). The proposed oxidative pathways for AMP are shown below;

- Formation of Acetone

The final oxidative degradative product of AMP is Acetone, as shown in Figure 2-9.

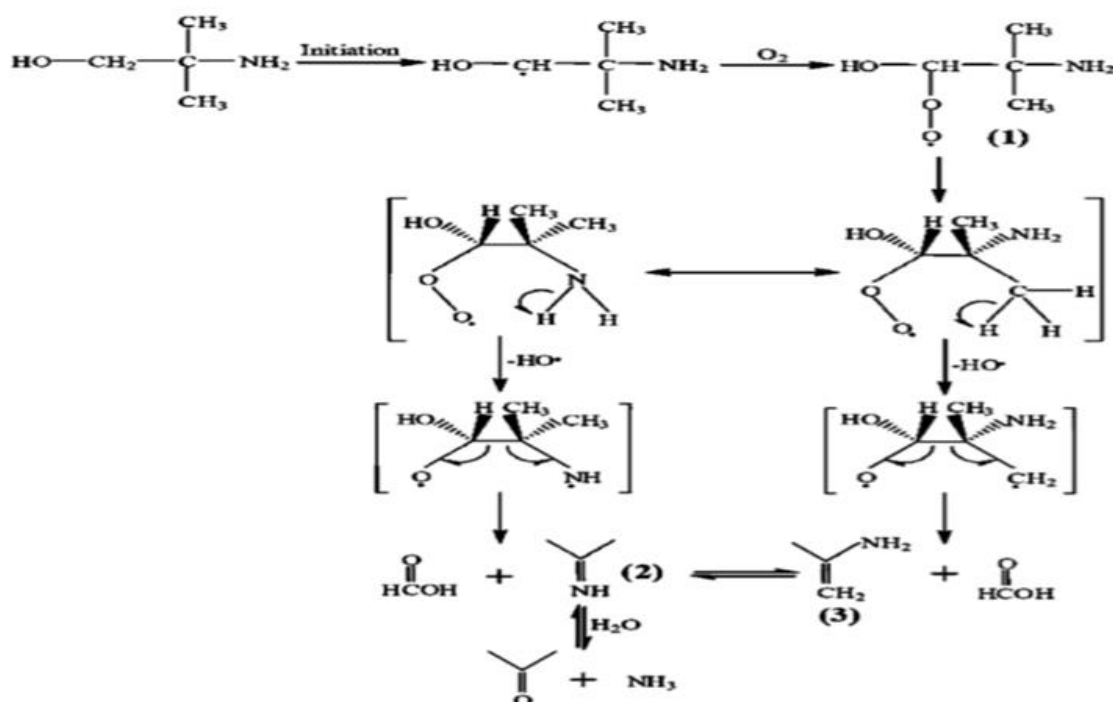
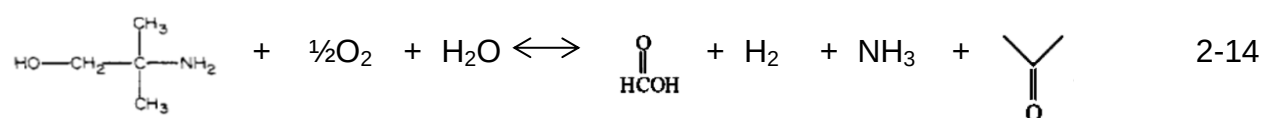


Figure 2-9: Scheme for oxidative degradation of AMP with O_2 (Wang & Jens, 2012)

Eliminating the intermediates, the reaction is as follows;



(AMP)

(Acetone)

- Formation of 4, 4-Dimethyl-2-Oxazolidinone

A major product observed in the thermally degrade AMP aqueous solutions was 4, 4-dimethyl-2-oxazolidinone, given in Figure 2-10.

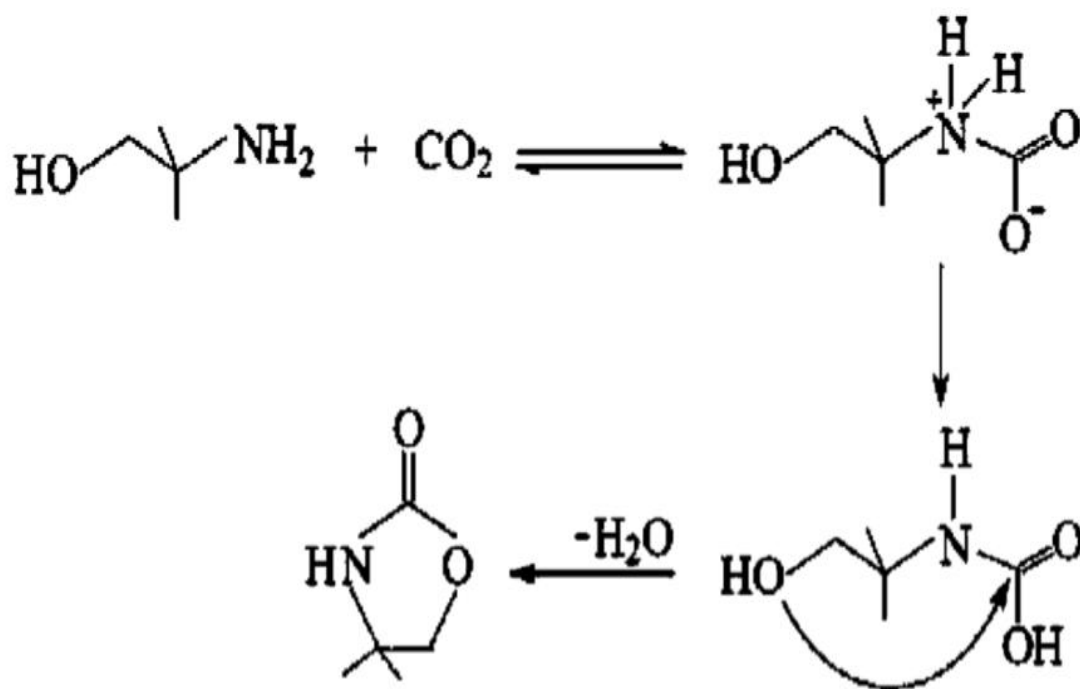
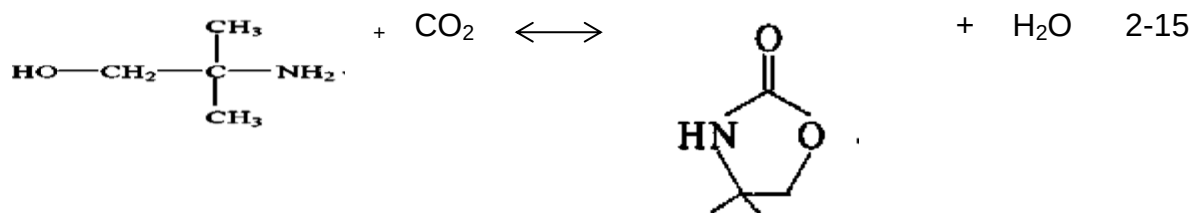


Figure 2-10: Scheme for oxidative degradation of AMP with CO_2 (Wang & Jens, 2012)

The stoichiometric coefficients of the degradation products are determined by eliminating the intermediates, and the equation is balanced as follows;



(AMP)

4,4 dimethyl-2-oxazolidinone

- Formation of 2, 4-Lutidine

A major oxidative degradation product of AMP is 2, 4-Lutidine. This involves the reaction of formaldehyde and an imine to form 2, 4-Lutidine, as shown in Figure 2-11.

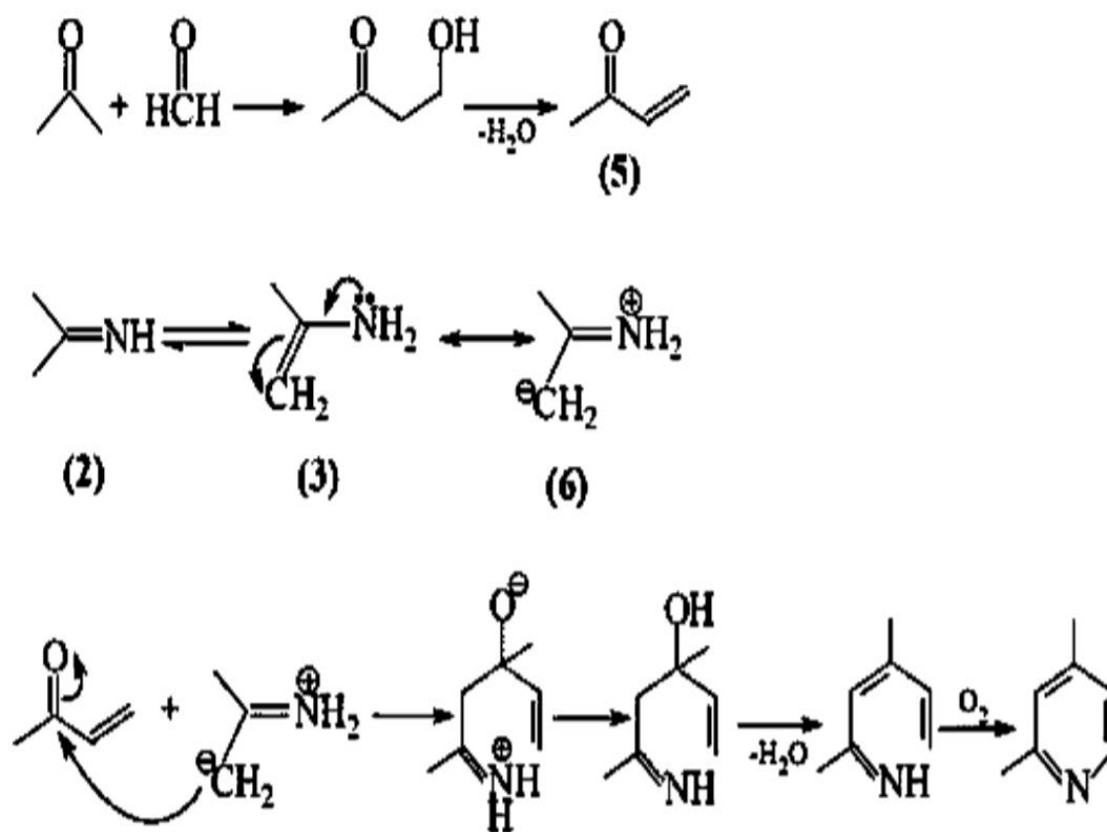
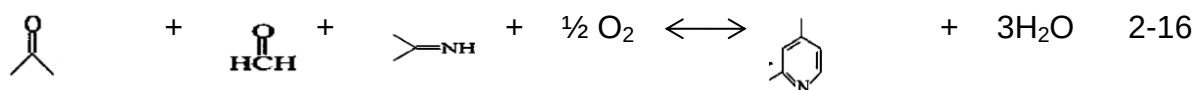


Figure 2-11: Scheme for oxidative degradation for 2, 4-Lutidine (Wang & Jens, 2012)

Eliminating the intermediates, the reaction is as follows;



(Acetone
)

(2,4-
Lutidine)

2.5 AMP-Based Process for CO₂ Capture Plant from NGCC Power Plant

A PCC plant utilising chemical solvent can capture CO₂ from the exhaust/flue gas of an existing NGCC power plant. With the integration of a PCC plant, it is essential to continue investing in and operating NGCC plants due to the relatively low emissions, high efficiency of up 58% (LHV basis), and security of gas supplies. Usually, various challenges are experienced. One of which is the energy required to regenerate the solvent and this is mostly provided by steam extraction from the power plant (Romeo et al., 2008). Importantly, the best location in the steam cycle to extract steam and how best to re-inject the condensate are decisions to be made. Thus, careful integration of the power plant steam cycle to the CO₂ capture process is required (Manassaldi et al., 2014).

In order to withdraw steam from the steam cycle in the power plant, some conditions must be met; steam needs to be at the saturation temperature and pressure (Manassaldi et al., 2014), and the extraction point needs to be accessible and be able to accommodate the required steam flowrate. In the extraction of steam for a solvent system, the optimal location is from the low-pressure (LP) turbine to provide steam at the lowest quality that satisfies the solvent system reboiler requirements (Aroonwilas & Veawab, 2007; Romeo et al., 2008). However, to extract a large amount of steam, the best location is the crossover pipe between the intermediate pressure (IP) and LP turbines (Lucquiaud & Gibbins, 2009).

It is pertinent to mention that different energy performances are encountered according to the solvent used (Neveux et al., 2013). Lucquiaud and Gibbins (2009) studied effective integration between the power plant and capture plant and pointed out that with the different solvents used in CO₂ capture plant, there will be different requirements to steam pressure, temperature, and flowrate extracted from the crossover pipe between IP and LP turbines.

Thus, analysing the integrated system at different operating conditions such as high stripper pressure of up to 3.5 bar as compared to the standard pressure, which is between 1.5-2 bar, requires a higher quality of steam. The steam requirement extracted from the IP/LP crossover pipeline will therefore change, and this will affect the interaction of the power plant with the capture plant. The higher operating temperature of AMP (up to 140 °C) compared to that of MEA (up to 120 °C) for integration, leads to a higher operating stripper pressure for the AMP-based process. This gives an opportunity for the AMP to produce a lower compression power compared to that of the MEA required in the preparation of CO₂ stream for transport (Lucquiaud & Gibbins, 2009).

Reduction in the compressor loads can lead to improving process performance by increasing the efficiency and also by reducing the cost of electricity (Chapel et al., 1999). Therefore, the integrated process can be improved by effective integration using the more favourable operating conditions for the AMP-based plant. This is because different requirements for steam pressure, temperature, and flowrate extracted from the crossover pipe between the IP and LP turbines will be required.

2.6 Solvent Storage System

With CO₂ capture, nearly 30% of generation capacity will be lost, and this means that existing capacity will not satisfy demand during the peak period. The demand for electricity varies and because of this; CCS plants will need a flexible operation. One way to achieve this is the storage of rich solvent, as this facilitates an increase in peak power available to the grid. Solvent storage enables solvent regeneration (the main consumer of energy in the capture process) to be deferred during the peak period and regenerate during off-peak when electricity demand is low.

The solvent storage system has potentials for improving the capture technology. A study (IEAGHG, 2012) has shown that addition of solvent storage to the amine integrated process can increase profit by approximately 14% during peak operating times of the power plant (IEAGHG, 2006; Chalmers and Gibbins, 2009). Thus, the AMP-based plant performance and operation can be improved by the incorporation of solvent storage.

The solvent storage process involves the addition of two solvent storage tanks (rich tank and lean tank) to the capture plant in order to store amine-CO₂ solution and

regenerate additional amine. The tanks need to be resized to accommodate additional solvent to be regenerated during hours of low electricity demand. The stripping of CO₂ occurs mainly at “off-peak” hours during the periods of low-cost electricity, and the storing of solvent occurs during hours of high electricity prices ‘peak’, while still maintaining a capture rate of 90%. The tanks present are used to temporarily store the amine-CO₂ solution that is not stripped off during times of high-energy costs. At times when the regenerator is turned off, a second storage tank is needed to supply regenerated amine to the absorber (Delarue et al., 2012). The most important benefit of the solvent storage technology is the increase in plant flexibility, by enabling the power plant to give maximum output during peak period (Chalmers & Gibbins, 2007). Figure 2-12 shows the flowsheet describing the solvent storage technology. The solvent storage process, which includes the same operating conditions as the PCC plant described earlier in section 2.2, involves the addition of the rich and lean amine tanks. The tanks operate at atmospheric conditions.

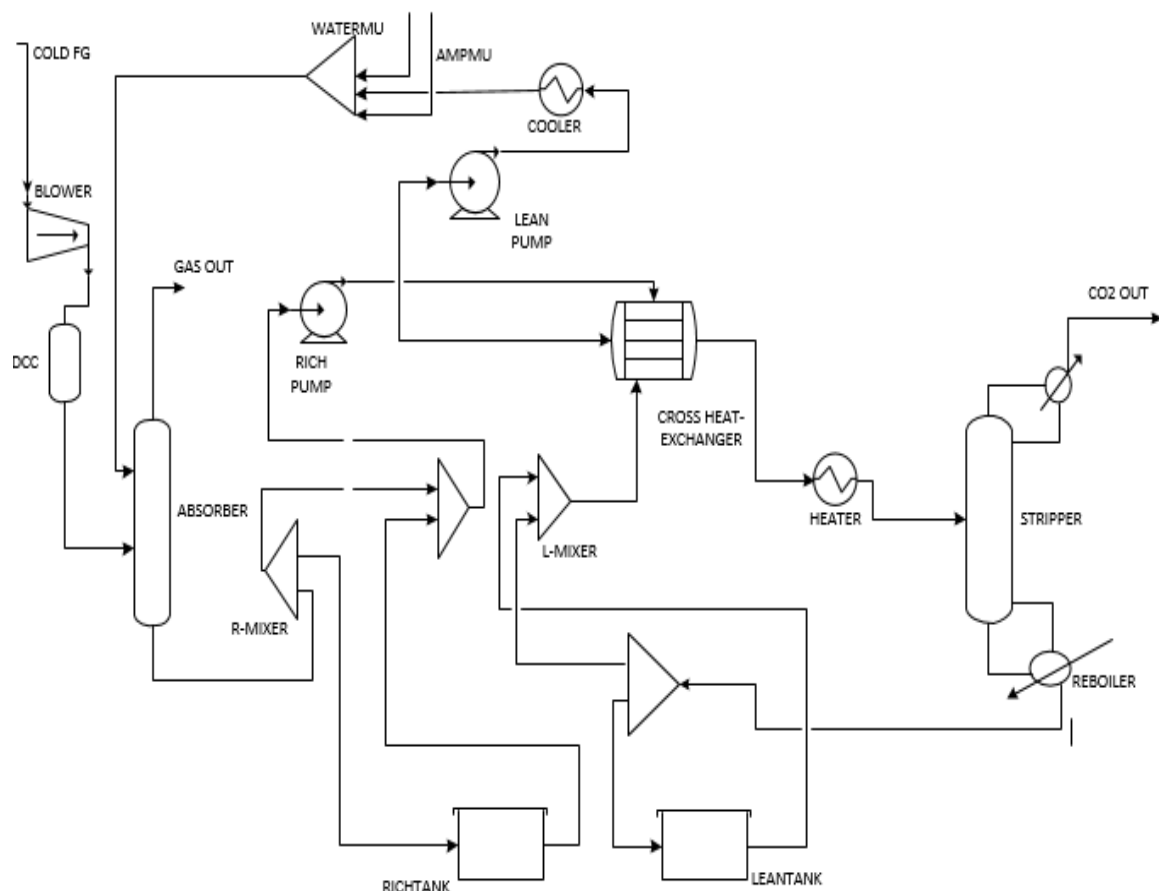


Figure 2-12: Solvent storage process flowsheet (Chalmers and Gibbins, 2007)

2.7 Different Flowsheeting Configurations

The study of the different flowsheeting configurations is necessary because it provides a means to reduce the energy consumption. This energy consumption in a CO₂ capture plant is about 15-30% of the net power (Jassim & Rochelle, 2006). The flowsheet configurations determine where it is possible to reduce the steam requirement in the amine capture process since it would lessen the extent of modification of existing steam cycles imposed by the retrofit of the power plant with the PCC plant (Ahn et al., 2013). With improved process configurations, it is expected that power demand of CO₂ removal by amine scrubbing should decrease between 20 to 30% of typical power plant output, this is because of the reduction in steam utilisation (Rochelle, 2009). The different flowsheeting options have also been suggested to reduce operating cost, an example is the cost of cooling water etc. but capital cost, such as cost of equipment is expected to increase, because of the additional equipment involved (Oyenekan & Rochelle, 2006; Jassim & Rochelle, 2006; Leites et al., 2003). Improved configurations such as absorber intercooling, split flow, rich split, vapour recompression etc. will reduce energy, but at the expense of complexity and capital cost (Cousins et al., 2011).

2.7.1 Split Flow Configuration

This involves splitting of the absorber and stripper into multiple stages in which regenerated solvent is recycled between the middle stages. It also comprises a partial solvent regeneration system and a stage feed to both absorber and stripper (Le Moullec & Kanniche, 2011) as shown in Figure 2-13. The rich amine exiting the absorber is split into lean and semi-lean, with split ratio 60% and 40% respectively (Ahn et al., 2013). The theory behind this configuration is to approach the theoretical level of inputting and removing all flow streams, which allows an evenly delivery of component concentration driving forces through the vapour and liquid phase (Amrollahi et al., 2012). This modification has the advantage of reducing CO₂ partial pressure in several stages, which increases the driving force of the absorption process. This is because the semi-lean solvent has a lower loading than the lean solvent, and the semi-lean solvent injection at the middle stage of the absorber affects the temperature profile resulting in higher rich loading (up to 0.503 mol/mol

for MEA), which reduces the heat required for regeneration by 12%. (Cousins et al., 2011).

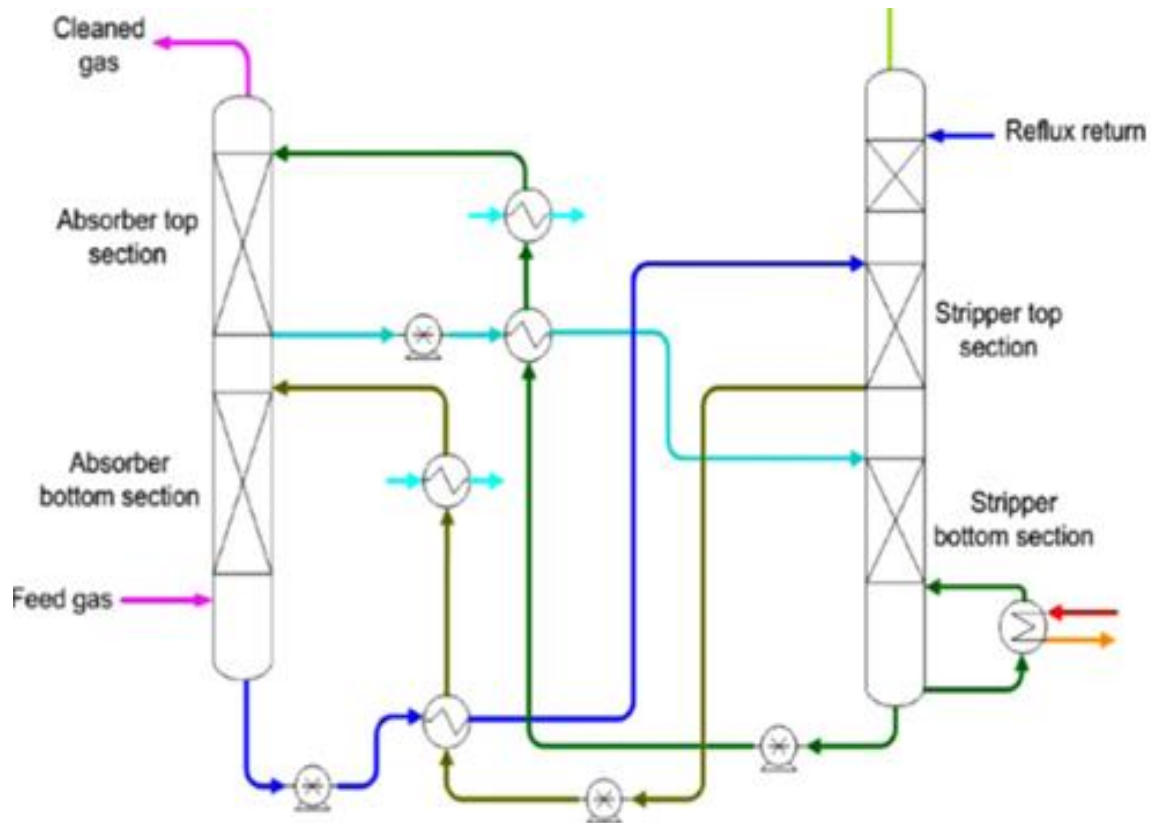


Figure 2-13: Split-flow process configuration (Cousins et al., 2011)

2.7.2 Intercooling Configuration

This process configuration enables the control of temperature within the absorber and is capable of enhancing CO₂ recovery (Cousins et al., 2011). In this configuration, given in Figure 2-14, the exothermic nature of CO₂ absorption in MEA results in a temperature bulge in the absorber, which can impact absorption negatively (Kvamsdal & Rochelle, 2008). This is because; temperature accelerates the reaction rate and increases the equilibrium partial pressure, which will lead to a reduction in the mass transfer gradient. The liquid to gas flow ratio is an important consideration in locating the bulge in the absorber. At the location where the temperature bulge occurs, the solvent is being extracted, cooled between 40-60 °C (Aroonwilas & Veawab, 2004) and returned into the absorber, which leads to the enhancement of absorption driving force (Cousins et al., 2011). The cooling at the

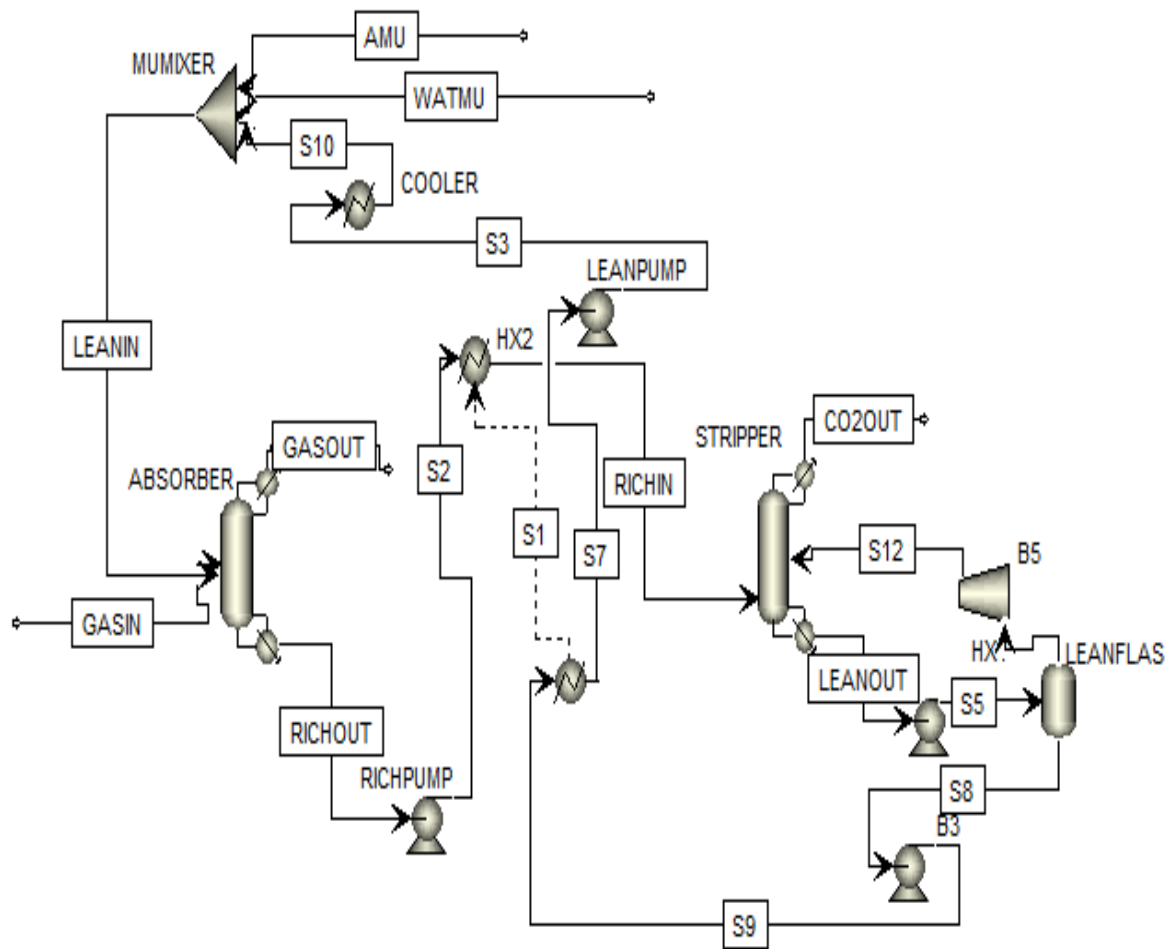


Figure 2-15: Lean amine flash process configuration (Ahn et al., 2013).

2.7.4 Rich Split Configuration

This involves the splitting of the rich stream where the split entering the top of the stripping column stays unheated. This configuration given in Figure 2-16, has the capability of pre-stripping the cold, rich solvent entering at the top of the stripping column. This can be attained due to the vapour released from the rich solvent steam, which moves up the stripping column. This configuration helps thermally to regenerate less solvent, thereby reducing regeneration energies by 7.1% (Cousins et al., 2011).

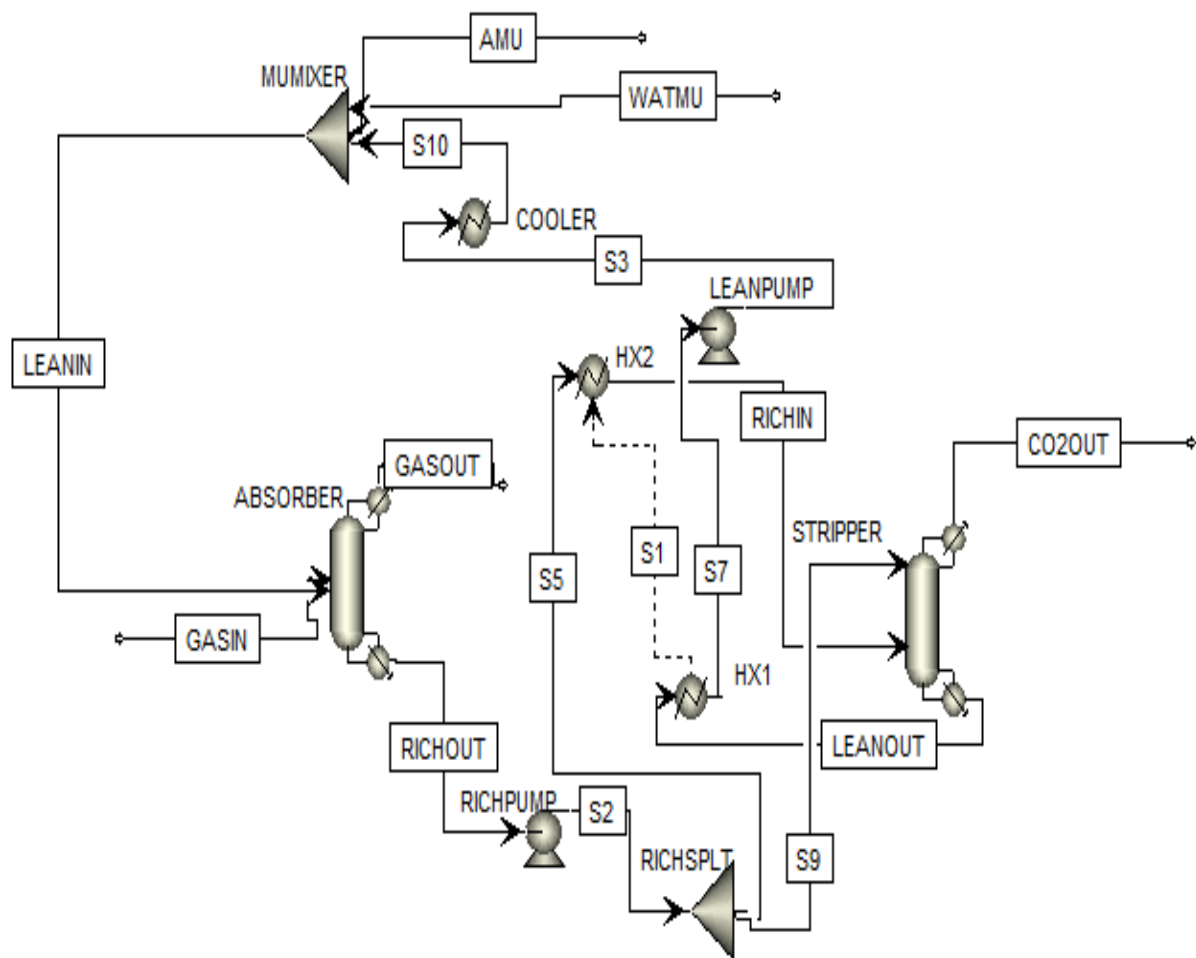


Figure 2-16: Rich split modification (Cousins et al., 2011)

2.7.5 Vapour Recompression

This involves the extraction of steam from a part of the stripping column, in which the overhead vapours are compressed 2-5 times the operating pressure of the stripper before being separated, and the condensate introduced back into the regenerator to provide more stripping steam, as shown in Figure 2-17. This leads to a decrease in the energy required for solvent regeneration between 11-24% but increases the consumption of electricity of the plant (Cousins et al., 2011).

model was used, and the results showed better performance of the retrofitted system in the case of AMP/PZ. The techno-economic analysis of the MEA and AMP/PZ processes, also considering the same operating conditions for both solvents has only been presented by Manzolini et al. (2015), and results showed 1% lower cost of electricity in the case of the AMP/PZ-based system. However, no study has yet evaluated the techno-economic performance of the PCC retrofit using only the AMP solvent with the stripper operating at elevated temperature and pressure.

Compared to MEA, AMP solvent has been shown to have a better performance as stated above. This is because AMP has the following properties over that of MEA:

- Lower energy required for regeneration of solvent
 - Higher absorption capacity
 - Higher concentration can be used with minimal degradation and corrosion problems (Gabrielsen et al., 2007; Aronu et al., 2009; Afkhamipour & Mofarahi, 2013).
- Thus, the characteristics of the AMP above could allow higher stripper pressure, lower solvent circulation, lower reboiler duty, and further cost reduction. This needs to be validated by investigating them through modelling and simulation.

Furthermore, several authors have addressed the concept of flexible operation of the MEA based capture plant with different power outputs for coal-fired power plants. Chalmers et al. (2009) presented short-run marginal cost and profits for the amine storage with different power outputs. Husebye et al. (2011) developed a model to generate the optimum operating strategy by maximising weekly profit using electricity prices from the German wholesale electricity market, EEX. Brasington (2012) presented a detailed assessment of the capital cost of amine storage. Van Peteghem & Delarue (2014) identified optimal operation strategies power plant with solvent storage by considering a 2-step block-shaped electricity price profile for analysis. Mac Dowell and Shah (2015) performed an optimisation study to maximise the short-run marginal cost profitability. In addition, Oates et al. (2014) maximised profits for amine storage with pulverised coal-fired and natural gas-fired power plants and employed an environmental model for analysis. There are limited studies on the use of process-based simulation models for flexible operation of CCS with NGCC. This has been the main motivation behind this study.

- In summary, it has been shown that solvent storage could potentially aid the flexibility of the capture plant as regards load following scenario. This has been thoroughly analysed for cases with MEA solvent but no studies with the AMP solvent.

Table 2-1 shows a review of the literature studies, which have considered modelling and simulation using the AMP solvent for the capture plant, and the power plant retrofits with the capture plant. Furthermore, the power plant retrofit with the capture plant and solvent storage using the MEA solvent is also given in Table 2-1, since no study employing AMP solvent for solvent storage analysis is presented in the literature.

Table 2-1: A review of different studies on the modelling with packed columns using AMP solvent for CO₂ capture technology

Author (s)	Methodology	Plant type	Research purpose outcome
Aboudheir et al. (2006)	Modelling	Capture plant	To anticipate the performance of CO ₂ absorption in AMP solutions in adiabatic packed columns
Gabrielsen et al. (2007)	Experiments & rate-based modelling	Capture plant	To validate a rate-based model
Kvamsdal et al. (2011)	Equilibrium-based modelling	Capture plant	To investigate the impact of two process modifications on the AMP capture process
Afkhamipour and Mofarahi (2013)	Rate-based and equilibrium-based modelling	Capture plant	To evaluate and compare mass transfer coefficients
Dash et al. (2014)	Rate-based modelling	Capture plant	To evaluate the effects of varying circulation rates, packing heights, and temperature and pressure of the columns
Sanchez et al. (2014)	Equilibrium-based modelling	Capture plant with coal-fired and NGCC power plants	To evaluate the performance of two types of power plants
Manzolini et al. (2015)	Equilibrium-based modelling	Capture plant with coal-fired and NGCC power plants	To evaluate the economics of the AMP process and compare with MEA
Spek et al. (2016)	Rate-based modelling	Capture plant with a coal-fired power plant	To improve the physical property model
Chalmers and Gibbins (2007, 2009)	Rate-based modelling	Capture plant with coal-fired power plant and solvent storage tanks using MEA	To evaluate short-run marginal cost and profits for the amine storage with different power outputs
Husebye et al. (2011)	Rate-based modelling	Capture plant with coal-fired power plant and solvent storage tanks using MEA	To develop a model to generate the optimum operating strategy by maximising weekly profit using electricity prices from the German wholesale electricity market, EEX
Brasington (2012)	Rate-based modelling	Capture plant with coal-fired power plant and solvent storage tanks using MEA	To evaluate a detailed assessment of the capital cost for amine storage
Van Peteghem and Delarue (2014)	Rate-based modelling	Capture plant with coal-fired power plant and solvent storage tanks using MEA	To identify the optimal operation strategies power plant with solvent storage by considering a 2-step block-shaped electricity price profile for analysis
Mac Dowell and Shah (2015)	Rate-based modelling	Capture plant with coal-fired power plant and solvent storage tanks using MEA	To maximise the short-run marginal cost profitability.
Oates et al. (2014)	Rate-based modelling	Capture plant with coal-fired and natural gas power plant and solvent storage tanks using MEA	To maximise profits for amine storage with pulverised coal-fired and natural gas-fired power plants and employed an environmental model for analysis.

3 PROCESS SIMULATION

3.1 Introduction

Process simulation is an activity that involves representing technical model-based processes using softwares. Process simulation tools, namely Aspen Plus®, Aspen HYSYS etc. are used to support modern process design and predict the performances of various processes. Models of fossil power plants derived using these tools can be used to study their behaviour and performance under different operating conditions (Tola & Pettinau, 2014). Usually, large numbers of process parameters and variables need to be specified for each simulation structure. With the use of Aspen Plus® software, the analysis is easy and straightforward. This is because Aspen has already made models for different unit operations and includes FORTRAN interface to modify these existing models to satisfy user's specific needs. The PCC process flowsheet is developed using models of the relevant unit operations in Aspen Plus®. The process flowsheet model is thereafter simulated to gain insight into the impact of different operating conditions.

The present study is therefore based on the development of building power cycle models in Aspen Plus® simulation software, which has high flexibility in predicting plant performance. Other software used include; ChemCad, PRO 11, etc. Furthermore, Aspen Technology Inc. has other products such as the Aspen Process Economic Analyser (APEA), which is used to perform economic analysis for process profitability.

Economic analysis can be done in several ways, namely; by estimating the capital cost of the major equipment and this can be achieved by having the price list from vendors. Another way is by using the available correlations/graphs for different types of common equipment in the literature, and using their cost data of past purchases. And lastly, by using the APEA which is based on the industry-standard Icarus System (Aspen Technology, 2010). This last option; the APEA is the preferred choice used in this research because it is readily accessible.

3.2 Methods/Approaches Available for Modelling and Simulation of Amine-Based Process for CO₂ Capture from NGCC Power Plant

The modelling of chemical absorption in packed columns involves two approaches, namely: rate-based and equilibrium-based modelling.

Rate-based involves multi-component mass and heat transfer, as well as chemical reactions, which are calculated using detailed mass transfer model such as the two-film theory. Conversely, the equilibrium-based approach assumes that vapour and liquid phases exist in equilibrium with theoretical stages, and the performance of each stage is usually designated by the height equivalent to a theoretical stage and Murphree Tray Efficiency (Kothandaraman, 2010). As a result, rate-based models are more accurate and robust than the equilibrium-based approach (Afkhamipour & Mofarahi, 2013).

Studies have been carried out on process simulations and thermodynamic modelling (Afkhamipour & Mofarahi, 2013; Linnenberg et al., 2012; Kwak et al., 2012; Zhang & Chen, 2011). The evaluation of the rate-based and equilibrium-based approaches demonstrated that the equilibrium approach resulted in an overestimation of rich loading, CO₂ removal rate and incorrect predictions of absorber temperature profiles. This confirms the fact that the application of the equilibrium modelling for reactive separation processes results in large deviations (about 11%) from literature (Asprion, 2006).

Rate-based modelling was applied in the amine capture plant to achieve reliable predictions of the capture plant performance. Aspen RateSep is a module inside Aspen Plus® that takes into account the rate-based simulation of absorber and stripper.

3.3 Aspen-Plus Rate Based Modelling

As shown in Figure 3-1, which illustrates the increasing model complexity, the Aspen Plus® model features rate-based approach, reaction kinetics, and no concentration gradient in bulk phases. It also shows the presence of electrolyte in the liquid phase and lastly, the film reactions, which include film discretization and the two-film theory (Kenig et al., 2001).

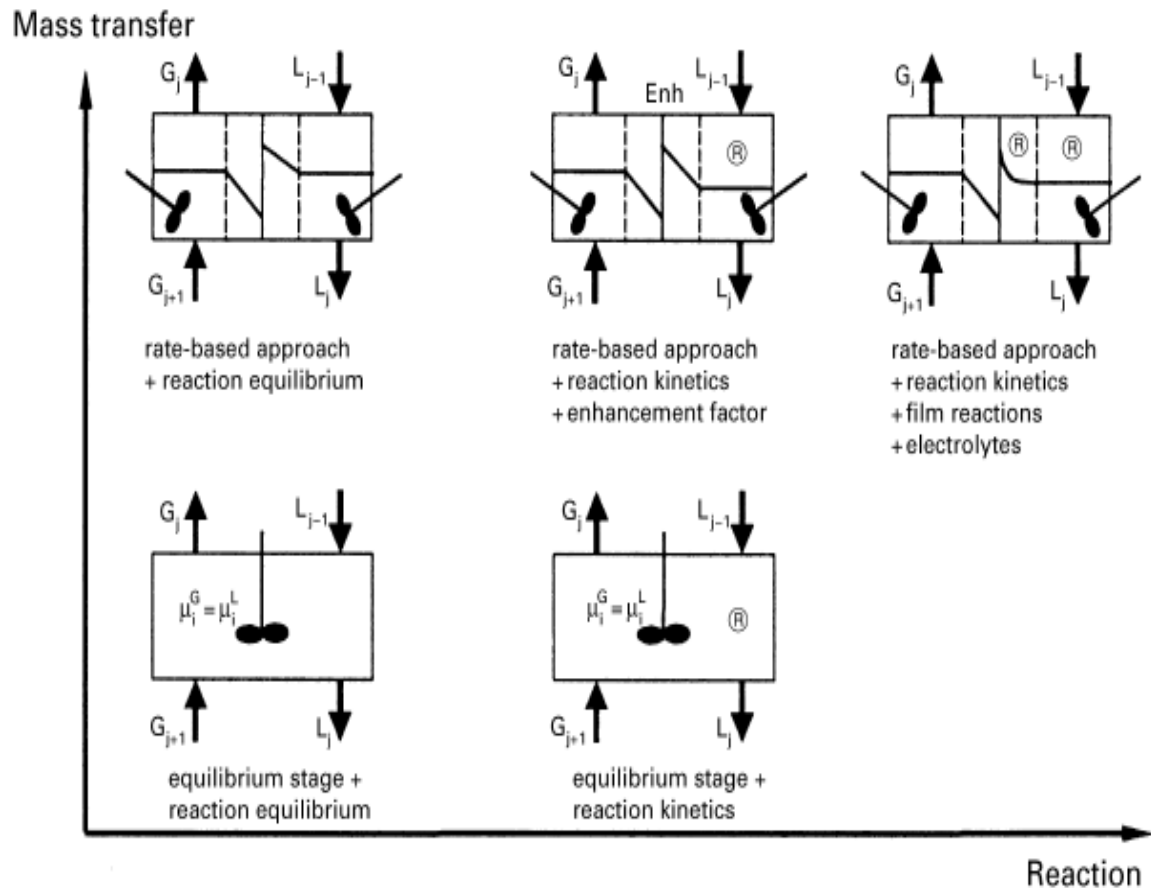


Figure 3-1: Approaches for modelling reactive absorption processes (Kenig et al., 2001)

The two-film theory is an approach widely used in modelling packed columns as shown in Figure 3-2.

The capture plant model is a steady state model, which employs the two-film approach. With the two-film theory approach, both liquid and gas phases consist of bulk and film regions. Components from the turbulent bulk vapour and liquid phases diffuse across the laminar vapour and liquid films respectively. Phase equilibrium between liquid and vapour phases is assumed at the interface. Each side of the interface are regions where mass transfer lies and this transfer is completely by molecular diffusion, the rate of diffusion across the gas-phase film must equal the rate of diffusion across the liquid-phase film. Mass transfer rates are calculated using the Maxwell Stefan's equation. This is because the Maxwell Stefan's formulation gives a better prediction for multiple component diffusion as compared to the Fick's

law (Krishna and Wesselingh, 1997). While heat and mass transfer resistance take place in the liquid and vapour films (Richardson et al., 2007).

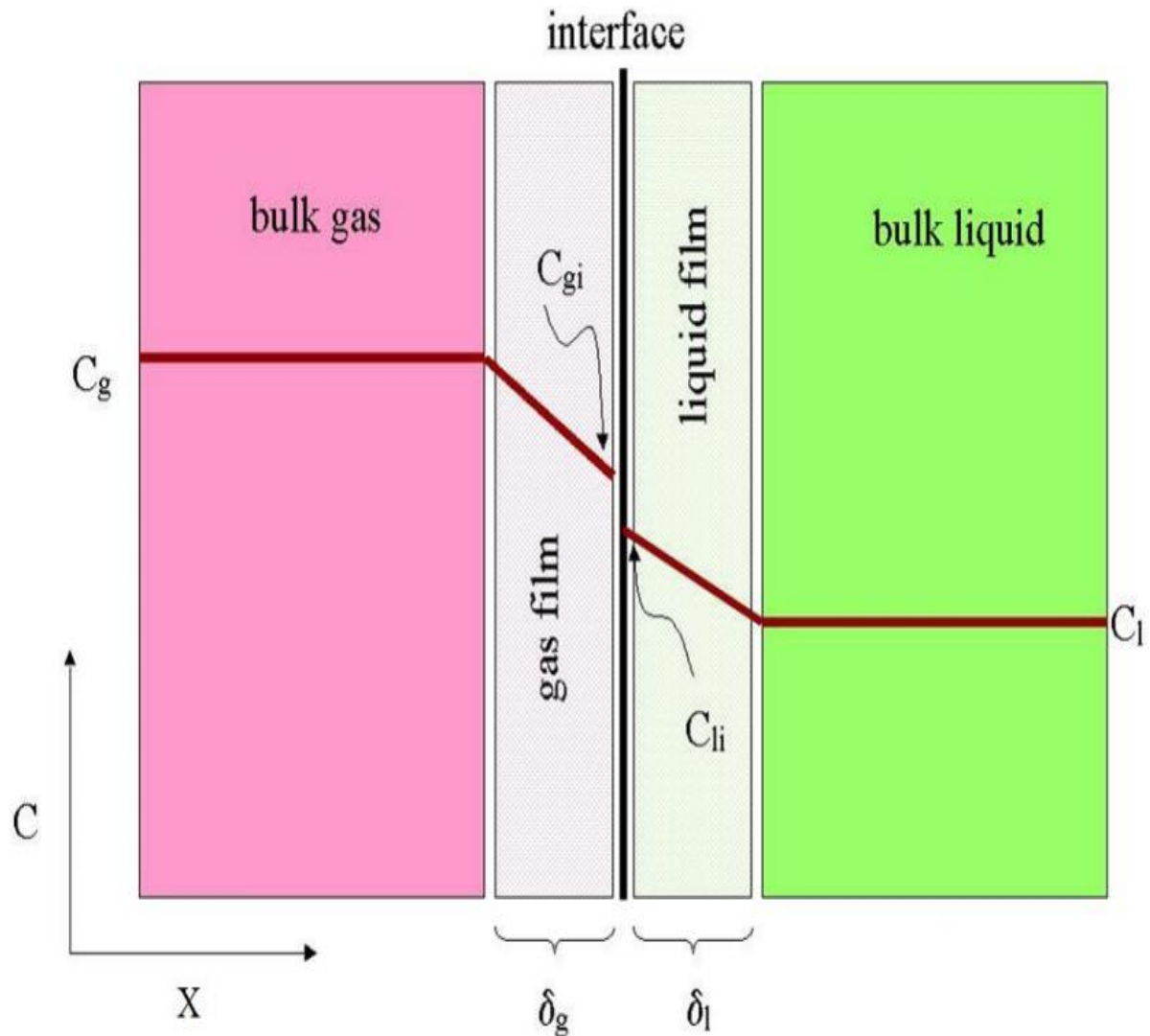


Figure 3-2: Two film theory approach (Richardson et al., 2007)

The counter-current flow of liquid and gas in a packed column describes the mass transfer in the system. The mass transfer parameters include the vapour and liquid mass and heat transfer coefficients, and the effective interfacial area. While the column hydraulics, are characterised by liquid holdup, pressure drop, and the column flooding capacity.

The thermodynamic modelling, which involves the vapour, liquid equilibrium, can be subdivided into two parts: physical equilibrium and chemical equilibrium. The physical equilibrium consists of the gas-liquid phase equilibrium. While the chemical equilibrium section, is used to describe the liquid phase speciation according to the chemical equilibrium equations.

3.4 Gas-Liquid Phase Equilibria

Phase equilibrium is a phenomenon, which occurs when the liquid and vapour phases are in equilibrium. However, in the liquid phase, non-volatile compounds such as ionic species are present. At equilibrium, the rate at which gas condenses into liquid is equal to the rate at which liquid evaporates into vapour. Thus, temperature, pressure and the phase change are the same for both liquid and vapour phases at equilibrium, but the compositions will be different. This is because of the vapour pressure of the pure component in the vapour phase and the non-idealities in the liquid phase. Due to this, the fugacity and activity coefficients are used to describe non-idealities in the vapour phase, and the liquid phase respectively.

3.5 Fugacity and Fugacity Coefficient

The concept of fugacity (Lewis & Randall, 1961) is used in the description of phase equilibria. Thus, under the same pressure (isobaric) and the same temperature (isothermal), the fugacity of species in the gas (F_g) and liquid phases (F_l) are equal, and expressed as given in Equation (3-1):

$$F_l = F_g \quad 3-1$$

For vapor-liquid phase equilibrium, a high pressure of up to 10 bar or greater is obtained. Thus, equations of states are used to calculate the fugacity coefficient for gas description.

3.5.1 Activity and Activity Coefficient

An activity can be defined as a measure of the effective concentration of species i in a mixture. However, activity describes how active a compound is in comparison to being under standard state conditions, and it depends on factors such as

temperature, pressure, etc. Activity coefficient of a species (γ_i) can be expressed as the ratio of the actual fugacity (f_i) to ideal fugacity (f_i^{id}) at the same temperature, pressure, and composition (Smith et al., 2005; Denbigh, 1981). This is given in Equation (3-2):

$$\gamma_i = \frac{f_i}{f_i^{id}} = \frac{f_i}{X_i f_i^0} \quad 3-2$$

3.6 Rigorous Vapour-Liquid-Equilibrium (VLE) Models for CO₂-Amines-H₂O Systems

On a basic level, the vapour-liquid equilibrium for electrolytic gas-liquid systems that is based on Henry's constant is ordinarily embraced. Accordingly, the supercritical components (i.e. components which are gases under typical conditions such as CO₂) are often referred to as Henry components (Aspen Technology, 2010; Austgen et al., 1989).

The Henry's constant of a supercritical component (i) in a given solvent (s) can be calculated from the following Equation (3-3) (Zhang & Chen, 2011):

$$\phi_i \gamma_i P = X_i \gamma_i H_i = X_i \gamma_i \left[\frac{H_i}{\gamma_i^\infty} \right] \quad 3-3$$

Where (H_i = Henry constant for component and ϕ_i is fugacity coefficient of species i , γ_i^∞ is the infinite dilution activity coefficient of Henry component i in the solution)

3.6.1 Models for the Fugacity Coefficient

Fugacity coefficient is calculated from pressure-volume-temperature (PVT) data using the equations of state (EOS) presented in the literature (Aspen Technology, 2010; Smith et al., 2005). Thus, EOS mostly employed in the modelling of the gas-phase non-ideal behaviour in CO₂-amines-H₂O systems are the Redlich-Kwong (RK) equation (Redlich & Kwong, 1949), the Soave's modification of the Redlich-Kwong (SRK) equation (Soave, 1972), and the Peng-Robinson (PR) equation (Peng & Robinson, 1976). Fugacity, which is viewed as a corrected partial pressure, is defined as shown in Equation (3-4):

$$f_i = \phi_i^{sat} P_i^{sat} \exp \left[\frac{V_i^l (P - P_i^{sat})}{RT} \right] \quad 3-4$$

Where, f_i is the fugacity of pure species i , at the temperature (T), and pressure of the solution. ϕ_i is the fugacity coefficient of pure species i at its saturation pressure, V_i is the liquid-phase molar volume of pure species i , and R is the gas constant.

3.6.2 Models for the Activity Coefficient

The activity coefficient defined by Equation (3-5) is used with the availability of the excess Gibbs energy (G^E) model present in the system.

$$\ln \gamma_i = \left[\frac{\partial (nG^E/RT)}{\partial n_i} \right]_{P, T, n_{j \neq i}} \quad 3-5$$

Most of the models used for the excess Gibbs energy of electrolytic systems, including CO₂ amine-H₂O systems, are a combination of short-range interactions, such as van der Waals type of interactions, and long-range electrostatic interactions as shown in Equation (3-6) (Kontogeorgis and Folas, 2009).

$$\frac{G^E}{RT} = \frac{G^{E,SR}}{RT} + \frac{G^{E,LR}}{RT} \quad 3-6$$

Where $G^{E, SR}$, and $G^{E, LR}$ are the short-range contribution and the long-range contribution respectively, to the excess Gibbs energy of the system.

The short-range interactions are taken into account by the Non-Random-Two-Liquid (NRTL) equation of Renon and Prausnitz (1968) and the Universal Quasi-Chemical (UNIQUAC) equation of Abrams and Prausnitz (1975).

Two of the broadly utilised models, which combine the short range and long range interactions are the electrolyte-UNIQUAC model; e-UNIQUAC) and the electrolyte-NRTL (e-NRTL) model (Kontogeorgis and Folas, 2009). The e-NRTL model applies in this work because it is the Aspen Plus® recommended model (Aspen Technology, 2008b).

- Electrolyte-NRTL Model (e-NRTL)

The model employed for the rigorous modelling of electrolyte systems, which includes the CO₂-alkanolamine-H₂O systems is the e-NRTL model. The e-NRTL

model, as first proposed by Chen and Co-workers (Chen et al., 1982) utilises the NRTL equation to represent short-range interactions and the PDH equation for long-range electrostatic interactions. However, the e-NRTL model represents the excess Gibbs energy transfer from infinite dilution in mixed-solvent to infinite dilution in the aqueous phase (Austgen, et al., 1989; Aspen Technology, 2011).

Chemical equilibrium expressions are used to model the liquid phase speciation. The liquid phase speciation is the equilibrium composition of the liquid phase and it is obtained by using the equilibrium reactions and the constant (Aspen Technology, 2008a). The equilibrium constants are determined from the equilibrium equations. The equilibrium constants (K_{eq}) for the reactions are defined as shown in Equation 3-7:

$$\ln K_{eq} = A + \frac{B}{T} + C \cdot \ln T + D \cdot T \quad 3-7$$

The values A, B, C, and D are given in the study (Austgen et al., 1989).

The kinetic expressions are useful in describing both absorption and regeneration processes. The reactions rates are determined by the power law expression given in Equation (3-8), which are useful for rate-controlled reactions.

$$r_j = k_j^o \exp \left(-\frac{E_j}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right) \prod_{i=1}^N C_i^{a_{ij}} \quad 3-8$$

Where r is the reaction rate of reaction j , k^o is its pre-exponential factor, E is the activation energy, C is the concentration (activity basis) of component i . N is the number of components in the reaction, and a is the reaction order of component i in reaction j . Values for the pre-exponential factors, and the activation energies of the reactions, are provided in the literature (Aspen Technology, 2008b).

4 AMP-Based Capture Plant Modelling and Simulation

4.1 Introduction

AMP is a primary amine, sterically hindered, and it was first considered by Satori and Savage (1987) as a substitute solvent for MEA. It has been noted that due to the steric effects when AMP absorbs CO₂, the stability of the formed carbamate is reduced, resulting in a lower heat of reaction compared to that in the case of MEA (Zhang et al., 2008). Also, AMP forms bicarbonates, and theoretical loading capacity is one (1) molCO₂/molAMP, which is double of that of MEA (Gabrielsen et al., 2007). Furthermore, AMP is more chemically and thermally stable with degradation rates close to half of those observed for MEA. For these reasons, saturated AMP solvent can be regenerated at higher temperatures, enabling the stripper operation under elevated pressure (up to 30% higher compared to that of MEA). This, in turn, reduces the CO₂ compression ratio, efficiency penalties, capital costs, and hence favours the economics of AMP-based CO₂ scrubbing. Due to the higher regeneration temperature, which can be up to 140 °C, 20 °C higher compared to MEA, the solvent viscosity is reduced (Wang & Jens, 2012). Also, AMP solvent is less corrosive than MEA enabling the use of higher concentrations of AMP, leading to a higher absorption capacity (Abu-Zahra et al., 2013; Aroonwilas & Veawab, 2004). Also, the absorption rate of AMP is lower than that of MEA, which appears to be the major drawback of AMP solvent (Gabrielsen et al., 2007; Abu-Zahra et al., 2013; Chowdhury et al., 2011).

The main aim of this chapter is the development of the AMP-based capture plant using default operating parameters in Aspen Plus®. Thus, the AMP-based process model for CO₂ capture is evaluated at a commercial scale and MEA-based process as a benchmark. Firstly, an AMP pilot-scale capture plant model is scaled up to commercial scale. Afterwards, the best mass transfer correlation set for the AMP-based process among three options is identified, and near-optimal operating conditions are determined by a sensitivity analysis.

Figure 4-1 shows a process flowsheet of the pilot-scale AMP-based plant as described in Dash et al. (2014). The AMP-based capture plant is modelled as a steady state process and consists of two columns (absorber and stripper), a cross heat exchanger represented by two heaters, a cooler and two pumps, connected in a closed cycle to achieve good prediction of the performance of the process (Biliyok & Yeung, 2013). Rich AMP leaving the bottom of the absorber is pumped to the cross heat exchanger, and exchanges heat with the lean solvent leaving the reboiler before entering the stripper. The lean solvent from the stripper is then pumped and further cooled down before it is fed to the absorber. More details on the design of absorber and stripper columns can be found in the literature (Aspen Technology, 2008b).

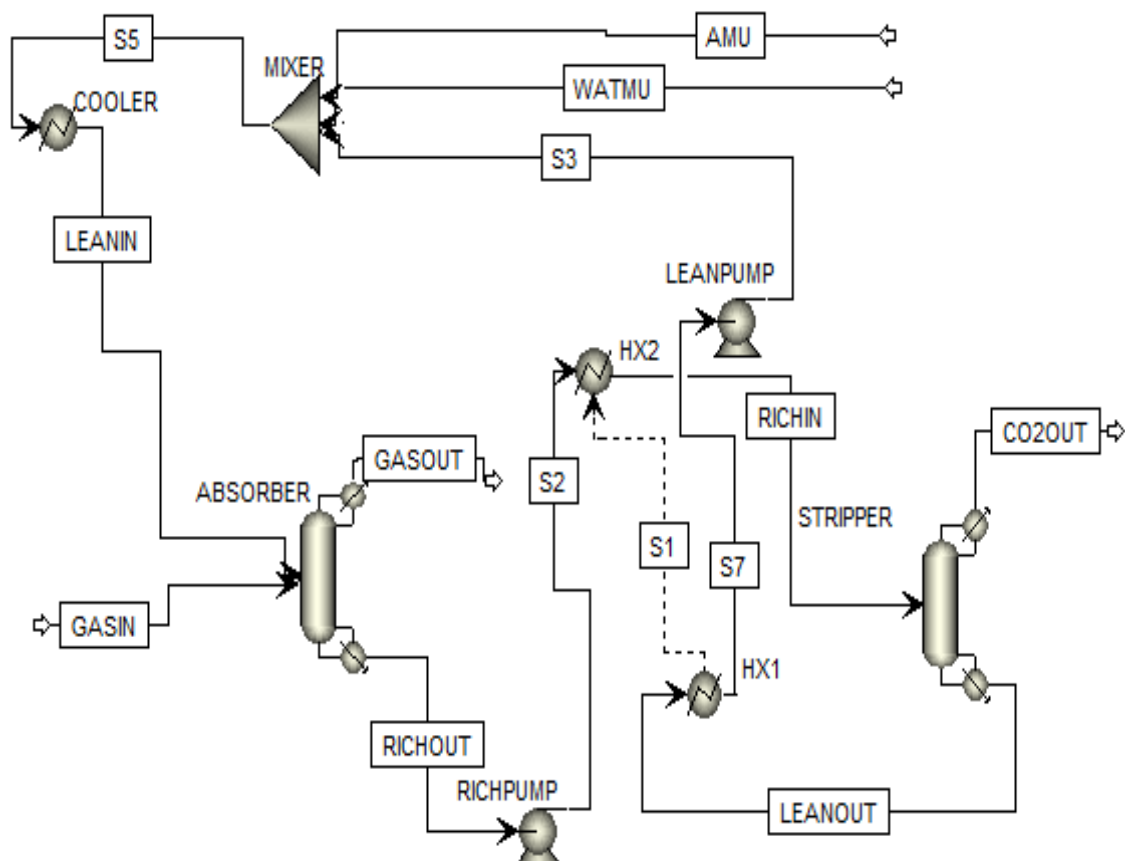
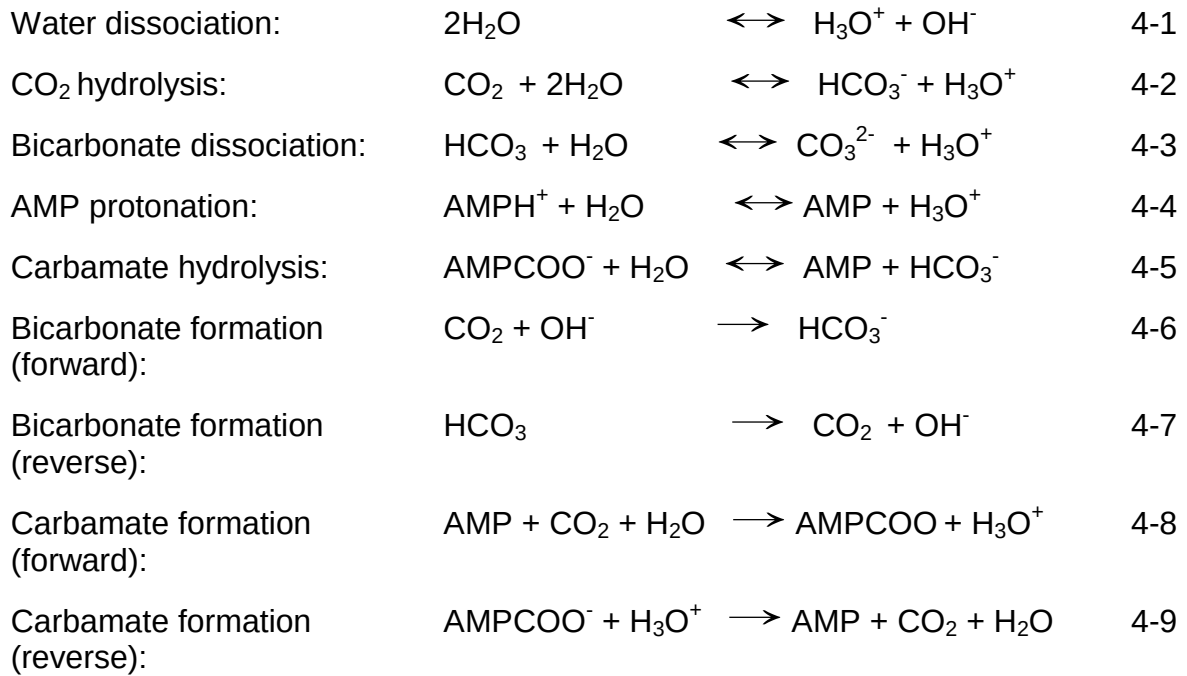


Figure 4-1: Process flowsheet of the AMP-based pilot plant for CO₂ capture
(Dash et al., 2014)

The rate-based AMP-based CO₂ capture plant model has been built using default parameters in Aspen Plus®. The thermophysical properties and reaction kinetics used in the model are based on experimental studies (Austgen et al., 1989). The transport property models and model parameters exist in the Aspen model (Aspen Technology, 2008b). Electrolyte NRTL model is used to describe the liquid phase thermodynamic state, while the Redlich-Kwong equation of state is used to describe the state of matter under physical conditions such as pressure, volume, and pressure of the molecular species of vapour phase (Aspen Technology, 2008a). To account for the CO₂-water-AMP system, the following solution chemistries were considered.



The equilibrium reactions defined by Equations (4-1:4-5) are modelled using equilibrium correlations (Austgen et al., 1989) as shown in Table 4-1.

Table 4-1: Coefficients of equilibrium constants

Reaction	A	B	C	D
Eq. (4-1)	132.889	-13445.9	-22.4773	0
Eq. (4-2)	231.465	-12092.1	-36.7816	0
Eq. (4-3)	216.049	-12431.7	-35.4819	0
Eq. (4-4)	2.1211	-8189.38	0	-0.007484
Eq. (4-5)	2.8898	-3635.09	0	0

While the kinetic reactions defined by Equations (4-6:4-9) are modelled using the power law expression with pre-exponential factors, and activation energies available in the literature (Aspen Technology, 2008b) given in Table 4-2.

Table 4-2: Power law expressions constants

Reaction	Pre-exponential factor (K_i (kmol/m ³ .s)	Activation energy E_i (cal/mol)
Eq. (4-6)	4.32×10^{13}	13249
Eq. (4-7)	2.38×10^{17}	29451
Eq. (4-8)	1.00×10^9	8202
Eq. (4-9)	1.52×10^{20}	12693

4.3 Model Validation

The AMP-based capture process model is validated with pilot plant data reported by Gabrielsen et al. (2007), for which the main design parameters are presented in Table 4-3. Three cases of experimental data (R4, R7, and R11) obtained for process parameters presented in Table 4-4 are chosen for model validation. These were selected from 11 experimental tests performed by Gabrielsen et al. (2007), due to their different operating conditions, and the accuracy of mass balances.

Table 4-3: Design data of the pilot plant (Gabrielsen et al., 2007)

	Absorber	Stripper
Diameter (m)	0.15	0.10
Packing height (m)	4.36	3.89
Packing	Sulzer Mellapak 250Y	Sulzer Mellapak 250Y
Type of packing	Structured	Structured

Table 4-4: Input parameters for validation of absorber model (Gabrielsen et al., 2007)

Input Parameters				
Case	Lean loading (molCO ₂ /molAMP)	AMP concentration (mol/L)	Gas flowrate (m ³ /h)	Solvent flowrate (L/h)
4	0.118	2.89	119	3
7	0.170	2.89	118	3
11	0.284	2.89	122	6

4.3.1 Absorber Model Validation

It can be seen in Table 4-5 that the best agreement between experimental and simulation results using the three different sets of mass transfer correlations given in Table 4-5, is in the case of Billet and Schultes (1993) correlation, with discrepancies for the capture level and rich loading having a relative error less than 0.1. The largest difference observed in the case of the other two sets of mass transfer correlations is almost 0.3 for the capture level (Case 4), implying that these correlations may have limited application for the AMP-based process.

Table 4-5: Comparison of model predictions with experimental data (Gabrielsen et al., 2007) **for the absorber**

Rich loading (molCO ₂ /molAMP)				Capture level (%)		
Bravo et al. (1985) correlations						
Case	Experiment	Model	Relative error	Experiment	Model	Relative error
4	0.379	0.403	0.063	29.85	24.79	0.170
7	0.459	0.412	0.102	24.15	21.44	0.112
11	0.400	0.399	0.003	22.00	19.40	0.118
Billet and Schultes (1993) correlations						
4	0.379	0.404	0.070	29.85	28.81	0.035
7	0.459	0.455	0.009	24.15	25.37	0.051
11	0.400	0.415	0.038	22.00	21.97	0.001
Bravo et al. (1992) correlations						
4	0.379	0.368	0.029	29.85	24.05	0.241
7	0.459	0.399	0.131	24.15	20.94	0.133
11	0.400	0.391	0.023	22.00	19.35	0.120

Figure 4-2 presents the comparison of temperature profiles in the absorber showing good agreement between the experimental data (Gabrielsen et al., 2007) and simulations for all three sets of mass transfer correlations. Specifically, the trend and the temperature bulge in the column for the three cases are properly predicted. This bulge is dependent on the liquid to gas (L/G) ratio and shows the location in the column where CO₂ absorption and heat release are the most intensive (Kvamsdal & Rochelle, 2008). Some deviations between experimental data and the results obtained from model remain, and they are more pronounced with increasing L/G ratio as shown in the temperatures profiles (Figure 4-2) for all three sets of the mass transfer correlations. Also, the results from the model underestimate the temperatures in the absorber, which implies that the model slightly underestimates the capture levels in the absorber; this is observed with the results presented in Table 4-5. In conclusion, the Billet and Schultes (1993) correlations enable the most accurate model predictions for the capture level, rich loading, and absorber temperature profiles which have a relative error less than 0.2 for all cases as shown in Table 4-6 and, therefore, can be used in a scaled-up and integrated process model.

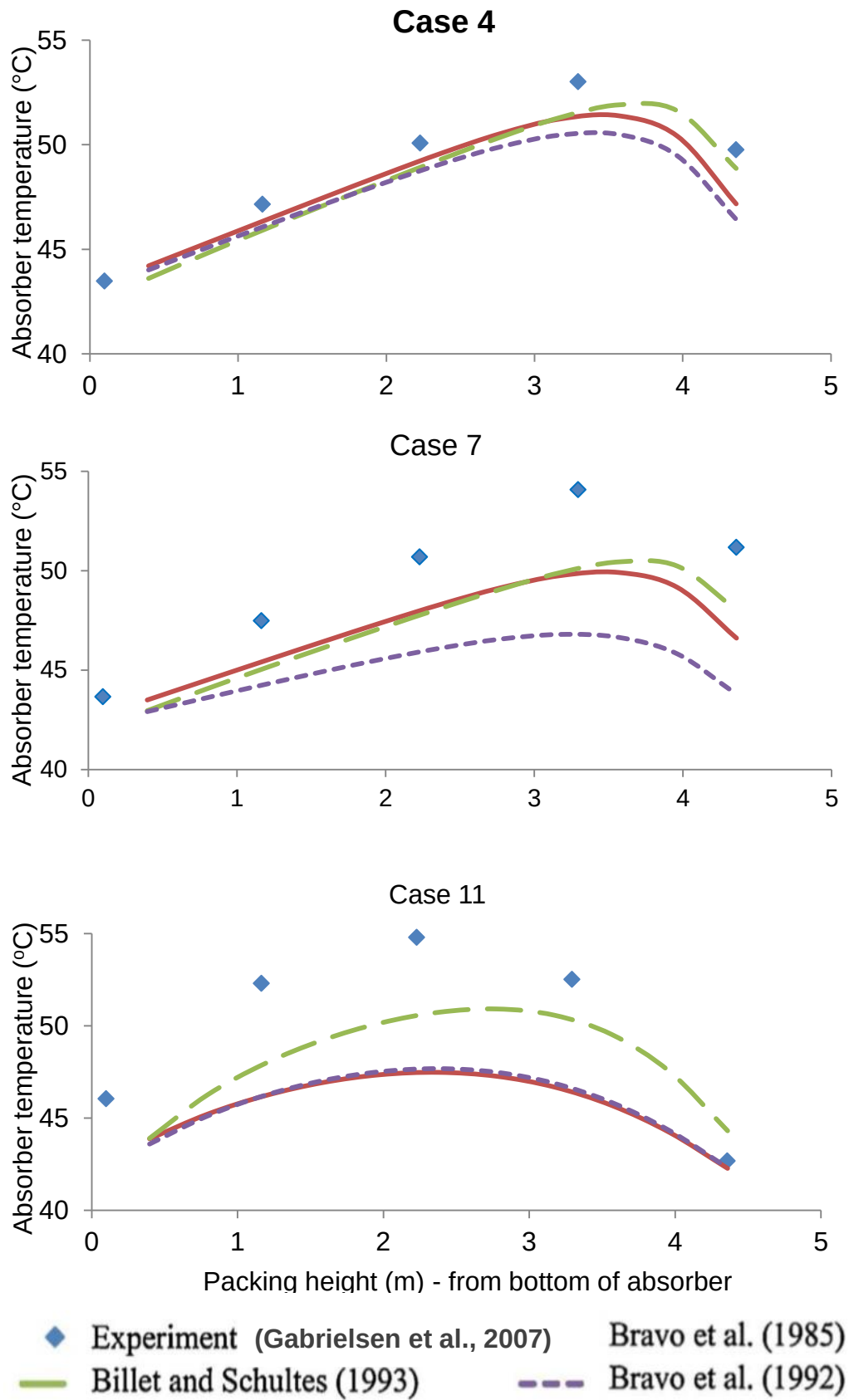


Figure 4-2: Liquid phase temperature profiles in the absorber

Table 4-6: Comparison of model predictions with experimental data (Gabrielsen et al., 2007) for the temperature profiles in the absorber

	Bravo et al. (1985) correlations				
	Case 4				
Packing height (m)	0.1	1.165	2.23	3.295	4.36
Temp °C (Experiment)	43.47	47.15	50.07	53.01	49.75
Temp °C (model)	46.58	46.85	46.74	45.93	43.90
Relative error	0.072	0.006	0.067	0.133	0.118
	Case 7				
Temp °C (Experiment)	43.66	47.48	50.68	54.07	51.17
Temp °C (model)	46.86	47.15	47.05	46.22	44.10
Relative error	0.073	0.007	0.072	0.145	0.138
	Case 11				
Temp °C (Experiment)	46.04	52.29	54.79	52.51	42.68
Temp °C (model)	47.26	46.72	45.74	44.28	42.32
Relative error	0.026	0.107	0.165	0.157	0.009
	Billet and Schultes (1993) correlations				
	Case 4				
Temp °C (model)	44.13	45.97	46.55	46.5	46.14
Relative error	0.062	0.014	0.07	0.132	0.113
	Case 7				
Temp °C (model)	46.41	46.79	46.84	46.26	44.34
Relative error	0.063	0.015	0.076	0.144	0.133
	Case 11				
Temp °C (model)	48.71	48.24	47.21	45.48	43.02
Relative error	0.058	0.077	0.138	0.134	0.008
	Bravo et al. (1992) correlations				
	Case 4				
Temp °C (model)	46.58	46.85	46.74	45.93	43.9
Relative error	0.072	0.006	0.067	0.133	0.118
	Case 7				
Temp °C (model)	46.57	46.8	46.65	45.81	43.79
Relative error	0.067	0.014	0.079	0.153	0.144
	Case 11				
Temp °C (model)	47.68	47.14	46.11	44.55	42.45
Relative error	0.026	0.107	0.165	0.152	0.005

4.3.2 Stripper Model Validation

Input parameters (Gabrielsen et al., 2007) for validation of the stripper model in Aspen Plus® are presented in Table 4-7. It can be seen in Table 4-8 that the model predictions closely fit the pilot plant data for all three sets of mass transfer correlations, with some better agreement in the case of the Bravo et al. (1985) and Bravo et al. (1992) correlations. Figure 4-3 shows the temperature profiles in the stripper for the three cases, which are very similar for all three sets of mass transfer correlations and fit the pilot plant data. Both pilot plant data and simulations show similar L-shape profiles expected for a stripper and the relative errors less than 0.2 for all cases as shown in Table 4-9. This confirms that the capture plant model can be scaled up and integrated, and the Bravo et al. (1985) correlation is selected due to the closest predictions to the experimental data (Gabrielsen et al., 2007)

Table 4-7: Input parameters for validation of stripper model (Gabrielsen et al., 2007)

Case	Rich loading (molCO ₂ /molAMP)	Reboiler duty (kW)	Condenser temperature (°C)
4	0.379	7.6	16
7	0.459	7.6	19
11	0.400	7.7	14

Table 4-8: Comparison of model predictions with experimental data for the stripper (Gabrielsen et al., 2007)

Lean solvent (molCO ₂ /molAMP)				Reboiler temperature (°C)		
Bravo et al. (1985) correlations						
Case	Experiment	Model	Relative error	Experiment	Model	Difference (%)
4	0.118	0.120	0.017	116.6	117.66	0.009
7	0.170	0.181	0.065	112.4	114.90	0.022
11	0.284	0.278	0.021	107.1	111.82	0.044
Billet and Schultes (1993) correlations						
4	0.118	0.115	0.025	116.6	117.77	0.010
7	0.170	0.182	0.071	112.4	114.99	0.023
11	0.284	0.278	0.021	107.1	111.84	0.044
Bravo et al. (1992) correlations						
4	0.118	0.121	0.025	116.6	117.63	0.009
7	0.170	0.182	0.071	112.4	114.93	0.023
11	0.284	0.278	0.021	107.0	111.82	0.045

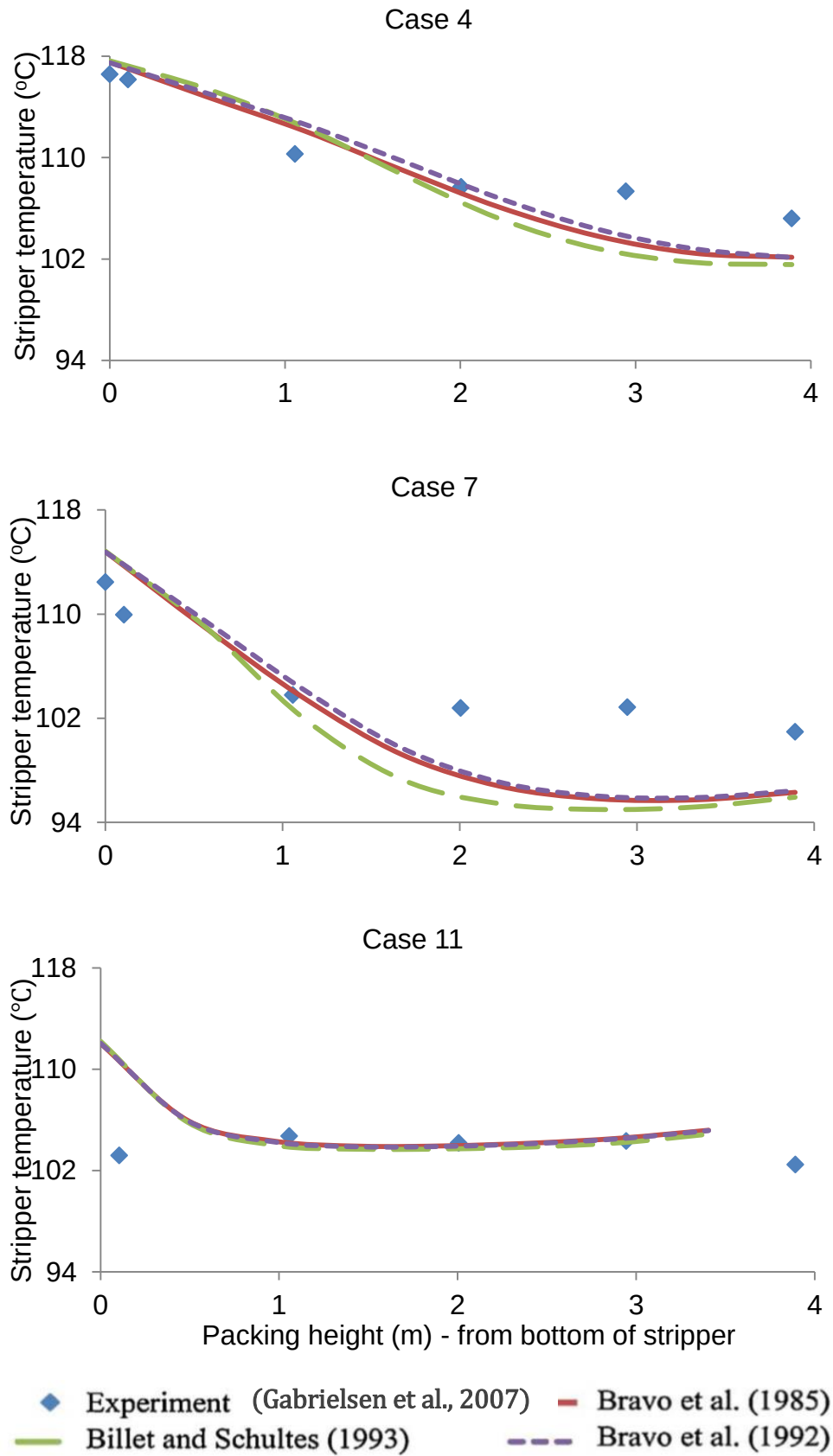


Figure 4-3: Liquid phase temperature profiles in the stripper

Table 4-9: Comparison of model predictions with experimental data for the temperature profiles in the stripper (Gabrielsen et al., 2007)

	Bravo et al. (1985) correlations				
	Case 4				
Packing height (m)	0.105	1.058	2.006	2.945	3.892
Temp °C (Experiment)	116.15	110.27	107.68	107.32	105.18
Temp °C (model)	112.19	106.32	104.71	104.30	104.27
Relative error	0.034	0.036	0.028	0.028	0.009
	Case 7				
Temp °C (Experiment)	109.93	103.78	102.78	102.85	100.95
Temp °C (model)	111.33	104.98	103.31	102.91	102.89
Relative error	0.013	0.012	0.005	0.001	0.019
	Case 11				
Temp °C (Experiment)	103.18	104.71	104.16	104.31	102.47
Temp °C (model)	112.03	105.97	104.32	103.91	103.95
Relative error	0.086	0.012	0.001	0.004	0.014
	Billet and Schultes (1993) correlations				
	Case 4				
Temp °C (model)	111.98	106.5	104.75	104.38	104.42
Relative error	0.036	0.034	0.027	0.027	0.007
	Case 7				
Temp °C (model)	111.12	105.21	103.4	103.04	103.11
Relative error	0.011	0.014	0.006	0.002	0.021
	Case 11				
Temp °C (model)	103.18	104.71	104.16	104.31	102.47
Relative error	0.084	0.013	0.002	0.003	0.016
	Bravo et al. (1992) correlations				
	Case 4				
Temp °C (model)	46.58	46.85	46.74	45.93	43.9
Relative error	0.072	0.006	0.067	0.133	0.118
	Case 7				
Temp °C (model)	46.57	46.8	46.65	45.81	43.79
Relative error	0.067	0.014	0.079	0.153	0.144
	Case 11				
Temp °C (model)	47.68	47.14	46.11	44.55	42.45
Relative error	0.026	0.107	0.165	0.152	0.005

4.4 Scale-Up of the Capture Plant Model

4.4.1 Considerations

As mentioned above, AMP has a lower absorption rate than that of MEA; this is a major drawback of AMP solvent compared to MEA. The absorption rate can be enhanced by increasing the surface area of packing, increasing the absorber pressure, or adding piperazine (PZ) to the AMP solution. Increasing absorber pressure would require flue gas compression, thicker vessel walls, and additional plant supports, leading to higher design and operational costs, which is undesirable. Although PZ is known to be a promoter for the amine systems, its main disadvantage is the narrow operating loading range due to solubility limitation (Freeman et al., 2010; Li et al., 2013). So increasing the surface area of packing is considered as the most suitable option, and the Mellapak 350Y packing was chosen for the scaled-up model because of the better capture efficiency (Chemtech - Sulzer Chemtech, 2010). The capture plant for the AMP solvent is scaled up to accommodate flue gas from an NGCC power plant (NETL, 2010). The flue gas composition is presented in the (Table 4-10).

Table 4-10: Flue gas composition (NETL, 2010)

Parameter	Value
Argon (mol/mol)	0.0089
CO ₂ (mol/mol)	0.0404
H ₂ O (mol/mol)	0.0867
N ₂ (mol/mol)	0.7432
O ₂ (mol/mol)	0.1209
Flue gas flow rate (kg/s)	897.4

4.4.2 Procedure for Scale-Up

Scaling up is done using the methodology described by Kister (1992) to achieve a capture level of 90%. The operational data for the scaled-up PCC plant obtained from this study are given in Table 4-11.

Table 4-11: Operating conditions for the full-scale AMP-based process model in Aspen Plus (Aspen Tech, 2008b; Lawal et al., 2010; Agbonghae et al., 2014)

Plant Specifications	Value
Absorber pressure (bar)	1.013
Absorber inlet pressure (bar)	1.2
Flue gas inlet temperature (°C)	40
Lean loading (molCO ₂ /molAMP)	0.2
Lean solvent concentration (wt%)	30.0
Packing type	Mellapak 350Y
CO ₂ capture level (%)	90
Reboiler temperature (°C)	120
Stripper pressure (bar)	1.65

An efficient packed column design is characterised by a good liquid and gas distribution that is achieved by operating at the highest economical pressure drop (Sinnott et al., 2005). Two criteria were used to determine the column diameter for given gas and liquid flow rates: the maximum pressure drop and the approach to maximum capacity. A maximum pressure drop per unit height of 20.83 mm-H₂O/m is assumed to be maximum for amine systems, this is because amine systems are prone to foaming (Kister, 1992; Sinnott and Towler, 2013). The vendor correlation for Mellapak 350Y structured packing was used for pressure drop calculation. While the approach to maximum capacity ranges from 70-80% of the flooding point velocity for packed columns (Kister, 1992). Generalised pressure drop correlation (GPDC) charts were established for both random and structured packing (Perry & Green, 2008; Strigle, 1994), the flooding line for the selected maximum pressure drop is represented in the GPDC chart as shown in Figure 4-4. Furthermore, the Bravo et al. (1985) correlation was used to calculate the mass transfer coefficients and the interfacial area, while the Bravo et al. (1992) correlation was used to calculate liquid holdup. Also, for prediction of the heat transfer coefficient, the Chilton and Colburn correlation was employed. The correlations listed above are in-built in Aspen Plus® (Aspen Technology, 2008b).

The capacity of the column is characterised by its cross-sectional area, and the column diameter (D), which is related to the superficial velocity of the gas stream is confirmed from the GPDC given in Equation (4-10):

$$D = \sqrt{\frac{4G}{\pi U_s}} \quad 4-10$$

Where G is the gas flow rate, and U_s is the superficial velocity of the gas stream, which is associated with the packed column capacity factor by Equation 4-11 (Strigle, 1994; Perry & Green, 2008).

$$C_o = U_s \left(\frac{\rho_G}{\rho_L - \rho_G} \right)^{0.5} F_p^{0.5} \mu^{0.05} \quad 4-11$$

Where C_o is the capacity factor; F_p is the packing factor; ρ_L and ρ_G are densities of liquid and gas, respectively; and μ is the kinematic viscosity of the liquid. The capacity factor for a packed column is dependent on the flow parameter (X) and the pressure drop per unit height of the packing (ΔP). The flow parameter is given by Equation 4-12 in which L is the liquid flowrate (Perry & Green, 2008; Strigle, 1994).

$$X = \frac{L}{G} \left(\frac{\rho_G}{\rho_L} \right)^{0.5} \quad 4-12$$

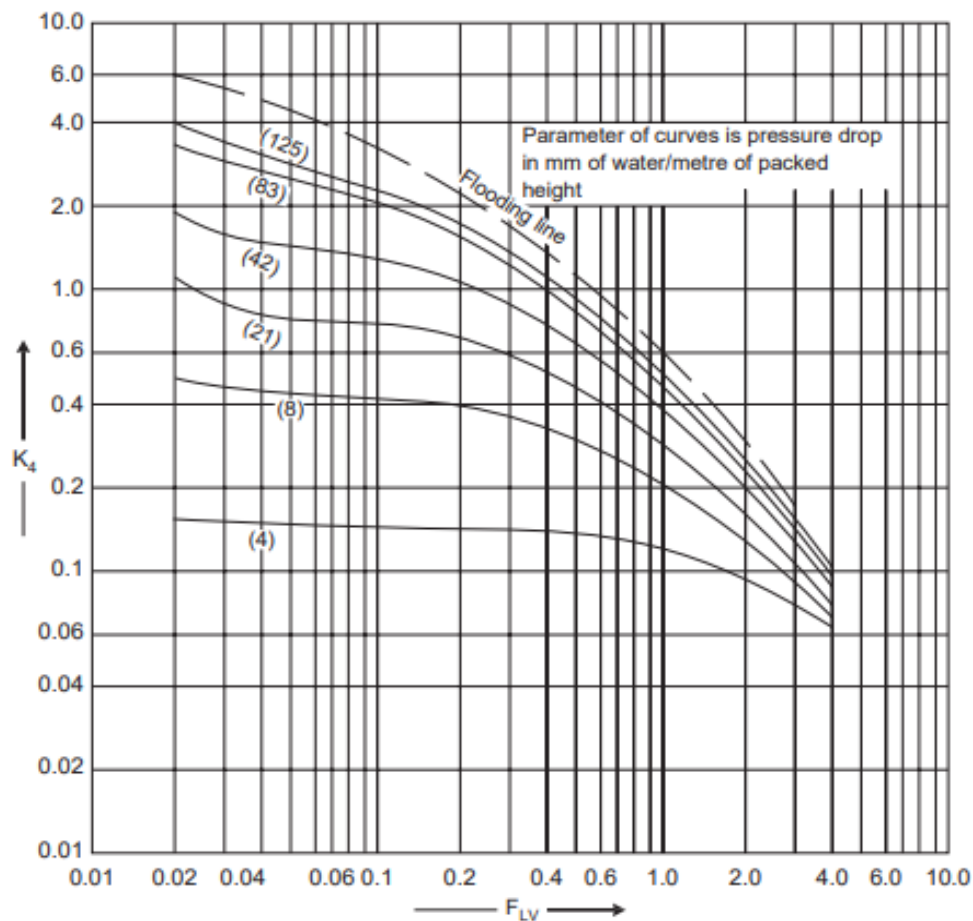


Figure 4-4: Generalized pressure drop correlation chart (Sinnott and Towler, 2013; Perry & Green, 2008)

Because of the turndown ratio limitations, packed column diameters should not exceed 15 m (Chemtech - Sulzer Chemtech, 2010), and the cross-sectional areas for the absorber and stripper should meet the capacity requirements. Therefore, the minimum number of absorbers and strippers depends on the desired column capacity. These calculated estimates were used as an initial guess to scale up the model in Aspen Plus® with the operating conditions set in order to prevent the column flooding to exceed 80%. Therefore, two absorption columns, each with a diameter of 15 m and one stripper with a diameter of 8.1 m are implemented into the model. The packing height method for both absorber and stripper involved using a generic height of 17 m (Lawal et al., 2010). Different packing heights are then trialled. The savings in the reboiler duty corresponding to each trialled height is considered the best packing height. The design and operations for the scaled-up AMP-based process obtained from this study are given in Table 4-12.

Table 4-12: AMP-based process full-scale plant preliminary design parameters in Aspen Plus

Parameter	Value
Absorber diameter (m)	14.5
Absorber packing height (m)	30
Stripper column diameter (m)	8.1
Stripper packing height (m)	30
Absorber column number	2
Stripper column number	1
Absorber cross-sectional area (m ²)	706.9
Stripper cross-sectional area (m ²)	51.5
CO ₂ stream purity (mass basis)	0.998
Liquid to gas ratio (mass basis)	1.05

AMP - 2-Amino-2-Methyl-1-Propanol

4.5 Process Analysis of Capture Plant

4.5.1 Sensitivity Analysis

The reboiler duty accounts for most energy consumed in a post-combustion chemical absorption capture process and, therefore, it requires the major consideration when comparing CO₂ solvents. The heat provided by the reboiler heats up the rich solvent from the absorber leading to the reverse of the CO₂ absorption reactions. CO₂ bonded in the form of carbamates and bicarbonates is released,

leaving the solvent behind, which is then recycled and reused in the absorber. The reboiler duty can be reduced by optimising the lean solvent loading, the solvent concentration, and the stripper operating pressure. The scaled-up capture plant is used to study the effects of these key parameters in order to determine near-optimal operating conditions, and the key parameters are varied in the range:

- AMP solvent concentration, 25–35 wt%;
- Lean loading, 0.15–0.36 molCO₂/molAMP;
- Stripper pressure, 1.5–3.5 bar.

Singh et al. (2011) employed a 35.6 wt% AMP for comparison with other solvents. In this study, an operating range of concentration of AMP (25–35 wt%) has been selected. Besides, Gabrielsen et al. (2007) highlighted difficulties in using up to 40 wt% AMP, due to the formation of a wax-like white solid, when absorbent is saturated with CO₂. Thus, these different conditions for the AMP-based process are varied around the different operating points to observe how the process responds to changes.

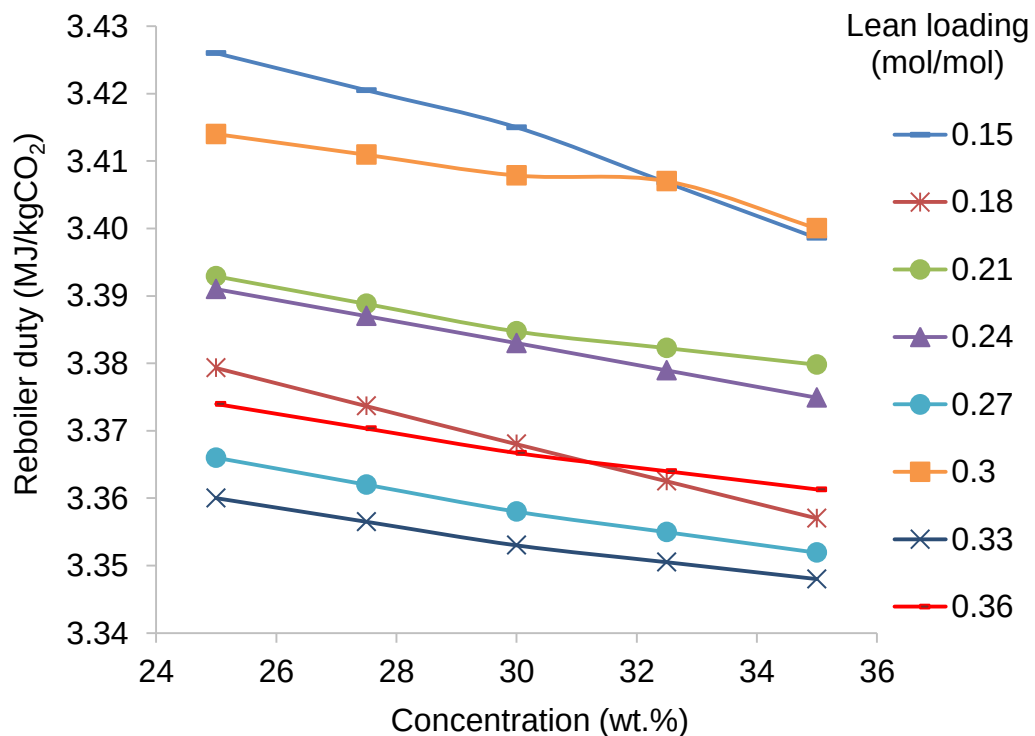


Figure 4-5: Effect of solvent concentration and lean loading on reboiler duty

As shown in Figure 4-5, an increase in solvent concentration results in a reduction in reboiler duty. This is driven by the slightly reduced circulation rate as shown in Figure 4-6, and because of the lower amount of water in the system, which means that less heat is needed to heat up and evaporate this water, which is later condensed and returned as reflux to the stripper column. With respect to lean loading, the trend is not as clear, as the lowest reboiler duty is observed for a lean loading of 0.33. The reason for this is that the reboiler duty achieves a combination of four functions:

- Providing sensible heat to the rich solvent to increase its temperature to the specified reboiler temperature
- Evaporating water in the reboiler, which acts as the stripping agent, aiding the CO₂ removal from the solvent
- Providing heat to reverse the absorption reaction in the absorber, which is in theory, equal to that released due to the exothermic reactions
- Providing heat to liberate dissolved CO₂ out of the solvent

Depending on the function which is most dominant under a given set of conditions, the reboiler duty will adjust accordingly to maintain a stripping rate that achieves a 90% capture level. Therefore, for the conditions under study, the lowest reboiler duty is achieved at around 0.33 mol/mol lean loading.

Finally, it can be seen from Figures 4-5 and 4-6 that minimum reboiler duty is achieved for 35 wt% AMP and a lean loading of 0.33 mol/mol and these values are selected to analyse the effect of stripper operating pressure.

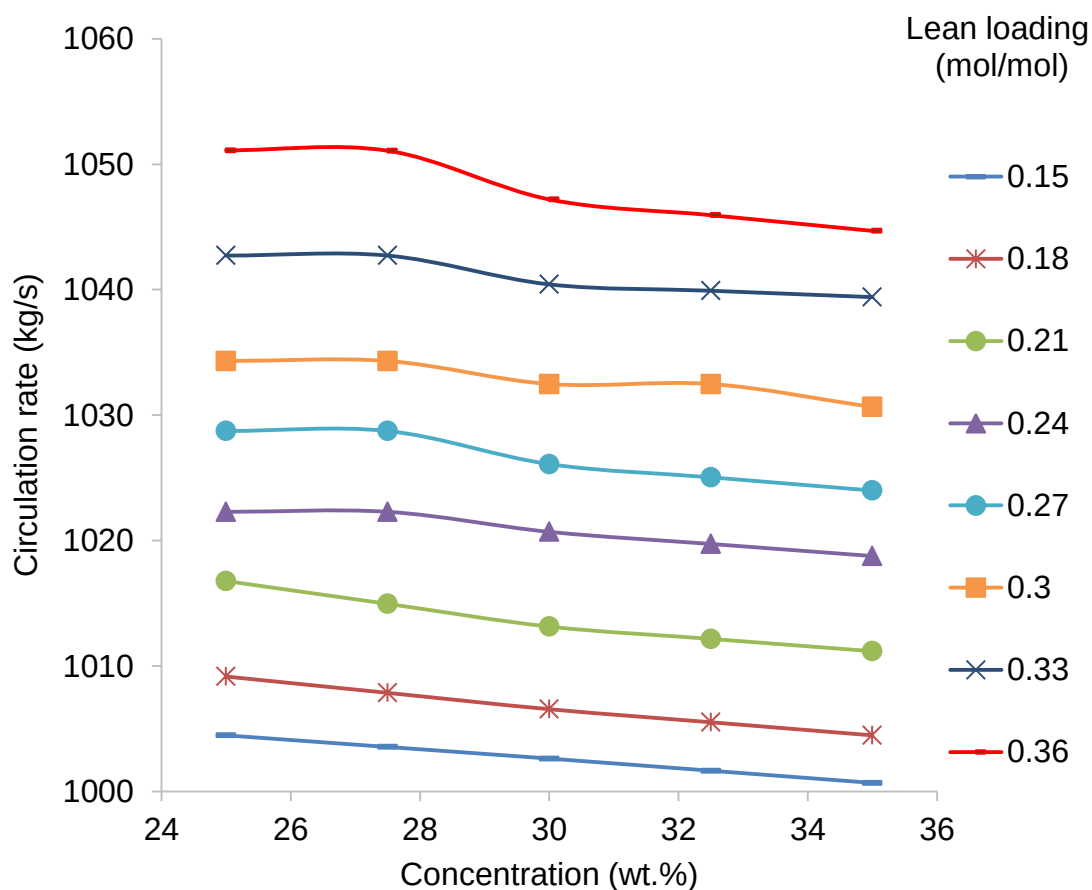


Figure 4-6: Effect of solvent concentration on circulation rate

Regeneration efficiency of amines depends on reboiler temperature, which is determined by the reboiler duty and stripper pressure (Tobiesen et al., 2008). As shown in Figure 4-7, with increasing stripper pressure, the reboiler temperature is higher while the reboiler duty decreases. For the range considered, the minimum reboiler duty is obtained at a stripper pressure of 3.5 bar and a reboiler temperature of 140 °C. This is the highest recommended, which is limited by the thermal degradation of AMP (Wang & Jens, 2012).

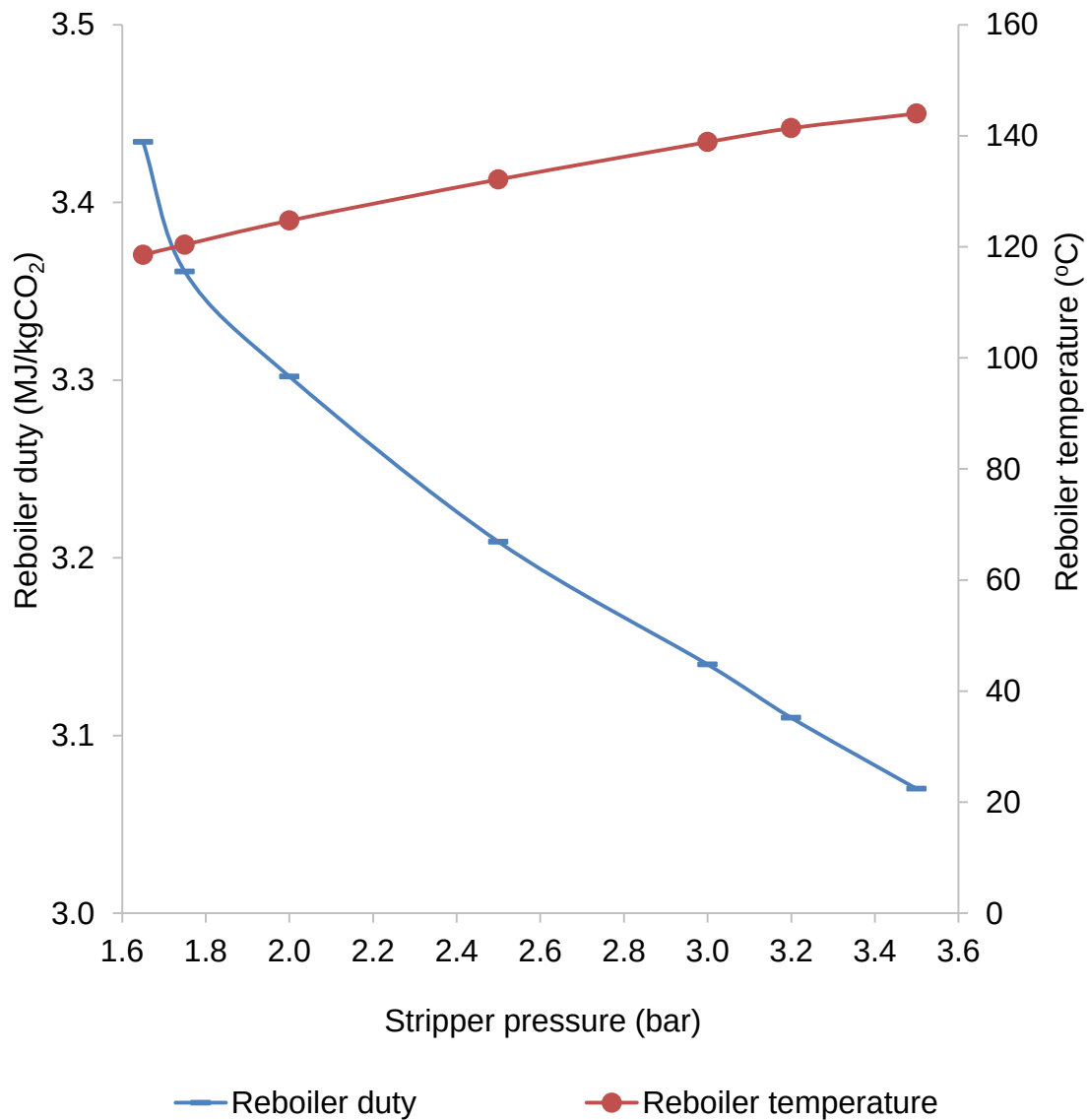


Figure 4-7: Effect of stripper pressure on reboiler duty and reboiler temperature for AMP solvent

In order to have a benchmark for comparison, an MEA-based process model is scaled up using the same procedure described in Sections 4.4, with operational requirements given in Table 4-13. The same flue gas composition and the plant specifications for the AMP-based process are used to design the MEA-based process used in this study.

Table 4-13: MEA-based process full-scale plant preliminary design with Aspen Plus

Specification	Value
Absorber diameter (m)	10.5
Absorber packing height (m)	20
Stripper column diameter (m)	8.61
Stripper packing height (m)	30
Absorber column number	4
Stripper column number	1
Absorber cross-sectional area (m ²)	346.4
Stripper cross-sectional area (m ²)	58.3
CO ₂ stream purity (mass basis)	0.979
Liquid to gas ratio (mass basis)	0.99

MEA - Monoethanolamine

4.6 Conclusion

In this chapter, a PCC process with the AMP-based process was evaluated. AMP solvent was considered to potentially replace traditional MEA solvent in the CO₂ capture processes. A detailed rate-based model implemented in Aspen Plus[®] was used to evaluate the PCC process. The model was developed in Aspen Plus[®] V8.4 at the pilot scale and validated using the experimental pilot plant data available in the literature (Gabrielsen et al., 2007). The simulation results indicated good agreement between the pilot plant logs and the model (developed using default operating parameters in Aspen Plus[®]), predictions especially when the Billet and Schultes (1993) and Bravo et al. (1985) mass transfer correlations were implemented in the absorber and stripper models, respectively. The model was then scaled up to process flue gas from a 474 MWe NGCC power plant. The effects of lean loadings, solvent concentration, and stripper pressure on reboiler duty were investigated. The simulations pinpointed the region for near-optimal operating conditions; AMP concentration of 35 wt%, a lean loading of 0.33 mol/mol with a stripper pressure and temperature of 3.5 bar and 140 °C, respectively, at these points, minimum reboiler duty for the AMP-based process was achieved.

5 INTEGRATION STUDIES

5.1 Introduction

Meeting the Paris Agreement targets is challenging as a high proportion of the existing power generation capacity is based on fossil fuels. CCS is expected to provide a cost-effective process of reducing CO₂ emission from the fossil fuel-fired power sector. Due to the low prices of natural gas, its demand is expected to rise compared to other fossil fuels such as coal. The amine solvent-based PCC is regarded as a suitable option for retrofitting the NGCC power plants (NETL, 2010). However, the energy requirement for solvent regeneration remains a major challenge, due to less electricity sold, and causing an energy penalty. By retrofitting the NGCC power plant with the CO₂ capture plant using chemical solvents, the net efficiency decreases by 7%-10% (Peeters et al., 2007). The parasitic load on the NGCC can be reduced by the use of substitute solvents (e.g. AMP), which has better overall performance than the MEA.

Furthermore, due to the energy penalty associated with capturing CO₂, if deployed in existing NGCC and coal-fired power plants, there will be a significant reduction in existing capacities. Until new power plants are built to make up for the shortfall, existing capacities will not be able to meet demand at peak periods. Hence, a way to address this challenge is the addition of the solvent storage system, which enables the energy penalty to be deferred until the times of low electricity prices. However, investing in solvent storage will only be profitable if there a substantial difference between the high and the low electricity prices. In addition, the operating mode of the plant, which defines the number of operating hours during peak and off-peak periods, determines the required capacities of the solvent storage and the solvent regeneration. Thus, the main benefits of the solvent storage system are increase in flexibility and additional profit opportunities (Chalmers & Gibbins, 2007).

In this chapter, the AMP-based process model is retrofitted into an NGCC power plant model, using the MEA-based process as a benchmark, with a key feature of implementation of the Stodola's ellipse law to account for the pressure drop due to steam extraction in order to provide better efficiency estimates. This chapter also

assesses the feasibility of retrofitting the CO₂ capture plant with solvent storage into the NGCC power plant, using AMP as a solvent.

5.2 Power Plant Modelling

A 474 MW_e NGCC power plant with a net efficiency of 47.5%_{LHV}, has been modelled in Aspen Plus[®] V8.4 and used in this study to explore the performance of the NGCC retrofit with the PCC. The NGCC plant comprises a single F-class gas turbine (GT), a HRSG, and a steam turbine. The gas turbine is modelled based on the Peng-Robinson equation of state with a pressure ratio of 18.4. The Gibbs reactor was used to model the combustor (NETL, 2012). The HRSG is configured with High-pressure (HP), IP, and LP steam drums, superheater, reheater, and economiser sections, and the steam/watersides are modelled using the steam tables (STEAMBS). The HRSG recovers heat from the flue gas and produces steam for the steam cycle that comprises the HP, IP and LP steam turbines characterised by design isentropic efficiencies of 85%, 91.1%, and 92.7%, respectively (NETL, 2012).

Furthermore, the reason for the feedwater framework is to pump feedwater streams from the deaerator storage tanks in the HRSG to the separate steam drums. The steam cycle condenser has a pressure of 0.07 bar, with a saturation temperature of 38.4 °C. The boiler feed water pumps are driven by a boiler feed water turbine and extracted steam from the IP-LP cross-over is extended in the boiler feed water turbine. The steam required by the CO₂ capture plant is also tapped from the IP-LP crossover while the condensate from the stripper reboiler is sent back to the steam cycle deareator.

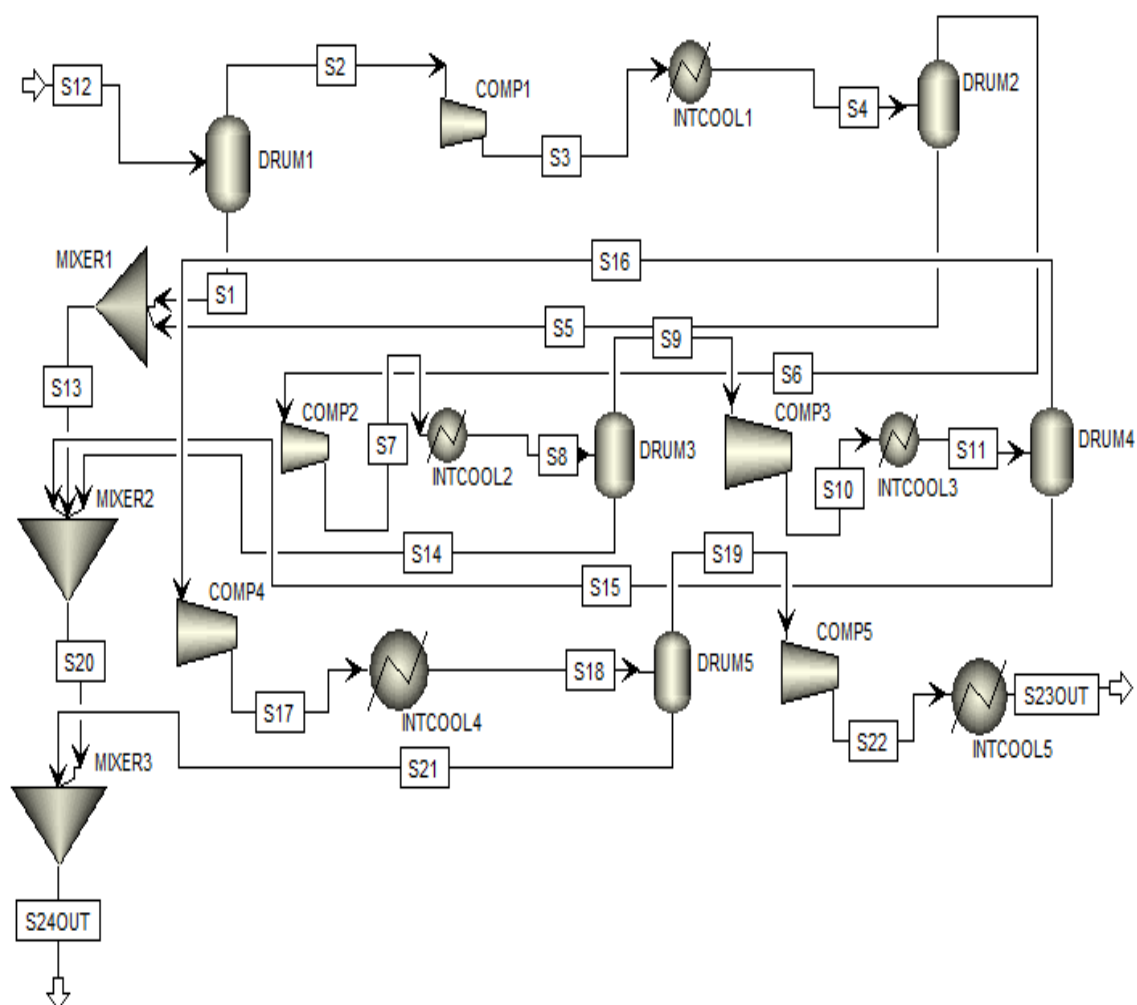
The design parameters of the NGCC plant are provided in Table 5-1, and the results from the model are validated with literature data (NETL, 2010). The NGCC plant model predicts a net output of 448.3 MW_e with a net efficiency of 45.0%_{LHV}. A comparison of the stream data provided in the Appendix A (Tables A-1 and A-2) shows that the model is in close agreement with the literature data, and all the parameters used, have a relative error less than 0.1.

Table 5-1: NGCC design specifications (NETL, 2010)

Parameter	Value
Fuel lower heat value L_{HV} (kJ/kg)	47,454
Natural gas flow rate (kg/s)	21.1
Ambient air temperature (°C)	15
HP steam turbine inlet pressure (bar)	166.5
IP steam turbine inlet pressure (bar)	24.8
LP steam turbine inlet pressure (bar)	5.2
Superheated steam temperature (°C)	565
Air to fuel combustion ratio (wt)	41.6
Gas turbine inlet temp (°C)	1273
Gas turbine inlet pressure (bar)	17.5
Condenser pressure (bar)	0.07
Thermal heat input L_{HV} (kW _t)	997,032
Generator efficiency (%)	98.5

5.3 CO₂ Compression Train

There is an additional energy penalty incurred due to the requirement for the concentrated CO₂ compression in the CO₂ compression unit (CCU). Incorporation of this subsystem in the analysis helps to fully assess the performance of the retrofitted system. CO₂ leaves the desorber at 40 °C and 3.5 bar and is then compressed to 110 bar (IPCC, 2005) in the compression section. The CO₂ compression unit comprises a multiple-stage centrifugal compressor with stage intercoolers, which helps to reduce the operating temperatures of the compressor and knock-out drums. This reduces the power requirements by removing water from the CO₂ stream and reducing the volumetric flow rate through the compressor stages. Power consumption for this unit was estimated assuming polytropic efficiencies of 78–79% for all stages (Pfaff et al., 2010; Posch & Haider, 2012). In order to achieve minimal compression work, a pressure ratio of 1.99 is used. Thus, it is assumed that each stage operates at the same pressure ratio, and each stage pressure ratio should not be higher than three because of equipment limitations (Syahrom et al., 2006). The process flow diagram for the compression train is presented in Figure 5-1, and the stage pressure ratio is obtained as shown in Appendix C. Preliminary design data obtained from this study are given in Table 5-2.



Where INTOOL= Intercooler, COMP = Compressor

Figure 5-1: Process flow diagram of the five-stage CCU model for the AMP-based process in Aspen Plus environment

Table 5-2: Compression train design data

Description	Value
Number of compressors	5
Compressor efficiency range (%)	80
Intercooler temperature (°C)	33
Inlet pressure (bar)	3.5

5.4 Process Integration with amine-based solvents

5.4.1 Integration of the AMP-Based Process into the NGCC Power Plant

The integration of the NGCC, AMP-based process and the CCU models is presented in this section. The flowsheet of the retrofitted system is shown in Figure 5-2. The NGCC plant supplies steam for solvent regeneration, and electricity for the CCU and other auxiliary equipment. The PCC plant is integrated into the power plant at four points (Global CCS Institute, 2011; Biliyok and Yeung, 2013):

- (i) The flue gas stream from the power plant is fed into a single absorber in the PCC plant,
- (ii) The steam from the IP/LP crossover pipe is used to regenerate solvent in the reboiler,
- (iii) Condensate is returned from the reboiler to the steam cycle,
- (iv) The concentrated CO₂ stream from the regenerator is sent to the CO₂ compression train.

A direct contact cooler (DCC) is used to cool down the flue gas coming from the power plant to 40 °C before it is fed to the absorber. The IP/LP crossover is used to draw off steam from the steam cycle, which employs a throttle valve ensuring that the pressure across the IP/LP crossover (steam pressure of 4.8 bar) does not fall below the required pressure in the reboiler of 3.5 bar. This steam supplied for regeneration needs to be at a minimum of 150 °C so that the saturated solvent in the reboiler can be heated up to 140 °C. In order to determine the pressure drop across the turbine sections, Stodola's ellipse law, which is widely used for determination of the off-design performance in power plants (Cooke, 1985), is used as shown in Equation (5-1).

$$\frac{m_1}{m_1^o} = \sqrt{\frac{T_1^o}{T_1}} \sqrt{\frac{p_1^2 - p_2^2}{p_1^{o2} - p_2^{o2}}} \quad 5-1$$

where m_1 , T_1 , and p_1 are mass flowrate, temperature, and pressure, respectively at off-design conditions, and m_1^0 , T_1^0 , and p_1^0 are at design conditions.

5.4.2 Thermodynamic Performance Analysis

The process thermodynamic performance parameters of the retrofitted AMP-based process are presented in Table 5-3. Also, for the purpose of comparison of the AMP-based process, the MEA-based process is also retrofitted, and the key thermodynamic performance parameters are presented in Table 5-3. As discussed above, the reboiler duty can be considered as a key performance parameter in the retrofitted systems, which reflects the benefits of the process employing AMP instead of MEA. The main differences in the operation of the AMP-based and MEA-based process retrofits are conditions in the stripper: 3.5 bar and 140 °C, and 1.8 bar and 120 °C respectively. Thus, this is enabled due to the better thermal stability of AMP. The pressure at the IP/LP crossover is 5.17 bar, i.e., more than required (4.76 bar, saturation temperature of 150 °C) to reach 3.5 bar in the stripper, which proves process feasibility under the conditions considered for AMP. It can be seen in Table 5-3 that the integration of the AMP-based process results in 13.3% lower net power output (465.3 MWe vs. 536.8 MWe) compared to the reference NGCC. In addition, the net efficiency reduced from 53.8%_{LHV} to 46.7%_{LHV}. Nevertheless, the thermodynamic performance of the AMP-based process with an efficiency penalty of 7.1% points is superior to that of the MEA-based process, for which the efficiency penalty was estimated to be 9.1% points. This is 2% higher for AMP compared to MEA. This compared to previous studies (Sanchez Fernandez et al., 2014; Van der Spek et al., 2016), the efficiency of the AMP-based process was between 0.86%-1% higher than that of the MEA.

The Stodola's ellipse law estimates that the pressure at the LP turbine inlet drops to 3.2 bar and 2.4 bar for AMP and MEA respectively. Thus, the efficiencies for AMP and MEA without the effect of Stodola are 47.3% and 45.6% respectively, amounting to an additional 1% efficiency loss, compared to the retrofitted plant process when Stodola is not taken into consideration; this is in accordance with the literature data (Biliyok et al., 2015; Hanak et al., 2015). This indicates that the effects of changes in

pressure profile across the turbine sections need to be accounted for in assessing the PCC integration impact.

Table 5-3: Energy performance of the AMP-based and MEA-based process retrofits

Parameter	NGCC power plant without capture	Integration with MEA-based process	Integration with AMP-based process
Input parameters			
Stripper pressure (bar)		1.8	3.5
Stripper temperature (°C)		124	140
Output parameters			
Net power output (MWe)	536.8	445.9	465.3
Power loss (%)		16.9	13.3
Efficiency, LHV (%)	53.8	44.7	46.7
Efficiency penalty (%)	-	9.1	7.1
Power plant auxiliary load (kWe)	2636.1	2631.0	2706.7
Other auxiliary loads (kWe) ^c	6730	9840	9840
Net specific emissions (kgCO ₂ /MWh)	377.3	33.5	51.1
Steam draw-off flowrate (kg/s)	-	75.5	53.8
LP turbine pressure (bar)	5.2	2.4	3.2
CO ₂ capture auxiliary load (kWe)	-	18142.7	16813.2
CO ₂ compressor power (kWe)		2331.9	984.7
Reboiler duty (MJ/kgCO ₂)	-	3.9	2.9
Required steam pressure (bar)	-	3.0	4.8
Capture level (%)		90	90

^cAssumed based on studies (NETL, 2010)

The CCU power requirement reduced from 2331.9 kW (MEA-based process, 1.8 bar) to 984.7 kW (AMP-based process, 3.5 bar), which leads to a parasitic load distribution of 2.7% for MEA and 1.5% for AMP as shown in Figure 5-3 and Figure 5-4, respectively. This is because the compressor train discharge pressure is fixed at 110 bar. Therefore, the higher suction pressure of 3.5 bar coming from the stripper results in reduced compression power required. Figures 5-3 and 5-4 show the parasitic load distribution using the MEA solvent and the AMP solvent, revealing that the most important driver causing a reduction in net power output was the LP steam extraction for solvent regeneration; with a pressure of 3.5 bar (68.7%) for AMP and 1.8 bar (72.8%) for MEA. The electricity demand imposed on the power plant because of auxiliaries and the CCU integration contributes about 27.2% and 31.4%

for MEA and AMP, respectively; this difference is due to the higher pumping duty for a pressure of 3.5 bar. As shown in Table 5-3, power output is higher for the AMP when compared to MEA. This, in turn, resulted in the less low-pressure steam generation and a drop in its pressure, which has been estimated according to the Stodola ellipse law; hence lower net power output is obtained for the MEA. Thus, the compressor load obtained for AMP was 58% lower than that of MEA. Previous studies (Van der Spek et al., 2016; Sanchez Fernandez et al., 2014), estimated between 0-18% lower compressor load for AMP as against MEA.

Reboiler duty which is heat required to strip off CO₂ from the solvent is obtained based on the solvent side energy balance (i.e. summation of the heat of reaction, sensible heat, and the heat of vaporisation) in the reboiler as stated in Section 4.5.1 above. The results in Table 5-3 show lower reboiler duty of the AMP compared to that of the MEA, which is 2.9 MJ/kg CO₂ vs. 3.9 MJ/kg CO₂, respectively, leading to 25.6% reduction in the reboiler duty for AMP as compared to MEA. This is due to a combination of reasons. Firstly, as previously stated in section 2.1.4, the heat of reaction (Q_{react}) for AMP (1730 kJ/kg CO₂) is lower than that of MEA (1920 kJ/kg CO₂) (Anthony, 2006). Secondly, the heat of vaporisation (Q_{vap}), which depends on the operating temperature and pressure in the stripper, is obtained as shown in Equation (5-2) (Perry & Green, 2008), and given as 69.4 MJ/s and 140.1 MJ/s for AMP and MEA respectively. Lastly, is the sensible heat (Q_{sens}), which is obtained using Equation (5-3) (Perry & Green, 2008), depends on the temperature and solvent flowrate in the stripper and given as 96.9 MJ/s, and 41.2 MJ/s for AMP and MEA respectively. Although sensible heat is higher for AMP than MEA, the total heat produced is still lower for AMP than MEA. This implies that less liquid must be heated in the reboiler for AMP, compared to that of MEA.

$$Q_{\text{vap}} = m_{H_2O, \text{ vap}} * \Delta H_{H_2O, \text{ vap}} \quad 5-2$$

$$Q_{\text{sens}} = m_s * C_p * \Delta T \quad 5-3$$

Where;

Q_{sens} = sensible heat, Q_{vap} = heat of vaporization, $\Delta H_{H_2O, \text{ vap}}$ = latent heat of vapourisation of water, C_p = specific heat capacity, $m_{H_2O, \text{ vap}}$ = vapour flowrate of

water and m_s = solvent flowrate in the stripper respectively, ΔT = change in temperature.

$$\text{Total heat requirement} = Q_{\text{sens}} + Q_{\text{vap}} + Q_{\text{react}}$$

Previous studies (Van der Spek et al., 2016; Sanchez Fernandez et al., 2014), estimated between 12.5%-19.5% higher savings in reboiler duty for AMP as against MEA. The main reason for this is the lower heat required for regeneration of AMP. It should also be noted here that the lower reboiler duty for AMP implies lower cooling duty, which results in additional benefits such as lower amounts of contaminated water to be treated and in general, smaller equipment and lower capital costs.

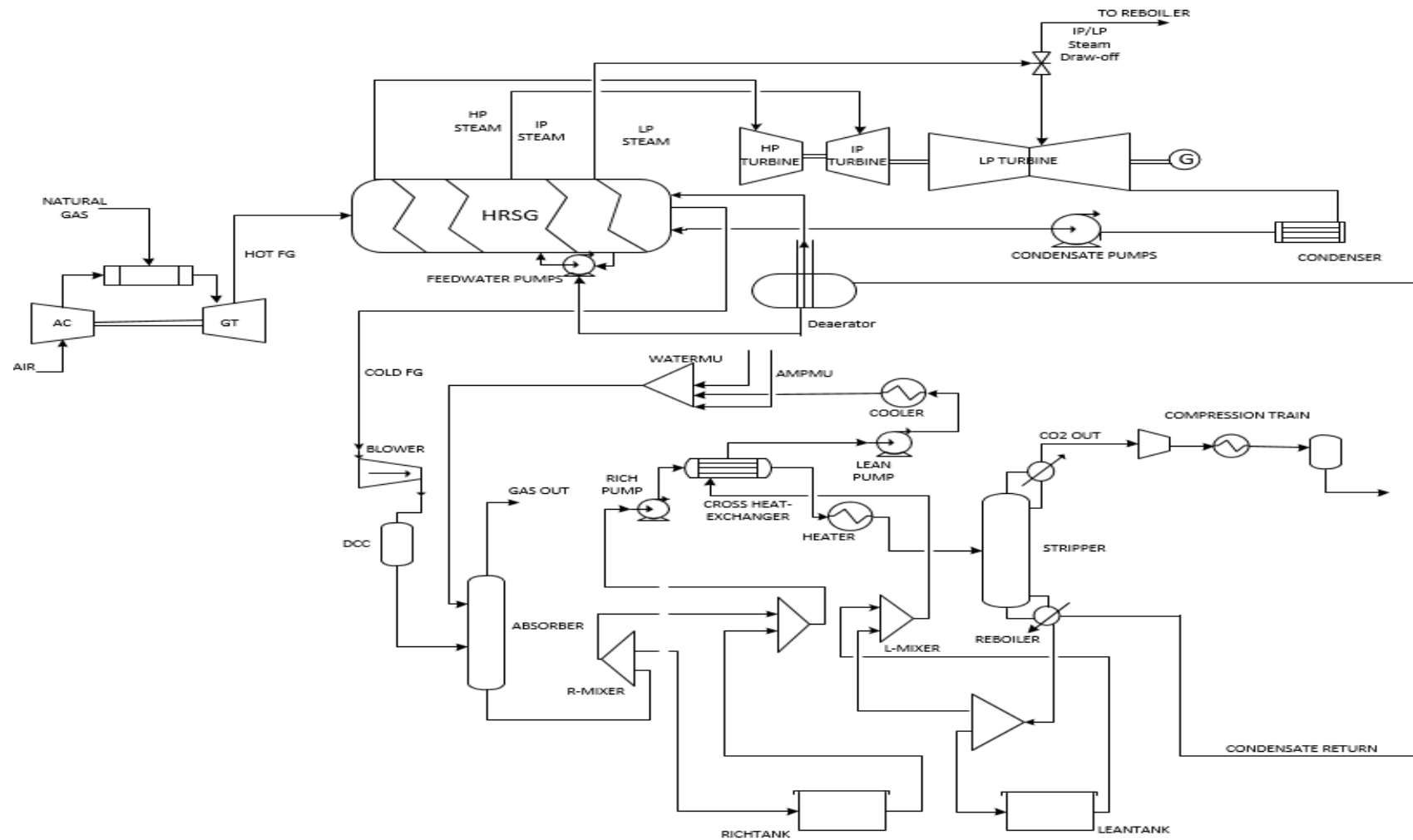


Figure 5-2: Process flowsheet of the NGCC power plant retrofitted with AMP-based process and CO₂ compression unit

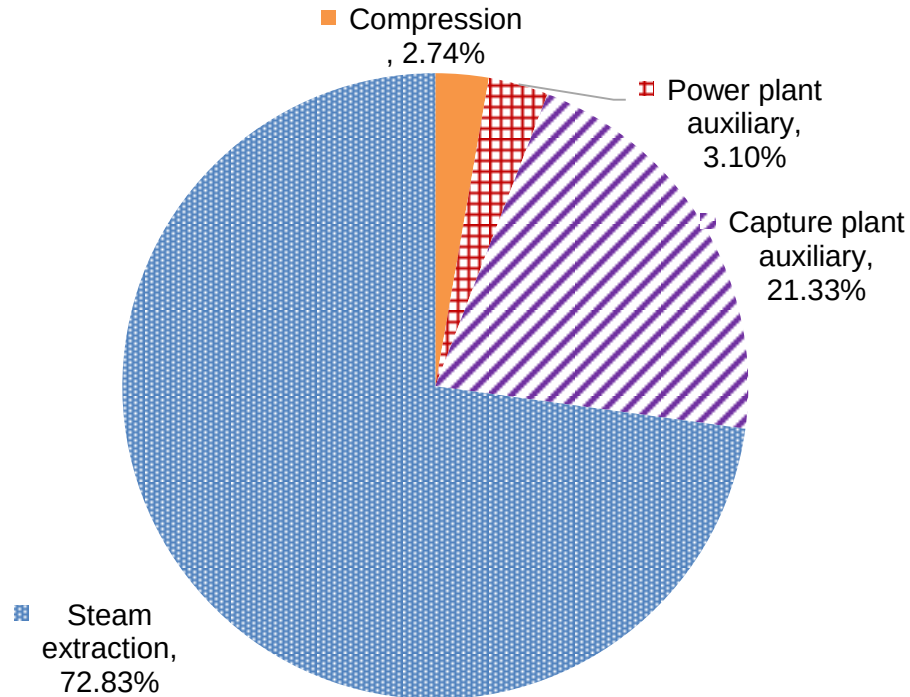


Figure 5-3: Parasitic load distribution for NGCC retrofit with MEA-based process

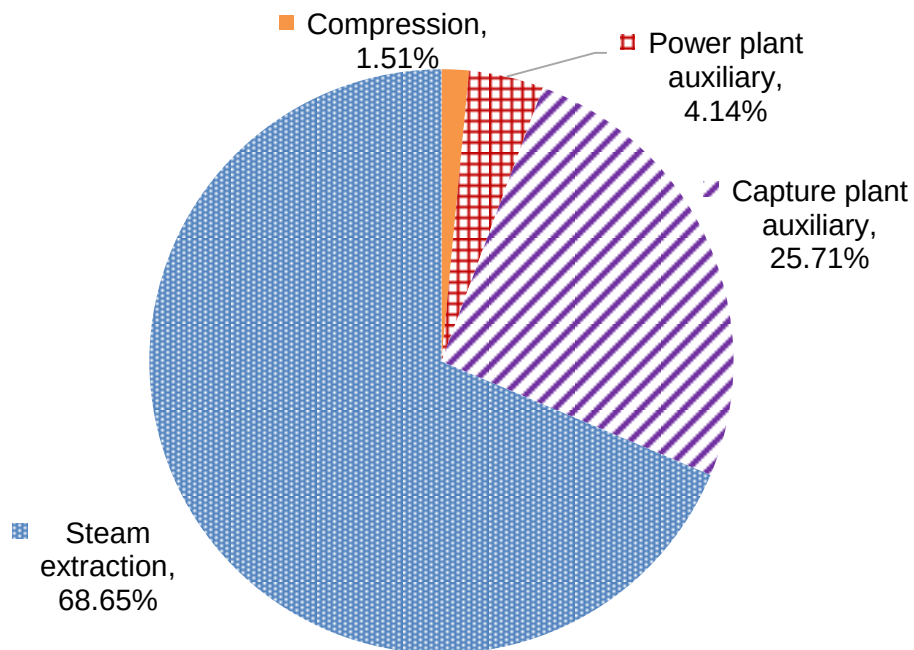


Figure 5-4: Parasitic load distribution for NGCC retrofit with the AMP-based process

5.5 Solvent Storage Tanks Description

This process involves the addition of two solvent storage tanks (rich tank and lean tank) to the AMP-based capture plant retrofit into the NGCC power plant in order to store both rich amine and lean amine solutions. This comprises sized equipment to enable increased AMP regeneration during hours of low electricity demand, and hence low electricity prices. The stripping of CO₂ will be done mainly at off-peak (12 hours) during the periods of low electricity prices, and rich amine solution will be stored during peak periods (4 hours) characterised by high electricity prices, while still maintaining a capture rate of 90%.

The storage tanks will be used to store the rich amine solution that is not stripped off during times of high-energy costs. At off-peak times when the regenerator is fully utilised, the second set of storage tanks is required to store the regenerated lean amine solution, which is later supplied to the absorber at peak times (Delarue et al., 2012). The most important benefit of this technology is that it allows the integrated facility to sell as much electricity as possible to the grid at peak times, getting a premium price, while utilising solvent regeneration as a way of ramping down power generation at off-peak times. Steady-state models have been utilised in the study with the regenerator operating at full capacity to regenerate rich solvent flowing from both the absorber and storage tank. Both tanks are the same size because the amount of rich solvent stored in one cycle is approximately equal to the amount of solvent stripped in the other cycle. The heat losses in the storage tank, were negligible as shown in the Appendix C. This is because the temperature of the solvent stored is close to ambient temperature. Therefore, heat losses are ignored. The amount of rich solvent withdrawn from the rich tank during the off-peak periods of operation is equal to the amount of lean solvent stored in the lean tank, along with additional makeup solvent from a fresh solvent storage tank, which is later utilised during peak periods. Finally, it is also assumed that the rate at which solvent is pumped into the tank is the same rate of pumping to the stripper. Thus, depending on how long it takes to empty the tank, solvent rate to stripper will be equal to the rich tank plus rich solvent from the absorber. The stripper is sized to accommodate the extra solvent from the storage tanks. The design specifications for the plant obtained from this study are also presented in Table 5-4.

Table 5-4: Aspen Plus AMP PCC large-scale PCC plant with solvent storage specification and operations

Specification	Value	Operations	Value
Absorber diameter (m)	14.5	Lean loading (mol/mol)	0.2
Stripper column diameter (m)	10.1	Absorber pressure (bar)	1.2
Stripper packing height (m)	30	Stripper pressure (bar)	3.5
Packing type	Mellapax 350Y	Flue gas inlet temperature (°C)	40
Absorber column number	2	Change in temp. before and after cooling (°C)	0.58
Stripper column number	1		

5.5.1 Process Integration with Solvent Storage

The integrated process (NGCC power plant, and the AMP-based capture plant with solvent storage tanks) using the appropriate operating conditions for AMP; a high pressure of 3.5 bar and a temperature of 140 °C, is presented in Figure 5-5. The model is employed to investigate the different scenarios:

- Reference NGCC power plant without CO₂ capture
- NGCC power plant with CCS without solvent storage
- NGCC power plant with CCS with solvent storage

The solvent volume flow rate and the number of operating hours determine the volume of the tank (Van Peteghem & Delarue, 2014). Thus, the flowrate of the solvent is obtained from simulation models given in Equation (5-4):

$$V = \frac{T_p \cdot 3600 \cdot V_s}{D} \quad 5-4$$

V = volume of tank (m³), T_p = (peak period duration), V_s = solvent flowrate (kg/s) and D = density (kg/m³). A 20% safety factor is assumed for the storage tanks (Oates et al., 2014).

The following daily operating periods are assessed:

- Peak period (T_p), the system operates during evening peak periods; (4 pm-8 pm)

- Off-peak period (Top), the system operates during the day and night times between (8 pm–12 am, and 12 am–8 am)
- CO₂ capture mode (no solvent storage – normal operation), the system operates in the remaining periods; (8 am–12 pm and 12 pm–4 pm)

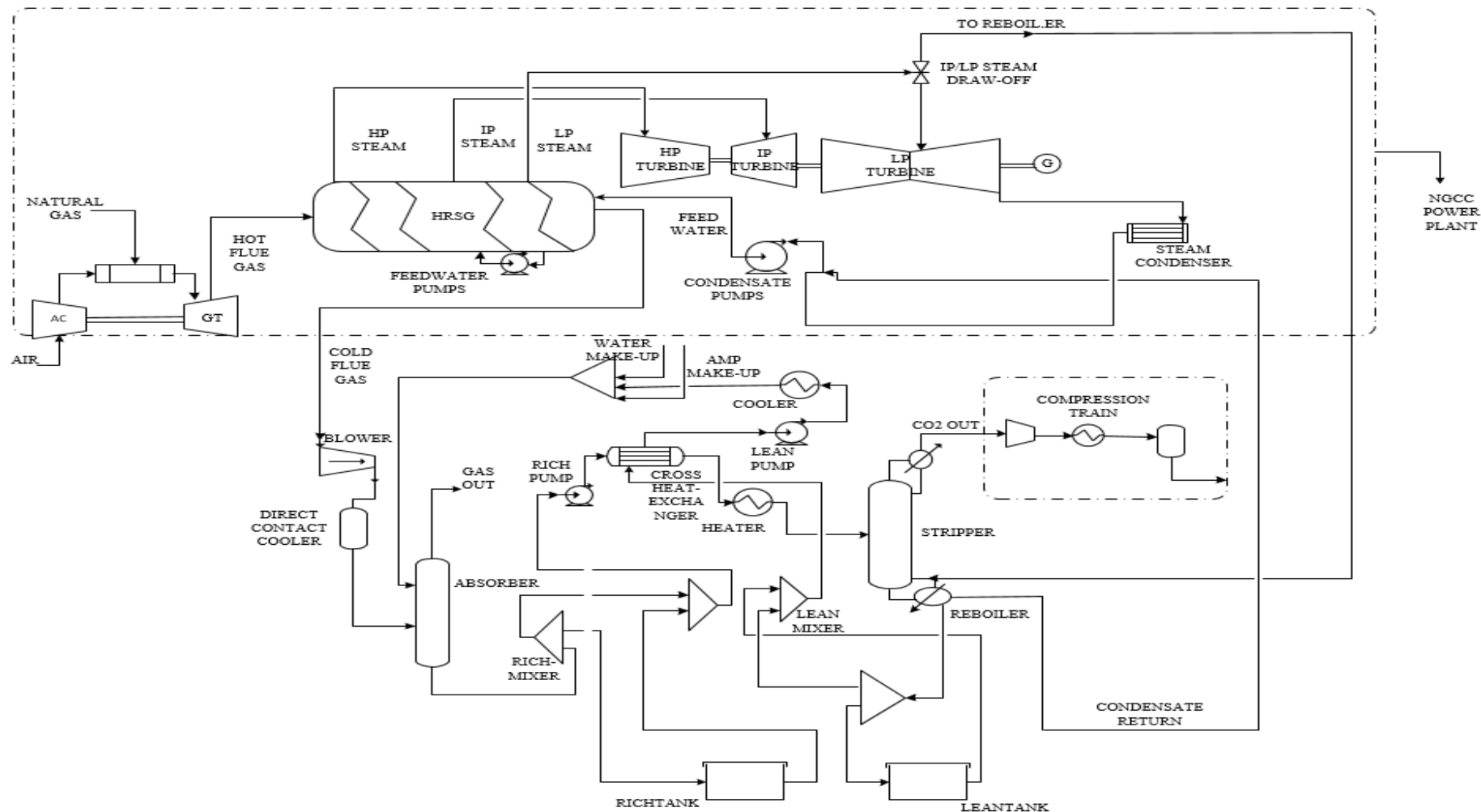


Figure 5-5: Process flowsheet of the integrated NGCC power plant, AMP-based capture plant, CO₂ compression unit (CCU) and solvent storage tanks

5.6 Integration with Solvent Storage Tanks

Table 5-5 shows the analysis for the NGCC power retrofit with the capture plant with solvent storage obtained from this study. The results reveal that to store solvent for 4 hours at a rate of 858 kg/s, a storage capacity of 6460 m³ is required. The performance evaluation is presented in Table 5-6. Results show that the NGCC retrofit with the plant with solvent storage decreased the maximum net power output from 471.81 MW_e (without solvent storage) to 471.75 MW_e, reducing, daily efficiency reduced from 47.32%_{LHV} to 47.31%_{LHV}. In addition, the heat required for solvent regeneration with solvent storage increases from 2.94 to 4.74 MJ/kg CO₂. This is because of the additional solvent to be regenerated. Thus, a higher percentage of steam is utilised during regeneration for the extra solvent. Therefore, it is important to assess the economic benefits of the addition of solvent storage to the AMP-based process.

Table 5-5: Results for solvent storage system

Parameter	Value
Solvent flowrate coming from absorber (kg/s)	858.0
Solvent density (kg/m ³)	963.0
Volume of solvent to be stored (m ³)	5383.3
Volume of each tank (m ³)	6459.9
Solvent flowrate to be regenerated (kg/s)	1218.0

Table 5-6: Results for integration with solvent storage

Thermodynamic performance	NGCC power plant	Integration without solvent storage	Integration with solvent storage
Net power output (MW _e)	536.89	471.81	471.75
Net efficiency (%LHV)	53.84	47.32	47.31
Net specific emission (kgCO ₂ /MWh)	377.28	50.39	45.63
Reboiler duty (MJ/kgCO ₂)		2.94	4.74

5.7 Conclusions

The AMP-based capture plant using the more favourable conditions; AMP concentration of 35 wt% with a stripper pressure and temperature of 3.5 bar and 140 °C, respectively, retrofitted into the NGCC power plant resulted in 25.6% reduction in the reboiler heat duty required for solvent regeneration compared to that of the MEA-based process. In order to assess the impact of integration, the effect of steam extraction on the pressure profile was considered using Stodola's ellipse law. Furthermore, the efficiency penalty due to the retrofit of the AMP-based capture plant into the NGCC power plant was estimated to be 7.1% points, compared to 9.1% points in the case of integration with the MEA-based process. In addition, the compressor load obtained for AMP was 58% lower than that of MEA. Hence, the results showed that AMP solvent is of superior performance from the thermodynamic point of view, as it can reduce the efficiency penalties associated with the MEA-based process retrofits.

Also in this chapter, the NGCC power plant retrofit with the AMP-based capture plant and with solvent storage was evaluated using Aspen Plus®. The results showed that at a rate of 858 kg/s, a storage capacity of 6460 m³ is required. The thermodynamic performance of the process with solvent storage revealed that the net efficiency reduced slightly from 47.32% to 47.31% LHV (basis) as compared to the process without solvent storage. In addition, the heat required to regenerate solvent was found to increase by from 2.94 MJ/kg CO₂ (process without solvent storage) to 4.74 MJ/kg CO₂ (solvent storage process). Thus, it is clearly observed that the process without solvent storage will be preferred to the process with solvent storage (average) when examining the thermodynamics (power output) of the process.

6 ECONOMIC ANALYSIS

6.1 Introduction

Economic analysis helps to determine feasible techniques in cases where the cost required for full-scale operations are ready for establishments. Therefore, the cost information will help in the design studies of the aqueous AMP-based systems, most especially in selecting the best designs and operating conditions for the CO₂ capture technology. Solvent regeneration is the main hindrance to the cost reduction of the CO₂ capture process (Freguia, 2003). The vital parameters in the economic analysis to consider for a process plant are capital cost, operating cost and interest rate (Karimi et al., 2011).

The operating costs have high potential savings between 13%-23% in the medium term and long term, in certain areas of operations in the plant (Peeters et al., 2007). These include integrating the power plant with the stripper reboiler of the PCC plant, which leads to a reduction in the utilization of steam of the entire plant and reducing the absorber packing pressure drop etc. This also applies to the capital cost with the NGCC efficiency improvements, where potential savings between 37%-42% (Peeters et al., 2007), are likely to occur in the plant equipment. These include equipment; such as the cooling vessels materials of the absorber, the reduced vessel size of the absorber, better oxidation inhibitors. Also, the use of new solvents with good physical, and chemical properties, and improved designs (Chapel et al., 1999; Peeters et al., 2007). An example is the use of both AMP and MEA solvents, and the different configuration options such as solvent storage, which will lead to the reduction of electricity consumption, reduced cost and increased profit. In summary, capital cost comprises; power plant specific cost, capture plant cost, and CO₂ compression cost. While the operating cost comprises; production cost (O&M cost, cooling water, chemicals, and labours, local taxes & plant overhead) and general expenses cost (R&D, administrative and marketing cost) (Aspen Technology, 2010).

In this chapter, the economic performance of the AMP retrofitted system is evaluated, and compared to that of the MEA retrofitted system. Also, the

economic performance of retrofitting the CO₂ capture plant with solvent storage into the NGCC power plant, using AMP as a solvent is evaluated. Furthermore, the output decisions of the power plant, which operates in the electricity market, are usually driven by electricity prices. However, due to the substantial changes in electricity demand at different periods, an electricity profile is required (Van Peteghem & Delarue, 2014; Husebye et al., 2011). Thus, the historical price data from EPEX SPOT electricity markets (EPEX SPOT, 2017) in Western Europe is used to conclude about the daily profitability of AMP storage.

6.2 Measures of Costs

6.2.1 Cost of electricity (COE)

The cost of electricity (COE) associated with the power generation technology, as shown in Equation (6-1), is the ratio of the total electrical energy that the power plant will produce in its lifetime (MWh/yr) to the sum of costs (operation & maintenance cost and cost generated from construction and investment) (Horlock, 1992). A parameter used in this calculation is the capacity factor; which is the average annual hours of plant operation.

$$COE = \frac{CF \cdot C_o + C_{fuel} + C_{O\&M}}{R \cdot U} \quad 6-1$$

C_o = capital cost of the plant (£)

C_{fuel} = cost of fuel supplied annually (£/yr)

$C_{O\&M}$ = cost of operation and maintenance annually (£/yr)

R = rating of the plant (MW_{net}) - power plant's output to the grid

U = plant utilisation - hours of operation per year (h/yr)

CF = capital charge factor

Where $CF = \frac{D(1+D)^Y}{(1+D)^Y - 1}$

CF corresponds to the maximum availability of each technology, and it is the factor that annualizes the capital cost of the plant (Rubin et al., 2005).

D = discount factor

Y = analysis period – Y years (life of the plant)

6.2.2 Cost of capture (COC)

The cost of capture (COC) given in Equation (6-2) is defined as the ratio of the difference in the cost of electricity between the reference plant and the plant with capture multiply by the cost of power for a given year to the volume of CO₂ captured (Breeze, 2010).

$$COC = \frac{(COE_{\text{capture}} - COE_{\text{ref}}) \times MWh_{\text{capture}}}{CO_2 \text{ captured}} \quad 6-2$$

6.2.3 Total cost (TC)

The total plant cost (TC) is the sum of the capital, O&M, and fuel costs. However, before we can sum these costs, we convert them into a common cost measure, known as the levelized electricity cost (LEC, \$/MWh) (Breeze, 2010).

6.2.4 Levelized cost of electricity (LCOE)

Levelized cost of electricity (LCOE) as shown in Equation (6-3) measures the entire competitiveness of different generating technologies (Ouyang & Lin, 2014). Both fuel cost and overnight cost highly affects LCOE (Short et al., 1995). The following are required to calculate LCOE;

- Capital cost
- Fuel cost
- Fixed and variable operations and maintenance cost (O&M)
- An assumed utilization rate for each plant type

$$LCOE = \frac{TC}{Q}(CF) \quad 6-3$$

TC = total lifetime cost

Q = energy output saved in Y years

6.2.5 CO₂ avoidance cost

The CO₂ avoidance cost given in Equation (6-4) is the incremental levelised capture costs for a year divided by the difference in emissions of CO₂ between the reference and capture cases (Abu-Zahra et al., 2007; Baker et al., 2012).

This is expressed as:

$$\begin{aligned} \text{Cost of } CO_2 \text{ avoided } \left(\frac{\text{€}}{\text{tonne}} \right) & \quad 6-4 \\ = & \frac{(\text{COE})_{\text{capture}} - (\text{COE})_{\text{reference}}}{(CO_2 \text{ emission})_{\text{reference}} - (CO_2 \text{ emission})_{\text{capture}}} \end{aligned}$$

6.3 Considerations

The estimation methodology employed for the capital cost, and the operating and maintenance cost (O&M) is discussed in this section. The cost figures (capital and O&M costs) for the NGCC power plant are obtained based on estimates from the DOE report (NETL, 2010). The year of cost estimation in the literature data (NETL, 2010) is different from this study. Therefore, the chemical engineering plant cost index (Peters et al., 2004), presented in Equation (6-5) is used to escalate the prices to 2013 US dollars. The annual averaged CEPCI for the years; 2007, 2011 and 2013 are 525.4, 585.7 and 567.3 respectively (Chemical Engineering, 2015).

$$\text{Present cost} = \text{original cost} \times \left\{ \frac{\text{CEPCI at present}}{\text{CEPCI at time original cost was obtained}} \right\} \quad 6-5$$

APEA V8.4, which is based on the industry-standard Icarus System (AspenTech, 2010) is used in performing the economic analysis of the PCC plant with compression train. The bottom-up approach is used to generate the

capital cost, which depends on material cost and wage rates, for estimation of equipment fabrication and cost of installation. The steps to obtain the capital and operating costs are described in Figure 6-1. As shown in Figure 6-1: The first step is to set up the model for process economics, followed by mapping unit operations to process equipment that involves quoted cost items; fixed material and labour cost, which is sized and designed, based on relevant design code. These equipment sizes form the basis for the cost estimation. Next, is the evaluation of the cost of process and project along with investment metrics; these are estimated by simulation of vendor fabrication procedures. The last step is to view and analyse the reported cost and investment metrics.

The capital cost and the O&M cost of the capture plant with the compression train are calculated using the costing template for the USA, which uses 2013\$ cost basis. Important cost inputs and assumptions are given in Table 6-1.

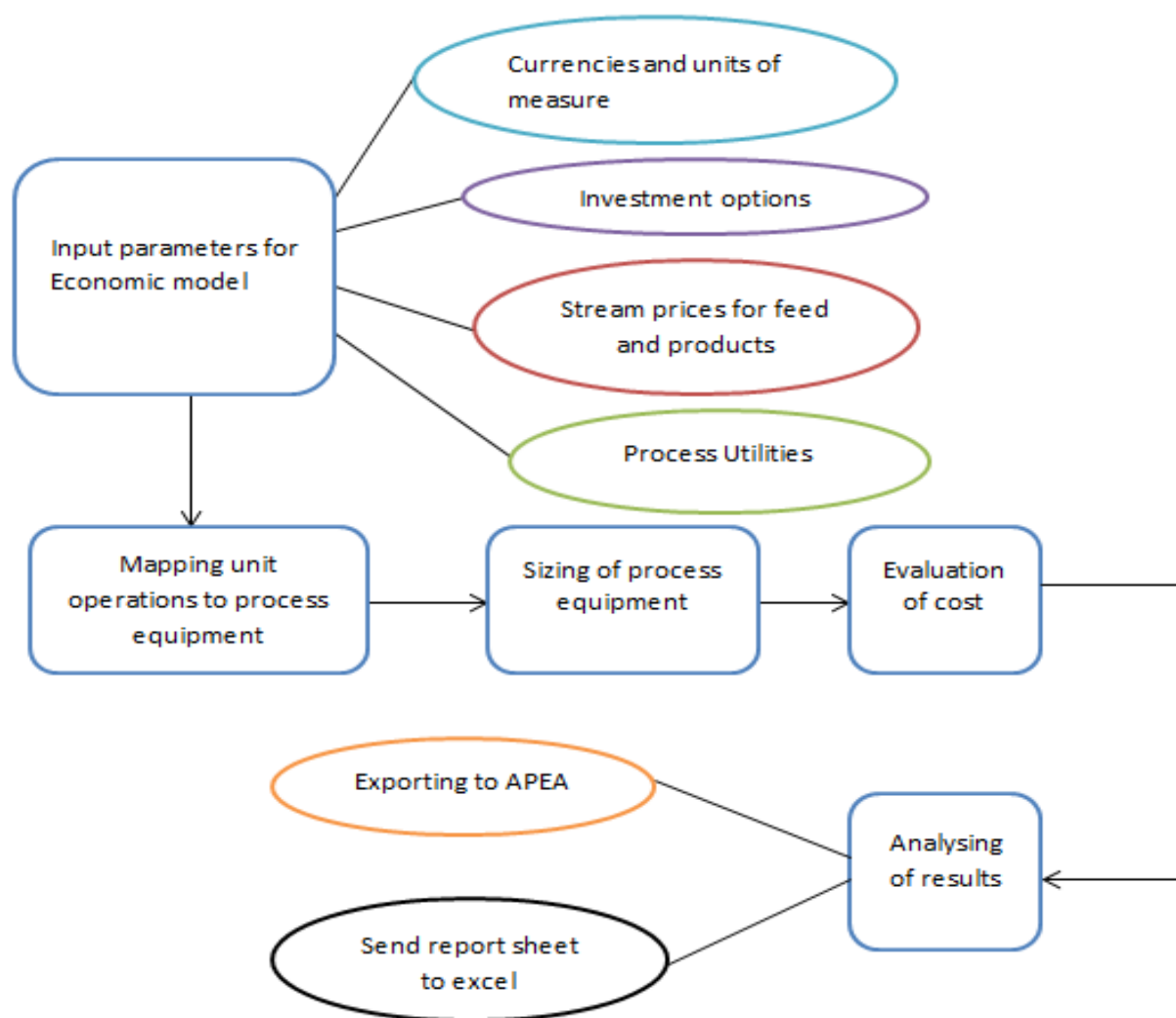


Figure 6-1: Flowchart of economic analysis framework (Aspen Technology, 2010)

6.3.1 Estimation of Cost for Solvent Storage

The cost data from literature is based on 2007 prices. Therefore, the Chemical Engineering plant cost index (Peters et al., 2004) is used to estimate the costs to 2015 prices. The Chemical Engineering cost indexes for 2007, 2011, and 2015 are 525.4, 585.7 and 556.8 respectively (Chemical Engineering, 2015). The cost of the solvent storage tanks was estimated using Perry's Handbook (Perry & Green, 2008) and scaled up using a scaling exponent of 0.57 for carbon steel tanks (Peters et al., 2004). Estimation of the cost of equipment, which involves different size parameters, is presented in Equation (6-6). The economic assumptions and cost inputs are also given in Table 6-1.

$$\begin{aligned} &\text{Cost of equipment for present analysis} \\ &= \text{cost of reference equipment} \times \left\{ \frac{\text{capacity of present}}{\text{capacity of reference}} \right\}^{\text{exponent}} \end{aligned} \quad 6-6$$

Table 6-1: Economic analysis assumptions and cost inputs

Input Parameters	Value
Plant location (NETL, 2010)	Greenfield, Midwestern USA
Plant capacity factor (%) (NETL, 2010)	85
Base year (year of capital expenditure)	2013
Operational period (year) (NETL, 2010)	30
Interest rate (%) (AspenTech, 2010)	10
Raw material escalation (%) (AspenTech, 2010)	3.5
Operating hours (h/year) (AspenTech, 2010)	8000
Natural gas price (\$/GJ) (U.S. Energy Information Administration, 2012)	3.94
AMP price (€/kg) (Manzolini et al., 2015)	8.0
MEA price (€/kg) (Manzolini et al., 2015)	1.042
Exchange rate (€/US\$)	0.95
Carbon tax (\$/tCO ₂) (Adams & Mac Dowell, 2016; Hanak & Manovic, 2016)	0.0
Fixed charge factor (FCF) (NETL, 2010)	0.11

The capital cost for the AMP storage process comprises; the cost of installing the storage tanks, the cost of additional solvent over the T-hours period; where 'T' is the number of hours required to store solvent and the cost of scaling up components of the CCS (Bandyopadhyay & Patino-Echeverri, 2013). It is important to mention that the limitation of this study is the historical price data from the national grid electricity markets in Europe, based on 2017 prices, which is used to conclude the profitability of AMP storage. Whereas the economic data used in this study is based on 2015 prices. The reason for this is the unavailability of electricity profile data for 2015 prices. The electricity profile considered in this study is the European national grid daily spot electricity prices (EPEX SPOT, 2017) as shown in Figure 6-2.

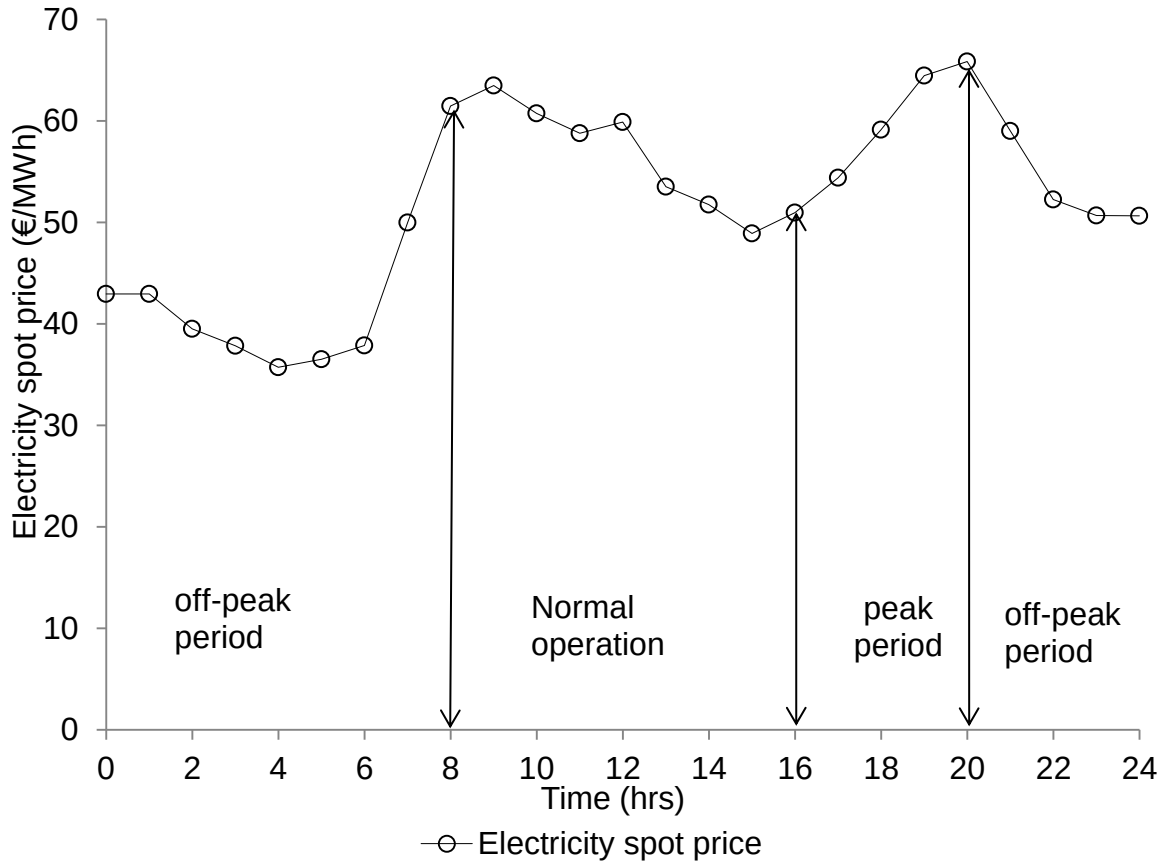


Figure 6-2: Variation of time against electricity spot price (EPEX SPOT, 2017)

To assess the profitability of the proposed processes with respect to the reference NGCC, four cost metrics are evaluated for the reference NGCC and the retrofitted capture plants.

- Levelised cost of electricity given in Equation (6-7), accounts for the total lifetime unit cost of electricity of the plant (NETL, 2010):

$$LCOE = \frac{FCF \times TOC + FOM + CF (VOM + FC)}{CF \times W_{net} \times 8760} \quad 6-7$$

Where $FCF = \frac{i(1+i)^n}{(1+i)^n - 1}$

- CO₂ avoidance cost is given in Equation (6-8):

$$= \frac{\text{LCOE}_{\text{with capture}} - \text{LCOE}_{\text{ref}}}{\text{tonne CO}_2 \text{ Emitted}/(\text{MW})_{\text{ref}} - \text{tonne CO}_2 \text{ Emitted}/(\text{MW})_{\text{with capture}}}$$

- The cost of CO₂ captured is given as shown in Equation (6-9) (Hammond et al., 2011):

$$\text{Cost of CO}_2 \text{ captured} = \frac{\text{LCOE}_{\text{capture}} - \text{LCOE}_{\text{ref}}}{(\text{tCO}_2/\text{MWh})_{\text{captured}}} \quad 6-9$$

Where $(\text{tCO}_2/\text{MWh})_{\text{captured}}$ is the difference between the CO₂ produced and the CO₂ emitted.

The short-run marginal cost of electricity (SRMC) given in Equation (6-10), expressed in €/MWh is the sum of fuel cost (F_C), carbon price (C_P) and specific CO₂ emission (E_R), O&M (operation and maintenance) variable O&M (VOM), transport and storage cost (T&S) (Mac Dowell & Shah, 2015):

$$\text{SRMC} = \frac{F_C}{\eta} + \text{VOM} + \text{T\&S} + (C_P \times E_R) \quad 6-10$$

η = Plant efficiency

To evaluate the economic viability of the retrofitted processes, these parameters: total overnight capital cost (TOC), fuel cost (FC), W_{net} (power output), fixed (FOM) and variable (VOM) operating costs and the fixed charge factor (FCF), which consider the total lifetime cost and the interest rate of the project, are estimated. These economic estimates are presented in Table 6-2 below.

6.4 Economic Performance Assessment of the NGCC Power Plant Retrofit with the AMP-Based and MEA-based Capture Plants

The economic performance of the AMP and MEA-based processes retrofitted into the NGCC power plant is shown in Table 6-2. The O&M for the capture plant comprises fixed cost (maintenance, plant overhead, operating charges, and operating labour costs) and variable cost (solvent make-up cost and utility costs).

Table 6-2: Economic analysis for AMP-based and MEA-based processes

	NGCC power plant	Integration with MEA-based process	Integration with AMP-based process
Total overnight cost (M\$)	430.1	781.1	762.7
Fuel cost (M\$/a)	123.9	123.9	123.9
Fixed cost (M\$/a)	13.2	40	39.5
Variable cost (M\$/a)	5.9	20	16
Total O&M costs (M\$/a)	142.1	183.9	179.3
LCOE (\$/MWh)	42.7	74.8	69.9
CO ₂ avoidance cost (\$/t)		93.4	83.4
Cost of CO ₂ captured (\$/t)		78.4	69.3

The results of the different scenarios considered showed that the fuel cost dominates the O&M cost. The overnight capital cost for the NGCC power plant is 430.1 M\$ which increased to 781.1 M\$, and 762.7 M\$ for the MEA and AMP, respectively, which is comparable with the data presented in the literature (Biliyok & Yeung, 2013; NETL, 2010). The operating cost for the MEA is 183.9 M\$ and reduced to 179.3 M\$ for that of the AMP. The better performance of the AMP-based process is mainly related to the reduced cost of compressors, while the operating cost is associated with the maintenance cost and the cost of utilities consumed, which includes the cost of steam, electricity, and cooling water.

The LCOE for the NGCC power plant is \$42.7/MWh, which increased to \$74.8/MWh and \$69.9/MWh, for the MEA and the AMP, respectively. Thus, the LCOE for the NGCC power plant retrofit with the AMP-based process is 6.6% lower than that of the plant with the MEA. The CO₂ avoidance cost, which

depends on the cost parameters and CO₂ emissions of the NGCC power plant, is estimated to be \$93.4/tCO₂ and \$83.4/tCO₂ for the retrofitted MEA and AMP-based processes, respectively. This aligns well with previous studies presented in the literature with a range of \$35/t–\$121/t for NGCC power plants (NETL, 2010; Rubin et al., 2015). In addition, the cost of CO₂ captured with AMP reduced from \$78.4/t to \$69.9/t, which is 11.6% lower than that of MEA, and it is in range of the literature data (\$48/t–\$111.1/t) (Rubin et al., 2015). Therefore, the retrofitted process with the AMP solvent employing more favourable operating conditions appears to perform better than MEA-based process since it reduces the LCOE. The distribution of the cost in dollars (\$) is presented in Figure 6-3.

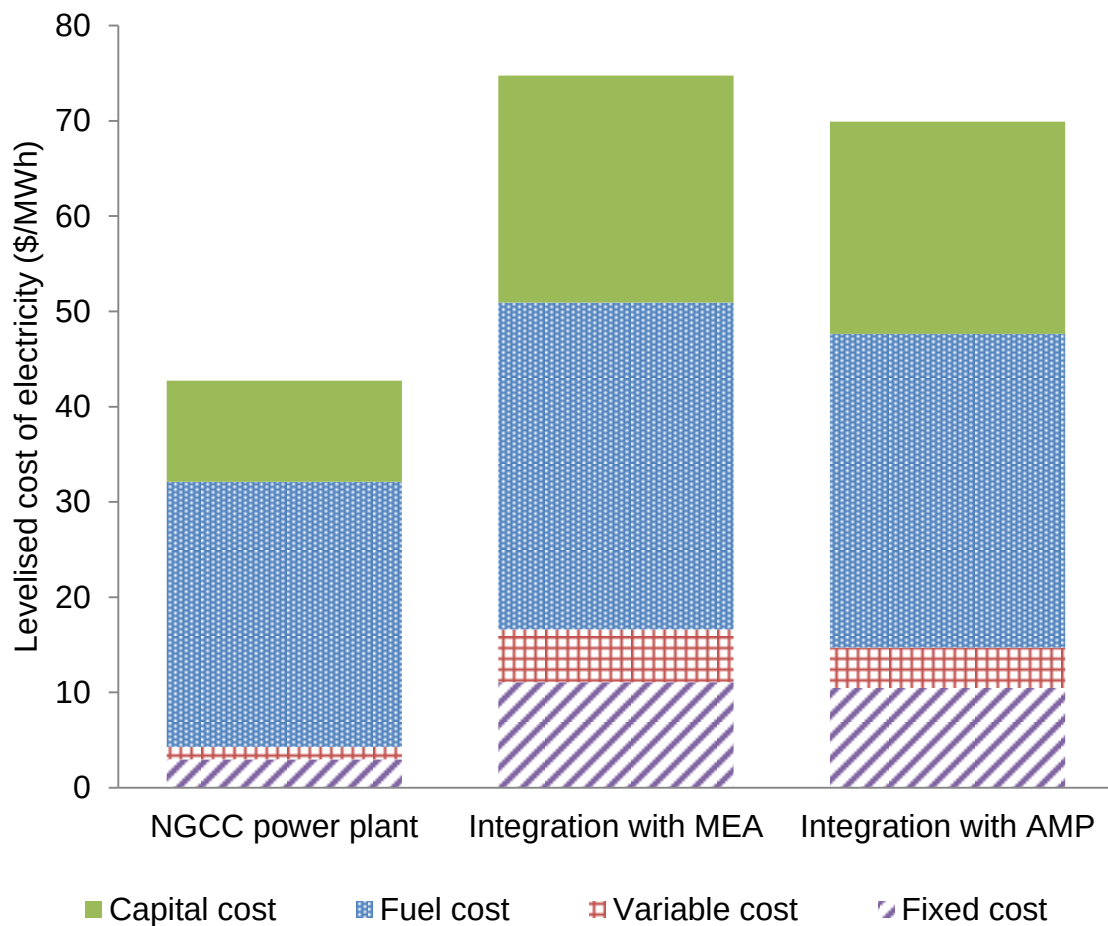


Figure 6-3: Distribution of LCOE by cost component

6.5 Sensitivity Analysis

6.5.1 Variation of Fuel Cost

Studies have shown that the cost of electricity is highly dependent on natural gas prices, and also for the NGCC power plants, the fuel cost is the dominating component of LCOE (Di Lorenzo et al., 2013; NETL, 2010). The sensitivity of LCOE to fuel cost is presented in Figure 6-4. It can be seen that for a fuel price of \$6.55/MMBTU (\$6.9/GJ), LCOE is \$62.8/MWh for the NGCC plant, which is close in range to COE values (\$58.9/MWh) in the study (NETL, 2010) using the same fuel cost. On the other hand, it is observed that the AMP-based process has a lower LCOE compared to that of the MEA-based process. This is mainly due to the lower energy intensity of the former process, as shown in Table 6-2. In addition, at a low fuel cost of up to \$1.94/GJ, the increase in LCOE for MEA is 7.1% higher than that of AMP, while at a high fuel cost of up to \$9.94/GJ, the LCOE for MEA increases up to 5.6% higher than for AMP.

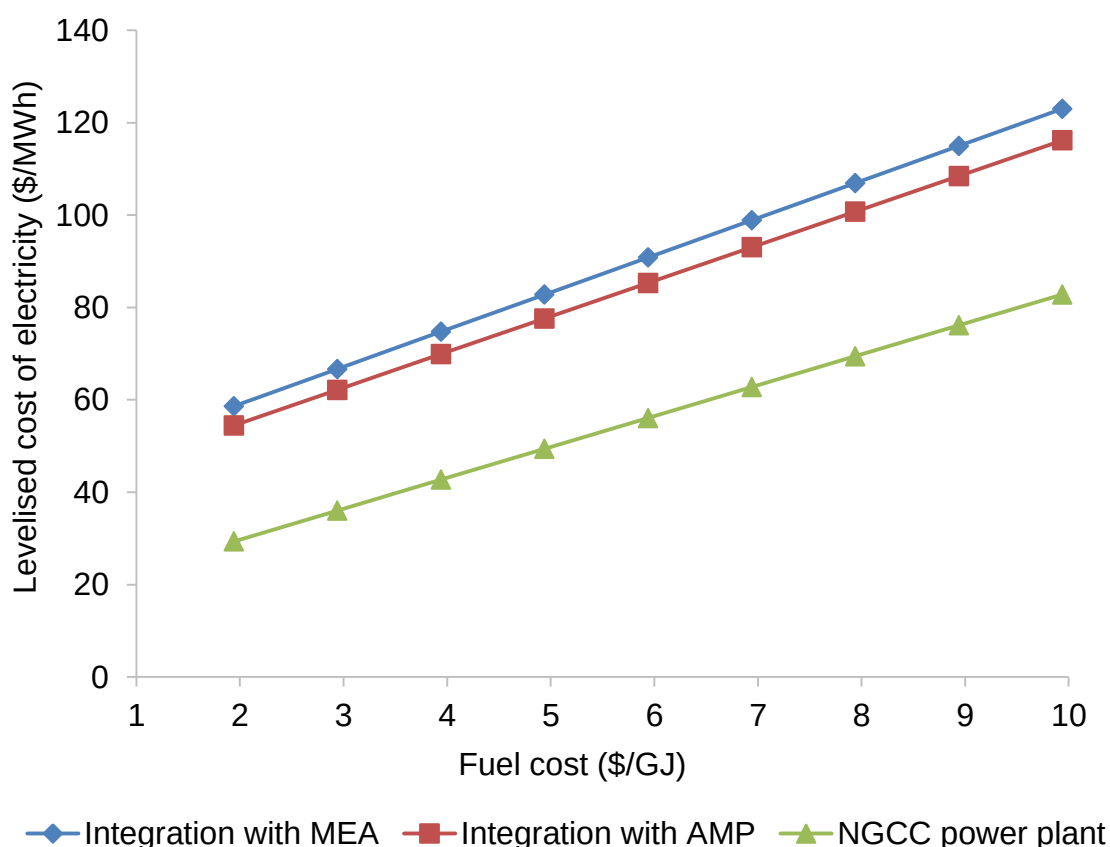


Figure 6-4: Effect of fuel cost on LCOE

6.5.2 Variation of Capacity Factor

The annual capacity factor (CF) of the NGCC is the ratio of its actual generation (that is, the unit's annual kWh) to the kWh it would generate if, hypothetically, it could operate at full capacity for every hour of the year without interruption. Most of the economic feasibility assessments in the previous study (NETL, 2010) assumed that this factor is constant. However, as CF directly affects the LCOE, it is essential to assess the effect of its variation on the LCOE. Therefore, CF of the retrofitted system with the different solvents considered in this study is varied between 30% and 85%.

The results presented in Figure 6-5 show that the LCOE decreases with increased CF. Due to the higher capital cost for the MEA-based process, the LCOE is higher by 6.3-7.0% than that of the AMP-based process across the considered CF range. Also, the NGCC power plant will always be the most economical option in respect of the changes in the operational pattern of the system to meet the market demand. These results are important for decision makers in order to estimate the costing structure for an NGCC plant with PCC.

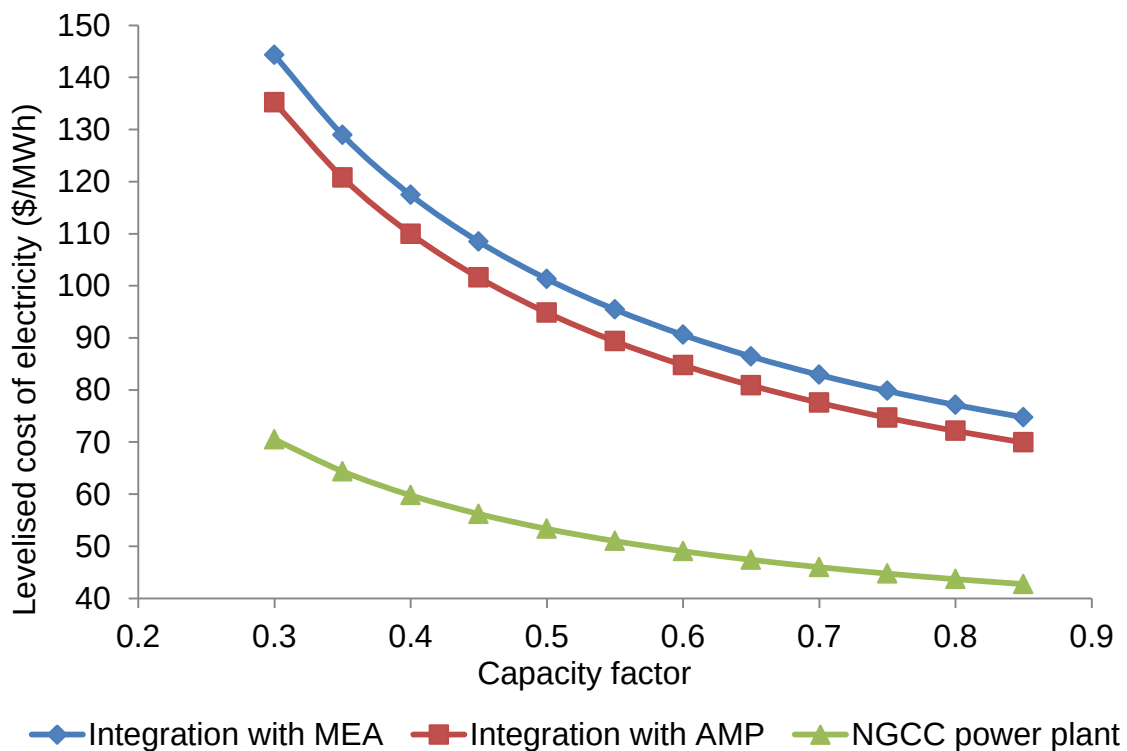


Figure 6-5: Effect of capacity factor on LCOE

6.5.3 Variation of Make-Up Flowrate

The solvent make-up flowrate is a key parameter that affects the economics of the process plant. However, for the solvent-based processes, the loss of solvent frequently occurs as a result of its volatility, degradation, and fugitive emissions (Vega et al., 2014; Nguyen et al., 2010; Rochelle, 2009). Therefore, feeding fresh solvent is needed in the system to make up for the losses. The case without makeup is presented in Section 6.2 (Table 6-2), while the solvent make-up rate is expressed as a percentage of total solvent flowrate in the PCC (Cormos & Cormos, 2017), as shown in Figure 6-6. This aims to evaluate the effect of solvent make-up on the LCOE.

As shown in Figure 6-6, the LCOE increases with increase in the make-up flow rate. Results also show that when the makeup is taken into consideration, the LCOE for the AMP-based process becomes higher than that of the MEA-based process. This can be associated with the higher specific cost of AMP solvent, which is the major contributor to the variable cost. As shown in Table 6-2, the cost of AMP solvent is about eight times the cost of the MEA solvent. In addition, AMP is known to be more volatile than MEA (Nguyen et al., 2010). This implies that more solvent will be lost during the operation, and the AMP system will require a higher make-up rate. Also, Figure 6-6 presents the sensitivity of LCOE to solvent price. The cost of solvent for both AMP and MEA is varied by $\pm 25\%$, and the results show that the LCOE in the AMP case is more sensitive to price changes, which is expected due to the higher price of AMP. Importantly, such results imply that although the use of AMP as a solvent in chemical solvent scrubbing can significantly reduce the efficiency penalty associated with CO₂ capture from NGCCs, it may not be the most economically feasible option if the make-up rate is above 0.03%. Thus, this make-up rate of 0.03% is below the expected value for amine scrubbing (Cormos & Cormos, 2017). It needs to be stressed, therefore, that development of novel CO₂ capture materials needs to be substantiated from both thermodynamic and economic standpoints.

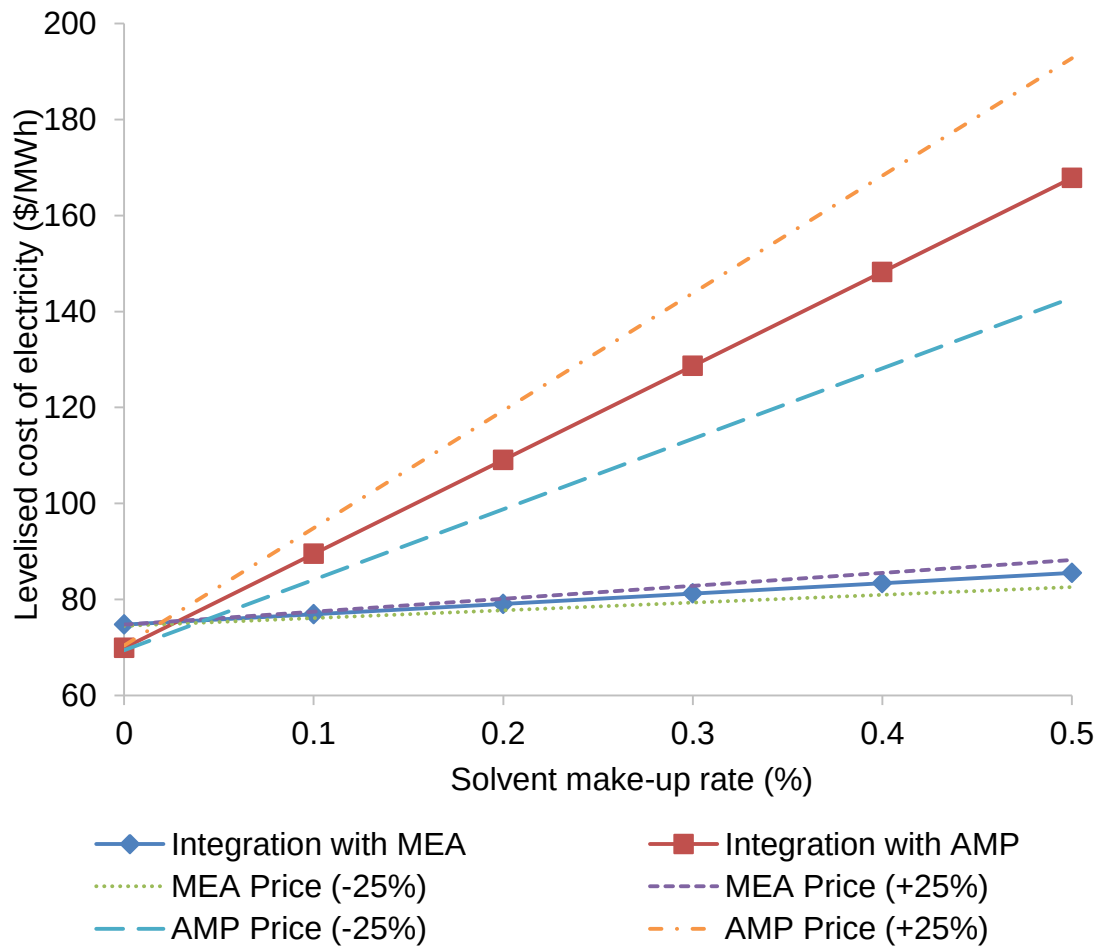


Figure 6-6: Effect of make-up rate on LCOE

6.6 Economic Performance of the NGCC Power Plant Retrofit with the AMP-Based Capture Plant and Solvent Storage

The economic performance, for the integration of NGCC power plant with the AMP-based capture plant and solvent storage tanks, is presented in Table 6-3 and comparison is made with the process without solvent storage. It is important to highlight that with solvent storage tanks, a larger capture plant is required because more solvent needs to be processed at off-peak times. This brings about additional sizing requirements, which have been accounted for in the simulation. This will have an impact on the economics. In Table 6-1 above, the cost of solvent is given, and it can be deduced that the specific capital cost for the process with solvent storage increases from €1536/kW (without solvent storage) to €1597/kW. Although, extra solvent (cost of solvent provided in Table 6-1 above) is required for operation, not much investment is needed for the

massive tanks. Furthermore, the fixed cost and variable cost increases for the process with solvent storage. An obvious reason is the extra cost of solvent and the maintenance cost required for the process. In addition, the LCOE for the NGCC power plant is €40.3/MWh, which increased to €65.5/MWh for the process without solvent storage and further increased to €74.3/MWh for the process with solvent storage. On the other hand, the CO₂ avoidance cost, which is dependent on the cost parameters and CO₂ emissions of the NGCC power plant, is estimated to be €77.1/tCO₂ and €102.5/tCO₂ for the process without solvent storage and with solvent storage respectively. Thus, the CO₂ avoidance cost increases for the process with solvent storage by 24.8% compared to the process without solvent storage. This is due to the lower power output generated, with solvent storage as shown in Chapter 5 (Table 5-6) above. Therefore, profit is required to ascertain if the savings in electricity can offset the higher cost, and be beneficial to the solvent storage system.

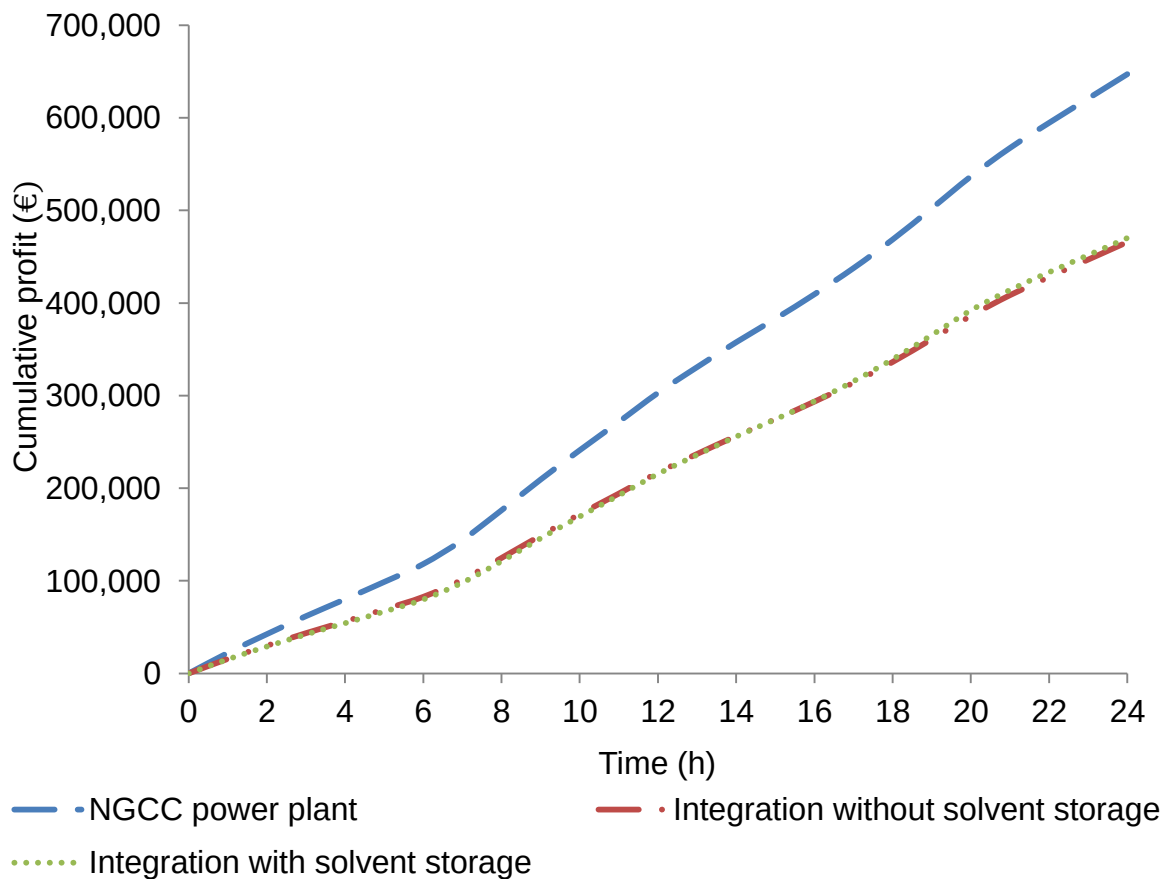
Table 6-3: Economic performance indicators

Economic indicators	NGCC plant	Integrated plant without solvent storage	Integrated plant with solvent storage
Specific capital cost (€/kW)	746.9	1535.7	1597.1
Cost of tanks (k€)	-	-	711.4
Fixed cost (€/kW)	23.0	79.5	117.3
Variable cost (€/kW)	10.2	32.2	47.5
Fuel cost (€/kW)	219.2	249.5	259.0
LCOE (€/MWh)	40.3	65.5	74.3
CO ₂ avoidance cost (€/t)	-	77.1	102.5

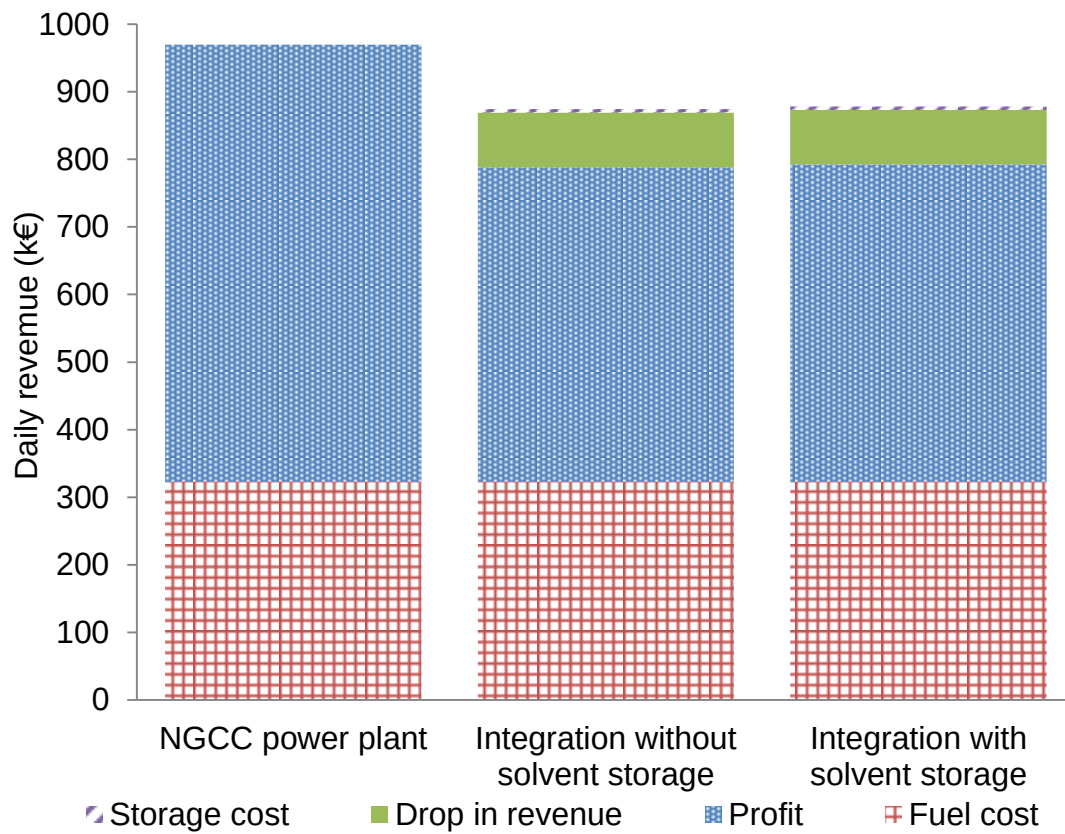
The peak and off-peak electricity prices are estimated using the electricity price profile presented in Figure 6-2 above. These electricity prices for the different periods are used in calculating the daily profit. The carbon price and transport and storage cost are used to calculate the SRMC. The short-run Profit (SRP) is obtained by subtracting the SRMC from the daily revenue from electricity sales (R). As shown in Figure 6-7a, the NGCC power plant generated the most profit of k€647 compared to the processes with and without solvent storage. The SRP for the process without solvent storage reduced by 28%, while the process with solvent storage reduced the profit by 27.3% compared to the NGCC power plant. The reason for this difference is because the power plant does not take

transport, and storage costs into consideration. This is also due to the drop in daily revenue from electricity sales as shown in Figure 6-7b, and the different loads associated with each process.

Importantly, the process with solvent storage increased the daily profit by approximately 1% compared to the process without solvent storage. This suggests some slight benefits when using solvent storage process. However, with part-load analysis, there is a high possibility of obtaining a higher profit for the process with solvent storage as presented in studies (Chalmers et al., 2009). In this study, the part-load analysis was ignored due to limitations in the steady-state model. The distribution of the daily revenue for the different cases is presented in Figure 6-7b. The results show that storage and transport cost had the lowest contribution.



(a)



(b)

Figure 6-7: Economic evaluation of the NGCC power plant with AMP-based plant and solvent storage; (a) Comparison of short-run profit, (b) daily revenue distribution

6.7 Sensitivity Studies

6.7.1 Variation of Price Change Difference

The electricity selling price differential would be important to allow a comparison between the values of additional output generated in the period when the solvent is stored. In Figure 6-8, the change in the peak price with respect to the electricity spot price is varied against the SRP.

As observed in Figure 6-8, increase in the peak price differential increases the SRP. Thus, the NGCC power plant will always generate the highest SRP compared to the processes with and without solvent storage. Moreover, results revealed that, if the peak price differential is increased up to €50/MWh, the

process with solvent storage increases up to 4%, higher than that of the process without solvent storage.

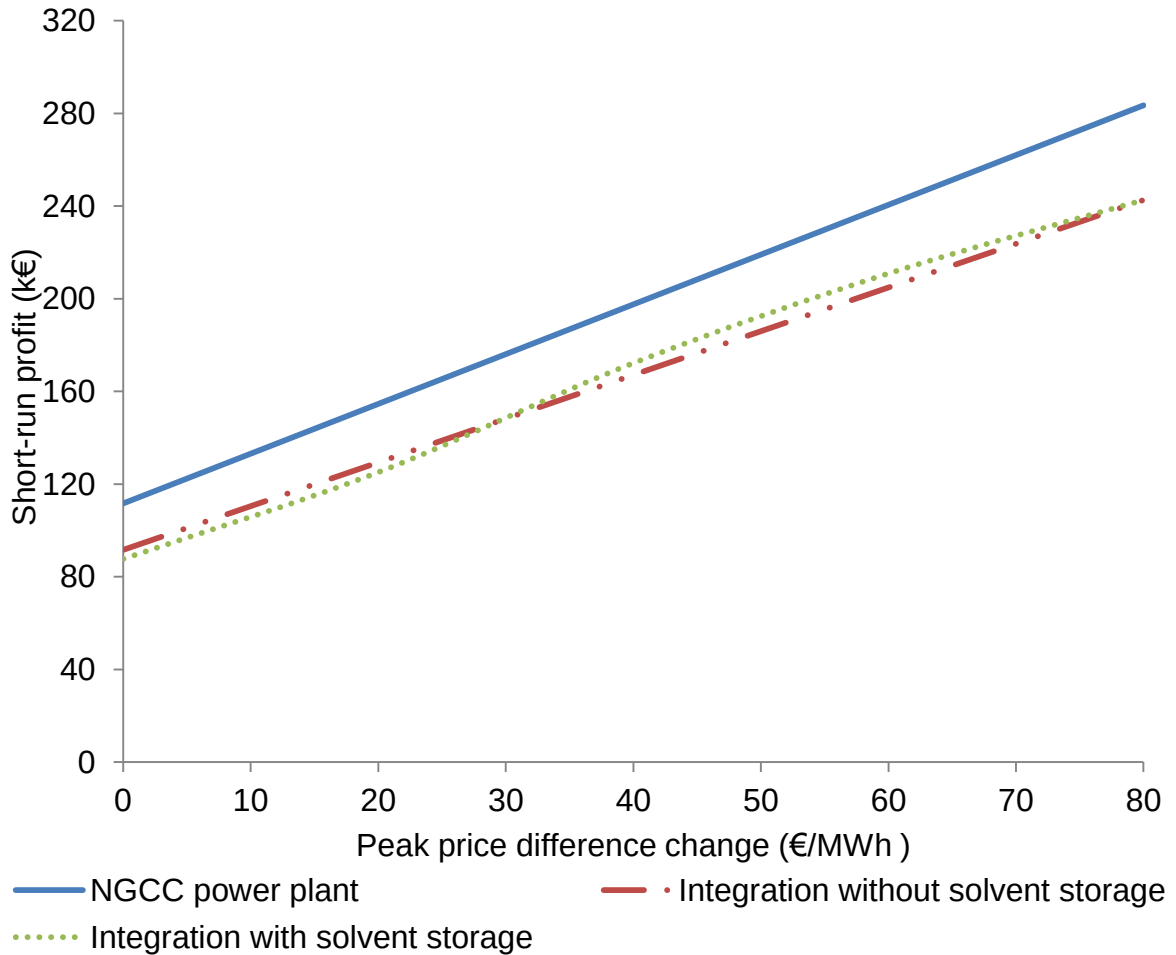


Figure 6-8: Effect of peak price differential on the short-run profit

6.7.2 Variation of Carbon Tax

Carbon tax is directly proportional to the effects of climate change, e.g. extreme weather, sea level rise, etc. (Symons et al., 1994). Based on predictions from studies (Department of Energy, 2014; EIA, 2010), the carbon tax varies between €10/tCO₂ to €150/tCO₂. This is because the profit is highly dependent on the economic climate. As shown in Figure 6-9, as carbon tax increases, the SRP reduces. The results also show that the NGCC power plant has the highest effect on the SRP due to its high CO₂ emissions content compared to the systems with CO₂ capture, which have very low CO₂ emissions content.

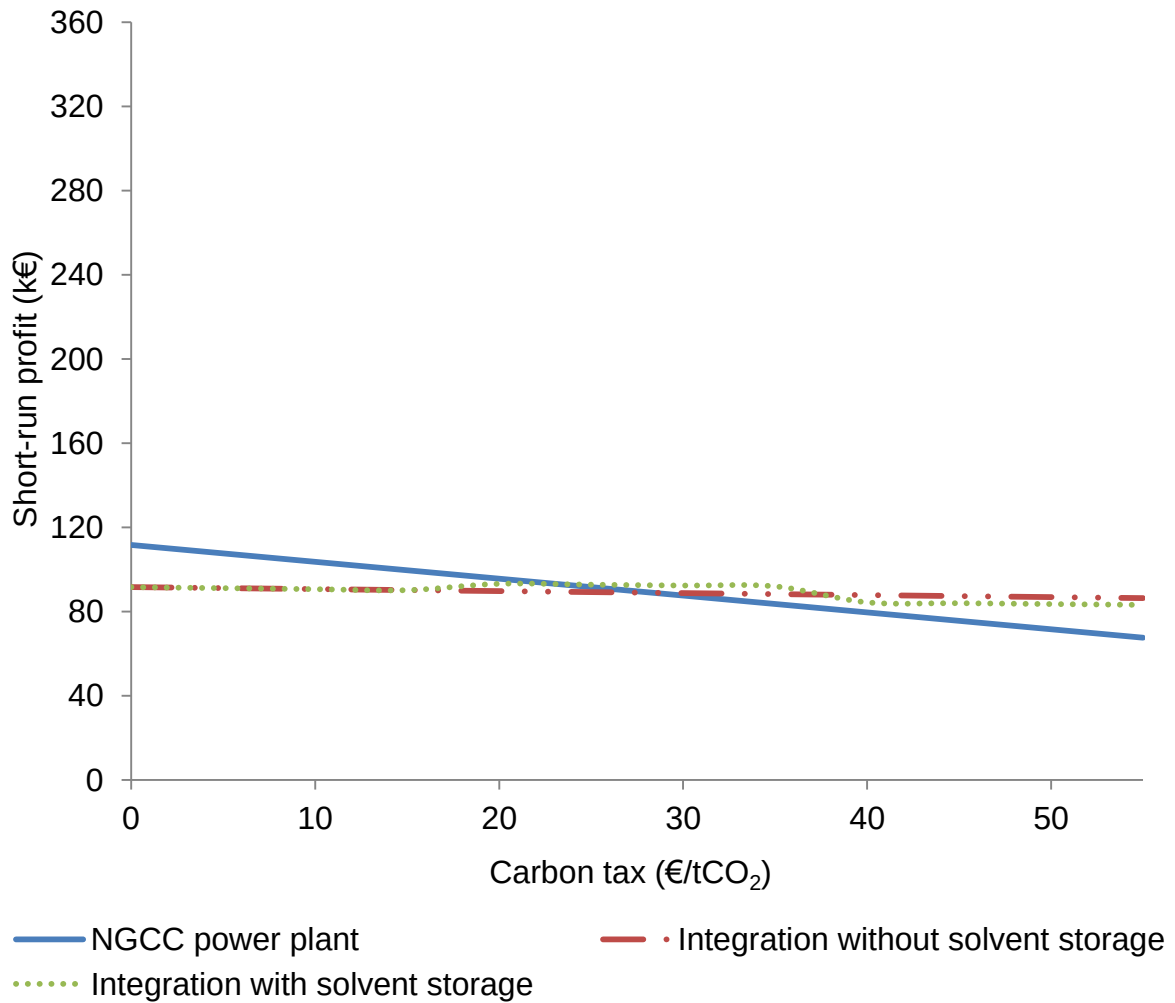


Figure 6-9: Effect of carbon tax on the short-run profit

However, if the carbon tax exceeds €30/tCO₂, and €25/tCO₂ for the processes without solvent storage, and with solvent storage respectively, these plants will be more profitable than the NGCC power plant. Although, the process without solvent storage, has a lower penalty (tax rate) compared to the process with solvent storage. Thus, if the range of carbon tax is between €23.9/tCO₂–€47.5/tCO₂, a higher profit for the power plant is expected for power systems with CO₂ capture (Adams and Mac Dowell, 2016; Hammond et al., 2011). This range agrees with the performance of the NGCC retrofit with AMP-based plants.

6.7.3 Payback period

The payback period, which is the expected number of years required to recover the original investment in the project is calculated for the PCC plant with solvent storage and without solvent storage. This is important because, if the payback period as shown in Equation 6-11 (Awomewe and Ogundele, 2008) is less than the required period, the project is accepted. Thus, shorter payback periods imply that money is gotten faster, and the business is better.

$$\text{Payback period} = \frac{\text{Total investment}}{\text{Annual net cash flow}} \quad 6-11$$

With an initial investment cost (includes the cost of procurement, engineering cost, VAT, construction cost, land, taxes, utility costs such as electricity cost and other cost incurred during the construction phase) of M\$793 and M\$763 for the retrofitted plant with solvent storage and without solvent storage respectively, the desired years of operation is 30 years. Results given in Table 6-4 show that it will take 9 years to recover the initial investment for the process with solvent storage and 10 years for the process without solvent storage.

In summary, the analysis in this research showed that LCOE is generally higher for the process with solvent storage by 11.8%, as compared to the process without solvent storage. In addition, the huge physical sizes of the storage tanks (6459.9 m³) will contribute to a larger footprint of the PCC process. The large volume of stored solvents, with a greater possibility of leakage/emission to the environment, will also have greater health and safety implication.

Table 6-4: Results for payback period

	Process with solvent storage	Process without solvent storage
Initial investment (M\$)	793	763
Number of operational period (years)	30	30
Payback period (years)	9	10

6.8 Conclusion

The economic evaluation was performed in the APEA for the AMP-based process using the bottom-up approach. The retrofitted AMP-based and MEA-based processes were evaluated. Results revealed that the LCOE for the AMP-based process was found to be 6.6% lower than that of the MEA if no solvent make-up was considered. However, the LCOE becomes equal for both solvents if the make-up is only 0.03% of total solvent flowrate. Beyond this point, the MEA-based process becomes more economically feasible, regardless of higher efficiency penalties. This implies that although the use of AMP as a solvent in chemical solvent scrubbing can significantly reduce the efficiency penalty associated with CO₂ capture from NGCCs, it may not be the most feasible option from the economic point of view. Therefore, evaluation of novel CO₂ capture materials should consider both thermodynamic and economic performance.

Furthermore, the economic performance of the NGCC retrofit with the capture plant and solvent storage was evaluated. The results revealed that the CO₂ avoidance cost for the process with solvent storage increased by 24.8% as compared to the process without solvent storage. More importantly, the process with solvent storage increased daily profit by approximately 1% as compared to the process without solvent storage. Thus, this performance would yield a higher short-run profit over the NGCC power plant if the carbon tax exceeds €25/tCO₂.

7 CONCLUSION and RECOMMENDATION

7.1 Conclusions

The AMP-based capture plant model was developed using the default operating parameters of the pilot-scale plant in Aspen Plus® software (Aspen Technology, 2008b) and validated using experimental data from the literature (Gabrielsen et al., 2007). Also, the predictions from the NGCC power plant were in good agreement with data reported in the literature (NETL, 2010) for the system modelled (most parameters had relative errors less than 0.1). Afterwards, the capture plant model was scaled up for 90% capture level from the 474 MWe NGCC power plant (NETL, 2010). The more favourable operating conditions for the AMP-based capture process were identified through sensitivity analysis. These include 35 wt% concentration, a lean loading of 0.33 mol/mol, a stripper pressure of 3.5 bar (temperature of 140 °C).

Also, the rate-based approach was used to estimate the energy requirement of the AMP-based plant, (2.9 MJ/kg CO₂) with the MEA-based plant (3.9 MJ/kg CO₂) used as a benchmark, and this was estimated to be 25.6% lower than that of the MEA-based plant, while the compressor load obtained for AMP was 58% lower than that of MEA. Previous studies (Van der Spek et al., 2016; Sanchez Fernandez et al., 2014), estimated between 12.5%-19.5% and between 0-18% higher savings in reboiler duty and compressor load respectively for AMP as against MEA.

Furthermore, the efficiency penalty due to the retrofit of the AMP-based plant into the NGCC power plant was estimated to be 7.1% points, compared to 9.1% points in the case of retrofit with the MEA-based process, which is 2% lower for AMP compared to MEA. This compared to previous studies (Sanchez Fernandez et al., 2014; Van der Spek et al., 2016), the efficiency of the AMP-based process was between 0.86%-1% higher than that of the MEA. Thus, the AMP-based capture process was simulated to operate under more favourable operating conditions. In addition, the economic assessment was performed in the APEA. The economic analysis performed revealed that the LCOE for the AMP-based process reduced by 6.5% compared to that of the MEA-based process only for make-up rates below 0.03% of total flowrate in the process. These results compared to a previous study (Manzolini et al., 2015) showed that the LCOE for the AMP-based process was 1% lower than that of the MEA-

based process. Thus, results demonstrate that operating under the more favourable conditions for the AMP-based process could reduce cost and provide higher energy savings.

Lastly, using the same NGCC power plant as a reference, the performance of the AMP-based plant with solvent storage has been evaluated, and a thermodynamic comparison of the process with solvent storage and without solvent storage was conducted. The results of the process analysis revealed that the average (peak and off-peak periods) net efficiency imposed on the process with solvent storage scenario was 47.31%, while without solvent storage scenario was 47.32%, LHV basis. Despite the lower thermodynamic performance, the cost of operating with solvent storage has been evaluated to be more profitable than that without solvent storage. Results revealed that NGCC retrofit with the AMP-based capture plant and with solvent storage increases the degree of energy utilisation during peak times. Thus, the process with solvent storage led to a higher profit of approximately 1% as compared to the process without solvent storage. However, a higher profit is achieved with the solvent storage scenario compared to the NGCC power plant if the carbon tax exceeds €25/tCO₂. The concept of solvent storage for decarbonisation of the natural gas-fired power plant with the AMP-based capture process is evaluated for the first time. Hence, a flowsheet with solvent storage for the AMP-based process has been developed.

In this research, AMP solvent was evaluated for the PCC process to identify approaches for reducing cost and increase the overall profitability of the process compared to existing literature. Results obtained in this study indicate that AMP is a technically and economically good option for decarbonisation of gas-fired power plants. However, regardless of the superior thermodynamic performance, the economic performance of the AMP-based process was shown to be better than that of the MEA-based process only for make-up rates below 0.03% of total flowrate in the system, which is not practical in real life scenario. Therefore, the use of AMP as a solvent in chemical solvent scrubbing may not be the most feasible option from the economic standpoint, even though it can significantly reduce the efficiency penalty associated with CO₂ capture from NGCCs.

7.2 Linkage of Projects Objectives

The thermodynamic and economic performance of the AMP-based plant has been investigated through modelling and process simulation (Dash et al., 2014; Van der Spek et al., 2016; Sanchez Fernandez et al., 2014; Manzolini et al., 2015). These studies (Objective 1,) used the MEA operating conditions (MEA-based process) for the AMP-based retrofit process, without exploring the more favourable operating conditions for AMP. Therefore, rate-based models of the amine capture plant have been built. The NGCC power plant retrofit with the capture plant using AMP solvent has been investigated, using the more favourable operating conditions such as higher concentration of up to 35 wt%, higher operating stripper temperature of 140 °C, and stripper pressure of 3.5 bar, compared to that of the MEA, (Objective 2,). Application of this approach leads to the process improvements such as increased energy savings, and reduced compressor load (Objective 3). It also leads to higher savings in the cost of electricity compared to that of the MEA PCC technology.

The NGCC power plant with capture is capable of quick start-up and load change as quickly as a plant without capture (IEAGHG, 2012). Furthermore, power plants are dispatched primarily based on their variable costs of operation; mainly the fuel prices (NETL, 2010). Plants with the most minimal variable costs generally operate continuously, and plants with higher variable costs are brought on line sequentially as demand for generation increases (EIA, 2012; NETL, 2010). Since natural gas prices influence variable costs, changes in natural gas prices can influence the selection of plants dispatched. Thus, price changes of natural gas have a high impact in the dispatch of combined-cycle power plants to meet intermediate load requirements (EIA, 2012). In order to attain a balance between electricity demand and supply, flexible plant operation strategy involving solvent storage in the capture cycle is employed. This technology would increase the energy generation by storing the excess amount of solvent during times when electricity demand is high and regenerate solvent when electricity demand is low (Chalmers et al., 2009). NGCC power plants with flexible operating conditions have been proposed and improved in recent years. Nevertheless, the process analysis with solvent storage has been presented with MEA solvent (Chalmers & Gibbins, 2007; Van Peteghem & Delarue, 2014; Oates et al., 2014). Therefore, process analysis with AMP as the solvent is

required for further evaluation. The AMP-based plant was improved by incorporation of solvent storage (Objective 4). This is expected to increase the profit for the PCC technology as compared to the process without solvent storage (Objective 5). The project objectives are linked together as presented in Figure 7-1.

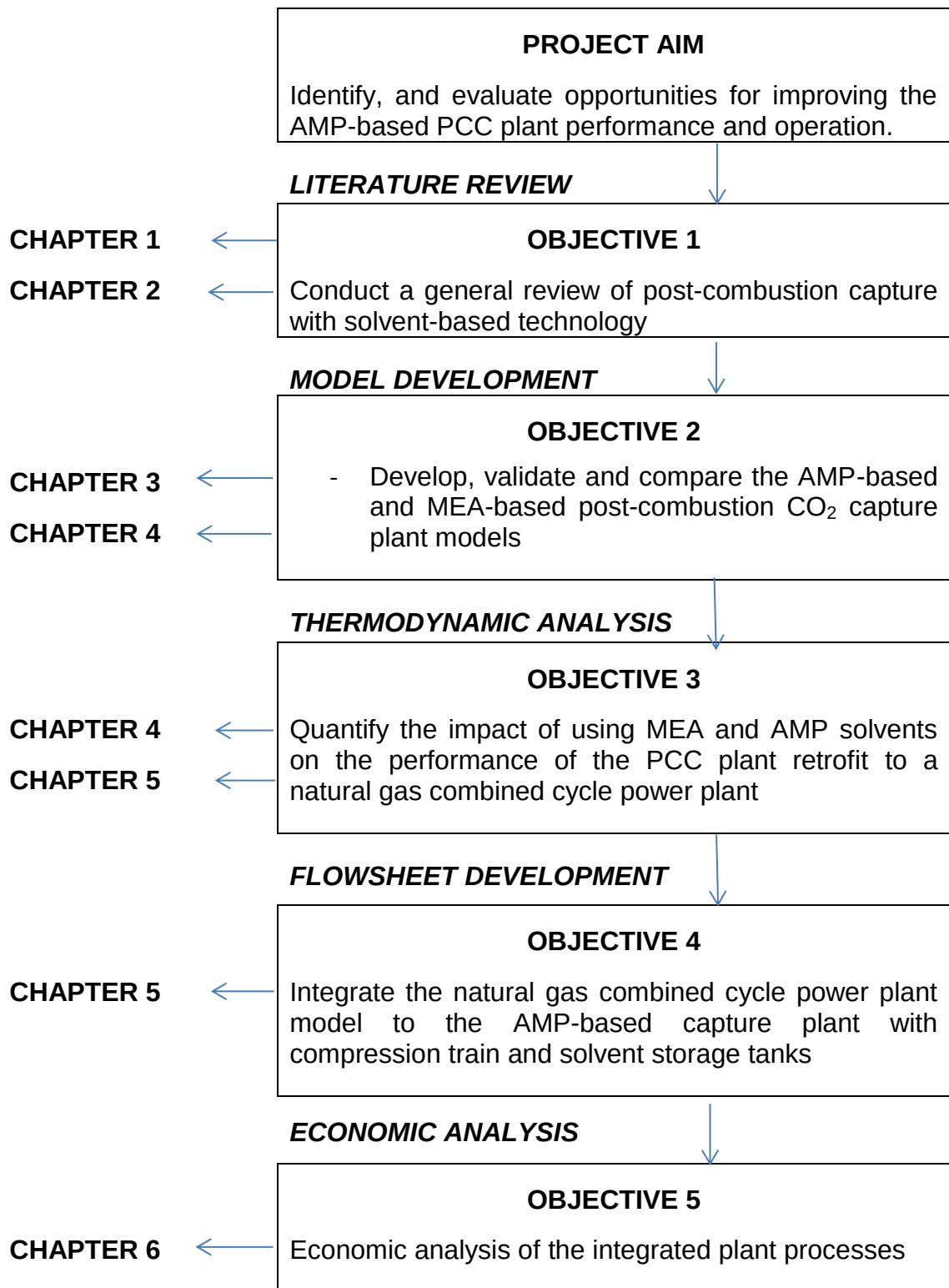


Figure 7-1: Linkage of project objectives

7.3 Recommendations for Future Work

- The present study demonstrates higher energy efficiency and cost savings for the AMP-based capture process (for make-up flowrate below 0.03% of total flowrate), over the MEA-based process as compared to studies presented in the literature. The study suggests that further improvements can be achieved by evaluating the different flowsheet process configurations for the AMP-based plant integrated into the power plant. Although these configurations yield better thermodynamic performances by enhancing absorption capacity, reducing steam requirements etc., they add more complexity to the process plant, which increases the cost for the CO₂ capture technology. Therefore, an economic evaluation of the configurations is also required to observe if any cost savings can be achieved.
- More experimental-based studies into the degradation reaction chemistry are required to improve the kinetics of AMP degradation reactions. Thus, future work should aim at generating reliable concentration versus time data over a wide range of temperatures. Furthermore, a simulation study on large-scale analysis of the AMP-based process with degradation reactions is required. The economic analysis should be performed to evaluate the cost of the AMP-based process with degradation taken into account, and compared with that of the MEA.
- The qualitative and quantitative assessment can be evaluated with exergy, unlike energy, which is based on quantitative assessment only. Thus, the main purpose of exergy analysis is to identify where exergy is destroyed. The destruction of exergy in a process is proportional to the entropy generation in it; which accounts for the inefficiencies due to irreversibility. Hence, this study recommends exergy analysis should be performed on the AMP-based capture plant and the integrated plant in order to improve the work potential.
- Carbon pricing varies in different locations, and the economic conditions such as wage rates, taxes, natural gas price vary for different countries. As a result,

new insights are expected regarding the cost of carbon capture in different plant locations. Therefore, techno-economic analysis of different plant locations for the AMP-based process should be evaluated, and compared, with that of the MEA-based process.

- Dynamic modelling and simulation of the AMP-based integrated process with solvent storage should be conducted to provide better insight. Furthermore, comparative analysis of the different flowsheeting configurations, including solvent storage process should be carried out to determine the highest cost savings plant.
- Lastly, since demand at peak and off-peak scenarios vary, the part-load performance of the power plant with the capture plant and solvent storage should be investigated, in order to study the plant performance at the condition.

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Appendix A NGCC Power Plant Validation

Table A-1: Aspen Plus NGCC power plant model with capture stream data
(NETL, 2010)

Stream	Temperature (°C)		Relative error	Mass flow rate (kg/s)		
	Report	Model		Report	Model	Relative error
Natural gas						
1	38	38	0.000	21.08	21.08	0.000
Air/flue gas						
2	15	15	0.000	876.32	876.32	0.000
Turbine outlet						
3	629	629	0.000	897.40	897.40	0.000
Water/steam						
Cold RH	308.83	308.83	0.000	104.55	104.55	0.000
HPFW	151.83	140.08	0.077	109.13	109.13	0.000
IPFW	149.28	138.06	0.075	21.86	21.86	0.000
LPFW	148.94	137.82	0.075	11.86	11.86	0.000
From condenser	41.56	41.56	0.000	67.47	67.47	0.000
Cold-FG	143.17	134.28	0.062	897.40	897.40	0.000
Hot RH	568.33	568.33	0.000	104.55	104.55	0.000
HP steam	565.56	565.56	0.000	108.04	109.13	1.000
IP steam	568.33	568.33	0.000	21.64	21.86	1.000
LP steam	280.56	280.56	0.000	11.74	11.86	1.000
Feed water	122.78	122.78	0.000	67.47	67.47	0.000

Abbreviations: RH - Reheat, HPFW – High-pressure feed water, IPFW – Intermediate pressure feed water, LPFW – Low-pressure feed water, FG - Flue gas, NGCC – Natural gas combined cycle.

Table A-2: Validation of the Aspen Plus NGCC power plant model

Parameter	Source (NETL, 2010)	Model	Relative error
Net plant efficiency (LHV) (%)	47.5	45.0	0.053
Net power (kWe)	473570	448319	0.053
Gas turbine power (kWe)	362200	339677	0.062
Steam turbine power (kWe)	148800	152741	0.026
Boiler feedwater pumps power (kWe)	2710	2553	0.058
Condensate pumps power (kWe)	80	77.95	0.026
Other auxiliary loads (kWe) ^c (NETL, 2010)	34640	34640	-

^cAssumed based on the values of other auxiliary loads reported in the US DOE report (NETL, 2010)

Appendix B Capture Plant Design and Operating Conditions

B.1 Liquid Phase Temperature Profiles in the Absorber for Different Packing for the AMP-Based Process

AMP has a lower absorption rate with CO_2 than MEA, which is the only drawback of AMP solvent compared to MEA. Ways to improve this rate are to increase the absorption rate, to increase the surface area of packing, to increase the absorber pressure and to mix AMP with PZ (Afkhamipour and Mofarahi, 2013; Kim et al., 2011). To minimize cost as much as possible, the option of increasing the surface area of different packing sizes as shown in Figure B-1, which are present in Aspen Plus® software, to increase the reaction rate of AMP is performed in this study.

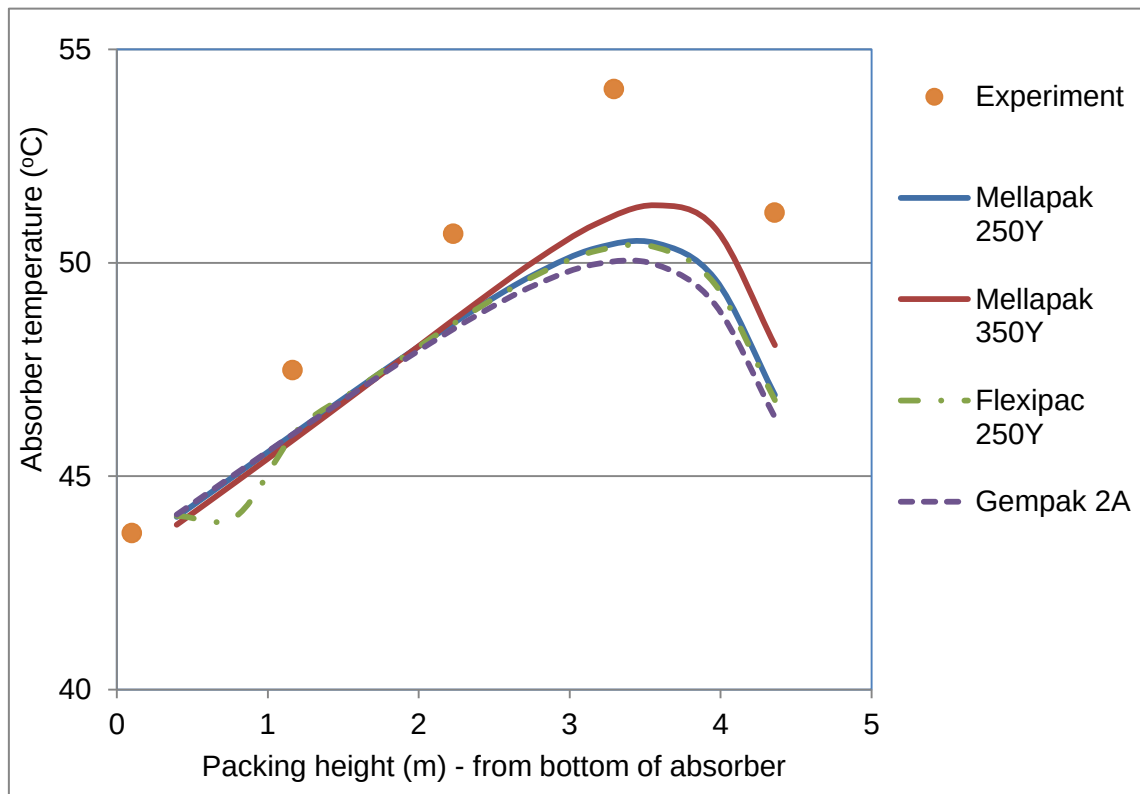


Figure B-1: Effect of packing height against temperature

Table B-1: Comparison of different packing materials (Aspen Technology, 2008b)

Packing type	Size (mm)	Surface area (m ² /m ³)	Rich CO ₂ loading (mol/mol)
Mellapak	250Y	250	0.4147
Mellapak	350Y	350	0.4427
Flexipac	250Y	250	0.4028
Gempak	2A	220	0.4007

As shown in Figure B-1, the highest temperature profile given for Mellapak 350Y has the closest fit compared to the experimental results. Also, this packing observed to have the highest rich loading given in Table B-1. However, as rich CO₂ loading increases, high amount of CO₂ can be absorbed using the fewer amount of solvent, which yields, to the high surface area of the packing. Thus, the preferred choice of packing to be used for further studies is Mellapak 350Y.

B.2 Model Validation for the MEA Capture Plant

The model validation strategy was based on the lean CO₂ loading by varying the stripper reboiler duty. Zhang et al. (2008) showed that one important parameter that affects the process most is the liquid to gas ratio. Notz et al. (2012) carried out several experiments. Experiments (1, 33, 34) representing low–1.06, medium-2.8 and high-4.5 L/G ratios respectively. Key pilot plant performance results for these 3 cases are summarized in Table B-2, and the percentage difference between experiments and models (Aspen Technology, 2008a) is less than 7%. Also, Figures (B-3: B-8), show the various temperature profiles present in the absorber and stripper, the results from the model compares with the experimental values from the pilot plant with a given constant L/G ratio. The figures clearly show that the model predictions agree with the experimental data. Therefore, this can be used for the scale-up of plant design.

Table B-2: Validation of aqueous MEA plant model against the pilot plant data by Notz et al. (2012)

	CASE 1			CASE 33			CASE 34		
	Exp	Model	Difference (%)	Exp	Model	Difference (%)	Exp	Model	Difference
Inlet flue gas flow rate(kg/h)	72	72	0.0	77.1	77.1	0.0	100.0	100.0	0.0
Inlet CO ₂ flow rate (kg/h)	6.12	6.12	0.0	12.10	12.10	0.0	8.4	8.4	0.0
CO ₂ absorption rate (kg/hr)	4.65	4.786	2.84	6.60	6.68	1.28	4.44	4.54	2.21
CO ₂ lean loading (mol/mol)	0.265	0.265	0.0	0.360	0.360	0.0	0.146	0.146	0.0
CO ₂ rich loading (mol/mol)	0.386	0.388	0.52	0.441	0.448	1.6	0.417	0.422	1.1
Reboiler duty (kw)	6.16	6.5	5.2	5.06	5.35	5.5	6.22	6.43	3.2
CO ₂ capture level (%)	75.91	78.2	2.93	54.59	55.15	1.01	75.87	76.71	1.1

B.2.1 Liquid phase temperature profiles in the absorber of experimental data (Notz et al., 2012) versus model used in this study

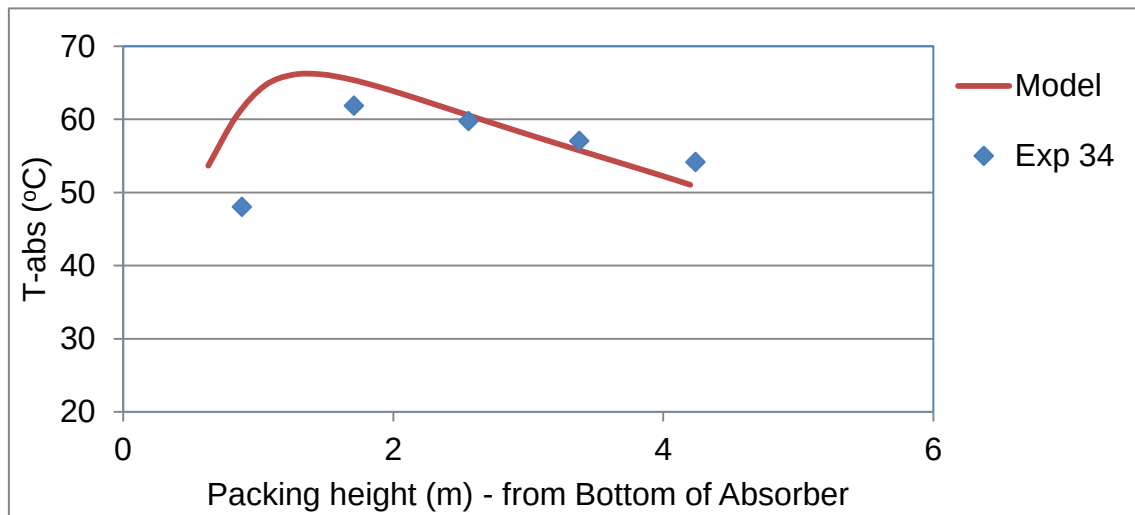


Figure B-2: Temperature profile for case 34

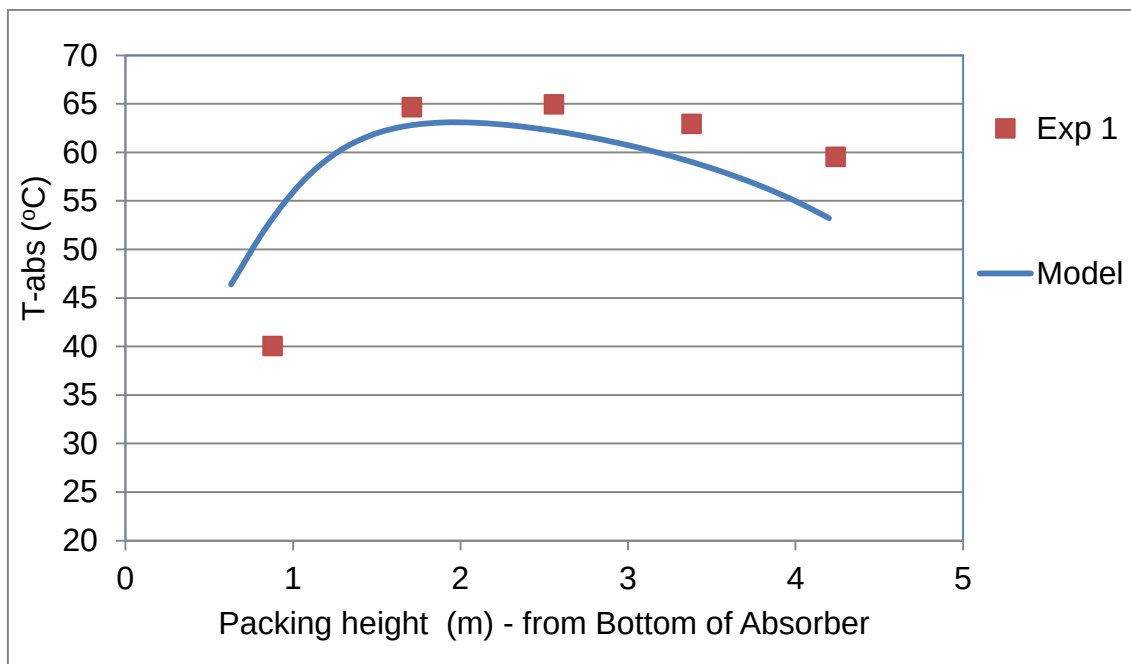


Figure B-3: Temperature profile for case 1

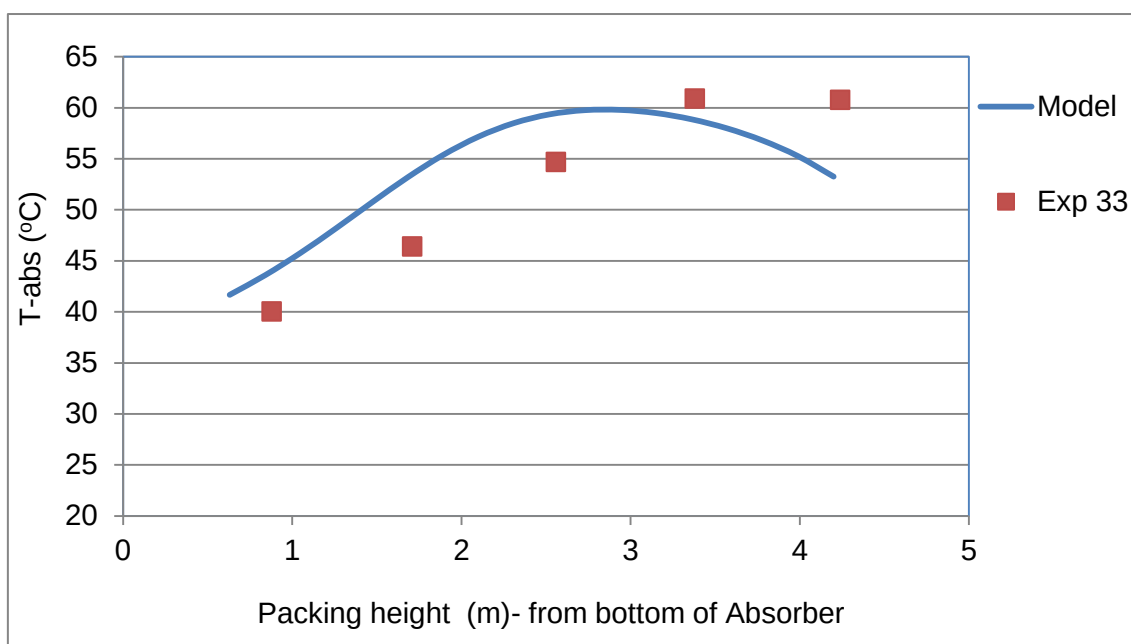


Figure B-4: Temperature profile for case 33

B.2.2 Liquid phase temperature profiles in the stripper of experimental data (Notz et al., 2012) versus model used in this study

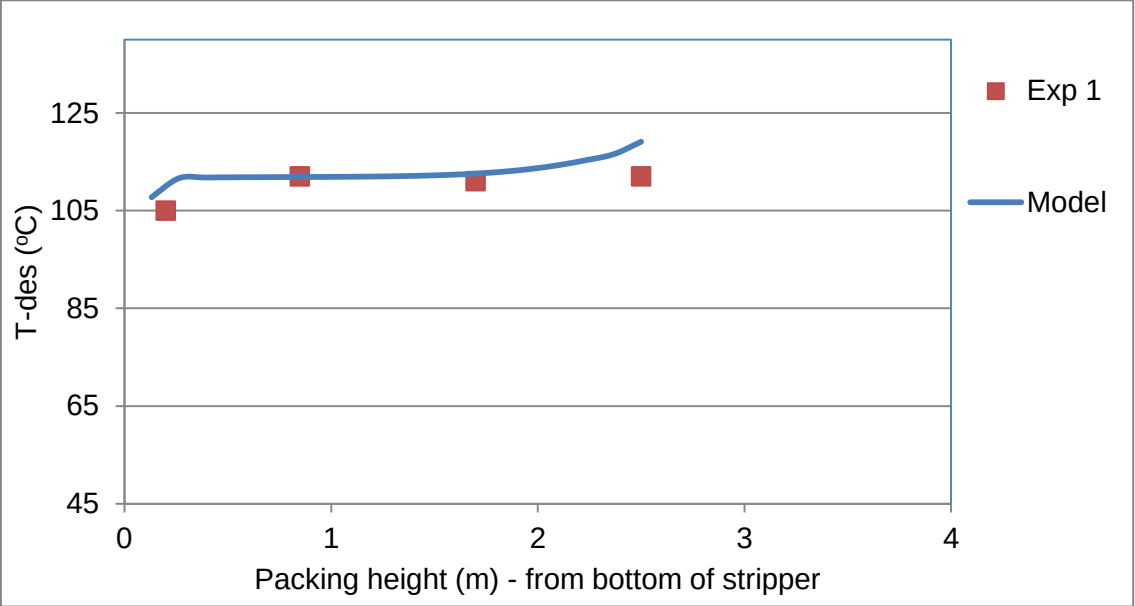


Figure B-5: Temperature profile results for case 1

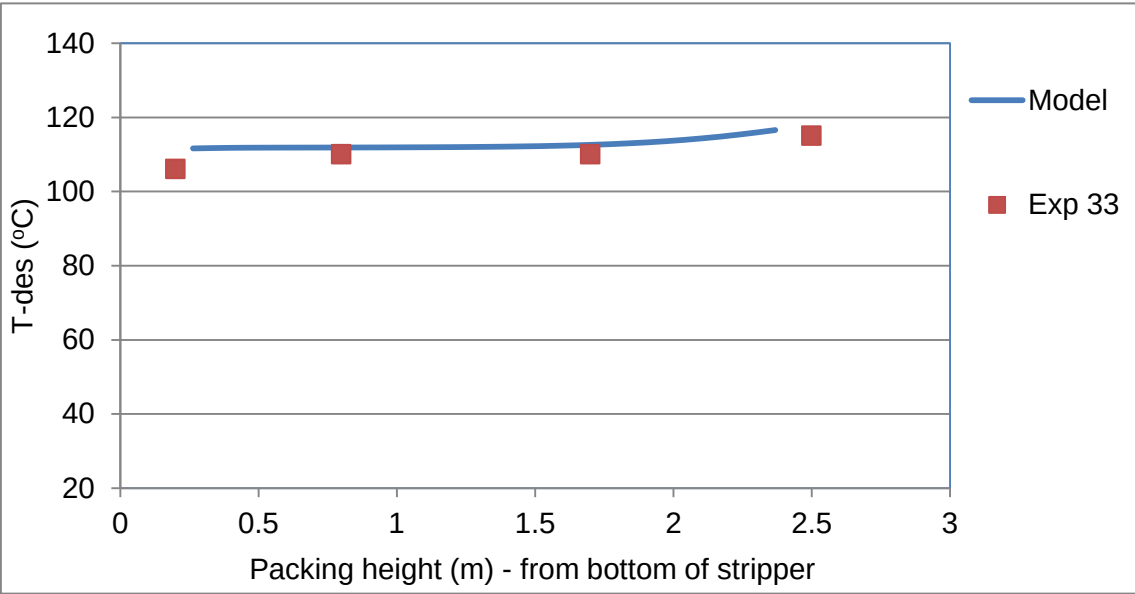


Figure B-6: Temperature profile results for case 33

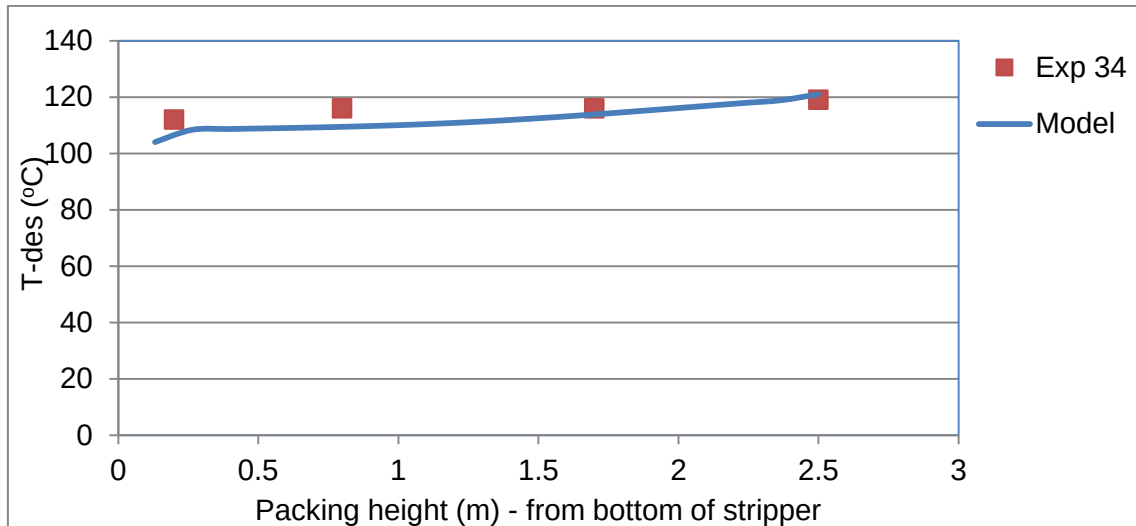


Figure B-7: Temperature profile results for case 34

Appendix C Integration Calculations

C.1 Sizing of the Compression Train

$$r = \frac{P_{CO_2,out}}{P_{CO_2,in}} \quad \text{C-1}$$

where r = overall pressure ratio

$$r_t = \sqrt[t]{\frac{P_{CO_2,out}}{P_{CO_2,in}}} \quad \text{C-2}$$

r_t = stage pressure ratio

t = t stages for the compressor

C.2 Sizing of Storage Tank

This is sized by doing a mass balance.

Assuming a time constant in order to calculate holdup volume, which is the tank volume. However, as the solvent is being pumped into the tank, the volume of solvent in the tank is not fixed.

Solvent storage scenario; for a given tank,

$$M_{in} - M_{out} = \frac{d_m}{d_t} \quad \text{C-3}$$

Where M_{in} and M_{out} are mass flowrates in and out of the tank respectively

m = mass holdup, (volume x density)

t = time

Density (ρ) is assumed fixed. Thus, the volume of solvent is changing, i.e.

$$\frac{d_m}{d_t} = \rho \times \frac{d_v}{d_t} \quad \text{C-4}$$

During storage, nothing leaves the tank, $M_{out} = 0$, and M_{in} = unknown

$$M_{in} = \rho \times \frac{d_v}{d_t} \quad \text{C-5}$$

Thus,

$$\frac{M_{in}}{\rho} \int_{t_1}^{t_2} dt = \int_{V_1}^{V_2} dv \quad \text{C-6}$$

$$\frac{M_{in}}{\rho} (t_2 - t_1) = (V_2 - V_1) \quad \text{C-7}$$

$t_1 = 0$ and $t_2 = 8$ hrs, are initial and final times respectively

$V_1 = 0$ and V_2 = unknown, are the initial and final volume of solvent in the rich tank

Thus, $V_2 = V_{final}$ = maximum solvent to be stored for a period of 8 hrs.

A 20% safety factor is assumed for the tanks (Oates et al., 2014).

Stripping scenario;

$M_{in} = 0$, because nothing is coming into the tank, and M_{out} = unknown

Substituting M_{in} with M_{out} in equation C-7 gives;

$$\frac{M_{out}}{\rho} \int_{t_1}^{t_2} dt = \int_{V_1}^{V_2} dv \quad \text{C-8}$$

Thus, V_2 and V_1 are known from equation C-7

C.2.1 Convective Cooling Calculation

Given;

$$Q = h_c A \Delta T \quad \text{C-9}$$

- Q is the heat transferred per unit time, can be defined as;

$$Q = \frac{m C_p \Delta T}{t} \quad \text{(i)}$$

Where;

{ m = mass of tank, C_p = specific heat, ΔT = temperature rise, t = time of heating}

A = heat transfer area

h_c = convective heat transfer coefficient

- Convective heat transfer coefficient, can be defined by Nusselt number

$$h_c = \frac{N_u K}{L} \quad \text{(ii)}$$

N_u = Nusselt no

K = thermal conductivity

L = length

Nusselt number for tanks given as: $0.030 (Re)^{4/5} Pr^{1/3}$, where $Re < 2000$

Where;

$Re = \frac{\rho D V}{\mu}$ = Reynolds number; ρ = density, D = diameter, V = velocity,

μ = viscosity (these parameters are derived from Aspen Plus data bank) (Aspen Technology, 2008a).

$Pr = \frac{C_p \mu}{K}$ = Prandtl number; C_p = specific heat capacity, k = thermal conductivity (these are derived from Aspen Plus data bank) (Aspen Technology, 2008a)

dT = rate of change of temperature

- Rate of change of temperature can be defined as;

$$\frac{dT}{dt} = -k (T_t - T_a) \quad (\text{iii})$$

Where T_t = difference between temperature = unknown

T_a = ambient temperature or initial temperature

k =constant which governs the rate of cooling

Appendix D **Publications and Conferences**

Journal Papers

Paper I

Ebuwa Osagie; Chet Biliyok, Giuseppina Di Lorenzo, Dawid P. Hanak, Vasilije Manovic, (2017); “Techno-economic evaluation of the AMP process as a substitute CO₂ capture technology for natural gas combined cycle power plant”. **International Journal of Greenhouse Gas Control 70 (2018) 45-56.**

Paper II

Ebuwa Osagie; Chet Biliyok, Giuseppina Di Lorenzo, Dawid P. Hanak, Vasilije Manovic, (2017); “2-Amino-2-Methyl-1-Propanol-based post-combustion capture process with solvent storage for decarbonisation of natural gas combined cycle power plant” **(in preparation).**

Conferences

Paper III

Ebuwa Osagie; Chet Biliyok, Giuseppina Di Lorenzo Vasilije Manovic, (2016); “Process Modelling and simulation of degradation reactions for the 2-amino-2-methyl-1-propanol (AMP) CO₂ capture process”. **International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland**

Poster I

Ebuwa Osagie; Chet Biliyok, Giuseppina Di Lorenzo, Hoi Yeung (2015); Modelling and evaluation of different process configurations for the post-

combustion CO₂ capture plant with AMP solvent. **Best poster won at UKCCSRC Biannual Meeting in Strathclyde, September 2015.**

Poster II

Ebuwa Osagie; Chet Biliyok, Giuseppina Di Lorenzo, Hoi Yeung (2015); New solvents for post-combustion capture as an efficient CO₂ capture technology for natural gas-fired power plants. **Cranfield Biannual Meeting, 2015, UK CCS Research Center**