

CRANFIELD UNIVERSITY



CHECHET SEAN BILYOK

STUDY OF POWER PLANT WITH CO₂ CAPTURE ABILITY
THROUGH MODELLING AND SIMULATION

SCHOOL OF ENGINEERING
Offshore, Process and Energy Engineering

PhD Thesis
Academic Year: 2012 - 2013

Supervisor: Professor Hoi Yeung
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This thesis is submitted in fulfilment of the requirements for the
degree of PhD in Process Systems Engineering

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ABSTRACT

With an increased urgency for global action towards climate change mitigation, this research was undertaken with the aim of evaluating post-combustion CO₂ capture as an emission abatement strategy for gas-fired power plants. A dynamic rate-based model of a capture plant with MEA solvent was built, with imposed chemical equilibrium, and validated at pilot scale under transient conditions. The model predicted plant behaviour under multiple process inputs and disturbances. The validated model was next used to analyse the process and it was found that CO₂ absorption is mass transfer limited. The model was then improved by explicitly adding reactions rate in the model continuity, the first such dynamic model to be reported for the capture process. The model is again validated and is observed to provide better predictions than the previous model.

Next, high fidelity models of a gas-fired power plant, a scaled-up capture plant and a compression train were built and integrated for 90% CO₂ capture. Steam for solvent regeneration is extracted from the power plant IP/LP crossover pipe. Net efficiency drops from 59% to 49%, with increased cooling water demand. A 40% exhaust gas recirculation resulted in a recovery of 1% efficiency, proving that enhanced mass transfer in the capture plant reduces solvent regeneration energy demands. Economic analysis reveals that overnight cost increases by 58% with CO₂ capture, and cost of electricity by 30%. While this discourages deployment of capture technology, natural gas prices remain the largest driver for cost of electricity. Other integration approaches – using a dedicated boiler and steam extraction from the LP steam drum – were explored for operational flexibility, and their net efficiencies were found to be 40 and 45% respectively. Supplementary firing of exhaust gas may be a viable option for retrofit, as it is shown to minimise integrated plant output losses at a net efficiency of 43.5%.

Areas identified for further study are solvent substitution, integrated plant part load operation, flexible control and use of rotating packed beds for CO₂ capture.

Keywords: post-combustion, MEA, dynamic modelling, model validation, combined cycle, NGCC, CCGT, Exhaust gas recirculation, EGR.

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LIST OF ABBREVIATIONS

2DS	2 Degrees Scenario
APEA	Aspen Process Economic Analyzer
BRICS	Brazil, Russia, India, China, South Africa
CAP	Chilled Ammonia Process
CC&ST	Carbon Capture & Sequestration Technologies
CCS	Carbon capture and storage/sequestration
CCT	Carbon capture and transport
CFD	Computational fluid dynamics
COE	Cost of electricity
DCC	Direct contact cooler
DEA	Diethanolamine
DOE	U.S. Department of Energy
EGR	Exhaust gas recirculation
EIA	U.S. Energy Information Administration
EOR	Enhanced oil recovery
ETS	Emissions Trading Scheme
EU	European Union
FC	Free Carbon
GHG	Greenhouse gas
HP	High pressure
HRSG	Heat recovery steam generator
IEA	International Energy Agency
IGCC	Integrated gasification combined cycle
ILs	Ionic liquids
IP	Intermediate pressure
IPCC	Intergovernmental Panel on Climate Change
L/G	Liquid to gas
LCOE	Levelised cost of electricity
LHV	Lower heating value
LP	Low pressure
MDEA	Methyl-Diethanolamine
MEA	Monoethanolamine

NETL	National Energy Technology Laboratory
NGCC	Natural Gas Combined Cycle
OECD	Organisation for Economic Co-operation and Development
O&M	Operational and Maintenance
PC	Pulverised coal
PCC	Post-combustion capture
PFD	Process flow diagram
PM	Particulate matter
PV	Photo-voltaic
RD&D	Research, development & demonstration
SF	Supplementary Firing
SRP	Separation Research Program
UNFCCC	UN Framework Convention on Climate Change
VLE	Vapour-Liquid Equilibrium

LIST OF SYMBOLS

A	cross-sectional area
a	reaction order
C	Concentration
E	activation energy
F	mass flow rate
F_H	energy flow
F_m	molar flow rate
h	specific heat
H	heat flux
k	rate constant
k^o	pre-exponential factor
L	length of the column
M	mass holdup
MW	molecular weight
N	mass flux
P	Pressure
P^L	saturation pressure
r	reaction rate
R	universal gas constant
SA	column surface area
Sp	specific area of the packing
T	Temperature
t	time
U	energy holdup
x	Composition
y,z	axial distance

Greek Symbols

α	activity coefficient
ω	wetted area ratio
γ	CO ₂ loading on solvent

Subscripts

abs	absorption
i	component
j	reaction

Superscripts

$cond$	conduction
$conv$	convection
I	interface
L	liquid
L_b	liquid bulk
L_f	liquid film
V	vapour
V_b	vapour bulk
V_f	vapour film

1 INTRODUCTION

1.1 Background

Recent extreme weather events such as Hurricane Sandy that devastated the US East coast and droughts that affected 60% of the US in late 2012, heat waves in Moscow and Texas in the summers of 2010 and 2012 respectively, floods in Northeast Australia in early 2011, and 50,000 deaths caused by the humanitarian disaster that resulted from the East African drought of 2011, are recognized with high certainty as the effects of human induced climate change (Barrett, 2012; Gillis, 2012; Marshall, 2013). This is due to greenhouse gas (GHG) emissions worldwide, which cause global warming by absorbing infrared radiation, thus tackling climate change would require global action.

Through a number of international agreements, like the Kyoto Protocol, the world is taking steps to address the issue. The intergovernmental Panel on Climate Change (IPCC, 2007) has recommended that emissions be cut by a minimum of 50% by 2050 compared to levels of 1990 to ensure that the average temperature increase worldwide does not exceed a potential catastrophic 2°C. This has led the European Union (EU) to commit to reducing GHG emissions by 80-95% by 2050 compared to 1990 levels (EC, 2011), with the UK government setting similar targets in its Climate Change Act passed in 2008.

The combustion of fossil fuels, which provides the energy for a variety of human activities such as transportation and manufacturing, is chief source GHG emissions. CO₂, a GHG, is one of the primary products of combustion, and accounts for the largest proportion of GHG emissions. With world energy demand expected to increase by 40% over the next 20 years due to an increasing world population and the emergence of the BRICS countries (IEA, 2009a), meeting the emission reduction targets is a daunting challenge. China, for example, commissions a new 1GW coal-fired power plant at the rate of about one per week (Insight Economics, 2011).

A pragmatic strategy to meeting this challenge would require deploying a portfolio of approaches like greater energy efficiency, a vast increase in renewable energy, waste recycling, smart grids, electric vehicle technology and carbon capture & sequestration (CCS). CCS involves the capture of CO₂ emissions from stationary sources like power plants, compression and then transport by pipeline or ship to a storage site, where the CO₂ is stored underground (at depths of 700 – 5000m) using natural mechanisms that have already “stored” CO₂, oil and gas underground for millions of years (Zero Emission Platform, 2011). It represents the bridge to a truly sustainable energy system. Studies by the International Energy Agency (IEA, 2009a) have shown that cutting emissions by 50% in a cost effective manner would require CCS to deliver a fifth of the reduction targets over the next 4 decades.

Features of CCS has been used for decades in the oil and gas industry for acid gas removal and enhanced oil recovery (EOR) activities worldwide, but it is still an emerging technology in other industries. In 2013, the Global CSS Institute (2013) identified 65 large scale integrated CCS projects, of which 12 are currently operating, 8 are under construction and the remaining are in the planning and engineering stages. Yet, CCS has to be commercially proven by 2020 to enable rapid and wide deployment if emission targets are to be met (Zero Emission Platform, 2011). Moreover, before investment in CCS can be contemplated by the private sector, governments will need to provide a policy framework that drives carbon prices to be significantly higher than their existing levels. One way is by reworking and expanding the Emissions Trading Scheme (ETS) used in the EU, or using policy instruments such as emission/energy taxation, feed-in tariffs for power plants with CCS, capital grants, government-backed lending, technological support and research funding to promote CCS deployment (EC, 2011; 2Co Energy Ltd, 2012)

1.2 Motivation

Currently, the cost of CCS has hindered its deployment and a large number of technical challenges and commercial risks remain, in addition to possible community opposition. Research, development, demonstration and early

deployment of CCS technologies are of paramount importance to ensure their cost-effective and large-scale penetration later on. This has enormous financial implications and would require substantial public funding, which prompted the EU to establish a legal framework for CO₂ storage, and provide funding for up to 12 CCS demonstration projects (Zero Emission Platform, 2011)

CO₂ has been transported by pipeline from oil and gas fields for the last four decades, and around 6000km of CO₂ pipelines operate on the US mainland alone to provide EOR from underground basins (Insight Economics, 2011). Many potential storage sites have been identified worldwide (Le Gallo and Lecomte, 2011), however detailed analysis and characterisation is still required. In addition, most estimates suggest that transportation costs make up only a relatively small part of the total costs of an integrated CCS operation. For example, a study by the Kiel Institute suggested that the costs of capture account for nearly 80% of an integrated CCS project, with transportation costs (depending on distance) representing less than 10% (Heitmann et al., 2010).

Therefore, as CO₂ capture is identified to account for an enormous share of CCS costs, research to improve capture costs has to be given top priority. Furthermore, with the 50,000 power plants around the world accounting for about a quarter of all GHG emissions (ENS, 2007), focus on the integration, performance and operability of CO₂ capture plants with power plants is vital. There are three main approaches of CO₂ capture for power plants – post-combustion, pre-combustion and oxyfuel – and each one has concomitant benefits and drawbacks. Among the varied technologies under the three options, post-combustion capture (PCC) via chemical absorption using monoethanolamine (MEA) solvent is the most mature technological option (MacDowell et al., 2010), and can be applied to new build power plants or retrofits.

A state-of-the-art pulverised coal (PC) power plant, operating under supercritical or ultra-supercritical conditions, emits around 800kg of CO₂ per MWh of power produced (Insight Economics, 2011), with natural gas combined cycle (NGCC) power plants producing around half of that amount. However, unconventional

gas production, pioneered in the US, has provided “cheap” gas and triggered a global tilt towards harnessing shale reserves. This underlines the significance of gas in the future energy mix, also evidenced by recent UK energy policy encouraging “a dash for gas”. As a result, implementation of CO₂ capture on NGCC plants is necessary.

Constructing pilot or demonstration plants for CO₂ capture, to investigate process integration concerns, requires high levels of investment. This has led to a number of high profile cancellations such as Scottish Power’s Longannet project (UK) in October 2011, TransAlta’s Project Pioneer (Canada) in April 2012 and most recently the full scale Mongstad project (Norway) in September 2013 (CC&ST, 2013a). These cancellations have been blamed on poor economic performance of the projects resulting from low carbon prices and the concomitant risks of CCS or being a “first mover”, as the expensive facilities would require substantial government subsidies and robust regulations to be competitive. None of the operating plants identified by the Global CSS Institute (2013) captures CO₂ from power plants and only 2 under construction are designed to do. Thus, building rigorous process models, validating them, and using them to explore possible problems is a priceless alternative. Modelling and simulation then becomes an invaluable tool for investigating CO₂ capture performance and power plant integration challenges.

1.3 Aim and Objectives

The aim of this research is the analysis of post-combustion chemical absorption CO₂ capture process for integration with gas-fired power plants, via modelling and simulation. MEA solvent would serve as the base option of the study.

The project objectives include:

- To develop a high-fidelity dynamic model of a PCC plant.
- To explore the PCC plant operation to identify improvement opportunities.
- To investigate the integration of a PCC plant to an NGCC power plant and analyse its performance.

- To perform an economic analysis of CO₂ capture plant integrated with an NGCC plant.
- To evaluate opportunities for improving integrated plant performance and operation.

1.4 Novelty

To achieve the objectives of this research, a number of contributions have been made to scientific body of knowledge. Firstly, an existing dynamic model of the PCC plant with MEA solvent, which was created using rate-based column models with an assumption that chemical reactions are in equilibrium, was used to explore the PCC process. It was validated both at steady-state (an improvement from Lawal et al. (2010)) and dynamically, the first successful attempt at a dynamic validation of such a model. Model predictions resulting from process inputs and disturbances were in agreement with plant responses. Pilot plant data were obtained from studies funded by the CO₂ Capture Pilot Plant Project of the Process Science and Technology Centre at the University of Texas at Austin (Dugas, 2006). The validated model was further used to investigate the effects of increasing inlet flue gas moisture content and the impact of intercooling on the PCC plant performance.

Second, the rate-based column model was improved by eliminating the assumption of chemical equilibrium and the implementing reaction kinetics to describe the rate of reaction between CO₂ and MEA. This ensures that the model captures all chemical interactions in the system. In addition, the performance of empirical correlations for describing mass transfer in the system was compared with that of theoretical-based correlations, in the predicting plant performance. As a result, as both the physical and the chemical behaviour of all components in the system are explicitly represented. This is the first such dynamic model in open literature for the PCC process. The model performance was validated and compared with the performance of the previous model to verify its efficacy. A dynamic analysis then is performed with the model.

Next, the performance of an integrated NGCC, PCC and CO₂ Compression plant was evaluated using validated and well-sized models. A thermodynamic analysis of the impact of exhaust gas recirculation (EGR) on the PCC plant performance, and hence on the integrated plant performance as a whole, was also completed. This revealed that PCC plant energy requirement can be greatly reduced by enhancing mass transfer in the absorber. Then, the feasibility and benefits of supplementary firing (SF) of the gas turbine exhaust on the design of the Rankine cycle and PCC plant performance were explored.

Economic analysis of the integrated plant located in Northern England, was done. Cost estimates were generated via a bottom-up approach, as opposed to the use of cost factors, while economic assumptions were also minimised. Overnight costs, the cost of electricity (COE) and Cost of CO₂ avoided were utilised as to analyse the viability of an NGCC power plant investment with or without CO₂ capture.

Finally, alternate approaches for the integration of the PCC plant in the NGCC plant were explored, with focus given to the retrofitting and operability. SF of the gas turbine was then evaluated as an operational procedure for boosting the plant output when PCC plant is in service.

1.5 Outline of Thesis

Section 2 of this report focuses on literature survey in terms of current energy trends and abatement strategies. Detailed description of capture processes and their application are also provided. Current research trends are highlighted, along with pilot facilities and advances in post-combustion capture technology. Model development strategies are described in Section 3, in conjunction with the modelling, simulation and cost estimation tools that are utilized in this research.

Section 4 covers the dynamic modelling, validation and analysis of a PCC plant with MEA solvent. Attention is given to the improvement of the dynamic PCC absorber model in Section 5. In Section 6, a techno-economic analysis of an integrated NGCC-PCC plant is performed, along with an investigation of the

effects of EGR on the plant. Alternate strategies for PCC plant integration in the NGCC plant are explored in Section 7.

Finally, the conclusions drawn from this work and recommendations for future research efforts are elucidated in Section 8.

1.6 Publications and Conferences

Journal Papers

Biliyok C. & Yeung H. (2013) Evaluation of Natural Gas Combined Cycle Power Plant for Post-Combustion CO₂ Capture Integration; *International Journal of Greenhouse Gas Control*, 19, 396-405.

Canepa R., Wang M., Biliyok C. & Satta A. (2013) Thermodynamic analysis of combined cycle gas turbine power plant with post-combustion CO₂ capture and exhaust gas recirculation; *Proc IMechE Part E: J Process Mechanical Engineering*; 227(2), 89–105

Biliyok C., Lawal A., Wang M. & Seibert F. (2012) Dynamic Modelling, Validation and Analysis of Post-Combustion Chemical Absorption CO₂ Capture Plant; *International Journal of Greenhouse Gas Control*, 9, 428-445.

Conferences

Biliyok C., Canepa R., Wang M. & Yeung H.; Techno-economic analysis of a natural gas combined cycle power plant with CO₂ capture; *Computer Aided Process Engineering*, 2013, 32, 187–192. 23rd European Symposium on Computer Aided Process Engineering (ESCAPE23) 9-12 June 2013, held at Lappeenranta University of Technology, Finland.

Biliyok C., Lawal A., Wang M. & Seibert F.; Dynamic Modelling and Validation of Post-Combustion Chemical Absorption CO₂ Capture Plant (Poster); *PSE Advanced Process Modelling Forum*, 17th-18th April 2013, held at Royal Garden Hotel London.

Biliyok C., Wang M. & Yeung H.; Dynamic Modelling and Validation of Post-Combustion Chemical Absorption CO₂ Capture Plant; *Royal Society of*

Chemistry (RSC) Energy Sector Early Career Energy Sector Chemists Symposium 2012, 17th November 2012, held at Cranfield University. **Winner of Best Fossil Fuel Poster Prize donated by the Coal Research Forum**

Biliyok C. & Wang M.; Improvement of Dynamic Model for Post-Combustion Chemical Absorption; *9th European Conference on Coal Research and It's Applications (ECCRIA9)*, 10th-12th September 2012, held at the University of Nottingham.

Biliyok C., Lawal A., Wang M. & Seibert F.; Dynamic Modelling and Validation of Post-Combustion Chemical Absorption CO₂ Capture Plant; *Computer Aided Process Engineering*, 2012, 30, 807-811. 22nd European Symposium on Computer Aided Process Engineering (ESCAPE22), 17 - 20 June 2012, held at University College London.

Workshops

Biliyok C., Canepa R., Wang M. & Yeung H.; Techno-economic analysis of a natural gas combined cycle power plant with CO₂ capture; *UKCCSRC Early Career Researcher Meeting*, 1st-2nd July 2013, held at Newcastle University.

Biliyok C., Lawal A. & Wang M.; Dynamic Modelling and Validation of Post-Combustion Chemical Absorption CO₂ Capture Plant; *Mathematical Modelling and Simulation of Power Plants and CO₂ Capture*, 20th-21st March 2012, held at the University of Warwick.

2 LITERATURE SURVEY

2.1 Greenhouse Gases and Energy Trends

In 2010, global average temperature and specific humidity was observed to have risen by 0.5°C and 4% respectively, compared to 20th century averages (Miller, 2012). Sea levels have also risen by 19cm due to thermal expansion of oceans and melting of ice across the globe (IPCC, 2013). The consequence has been a dramatic increase in the frequency, intensity and duration of floods, droughts and heat waves globally. Precipitation has increased noticeably in Eastern parts of the Americas, Northern Europe, Northern and Central Asia, while it has declined in the Sahel, Mediterranean, Southern Africa and South Asia (IPCC, 2007).

A recent report by the IPCC (2013) identifies GHG emissions from human activities, with 95% certainty, as the dominant cause of this global warming effect. Figure 2-1 illustrates the World GHG Emissions Flow Chart as of 2000, and shows CO₂ as the most abundant GHG. To avoid further temperature increases, the EU and G8 leaders in 2008 agreed to cut CO₂ emissions by 80% by 2050 so as to stabilise atmospheric CO₂ at 450 ppm, thereby keeping warming below 2°C. This was the global target agreed in December 2009, yet atmospheric CO₂ concentration has already reached 397 ppm, and is rising by 2-4 ppm every year (Mauna Loa Observatory, 2013). Consequently over the past year, a number of troubling trends have emerged (Le Page, 2012):

- The artic is warming faster than predicted as observed from record ice loss in 2012.
- Extreme weather is getting more extreme – record blizzards and heat waves in North America, record deluges in the UK
- Food production is falling, caused by droughts mainly in North America.
- Sea levels are rising faster than expected due to melting ice sheets in Greenland and Antarctica.
- GHG levels could keep rising even if our emissions stop as a result of melting permafrost globally, which release trapped CO₂.

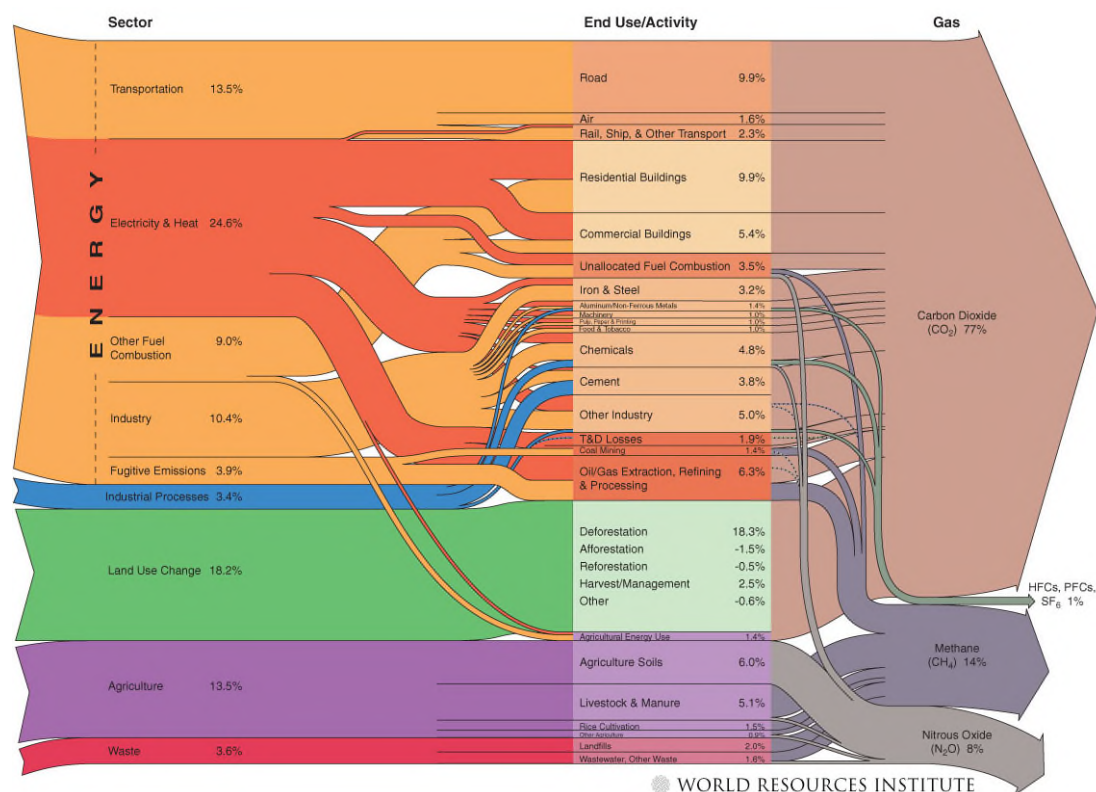


Figure 2-1: World GHG Emissions Flow Chart (World Resources Institute, 2008)

The IPCC (2007) estimates that 69% of all CO₂ emissions and 60% of all GHG emissions are derived from stationary sources like power plants, and Figure 2-1 shows electricity and heat i.e. power generation as the biggest single contributor of GHG emissions.

Although renewable energy supply has grown in recent years due to market-creating policies and cost reductions, the growth of fossil fuels has matched — or even outpaced it — as coal and gas have met 80% of new energy demand globally over the past decade (IEA, 2011), and are projected to continue to do so, according to Energy Information Administration (EIA) estimates (Figure 2-2). Hence, CO₂ emissions are expected to rise from 29.7 billion tonnes in 2007 to 33.86 and 42.4 billion tonnes in 2020 and 2035 respectively.

There is also a rising difference the manner in which energy demand is being met between developed countries, which make up the Organisation for Economic Co-operation and Development (OECD), and non-OECD regions, which are led by BRICS countries.

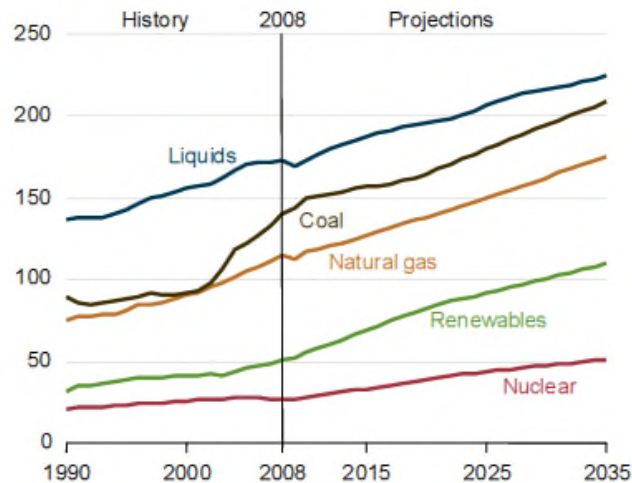


Figure 2-2: Projected World Energy Consumption (Quadrillion BTU) (EIA, 2011)

Growing energy demand in non-OECD countries is largely met by coal, while in OECD countries it is met by natural gas and renewable energy; especially wind (IEA, 2011). In fact, energy consumption in developing countries has now overtaken that in the developed world, with China and India leading the way (Clark, 2011). Even if the OECD countries succeeded in completely eliminating their emissions, emissions from non-OECD countries would still lead to a greatly different climate dominated by extreme weather events, if we remain on today's path. Thus, international agreements are required, accompanied by strict enforcement to meet realistic emissions reduction targets.

2.2 Emission Abatement Strategies

With no firm global action against climate change, temperatures might increase to 6°C by 2050 (IEA, 2013). With the IEA (2011) projecting fossil fuel prices to increase significantly over the coming years regardless, they have come up with a number of scenarios for cutting global emissions in a cost effective manner. For example, the 2 Degrees Scenario (2DS) sets a goal of halving global energy-related CO₂ emissions by 2050 (compared to 2009) and ensure that emissions continue to fall thereafter, by deploying existing low-carbon technologies so as to limit temperature rise to 2°C. Figure 2-3 shows how different technologies contribute to meeting the targets of 2DS compared to a path where no action is taken.

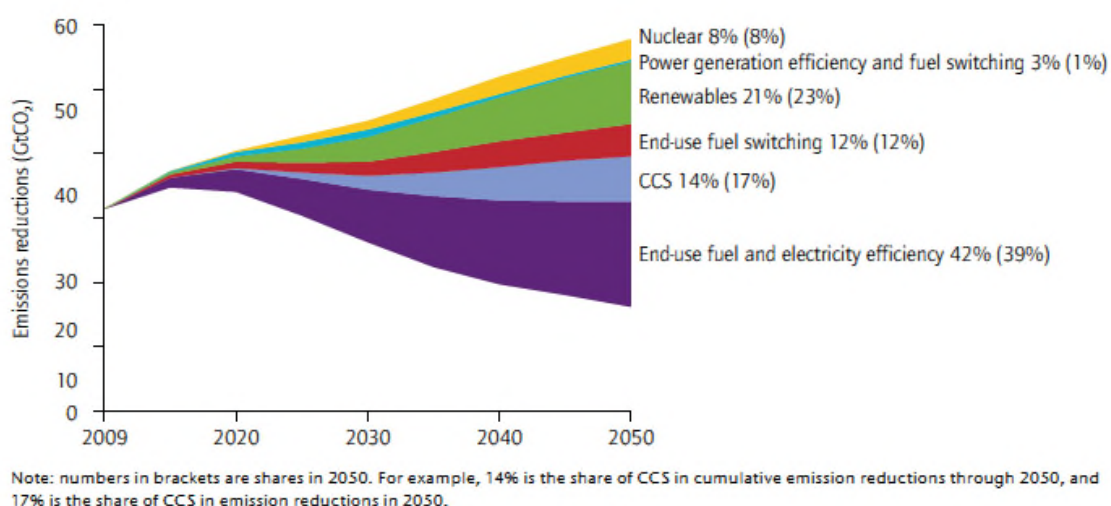


Figure 2-3: Key Technologies for the 2DS (IEA, 2013)

In 2DS, CCS is projected to play a major role and contribute 17% of emission cuts by 2050. This translates to 130 large-scale projects are needed by 2020, and 3400 by 2050 (IEA, 2012). With 12 such facilities currently operating, 8 under construction and a further 45 being planned (Global CCS Institute, 2013), meeting the 2DS target would be challenging. There is also considerable uncertainty on how many of these projects will be realised, in light of cancellations this year of PGE's Belchatow project (Poland) in April, Tenaska Trailbrazer (USA) in June and StatOil's Mongstad project in September (CC&ST, 2013a). In addition, available public funding for large-scale demonstration projects (USD25 billion) is insufficient (IEA, 2011). Still, as projected by 2DS, a total cumulative of about 120Gt of CO₂ would need to be captured and stored around the world between 2015 & 2050.

2.3 Carbon Capture and Sequestration

The process of CCS (Figure 2-4) involves the capture of CO₂, compression and transport to storage sites via pipelines or ships, then storing the CO₂ in geological formations like saline aquifers, depleted petroleum reservoirs and coal seam beds. Studies of potential GHG mitigation strategies have found that a minimum of 90% CO₂ capture from stationary emitters like power plants is required before substantial impact can be made in stabilizing atmospheric CO₂ levels (Ciferno et al., 2010), underlining the urgency of CCS deployment.

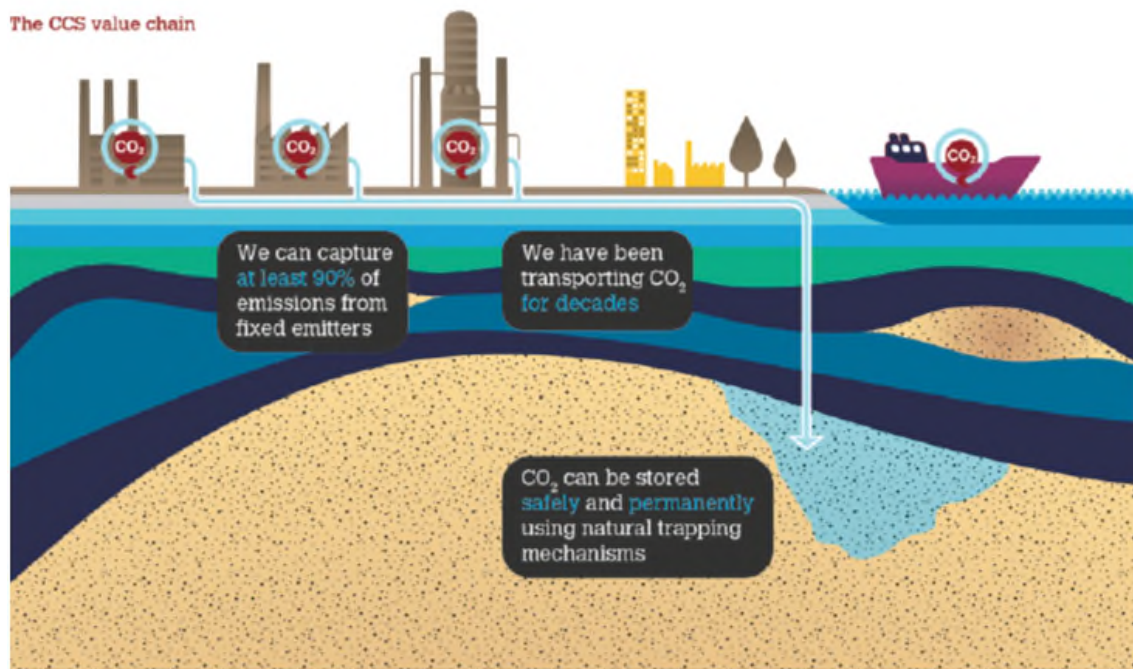


Figure 2-4: CO₂ Capture and Storage System (Zero Emissions Platform, 2012)

Meeting the CCS targets of 3400 industrial-scale CCS projects by 2050 would require a colossal undertaking in terms of infrastructure and storage capacity, necessitating the construction of over 200,000km of pipelines for transport of captured CO₂ (IEA, 2009b). To efficiently transport CO₂ by pipeline, it has to remain in a supercritical state, equivalent to very dense gas behaving as liquid. Either compression or a combination of pumping/refrigeration is required for supercritical CO₂ to be transported to sites for safe underground storage or use in EOR (Ciferno et al., 2010). CO₂ becomes supercritical at a temperature of 31°C and pressure of 74bar, increasing its density approximately 235 times. The presence of impurities can exert significant changes on the properties of the CO₂. For instance, nitrogen can drastically reduce its supercritical point, so that far greater energy is required for compression and transport (Davies, 2010).

Monitoring, verification and accounting (MVA) capabilities will be critical to ensuring the long-term viability of CCS, i.e. satisfying both technical and regulatory requirements. This encompasses the ability to measure the amount of CO₂ stored at a specific storage site, to monitor the site for leaks, to track the location of the underground CO₂ plume, to verify that the CO₂ is stored

permanently, validate simulations, and optimize injection operations and mitigation strategies (Ciferno et al., 2010). A key challenge for carbon storage is the development of robust, equitable, and transparent accounting procedures with the flexibility to adjust to future regulatory and market situations.

The distance of a storage site from the stationary emitter is the most important factor that drives transport costs. The Carbon Sequestration Atlas of the US and Canada shows that over 40% of current U.S. coal-based power plant capacity is located directly above potential geologic sequestration sites, yet NETL estimates that using available CCS technologies would increase COE of a new coal-fired plant, an NGCC plant and COE of a new advanced gasification-based plant by 80%, 60% and 35% respectively, due to additional energy and operational requirements (Ciferno et al., 2010). So efficiency improvements in power plants and reduction of CCS energy requirements are vital. Recently constructed coal plants are highly efficient, emitting around 800kg CO₂ per MWh (Insight Economics, 2011), compared to a global average of more than 1Mt CO₂ per MWh (IEA, 2011). On-going improvements in gas turbine technologies, is also expected to provide significant boosts to NGCC and gasification-based plant efficiencies.

According to 2DS, in addition to power plants, CCS must be employed on a variety of stationary emitters such as iron/steel plants, refineries and cement plants. By 2050, it is projected that 70% of CCS projects would need to be implemented in non-OECD countries, where the largest share of global industrial growth will take place (Figure 2-5). However, the cost of deploying current CCS technologies is very high, and a number of technical challenges and commercial risks also remain, including possible community opposition. For CCS to become commercially viable, a strong regulatory framework and a manageable risk exposure are required (Zero Emission Platform, 2011). Public outreach is also critical as projects like Barendrecht in the Netherlands, have been cancelled due to public opposition (IEA, 2011).

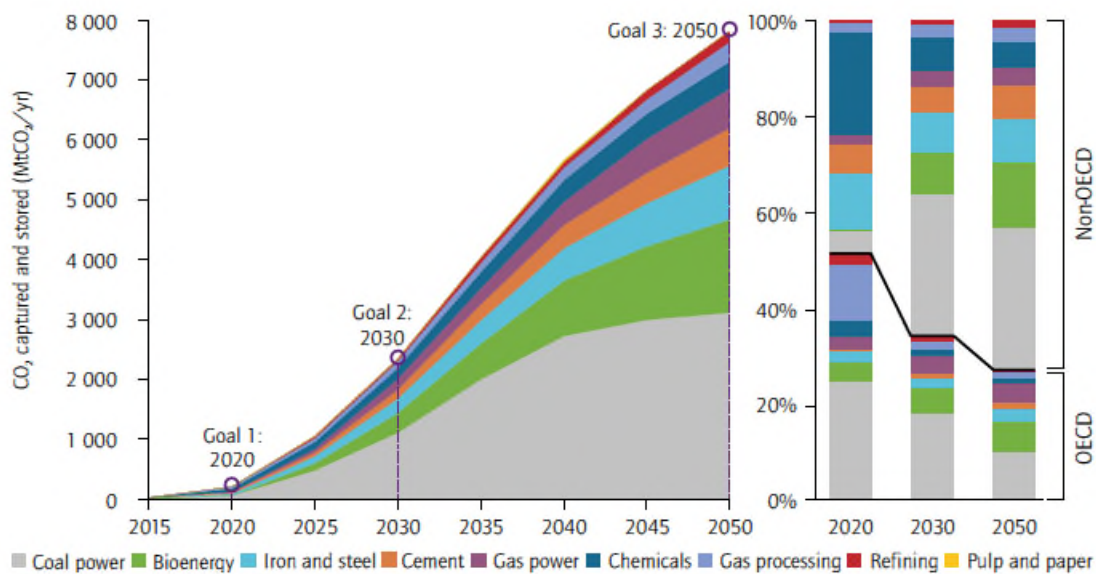


Figure 2-5: CCS in Power and Industrial Sectors in 2DS (IEA, 2013)

2.4 Capture Technologies

There are different technologies that can be applied to CO₂ capture (Figure 2-6), with the choice mainly driven by the concentration or partial pressure of CO₂ in the gas stream. Absorption technologies use a solvent that must be thermally regenerated after CO₂ has been absorbed, introducing considerable energy requirements for the process. Chemical solvents are used when CO₂ partial pressures are lower than 15%, and require substantial energy to regenerate. Physical solvents require less energy, and are used when there is larger partial pressure of CO₂. Adsorbent beds and membranes require CO₂ partial pressures well above 20% to be effective, while cryogenic separation involves CO₂ condensation from the flue gas via refrigeration (IEA, 2004).

Three distinct approaches to CO₂ capture from power plants using these technologies have emerged. Descriptions are adapted from the NETL CCS RD&D Roadmap (Ciferno et al., 2010).

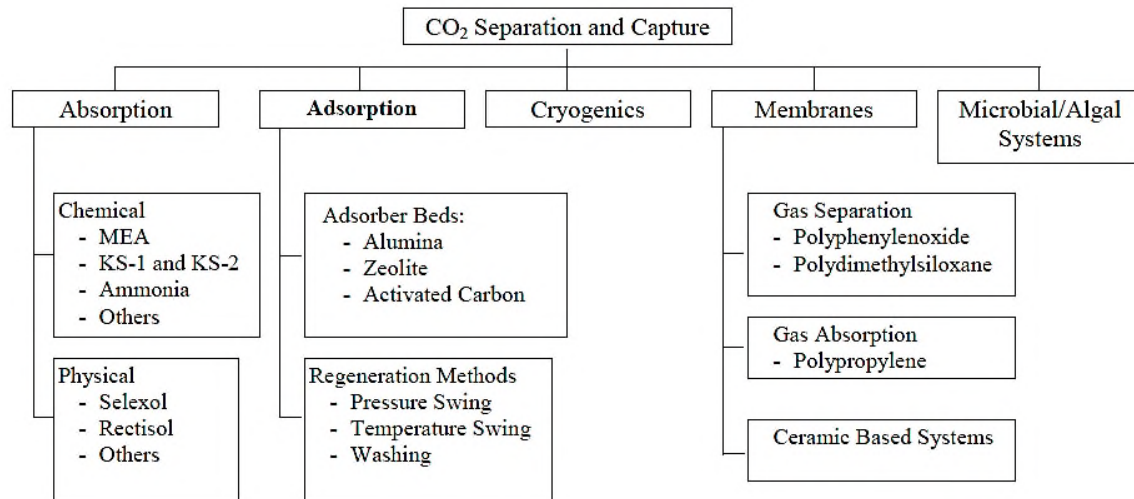


Figure 2-6: CO₂ Capture Technology (Rao and Rubin, 2002)

2.4.1 Pre-combustion Capture

Pre-combustion capture is mainly applicable to integrated gasification combined cycle (IGCC) plants, where fuel (coal or biomass) is converted to synthesis gas (syngas) by applying heat under pressure in the presence of steam and sub-stoichiometric oxygen (O₂). The produced syngas is a mixture of hydrogen (H₂) and carbon monoxide (CO), with minor amounts of other gases. To enable pre-combustion capture, the syngas is further processed in a water-gas-shift reactor, converting CO into CO₂ and producing more H₂, thus increasing the CO₂ and H₂ concentrations. CO₂ is separated from the H₂ prior to combustion by absorption using physical solvents like the glycol-based Selexol™ or the methanol-based Rectisol®, which are only effective with high partial pressures of CO₂. The H₂-rich syngas is then used as a fuel in a combined cycle to generate electricity.

2.4.2 Oxyfuel Combustion

Oxyfuel combustion is applicable to both new and existing coal-fired power plants. Coal is burnt in pure O₂, diluted with recycled CO₂ or CO₂/steam mixtures, producing mostly water and CO₂. CO₂ concentration is around 60%, so water is further removed by condensation via cooling and compression. Minor products of combustion like excess O₂, SO₂, and NO_x, may also be removed to produce a relatively pure CO₂ stream. However, co-sequestration of

CO₂ with minor amounts of such gases could be technically acceptable, as demonstrated successful H₂S/CO₂ injection experience in EOR. The appeal of Oxyfuel-combustion is tempered by a few key challenges: significant capital costs and energy consumption for air separation unit, boiler air infiltration that dilutes the flue gas with nitrogen, and excess O₂ contained in the concentrated CO₂ stream. Flue gas recycle (~70 to 80%) is necessary for Oxyfuel-combustion retrofit to existing air-fired boilers in order to match the boiler combustion and heat transfer characteristics of combustion with air.

2.4.3 Post-Combustion Capture

PCC involves CO₂ removal from the flue gas produced from fossil fuel combustion. It is primarily applicable to conventional coal-fired power plants, but could also be used in IGCC and NGCC plants. In a typical coal-fired power plant, fuel is burned with air in a boiler to produce steam that drives a turbine to produce electricity. Flue gas from the boiler consists mostly of nitrogen and CO₂. The CO₂ capture process would be located downstream of the pollutant controls for nitrogen oxide (NO_x), particulate matter (PM), and sulphur dioxide (SO₂). Chemical absorption technologies used for acid gas removal in the oil and gas industry are most suited to this application. The chemical solvent regeneration requires the extraction of a relatively large volume of low-pressure steam from the power plant's steam cycle, decreasing the gross electrical generation. In addition, separating CO₂ from this flue gas is challenging for several reasons:

- High volume of flue gas must be treated (~1 mil. L/s for 550MWe plant);
- CO₂ is dilute (<14% CO₂ for PC plants & <5% for NGCC plants);
- Flue gas is at atmospheric pressure and requires a large auxiliary power load to compress to pipeline pressure; and
- Trace impurities (PM, SO₂, NO_x, etc.) can degrade chemical solvent.

In spite of the low CO₂ concentration in the flue gas, amines are capable of achieving high levels of CO₂ capture due to strong chemical reactions.

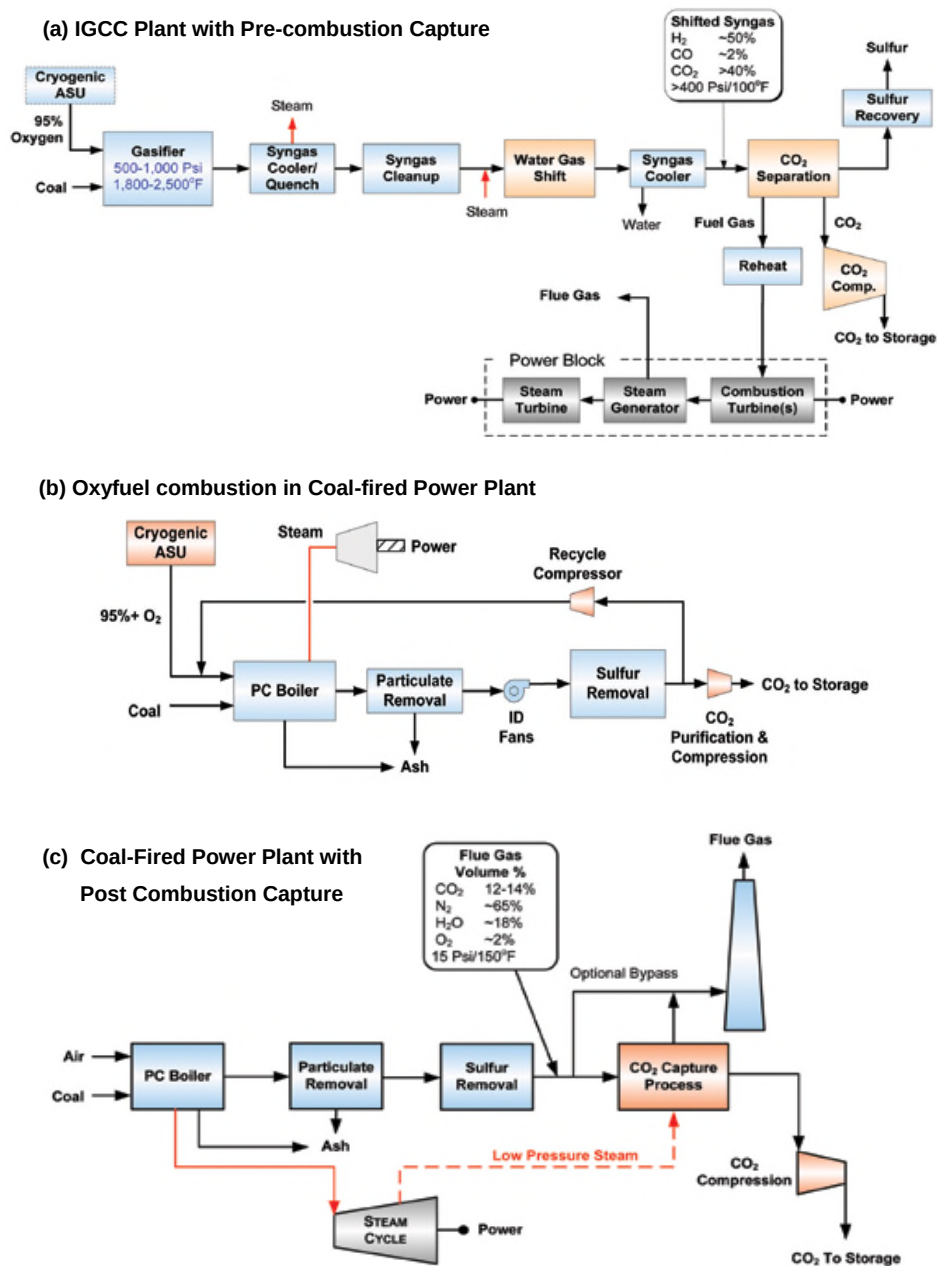


Figure 2-7: Process Schematic of Capture Approaches (Ciferno et al., 2010)

2.5 Challenges of Carbon Capture

2.5.1 Cost-Effectiveness

Considering a nominal 550-MWe net output coal-fired power plant (Ciferno et al., 2010), the addition of CO₂ capture increases the capital cost by \$900 million, \$700 million and \$400 million for a PCC, an Oxyfuel-combustion capture and an IGCC facility respectively, with energy penalties increases of 30%, 25%

and 20%. For an NGCC plant, the capital cost would increase by \$340 million and an energy penalty of 15% would result. The resulting levelized cost of electricity (LCOE) and CO₂ avoided costs due CO₂ capture are shown in Figure 2-8. Improvements to CO₂ capture and compression processes, along with the development of advanced capture technologies, are vital for cost reduction.

2.5.2 Capture and Compression Parasitic Power

Net output from a PC power plant with CO₂ capture and compression is significantly less than that for the same plant without capture. Energy produced at the plant must be used to operate the CO₂ capture and compression processes. Figure 2-9 shows the change in net plant efficiency as a result of implementing available CO₂ capture and compression technologies on conventional PC, IGCC, and NGCC power plants.

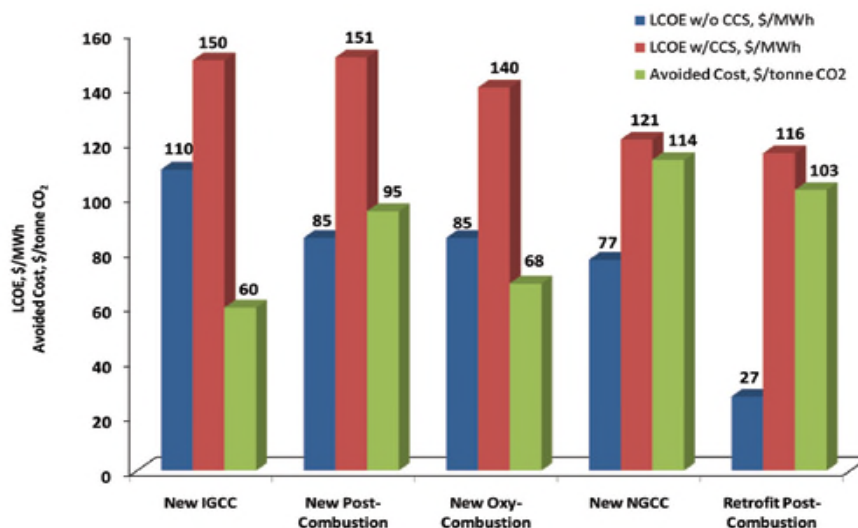


Figure 2-8: Cost Comparison of Different Power Plants (Ciferno et al., 2010)

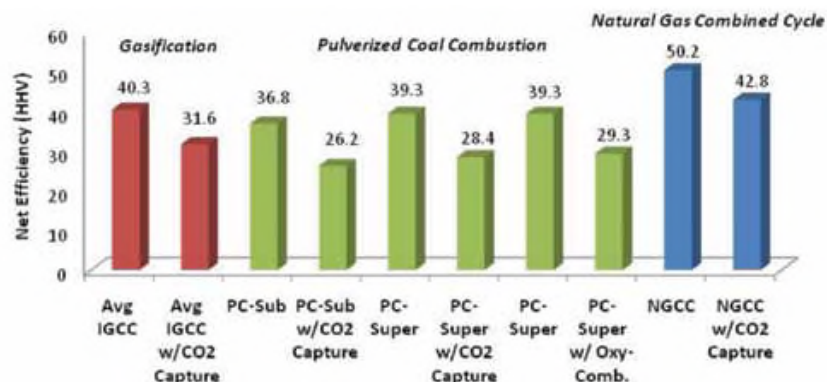


Figure 2-9: Net Efficiency with or without Capture & Comp. (Ciferno et al., 2010)

2.5.3 Integration with Existing Plant Infrastructure

As the energy required to regenerate the solvent in current technologies would mostly be provided by steam extraction from the power plant, a careful integration of the power plant steam cycle to the CO₂ capture process would be required. A high level of integration is necessary to optimize both power generation and CO₂ capture efficiencies under all operating conditions.

2.5.4 Plant Control and Flexibility

The control philosophy of a power plant dictates that net output changes to match power demand, leading to load fluctuations. For a chemical process like CO₂ capture, process control involves damping of disturbances to meet product specifications of quality and quantity. Managing these competing requirements in an integrated plant requires some ingenuity. In addition, the differing process speeds between power plant and CO₂ capture adversely impact on operating procedures like start-up, shut down, and load cycling.

2.5.5 Cooling Water Requirements

CO₂ capture and compression requires ample quantities of cooling water. The impact of this has been evaluated for subcritical, supercritical, and IGCC power plant configurations on water withdrawal and consumption requirements (Figure 2-10). Water consumption is used to describe the loss of withdrawn water, typically through evaporation into the air, which is not returned to the source.

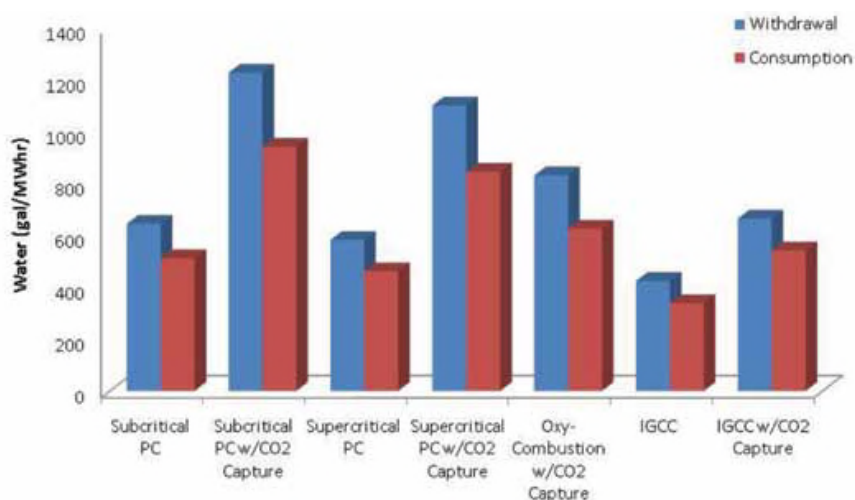


Figure 2-10: Water Requirement Comparison (Ciferno et al., 2010)

2.5.6 Plant Layout

In view of the sizes of process equipment that have been proposed for current capture technologies, a substantial floor space would be required. This footprint introduces layout problems, with difficulty arising in the locating piping and plant supports that link the CO₂ capture process to the power plant.

2.5.7 CO₂ Capture Impacts on Existing Plant Retrofits

EIA estimates that 95% of the coal-based CO₂ emissions in the US projected to be released through 2030 will originate from existing coal-fired power plants. Therefore, retrofits for CCS will likely be required on a large portion of existing plants. Retrofitting is anticipated to be more challenging than new builds, as depending on plant age and/or size, CCS might not be cost-effective for existing power plants. If a plant is too old, or too small, owners may not be able to justify the large capital investment required to retrofit CCS. The space requirement for CO₂ capture retrofit may also be a problem. And it is likely that optimizing the energy integration of the CO₂ capture and compression system with an existing plant's steam cycle will be more difficult than for a new plant.

2.6 Post Combustion Capture with Chemical Absorption

The Post-combustion CO₂ capture process through chemical absorption using MEA solvent is the most mature capture approach (MacDowell et al., 2010). It involves the use of at least two packed columns, an absorber and a regenerator. Flue gas from a power plant, reduced to temperatures of 40 – 50 °C, is introduced to the bottom of the absorber at atmospheric pressure and an amine solution (about 30wt%) is fed in at the top. CO₂ in the flue is absorbed into the solvent, and the treated gas exits the absorber, without 80 – 95% of the CO₂ originally in the flue gas. Often a water wash section is provided in the column to trap fugitive amine that can escape to the atmosphere, while also maintaining a water balance in the column, which is lost through vaporisation caused by heat released from exothermic absorption of CO₂.

The rich amine solution, containing the absorbed CO₂, is pressurised to 4bar to prevent flashing before it is sent to the top of the regenerator via a cross heat

exchanger. As the solvent falls through the packing, the chemical bonds of CO₂ and the amine are broken up thermally (heat provided by steam in the reboiler) and the rising CO₂ and water vapours acts as stripping agents, releasing more CO₂ vapour. Water is condensed and returned as reflux to the top of the regenerator, leaving a high purity CO₂ vapour stream (up to 95%) exiting the condenser, from where it can be compressed and transported.

The temperature at the bottom of the regenerator is kept below 125°C to avoid the thermal degradation of amine. The lean amine solution, having lost much of its CO₂, exits the reboiler and exchanges heat with the rich solution in the cross heat exchanger. It is then returned to the top of the absorber to close the process loop. A cooler is usually required for temperature control, and a make-up vessel to cater for solvent losses.

Solvent degradation is also caused by the presence of SO_x and NO_x gases in the flue gas, which form heat stable salts with amines, and therefore must be removed using a desulphurisation unit for SO_x and an electrostatic precipitator for NO_x. Oxidative degradation of the solvent due to O₂ in the flue gas is also a problem, but it can be minimised by treating the amines with oxygen inhibitors.

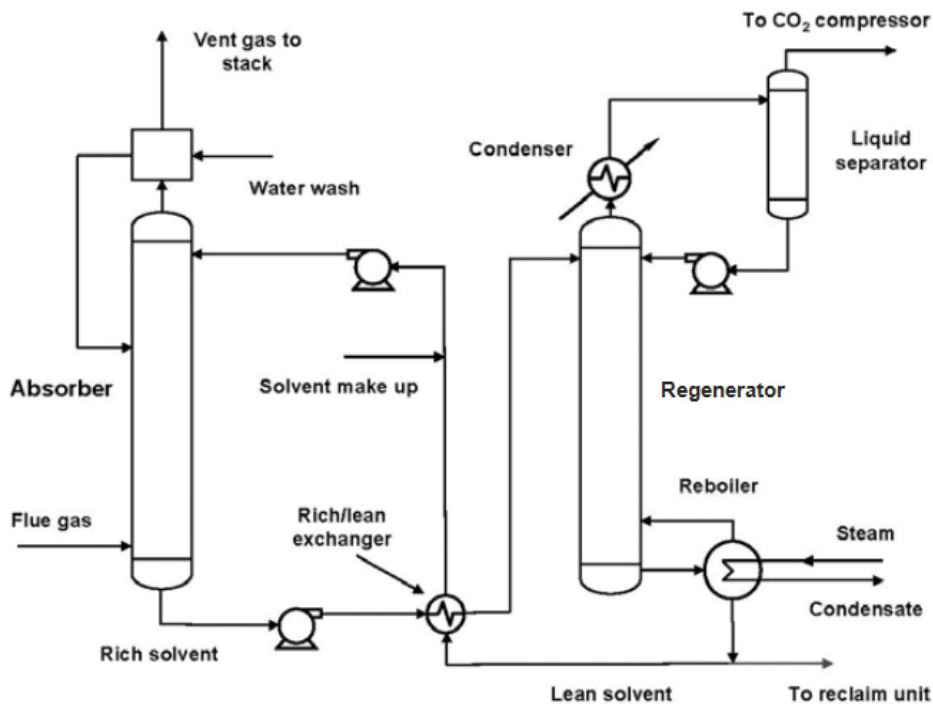


Figure 2-11: Flow Diagram of PCC Process (Global CCS Institute, 2012)

NETL conducted a study to determine the cost and performance of a PCC technology retrofit on a coal-fired unit and determined that the process would require extraction of approximately 50% of the steam that normally flows through the low-pressure turbine for a 90% CO₂ capture (Ciferno et al., 2010). This combined effect of a steam draw and auxiliary power requirements for capture and compression, resulted in a 30% decrease in net power output.

Ciferno et al. (2010) estimated the theoretical minimum energy required for CO₂ capture and compression to be 440kJ/kgCO₂ and the energy required for a state-of-the-art MEA-based solvent PCC process to be 1,500kJ/kgCO₂, translating to a thermodynamic efficiency of about 30%. This poor performance can be improved with smart design modifications. Yet, PCC process designs with very high efficiencies will also be expensive due to the addition of costly equipment required to achieve these efficiencies. An optimum must be found that balances decreased operating costs due to improved efficiency against the additional capital costs associated with higher efficiency process designs. This optimal design can be investigated through demonstration plants or through process modelling and simulation. Pilot/demonstration plants that are currently operating are listed in Table 2-1.

It is important to note that while demonstrations can result in limited improvements over time, it is unlikely to provide the significant step changes in cost and performance required to make CO₂ capture more economically viable. Significant process modifications and new process designs are required. This underlines the importance of modelling and simulation CO₂ capture.

Table 2-1: Pilot/Demonstration PCC Facilities in Operation (CC&ST, 2013b)

Pilot Plant	Company	Location	Size	Operational
Shidongkou	Huaneng	China	0.1Mt/yr	2011
Brindisi	Enel &Eni	Italy	48MW	March 2011
Mongstad	StatOil	Norway	0.1Mt/yr	May 2012
Plant Berry	Southern Energy	USA	25MW	August 2012
Ferrybridge	SSE	UK	5MW	November 2012
Aberthaw	RWE	UK	3MW	January 2013

2.7 Integration of PCC in a Power Plant

Natural gas is expected to continue to play an important role in the global energy mix as shown in Figure 2-2. The proliferation of hydraulic fracturing technology in the US, which enables the production of gas from shale formations, has increased the significance of natural gas. This unconventional gas production has engendered a glut, and hence, cheap gas in the US, which led to the recent approval of LNG exports by the US government. Thus, there presently exists enormous global interest in shale gas production, as countries like the UK, China and Argentina taking steps to harness their unconventional gas reserves.

A lot this gas is used for power generation in NGCC power plants. As these plants produce about half the emissions that PC power plants generate, net GHG emissions fall noticeably, as witnessed in the US over the past couple of years (EIA, 2012). Yet even if all coal consumption were replaced with natural gas, the reductions would not be enough to meet the global emission reduction targets proposed by the IPCC (2007). Therefore, analysis of implementation of CO₂ capture on NGCC plants is essential.

2.7.1 Natural Gas Combined Cycle Power Plants

Power is generated in an NGCC power plant through integrated Brayton and Rankine Cycles. Natural gas is fired in compressed air to release its thermal energy, and the combustion products are then expanded in a gas turbine to generate power. The turbine exhaust gas is fed into a heat recovery steam generator (HRSG), where heat is captured to complete the Brayton Cycle and produce pressurised steam for the Rankine Cycle. The steam is then expanded in steam turbines to also generate power. These combined cycles (Figure 2-12), depending on the gas turbine utilised, are able to achieve net efficiencies approaching 62% based on the gas lower heating value (LHV).

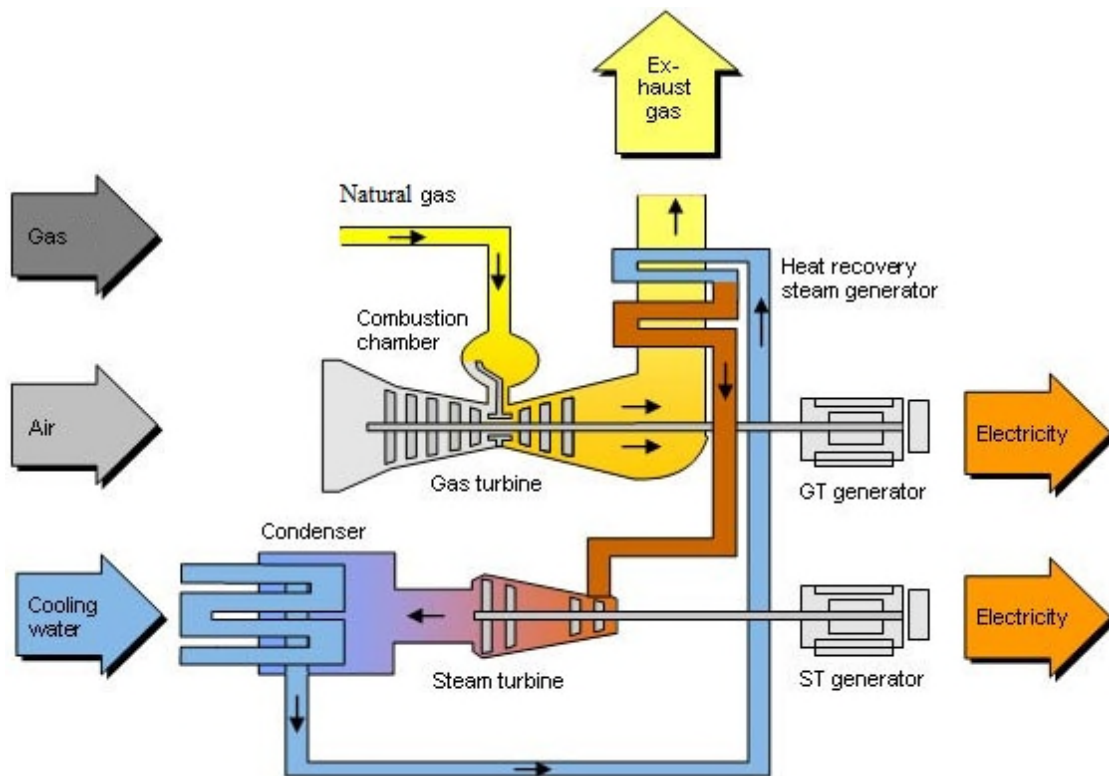


Figure 2-12: Natural Gas Combined Cycle Power Plant (Siemens, 2012)

Compared to coal-fired power plants, an NGCC power plant has the following advantages:

- Lower capital outlay
- Half the CO₂ per MWh, along with negligible SO_x and particulates.
- Lower environmental profile i.e. less than a quarter of the footprint.
- High operational flexibility, easily handling cyclic loading.
- Smaller number of staff requirement, hence lower operating costs.
- Reliability, leading to lower risk, and hence cost of capital.

2.7.2 NGCC and PCC Integration Modelling Research Activity

As highlighted in Section 2.4.3, a PCC plant using chemical solvent can capture CO₂ from the exhaust/flue gas exiting an NGCC plant. While integrating a PCC plant, it is important that the advantages of investing in and operating an NGCC plant are maintained. A number of daunting challenges are encountered, most of them already covered in Section 2.5 of this report. However, a problem that is specific to NGCC plant is the low CO₂ concentration in the flue gas, which is

less than 5Vol% (Amann and Bouallou, 2009). This results in large flow rates of flue gas would need to be processed, requiring large equipment (packed columns, heat exchangers and vessels), a lot of solvent circulation and hence, large amount of steam for solvent regeneration. Therefore, a key element of integration is exhaust gas recirculation (EGR), which involves the return of part of the NGCC exhaust gas to the inlet of the air compressor. EGR can increase the CO₂ concentration in the flue gas to 8Vol%, leading to a smaller PCC plant for integration and reduced regeneration energy. Consequently, a lot of conceptual and modelling work has been recently undertaken to assess the viability of integrating a PCC plant in an NGCC power (Figure 2-13).

Berstad et al. (2011) performed a parametric study of NGCC, coal-fired and biomass-fired power plants with PPC and CO₂ compression, and found that although the NGCC plant had the largest specific electricity losses, its energy penalty for was the smallest among the three. Botero et al. (2009) evaluated the best integrated concept for a PCC plant for a 400MW NGCC power plant by assessing the process performance and economics. They also considered compression requirements, EGR and integration of the PCC reboiler into the power plant HRSG. Sipöcz and Tobiesen (2012) performed a similar analysis on a 440MW plant, considered the impact of EGR, and found it to be beneficial to the integrated process. Amrollahi et al. (2012) compared different PCC plant configurations integrated to an NGCC plant and found that combining absorber intercooling with vapour recompression introduced a smaller energy penalty to the power plant. Peeters et al. (2007) performed a techno-economic analysis of NGCC plant linked to PCC and CO₂ compression plants, and considered technological improvements in the short, medium and long terms. Singh et al. (2011) performed a life cycle assessment of a CCS chain of NGCC plant, PCC plant, CO₂ transport and storage, and found that 90% CO₂ capture can reduce global warming potential by 64%.

Most models used for the analyses covered were not validated. Therefore, high fidelity models of an NGCC power plant integrated with a PCC plant and compression train are required for robust and rigorous analysis.

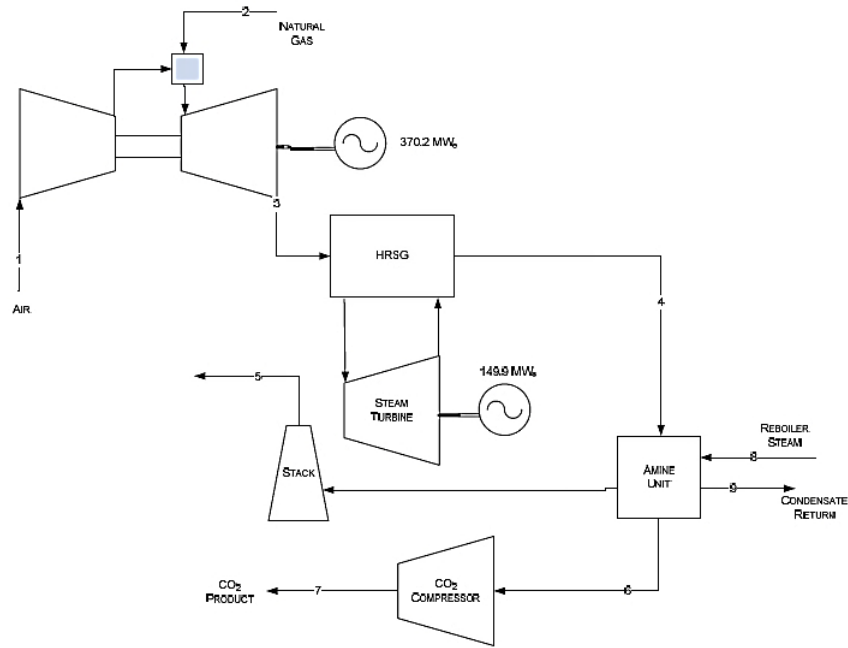


Figure 2-13: NGCC with Post-Combustion Capture (Skone and James, 2010)

2.8 Research Trends in PCC Absorption Technology

Research focus in PCC has been primarily on reducing the energy needed for solvent regeneration and on other capture mediums, to lower the parasitic load on a power plant. Reducing the investment costs of installing a capture plant is also an important target as large scale capture plants would require enormous columns and possibly, multiple trains of equipment (Ciferno et al., 2007) .

2.8.1 Alternative/Advanced Solvents

A lot of effort has gone into finding on solvents that can replace amines in the conventional PCC process that possess higher absorption capacity, faster reaction rates with CO_2 , and lower heat of absorption, which translates to smaller regeneration energy requirements. Secondary and tertiary amines such as diethanolamine (DEA) and methyl-diethanolamine (MDEA) respectively, have greater CO_2 absorption capacity with slower reaction rates. Therefore, amine blends – primary, secondary and tertiary – have been proposed to take advantage of the strength of each solvent (Adeosun and Abu-Zahra, 2013).

A promising alternative to amines is ammonia (NH_3), which being relatively cheap, ticks the boxes of having a relatively high CO_2 absorption capacity and

lower heat of absorption compared to MEA, yet with a drawback of slower reaction rates. It is not as corrosive as MEA and can be used as a multi-component capture solvent for SO_x and NO_x (Wang et al., 2011). NH_3 -based PCC can be operated either as an aqueous NH_3 process taking place at ambient temperature (25-40°C), which has a downside of substantial NH_3 slip to the atmosphere, or a chilled ammonia process (CAP) at a low temperature (2-10°C), which minimises NH_3 slip but introduces a significant cooling duty (Bandyopadhyay, 2011). Alstom Power (2011), who own the patent of the CAP, ran a demonstration that proved the efficacy of the process, and estimated that the COE generated by a coal-fired power plant fitted with CCS will be €0.65-0.85/kWh when the technology is commercially available in 2015.

Another alternative solvent is potassium carbonate (K_2CO_3), with advantages similar to NH_3 . In addition, it does not degrade thermally, but is also known to have slower reaction kinetics compared to MEA. The use of piperazine as a promoter for K_2CO_3 to enhance reaction rates results in superior performance over MEA (Rochelle et al., 2007). A number of commercial proprietary solvents also exist, claiming improved performances and advantages over MEA such as Fluor's Econamine FG Plus solvent, Mitsubishi's KS-1™, Cansolv's DC-103™, Hitachi's H3-1™, KEPCO's KoSol-3™, and so on.

Ionic liquids (ILs) are being considered as solvents for CO_2 capture, with a potential of reducing regeneration energy by 16% compared to MEA (MacDowell et al., 2010). ILs are composed entirely of ions, non-volatile at ambient conditions and have melting points below 100°C. ILs can be used as "designer solvents", as the cation and anion can be independently manipulated to tailor solvent properties to specific process needs. Also, ILs have desirable capture properties: a large liquid range, high thermal stability, extremely low volatility and good CO_2 solubility. A pressure-swing approach has been proposed, where CO_2 is preferentially absorbed from other gases and the IL is regenerated through a pressure decrease, with zero solvent loss, owing to the very low volatility of ILs. Thermal solvent regeneration is also possible, and could be very efficient if the CO_2 is physically absorbed into the IL.

2.8.2 Capture Plant Configurations

PCC configuration changes that can reduce the reboiler heat duty requirement, enhance the absorption of CO₂ or do both are being explored. They include:

- Addition of intercooling to the absorber (Aroonwilas and Veawab, (2007)
- Split flow of solvent into absorber and/or regenerator (Towler et al., 1997)
- Vapour recompression in regenerator (Woodhouse and Rushfeldt. (2008)
- Reduction of rich solvent into regenerator

The intercooler process configuration (Figure 2-14) is of particular interest, due to the exothermic nature of CO₂ absorption in amine-base solvents, which results in a temperature bulge that impacts absorption negatively (Kvamsdal and Rochelle, 2008). The location of this bulge in the absorber depends on the liquid to gas flow (L/G) ratio. At such locations the solvent can be extracted, cooled, and then sent back into the absorber to continue CO₂ capture with an enhanced absorption driving force (Cousins et al., 2011).

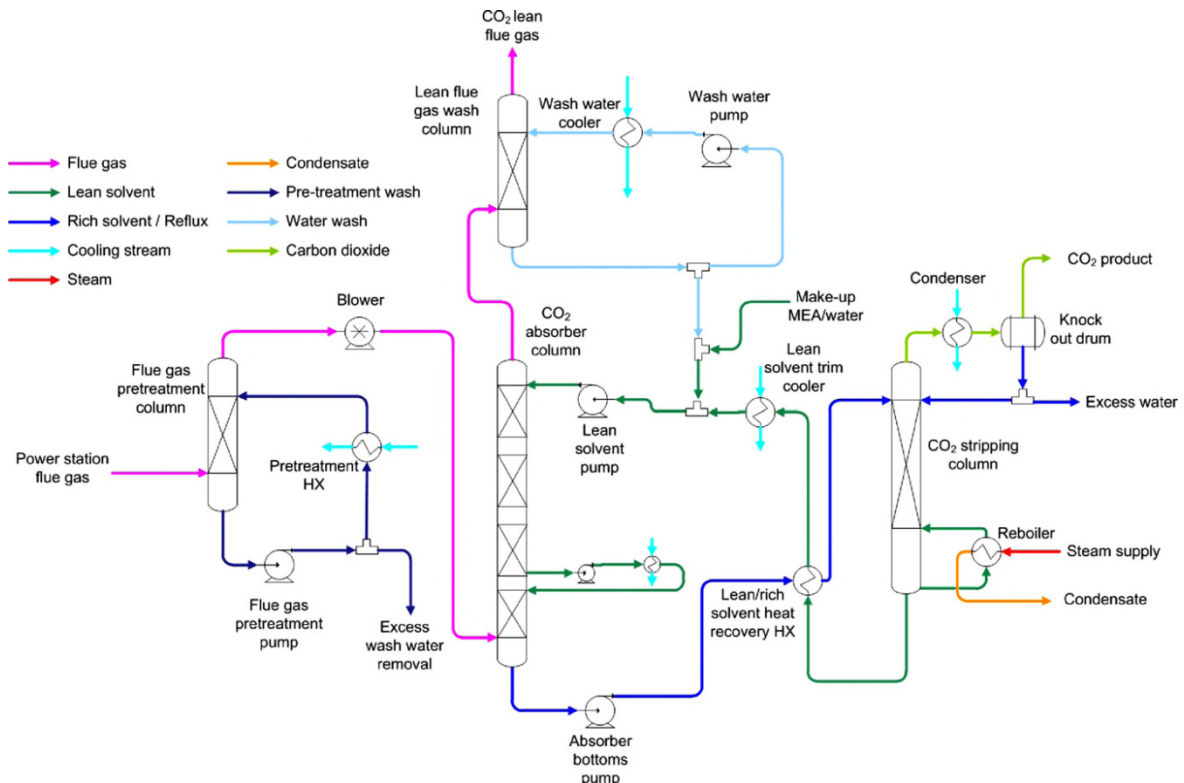


Figure 2-14: Intercooled Absorber Configuration (Cousins et al., 2011)

In a rich split flow process (Figure 2-15), the regenerator is split in two or more stages, and vapour released from the heated portion of the solvent acts as the stripping agent on the cold rich solvent entering the top of the regenerator, thermally regenerating less solvent, and hence reducing regeneration energies.

A lean split configuration (Figure 2-16) involves feeding lean solvent to different stages of the absorber. A temperature bulge is minimised as the multiple lean solvent inlets ensure that CO₂ absorption takes along the length of the absorber, maintaining a driving force. Solvent regeneration energy for this configuration was determined to be 11.9% less than the conventional process (Knudsen et al., 2009).

In a split flow process (Figure 2-17), the absorber and regenerator are both split in two or more stages, and partially regenerated solvent is recycled between the middle stages. This ensures less solvent regeneration, reducing the energy requirement, while also providing intercooling for the process.

The vapour from the reboiler can be compressed before it is introduced into the regenerator to provide additional stripping, thereby reducing the energy required for solvent regeneration, although at the expense of increased investment in a compressor and electricity consumption for the compressor (Figure 2-18).

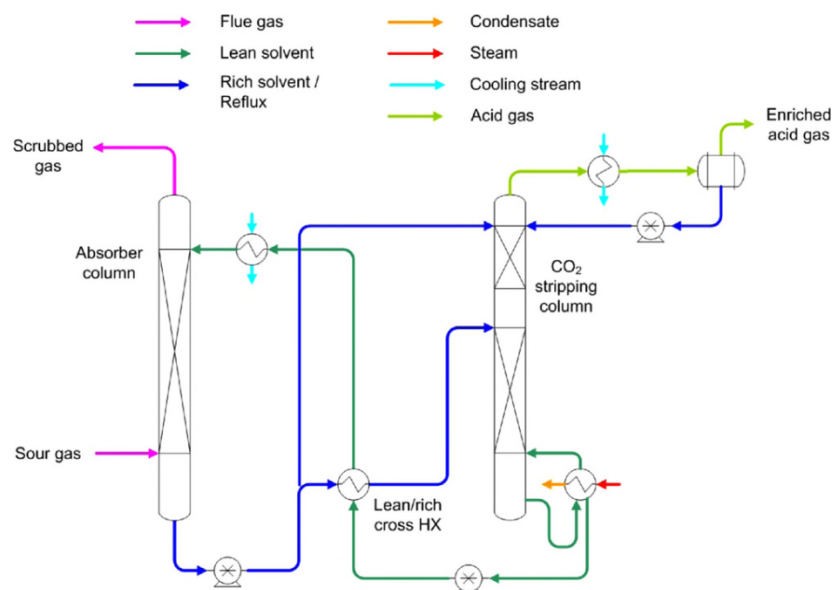


Figure 2-15: Rich Split Configuration (Cousins et al., 2011)

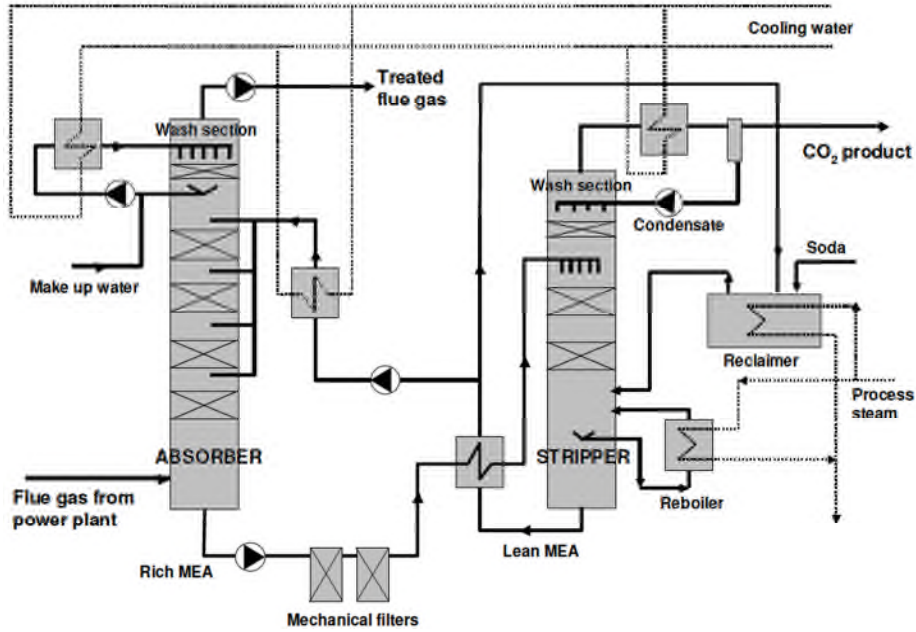


Figure 2-16: Lean Split Configuration (Knudsen et al., 2009)

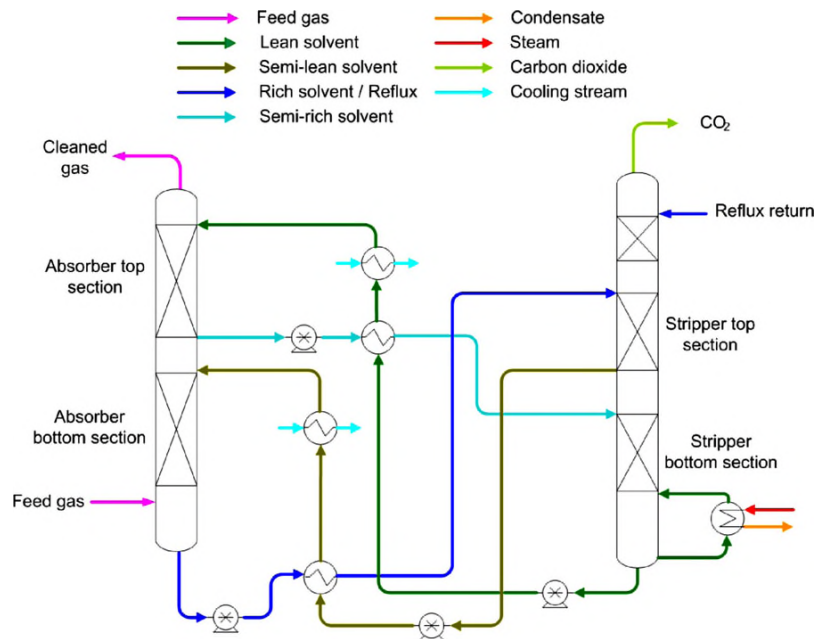


Figure 2-17: Split Flow Configuration (Cousins et al., 2011)

The DMXTM process (Figure 2-19) takes advantage of the immiscible liquid phases of the solvent solution at different temperatures. A light aqueous phase is decanted from the rich solvent, leaving a smaller entering the regenerator, requiring less energy for regeneration. The light phase from the decanter is then mixed with the lean solvent from the reboiler, before it is fed into the absorber.

Solvent regeneration energy for the DMX™ process is estimated to be 43% less than the conventional process (Raynal et al., 2011).

There is also ample opportunity for heat integration between the power plant, PCC plant, and compression stage which can potentially reduce the energy penalty in an integrated plant.

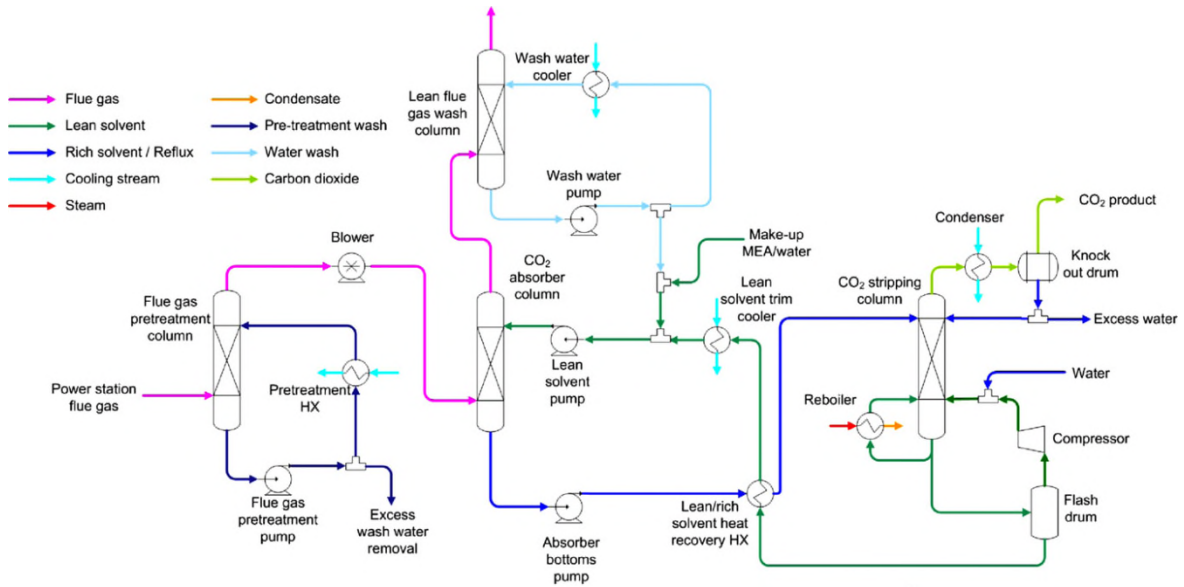


Figure 2-18: Vapour Compression in Solvent Regeneration (Cousins et al., 2011)

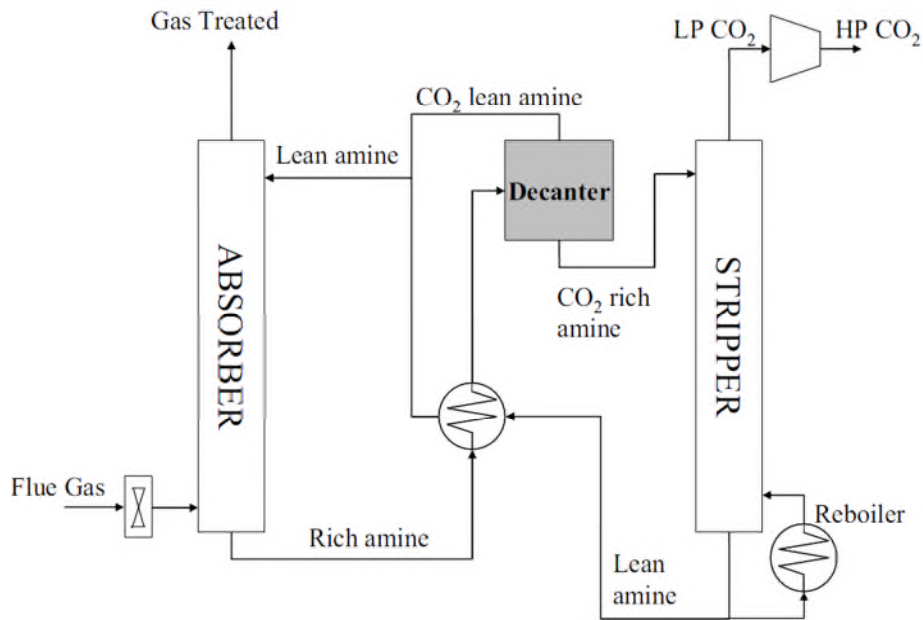


Figure 2-19: DMX™ Process Configuration (Raynal et al., 2011)

2.8.3 Novel Equipment and Regeneration Approaches

Other key technology components under development include membranes and advanced generation post-combustion sorbents for CO₂ capture and advanced CO₂ compression. Some membranes and sorbents are claiming potential savings of up to 50% capture energy and 60% capital investment (Carbon Capture Journal, 2011).

To avoid drawing steam from the power plant, the addition of a boiler solely dedicated to steam generation has been suggested, which appears unattractive due to the increase in both capital and operating costs, but may be essential to the flexible operation of a power plant. Alternatively, concentrated solar power is being explored as an alternative sustainable effective approach, where solar thermal energy is exploited to produce steam in a parabolic trough (Parkinson, 2012).

Stern et al. (2013) recently proposed an electrochemical regeneration cycle, where metal cations that are generated at an anode react with the amines in the solvent, displacing the CO₂, which is then flashed off, leaving the amines to be regenerated by the reduction of the metal cations in a cathode cell. In addition to lower energy demands, a major advantage of this approach is that it allows higher CO₂ regeneration pressures, leading to smaller process equipment.

Application of process intensification techniques, such as the Higee technology, is also being evaluated for the PCC plant (Wang et al., 2011). The absorber and regenerator columns are replaced with rotating packed beds, where the enhanced gravity caused by centrifugal forces due to rotation increases mass transfer greatly for CO₂ absorption and desorption. The consequence of this is smaller solvent regeneration energies, reduced process equipment sizes and substantially smaller plant footprint.

3 MODEL DEVELOPMENT CONSIDERATIONS

3.1 Modelling Approach/Complexity

There are a number approaches to modelling packed columns in a PCC process. The complexity of model is dependent on the extent to which the phenomena of mass transfer and chemical reaction are handled in the model. The simplest models assume a vapour-liquid equilibrium (VLE) and a chemical equilibrium, which results in equilibrium stages, where performance is adjusted by tray efficiency (Schneider et al., 1999). The most complex model accounts for mass transfer between vapour and liquid, as well as the reactions kinetics and electrolytic interactions between the components present (Noeres et al., 2003). An increasing model complexity is illustrated in Figure 3-1. Model 1 is adequate for systems where there is no chemical reaction or very fast chemical reaction. Model 2 is an improvement, yet it has been shown to poorly predict the performance of an absorber in a capture process (Aspirin, 2006). Model 3 performs satisfactorily when the rate of the reaction under consideration is fast, and Model 4 is only a slight improvement from Model 3 as an enhancement factor is utilized, making it only applicable to pseudo first order reactions (Kucka et al., 2003). Model 5 is the most accurate representation as it accounts for all physical and chemical interactions. A rate-based approach is strictly considered in this work.

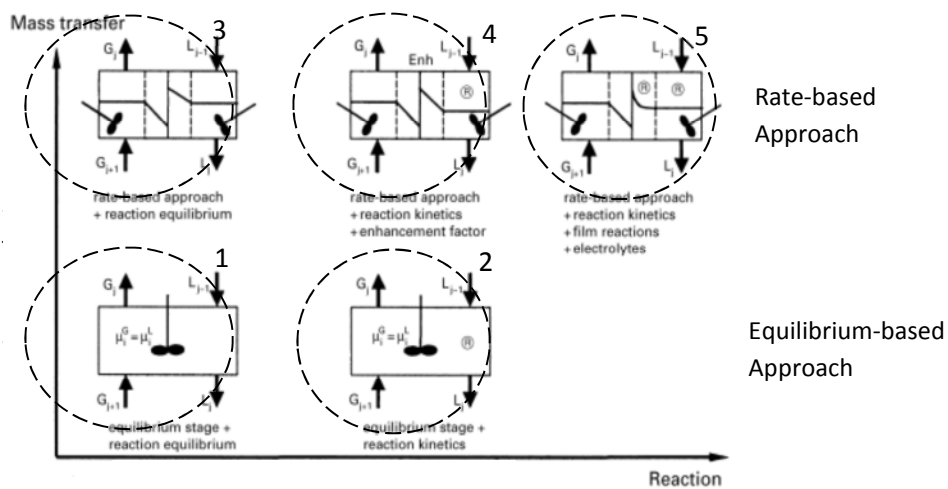


Figure 3-1: Different Column Stage Modelling Approach (Kenig et al., 2001)

3.2 Two Film Theory

Mass transfer in the model can be described by two-film theory, the penetration theory, the film-penetration theory or the turbulent boundary layer theory (Krishna and Wesselingh, 1997). The two-film theory is the most utilized approach in modelling packed columns for the PCC process (Figure 3-2). It assumes two laminar film layers of vapour and liquid films exist between the turbulent regions of counter flowing vapour and liquid phases, which interact across an adjoining interface.

To implement two-film theory, material and energy continuities are imposed on the bulk vapour phase, bulk liquid phase, vapour film and liquid film. These continuities may also account for chemical interaction between components. Components from the turbulent bulk vapour and liquid phases diffuse across the laminar vapour and liquid films respectively. A VLE exists at the interface between the films, implying that mass and energy fluxes between the vapour and liquid films are equal at the interface. Although Fick's law can be used to describe the diffusion of components across films, the Maxwell Stefan formulation provides a better prediction for multiple component diffusion (Krishna and Wesselingh, 1997).

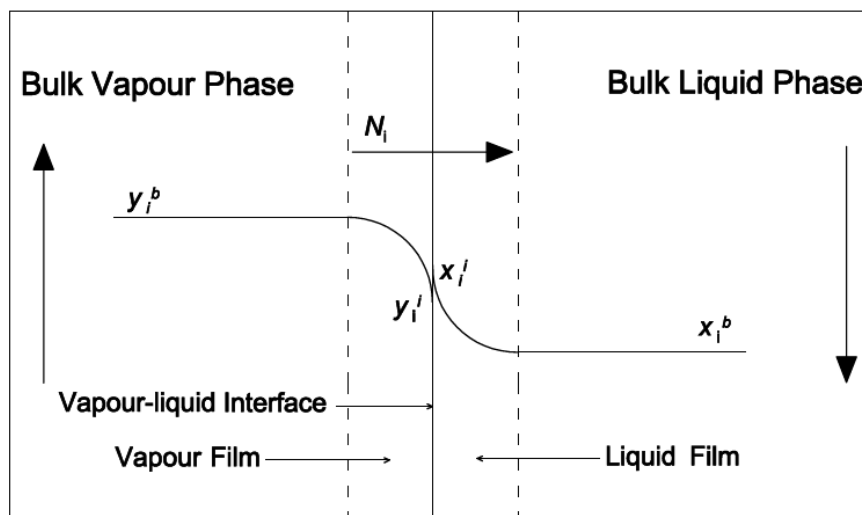


Figure 3-2: Two-Film Approach to Modelling

3.3 Mass Transfer

A good understanding of the counter-current flow of liquid and gas in a packed column is essential for the describing mass transfer in the system. The hydraulic behaviour of the flowing gas and liquid are governed by the parameters such as the packing specific area and void fraction; the densities, viscosities and flow velocities of the phases; and the surface tension between the phases (Billet and Schultes, 1999.) These combined to define the following mass transfer parameters:

- Vapour and liquid mass transfer coefficients;
- Effective interfacial area;
- Liquid Hold up;
- Pressure Drop; and
- Column flooding capacity

Onda et al. (1968) developed empirical correlations for the interfacial area and liquid and gas mass transfer coefficients using data from a randomly packed column. They made the distinction between the interfacial area and total specific area of packing, as in most cases the total specific area is not used for mass transfer due to hydraulic conditions and physical interactions that influence the spreading of liquid. Billet and Schultes (1999) proposed semi-theoretical correlations for interfacial area, liquid and gas mass transfer coefficients, pressure drop, column flooding limit and liquid holdup, which can be applied to both random and structured packings. Structured packing is commonly used in absorption processes, as it offers larger area for gas–liquid contacting, excellent mass transfer and better hydraulic performance compared to random packing (Wang et al., 2006).

Mass transfer in a packed column is largely affected by the interfacial area. Wang et al. (2006) performed an extensive review of the numerous interfacial area correlations and found considerable discrepancies in the estimated areas. They observed that the effective surface area predicted by the Onda correlation differs significantly from the experimental results and is usually smaller. Correlations of Billet & Schultes, Rocha et al. and Gualito et al predict the

interfacial area effectively at lower pressures, but begin to struggle at pressures above 20bar. Therefore, they proposed incorporating a correcting factor which is a function of gas velocity to improve predictions.

Gaspar and Cosmos (2012; Cormos and Gaspar, 2012) compared the prediction of several mass transfer and hydraulic models in a PCC application and found the interfacial areas predicted by the Wang correlation to be the most effective for most amine solvents, with the Billet-Schultes correlation to be very effective for MEA and DEA. Shojaee et al. (2011) next used a 3D computational fluid dynamics (CFD) model to evaluate correlations and found the Brunazzi correlation, which requires specification of the structured packing angle, to be the most effective. Tsai et al. (2011) proposed an interfacial area correlation that was formulated independent of the liquid and gas mass transfer correlations, and suggested that the impact of surface texture and angles on interfacial area is weak.

Razi et al. (2012) then performed an extensive review of mass transfer correlations for PCC applications, noting that none of the proposed correlations have been verified for large scale application, with ranges that can lead to sizeable errors and deviations. Afterward, Hanley and Chen (2012) developed tailored mass transfer expressions for four types of packing (two random and two structured) that showed good performance for a wide range of systems and operating ranges, but predicted effective interfacial areas for mass transfer well in excess of the packing specific surface area

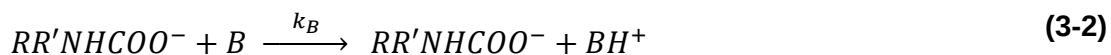
Therefore, the effectiveness of a rate-based column model is ultimately tied to underlying mass transfer-related correlations, which have questionable predictive capability outside the operating range that they were developed.

3.4 Chemical Reaction Kinetics

Amines are the most common solvents used in PCC. The reaction of CO₂ with primary, secondary and sterically hindered amines (RR'NH) is described by the zwitterion mechanism, which suggests the formation of a zwitterion as an intermediate (Vaidya and Kenig, 2007):



The zwitterion then undergoes deprotonation by a base (B) forming carbamate:



So the reaction rate of CO₂ in aqueous amine solution can be expressed as:

$$r = \frac{k_1[CO_2][RR'NH]}{1 + \frac{k_{-1}}{k_B[B]}} \quad (3-3)$$

The base may be the amine itself, H₂O, a hydroxide ion present or a combination of these. Thus $k_B[B]$ represents the sum of the rates of all occurring deprotonation reactions. When deprotonation is almost instantaneous compared to the zwitterion formation ($k_{-1} \ll k_B[B]$), the latter is rate limiting and Equation (3-3) becomes:

$$r = k_1[CO_2][RR'NH] \quad (3-4)$$

When the contribution of the amine to the zwitterion deprotonation is significant and a fractional reaction order between one and two with respect to the amine is observed, the deprotonation step becomes rate limiting ($k_{-1} \gg k_B[B]$), therefore Equation (3-3) becomes:

$$r = \frac{k_1 k_B[B]}{k_{-1}} [CO_2][RR'NH] \quad (3-5)$$

Alternatively, termolecular mechanism can be used to describe the absorption process, with some studies suggesting that it provides a better description (Aboudheir et al., 2003). This mechanism assumes that the reaction between the amine and CO₂ and the proton transfer to the base occurs simultaneously, rather than in two steps as the zwitterion mechanism suggests. A loosely-bound encounter complex is formed as an intermediate, which breaks up to form reactant molecules (CO₂ and amine), while a small fraction reacts with a second molecule of the amine or a water molecule to give ionic products. The resulting

rate expression can then be used to describe fractional and higher-order kinetics (Vaidya and Kenig, 2007).

In the past, the absorption of CO₂ in MEA has been described as first order (Hikita et al., 1977a; Freguia and Rochelle, 2003), however there have been conflicting estimate of the reaction rate coefficients reported (Vaidya and Kenig, 2007). Consequently, three kinetic models, among many, are considered:

3.4.1 Aboudheir et al

Aboudheir et al. (2003) explained that previous discrepancies in rate coefficients are a result of the assumption of a pseudo-first order reaction (among other factors), and showed that the assumption is only valid for low MEA concentrations or high CO₂ loadings. Therefore, a robust rate expression for the forward reaction using the termolecular mechanism is given as:

$$r = k_{app}[CO_2] \quad (3-6)$$

Where;

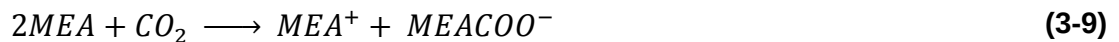
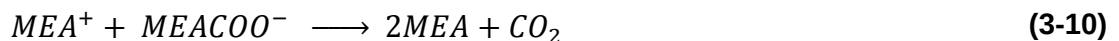
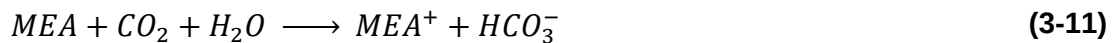
$$k_{app} = (k_{H_2O}[H_2O] + k_{MEA}[MEA]) [MEA] \quad (3-7)$$

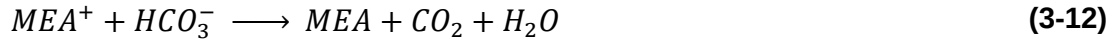
Where;

$$k_{MEA} = 4.61 \times 10^9 \exp\left(-\frac{4412}{T}\right) \text{ m}^6/\text{kmol}^2.\text{s} \quad (3-8)$$

3.4.2 Zhang et al & Plaza et al

Zhang et al. (2009) and Plaza et al. (2010) employed the rate data for CO₂ absorption in MEA generated from experiments by Aboudheir et al. (2003) to come up with the following kinetic expressions:





The four reactions are two forward and two backward directions of two distinct reactions. This makes the kinetic expressions useful in describing both the absorption and regeneration processes. The reaction rates can be determined by the power law:

$$r_j = k_j^o \exp\left(-\frac{E_j}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \prod_{i=1}^N C_i^{a_{ij}} \quad (3-13)$$

Here r is the reaction rate of reaction j , k^o is its pre-exponential factor, T is the temperature, E is its activation energy, R is the gas constant, C is the concentration (activity basis) of component i , 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, along with component reaction orders, are given by Zhang et al. (2009) and Plaza et al. (2010).

These differences observed in the kinetic constants of the two models given in Table 3-1 results from the fact that the model proposed by Zhang et al. (2009) incorporates the electrolytic interactions of water dissociation and bicarbonate dissociation reactions:

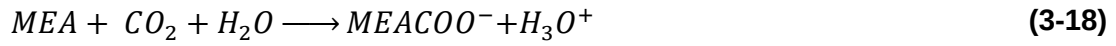
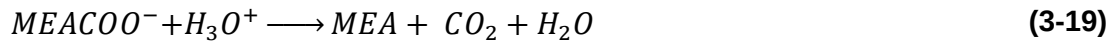


Table 3-1: Power Law Expression Constants for CO₂ Absorption in MEA

	Zhang et al		Plaza et al	
	k_j^o (kmol/m ³ .s)	E_j (kJ/kmol)	k_j^o (kmol/m ³ .s)	E_j (kJ/kmol)
(3-9)	4.73×10^9	19340	5.31×10^9	14610
(3-10)	423000	107470	475000	102740
(3-11)	9026	49000	9026	49000
(3-12)	3313	112740	2917	114250

3.4.3 AspenTech

AspenTech (2008) released a sample model of CO₂ capture process using MEA, accompanied by the following kinetic expressions:



Electrolytic interactions such as water dissociation (reaction (3-14)), bicarbonate dissociation (reaction (3-15)) and MEA hydrolysis are also accounted for. The expression for MEA hydrolysis:



Kinetic parameters of reaction (3-16) are taken from Pinsent et al. (1956) and those for reaction (3-17) are derived using equilibrium constants from Hikita et al. (1977a), considering the reversibility of (3-16) and (3-17). These are then adapted to the power law (Equation (3-13)) by AspenTech (2008), who also provide the kinetic parameters of reactions (3-18) and (3-19). The basis of concentration used in the power law is molar concentration, with the appropriate component reaction order also provided. As with the kinetic models described in 3.4.2, the reversibility of this formulation makes the model application to both CO₂ absorption and solvent regeneration.

Table 3-2: AspenTech Power Law Expression Constants

	k_j^o (kmol/m ³ .s)	E_j (kJ/kmol)
(3-16)	4.32×10^{13}	55433
(3-17)	2.38×10^{17}	123330
(3-18)	9.77×10^{10}	41237
(3-19)	3.23×10^{19}	65500

3.5 Thermodynamic Considerations

As already stated in Section 2.8.2, the absorption of CO₂ into MEA is an exothermic process, which results in the release of heat that rises temperature in the absorber and erodes absorption. Experiments performed by Kim et al (2007; 2009; 2011) at the Norwegian University of Science and Technology to determine heat of absorption of CO₂ in MEA have shown the value to be greatly dependent on the CO₂ loading of the solvent and temperature. Oyeneke (2007) then formulated a correlation, based on data from pilot campaigns at the University of Texas at Austin, which is a function of both CO₂ loading and temperature. Zhang and Chen (2011) proposed that heat of absorption can be determined as combination of the heat of formations of the reacting components and changes in enthalpy.

3.6 Modelling Tools

The chemical absorption capture plant using MEA is a commonly modelled process both academically and commercially. The following simulators would be utilised in this research:

3.6.1 gPROMS[®]

gPROMS (general PROcess Modelling System) is developed by Process Systems Enterprise Limited. It is an equation-based modelling system that enables user developed process models. These models could then be used for steady state and dynamic simulation, as well as optimization. Through the CAPE-OPEN interface, gPROMS could be used with other compatible process modelling tools such as the physical property methods and models of Aspen Properties[®].

3.6.2 Aspen One Engineering[®]

AspenTech has provided simulation solutions for CCS consisting of a rate-based column, which is a rigorous rate-based distillation model that is available in either of its flagship simulators – Aspen HYSYS and Aspen Plus. Aspen HYSYS is mainly used for the oil and gas applications while Aspen Plus strengths mainly lie in simulating chemical processes. Aspen HYSYS can

perform simulations in both steady-state and dynamics, while Aspen Plus is restricted to steady state.

The biggest advantage of using AspenTech's tool is that all required property models and parameters for CO₂ absorption solvents are already available in it. These are available in Aspen Properties, a dedicated property database, which can also be used in either simulator. Available solvents include MEA, DEA, TEA, MDEA, DGA, AMP, Hot Carbonate, and Ammonia as chemical solvents; Rectisol (Methanol) and Selexol as physical solvents. Process analysis can be performed with these solvents. In addition, AspenTech is actively developing new solvent property models: Sodium Carbonate, DIPA, and Piperazine as chemical solvents; NMP, Sulfolane, Propylene Carbonate as physical solvents; also mixed amine solvents.

Finally, AspenTech offers Aspen Process Economic Analyzer, which is a cost estimation tool that is part of Economic Evaluation Suite used to perform detailed economic analysis and process comparison to assess the most cost effective option available from a number of process choices.

4 DYNAMIC MODEL VALIDATION AND ANALYSIS

4.1 Motivation

To understand the operational characteristics of a CO₂ capture plant and identify possible difficulties that may arise, process analysis is required via modelling and simulation. The chemical absorption capture plant using MEA is a commonly modelled process both academically and commercially in process simulators like Aspen HYSYS, Aspen Plus and gPROMS. Although there are a number of pilot and demonstration CO₂ capture plants currently running campaigns (Wang et al., 2011), acquiring data of these campaigns is difficult, making model validation a challenging task. Nevertheless, data is available (Dugas, 2006; Cottrell et al., 2009), thus steady-state validation and analysis of a rate-base absorber model has been performed, using the temperature profile and capture level of the absorber to compare with experimental data (Zhang et al., 2009; Lawal et al., 2009a; Kvamsdal et al., 2009; Simon et al., 2011). In addition, Lawal et al. (2009b, 2010) were able to perform steady-state validation of an standalone regenerator model, before finally performing the steady-state validation of the entire capture process model with the integrated columns.

Models validated at steady-state can predict process performance at different operating points. However, it is not clear how fast/slow the process will move from one steady-state to another without dynamic models. Dynamic validation of the model of the integrated process has not been performed due to the challenging nature of running a CO₂ absorption pilot campaign in dynamic mode (Kvamsdal et al., 2011), which makes acquiring data for such an endeavour very difficult. Nevertheless, Faber et al were able to perform step response test at a 1 tonne CO₂/hour pilot plant and found that the overall system acts like a buffer for any perturbation at the absorber flue gas inlet (Faber et al., 2011).

4.2 Development of Dynamic Model

4.2.1 Continuity and Mass Transfer

The model developed for this study has been described by Lawal et al (2009a, b, 2010). Model assumptions include:

- Plug flow regime with linear pressure drop along the column.
- No material accumulation in the liquid film, the vapour film and the bulk vapour.
- Phase equilibrium at interface between liquid and vapour films.
- Reactions are also assumed to attain chemical equilibrium at interface.
- Negligible oxygen concentration in the flue gas and solvent degradation and heat loss in the absorber to the surroundings.

The following continuity equations are applied to the bulk vapour and bulk liquid phases:

$$\frac{dM_i}{dt} = \frac{-1}{A} \frac{\partial F_i}{\partial y} + N_i \cdot MW_i \cdot Sp \cdot \omega \quad (4-1)$$

$$\frac{dU}{dt} = \frac{-1}{A} \frac{\partial F_H}{\partial y} + Sp \cdot \omega \cdot (H^{cond} + H^{conv} + H_{abs}) + Heat Loss \quad (4-2)$$

In the mass transfer regime, the vapour diffusion coefficients are calculated by a method given by Fuller et al (1966) and the liquid diffusion coefficient of CO₂ in water is provided by Versteeg and Van Swaaij (1988). These were in turn applied in the Maxwell-Stefan formulation to determine the mass fluxes of components in both the vapour and the liquid film (Krishna and Wesselingh, 1997). The mass transfer coefficient for both the vapour and liquid film, in addition to the wetted area on the packing were calculated by empirical expressions provided by Onda et al. (1968).

The heat flux due to absorption of CO₂ in MEA is determined as:

$$H_{abs} = N_{CO_2} \cdot h_{abs} \quad (4-3)$$

Where the specific heat of absorption h_{abs} is given as (Oyenekan, 2007):

$$h_{abs} = R \cdot \left(-14281 - \left(\frac{1092554 \cdot \gamma^2}{T} \right) - \left(\frac{6800882 \cdot \gamma}{T} \right) + 32670.01 \cdot \gamma \right) \quad (4-4)$$

The Heat Loss in the energy balance equation applies to the regenerator only and is determined as:

$$Heat\ Loss = \frac{342.88 \times SA \times (T_{RegenBottom} - T_{ambient})}{L \times A} \quad (4-5)$$

The constant in the equation is derived from a correlation from the University of Texas at Austin test (Dugas, 2006).

Due to the assumption of negligible material accumulation in the vapour phase, both the material and energy accumulation terms in the continuity equations are eliminated. Another important assumption is made that phase equilibrium is attained at the vapour-liquid interface, equating the vapour fugacity to the liquid fugacity.

4.2.2 Physical Properties and Chemical Equilibrium

The Electrolyte Non-Random-Two-Liquid (ElecNRTL), an activity coefficient model available in Aspen Properties[®], is used to describe the Vapour-Liquid Equilibrium, the chemical equilibrium, the physical properties of the system through the CAPE-OPEN Thermo interface. The equilibrium reactions, which are assumed to occur in the liquid film, are defined as:



The equilibrium constants (K_{eq}) for the reactions presented in Equations (4-6) – (4-10), given on a molar concentration basis, are temperature dependent and are defined as:

$$\ln K_{eq} = A + \frac{B}{T} + C \cdot \ln T + D \cdot T \quad (4-11)$$

The values of A, B, C and D for Equations 6 – 10 are given in Table 4-1.

Table 4-1: Coefficients of Equilibrium Constants (AspenTech, 2010)

	(4-6)	(4-7)	(4-8)	(4-9)	(4-10)
A	132.889	98.566	216.049	0.7996	1.282562
B	-13445.9	1353.8	-12431.7	-8094.81	-3456.176
C	-22.4773	-14.3043	-35.4819	0	0
D	0	0	0	-0.007484	0

4.3 Steady-State Validation

4.3.1 Pilot plant data logs

The model of the conventional process was validated by Lawal et al. (2010) at steady-state using data logs from the Separation Research Program (SRP) pilot plant at the University of Texas in Austin (Dugas, 2006). Seibert et al. (2011) described the operating procedure of the pilot plant. Lawal et al. (2009a, 2010), Kvamsdal et al. (2009) and Zhang et al. (2009) had previously showed that the process more affected by the L/G ratio into the absorber, than any variation in the individual input of solvent or gas. Consequently, two data sets or cases – Cases 32 and 47 – representing high and low L/G ratios respectively are validated against the model results. The process conditions of Cases 32 and 47 are given in Table 4-2 and unit specifications are given in Table 4-3.

Table 4-2: Process Conditions for Steady-state Validation (Dugas, 2006)

	Case 32			Case 47		
Stream ID	Flue	Lean MEA	Rich MEA	Flue	Lean MEA	Rich MEA
Temperature (K)	320	316	358	332	313	356
Total flow (kg/s)	0.130	0.720	0.745	0.158	0.642	0.746
Mass fraction						
H ₂ O	0.0148	0.6334	0.6122	0.0193	0.6334	0.6085
CO ₂	0.2520	0.0618	0.0971	0.2415	0.0618	0.0966
MEA	0.0000	0.3048	0.2901	0.0000	0.3048	0.2943
N ₂	0.7332	0.0000	0.0006	0.7392	0.0000	0.0006
Loading (mol CO ₂ /mol MEA)	-	0.2814	0.4646	-	0.2814	0.4556

Table 4-3: Equipment Specifications for Steady-state Validation (Dugas, 2006)

Description	Value
Column inside diameter (Absorber & Regenerator) (m)	0.427
Height of packing (Absorber & Regenerator) (m)	6.1
Nominal packing size (Absorber & Regenerator) (m)	0.0381
Packing specific area (Absorber) (m ² /m ³)	145
Packing specific area (Regenerator) (m ² /m ³)	420
Cross heat exchanger heat transfer area (m ²)	7
Reboiler volume (m ³)	1
Condenser volume (m ³)	2

4.3.2 Model Topography and Control

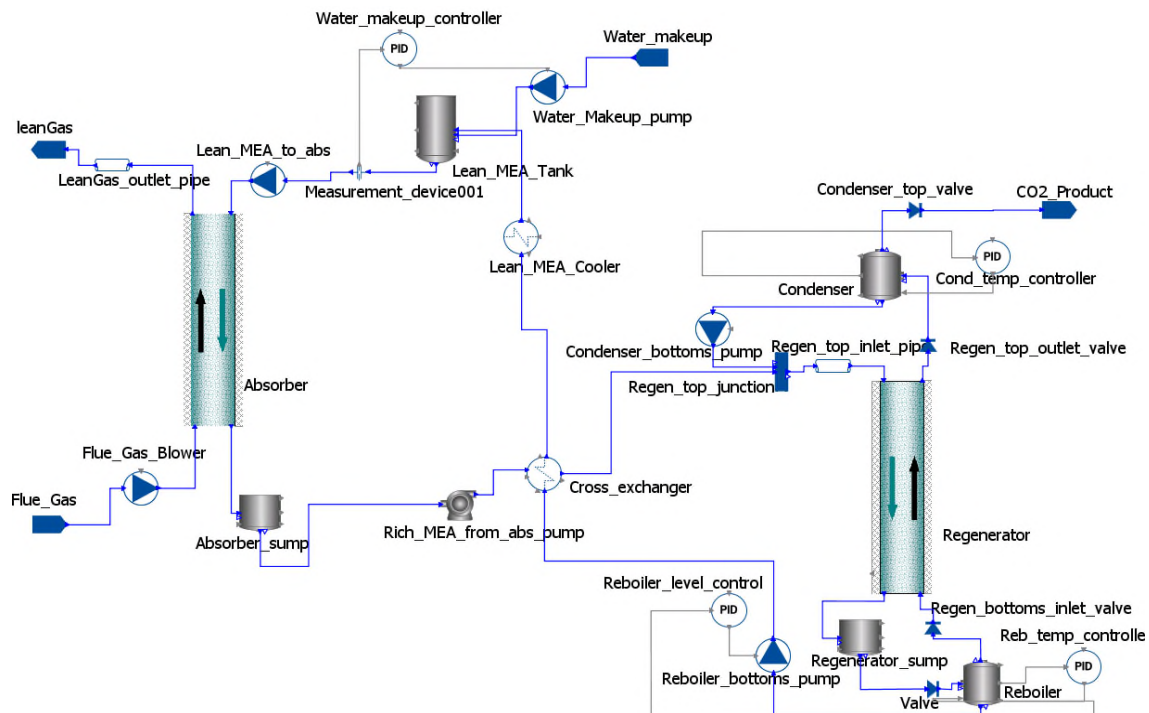


Figure 4-1: Conventional Amine plant model in gPROMS® (Lawal et al., 2010)

This being a dynamic model, appropriate control schemes were implemented to ensure the model arrived at a steady-state where comparison can be done between the model predictions and the pilot plant data logs. This control scheme is given in Table 4-4.

Table 4-4: Model Control Scheme for Steady-state Validation (Lawal et al., 2010)

Controlled Variable	Manipulated Variable	Set Point
Condenser Temperature	Condenser duty	320 K
Reboiler Temperature	Reboiler duty	387 K
Reboiler Level	Reboiler Bottoms flow rate	50 vol%
Water Make-Up	Water Make-Up flow rate	0.6332 Mass fraction
Capture Level	Lean MEA Solvent flow rate	97 wt%

Simulations were first performed for standalone absorbers and regenerators for Cases 32 and 47. In the standalone regenerator model, there is no sump as it was only added to the integrated process model to ensure robust process control. Instead, constant heat duties are imposed on the reboiler and condenser to achieve the constant temperatures required for the two stages. The two columns of Case 32 were then linked, the integrated capture process was simulated and the results (taken from Lawal et al. (2010)) were analysed.

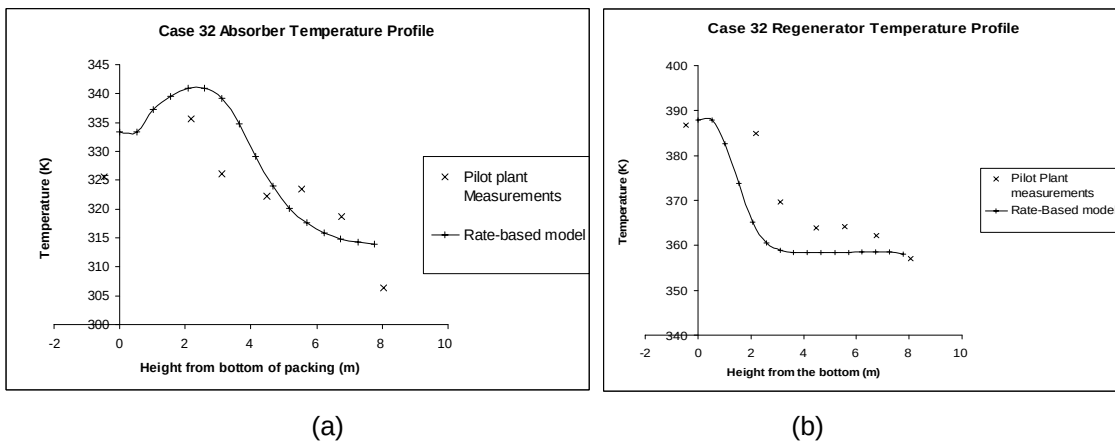


Figure 4-2: Standalone Absorber & Regenerator Temperature Profile for Case 32

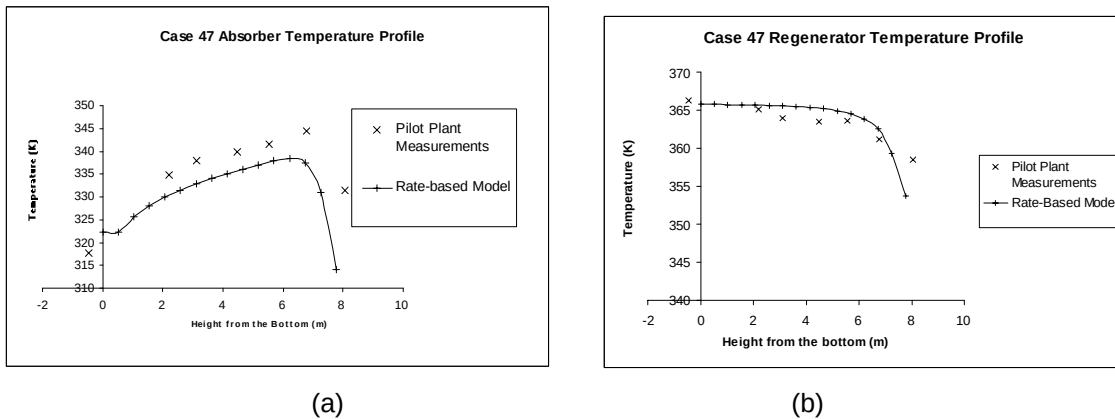


Figure 4-3: Standalone Absorber & Regenerator Temperature Profile for Case 47

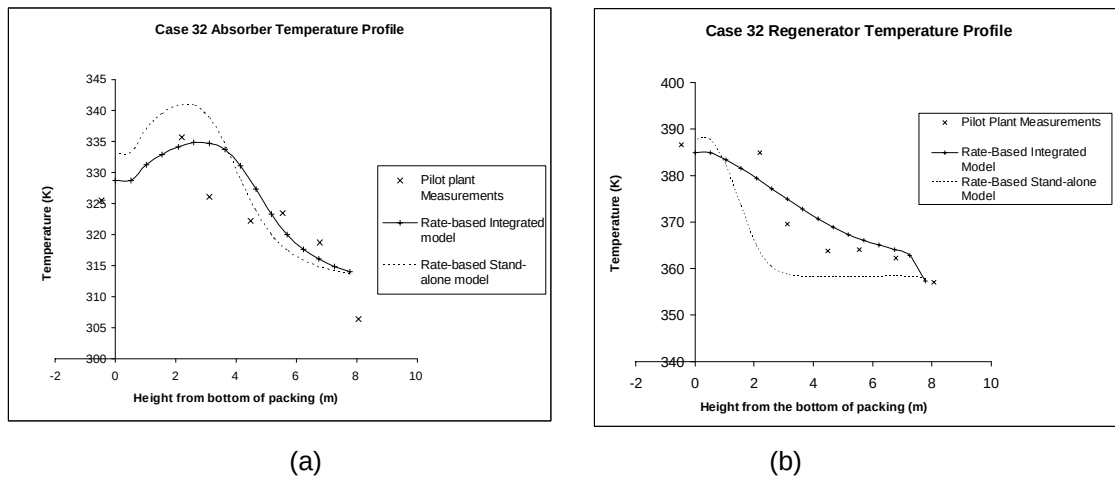


Figure 4-4: Integrated Absorber & Regenerator Temperature Profile for Case 32

4.3.3 Discussion of Results

An initial analysis of the results has been provided by Lawal et al. (2010) Figure 4-2 and Figure 4-3 show the temperature profile comparison of the standalone columns of Cases 32 and 47 respectively. Although there is some deviation, it is observed that the prediction of the standalone models generally agrees with data logs of the pilot plant, which implies that the model performs satisfactorily.

For the standalone absorber models, the inlet flue gas flow rate were slightly adjusted from 0.130kg/s to 0.110kg/s and from 0.158kg/s to 0.172kg/s for Cases 32 and 47 respectively, to match the capture level achieved in the pilot plant.(Zhang et al., 2009; Lawal et al., 2009) The temperature bulges are clearly observed in the absorbers, at the bottom for Case 32 (Figure 4-2(a)) and at the top for Case 47 (Figure 4-3(a)), which is expected considering the L/G ratios of the two cases (Kvamsdal and Rochelle, 2008). In Figure 4-3(a), it is also clear that the model consistently underestimates the temperatures in the absorber at low L/G ratio, notwithstanding the agreement with the pilot plant data.

Considering the standalone regenerators, an abrupt temperature drop of about 20K is observed around the middle of the column length for Case 32 (Figure 4-2(b)) in both pilot plant and model, while lower temperatures are detected for Case 47 (Figure 4-3(b)). From Table 2, it is clear that the flow rate of the rich solvent inlet to both regenerators is roughly the same, and significant difference only is observed in CO₂ loadings of the rich solvent. However, it is the reboiler

temperature that is the main driver of the regenerator temperature profiles, as it is 387K for Case 32 and 366K for Case 47. Therefore, the steep temperature drop in Case 32 implies that the reboiler is being operated at a temperature higher than is required for solvent regeneration.

Figure 4-4 displays the temperature profiles comparison of the integrated columns, the standalone columns and the pilot plant measurements for Case 32. The results reveal an improved temperature profile prediction in Figure 4-4(a) for the absorber when the connected column is compared with the standalone column, which only required a reduced adjustment of the inlet flue gas flow rate from 0.130kg/s to 0.120kg/s, to match the capture level achieved in the pilot plant. In Figure 4-4(b), the model prediction appears to take the form of a constant gradient between the inlet (top) and outlet (bottom) temperature along the length of the regenerator, making the abrupt temperature drop observed in the pilot plant around the middle of the column length no longer as pronounced. This is as a result of the regenerator column configuration that is used in the integrated process, as the added sump and temperature control results in a higher heat duty requirement in the reboiler, which increases the temperatures in the column. A less influential factor is the change in rich solvent composition due to the recycle, which is highlighted in Table 4-5.

Table 4-5: Case 32 Standalone & Integrated Columns Solvent Inlet Comparison

Column	Lean MEA		Rich MEA	
	Standalone	Integrated	Standalone	Integrated
Flue gas rate (kg/s)	0.110	0.120	-	-
Solvent rate (kg/s)	0.720	0.719	0.745	0.746
Solvent Mass fraction				
H ₂ O	0.6334*	0.6334*	0.6122	0.6083
CO ₂	0.0618	0.0605	0.0971	0.0971
MEA	0.3048	0.3061	0.2901	0.2939
N ₂	0.0000	0.0000	0.0006	0.0007
Loading (mol CO ₂ /mol MEA)	0.2814	0.2743	0.4646	0.4586

*Water concentration is kept constant by a controller to meet a water balance in the absorber (please refer to Figure 4-1)

The heat capacity of MEA solution decreases with increasing MEA concentration (Weiland et al., 1997), meaning a higher MEA content would result in the higher temperatures observed in the integrated regenerator.

Notwithstanding this qualitative change in the regenerator profile prediction, the integrated system still provides a better prediction than the standalone one. This is expected as the real process comprises of linked columns with a recycle and not standalone columns which, as previously stated, causes the composition of the rich solvent that is fed to the top of the regenerator to be updated. Similarly, the composition of the lean solvent is also updated and returned to the absorber as recycle, though the water concentration is kept constant using a controller to maintain the water balance in the absorber. The updated inputs of the integrated absorber model were then applied to the standalone absorber to ascertain the impact of the recycle update on the process, and the results obtained were essentially identical to the results of the integrated absorber, confirming the significance of the recycle. Therefore, the model prediction in the integrated system is better, increasing the reliability of the validated model.

Lastly, it should be noted a control scheme for lean solvent composition implemented in the model is slightly different from what is in the pilot plant. While the plant uses MEA concentration as the controlled variable with a set point at around 30 wt%, water concentration is kept constant at 63.34 wt% in the model due to numerical difficulties. This has been done to maintain a water balance in the system, which ultimately maintains the MEA concentration. This implementation may contribute to some model deviation from the pilot plant; however the impact appears to be very limited, as the integrated model satisfactorily predicts the pilot plant performance.

4.4 Dynamic Validation

4.4.1 Case 1 – Conventional process

4.4.1.1 Pilot plant data logs and comparison

The dynamic validation of the conventional process was also carried out using logged data from the SRP pilot plant, with equipment specifications the same as

those given in Table 4-3. Although there are no dynamic step tests available in the data, a case study was selected from the data logs based on the following criteria:

- Significant change in plant input that would affect CO₂ capture.
- Negligible variation in regenerator reboiler temperature.
- Minimal number of additional disturbances in other inputs.

4.4.1.2 Process Inputs and Disturbances

The process flow diagram of this case is the same as displayed in Figure 4-1. Based on the data log selection criteria discussed, a data set corresponding to Case 25 (with initial process conditions given in Table 4-6) was chosen. The data log is presented in Figure 4-5. Three main inputs/disturbances in this case were identified:

- A slow decrease in lean solvent flow rate to the absorber
- The concentration of CO₂ in the inlet flue gas stream to the absorber
- The temperature of the inlet flue gas stream to the absorber.

The reboiler temperature reading in the pilot plant was used as the set point of the temperature controller in the reboiler model. All other variables were either constant or assumed to have negligible effect on the validation results. To account for the changing process variables, a gPROMS[®]-Microsoft Excel foreign process interface was developed, and the process values were read off an Excel Spreadsheet onto gPROMS[®] with a time sequence for the lean MEA mass flow, the CO₂ and nitrogen concentrations of the inlet flue gas, as well as the inlet flue gas temperature to the absorber. The moisture content (i.e. the water concentration) in flue gas was assumed constant for the duration of the run and calculated as a function of the ambient air relative humidity during the pilot plant campaign, so that the nitrogen concentration of the inlet flue gas can be estimated. This procedure is used in all subsequent runs in this work.

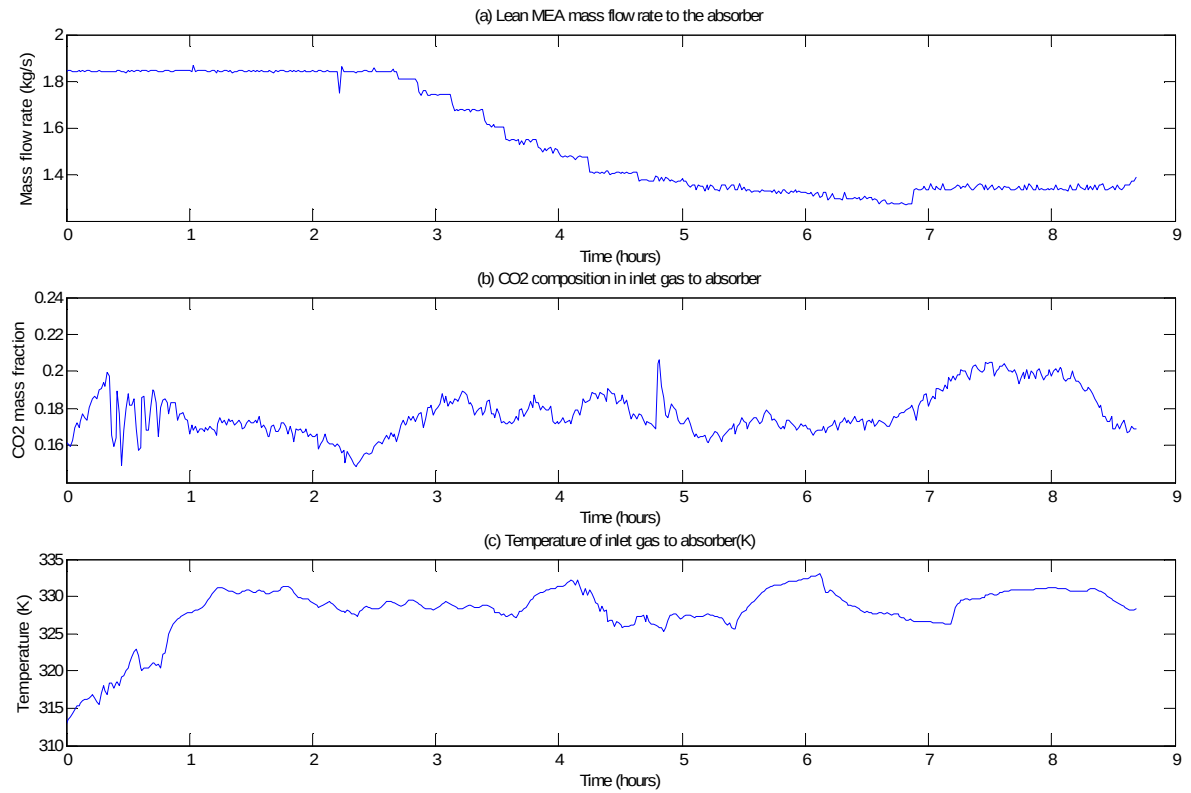


Figure 4-5: Process Inputs / Disturbances Applied in Case 4.1 (Lawal, 2010)

Table 4-6: Initial Process Conditions for Dynamic Test Case 25 (Dugas, 2006)

Stream ID	Flue	Lean MEA
Temperature (K)	313	316
Pressure (10^5 Pa)	1.05	1.05
Total flow (kg/s)	0.235	1.840
Mass fraction		
H ₂ O	0.015	0.633
CO ₂	0.159	0.059
MEA	0.000	0.308
N ₂	0.826	0.000

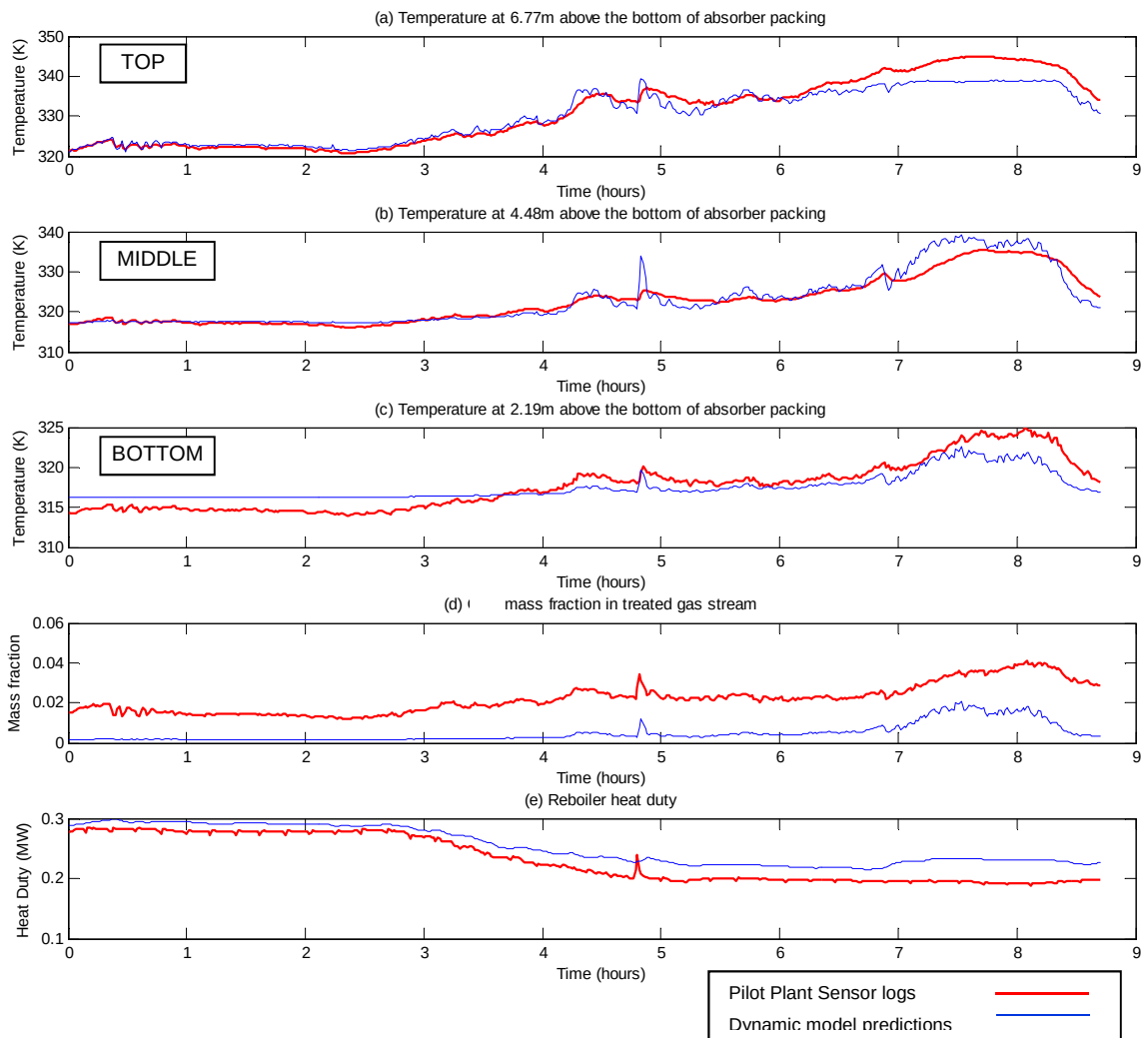


Figure 4-6: Comparison of Pilot Logs and Model Response for Case 4.1

4.4.1.3 Discussions of Results

The comparison of the logged pilot plant data and the model responses due to the input and disturbances shown in Figure 4-6(a)-(c) is presented in Figure 4-7(a)-(e), culled from Lawal (2010). Figure 4-7(a)-(c) compare the temperature readings in the absorber at the top, middle and bottom of the absorber respectively. Figure 4-7(d) compares the CO₂ concentration in the treated gas exiting the absorber and Figure 4-7(e) compares the reboiler duty.

Considering Figure 4-7(a)-(c), it is clear from the absorber temperature profile that the model prediction as a result of the disturbances tracks the data logs very well, especially at the top and the middle of the column, and throughout the

run. This demonstrates the effectiveness of the absorber model. A steady rise and fall in temperature is observed in the column between the 7th hour to the end of the run. This response appears to coincide with a disturbance of a rise in flue gas CO₂ concentration as seen in Figure 4-6(b). Again, the model predicts this trend quite well, but does not predict the magnitude of the changes as well as it did before the 7th hour mark. The model response accuracy decreases due to a 25% drop in lean solvent flow rate as seen in Figure 4-6(a). This is in agreement with the observations in Figure 4-3(a), where the model underestimates the temperature at a low L/G ratio. Furthermore, other factors such as a fluctuating inlet flue gas moisture content and heat loss in the absorber are likely to take on increased significance in long runs in the pilot plant, influencing the measured temperature profile. However, this has not been accounted for in the model, as moisture content was assumed constant throughout the run and heat loss in the absorber was assumed to be negligible. The impact of a changing inlet flue gas moisture content on absorber performance would be analysed in Section 4.5.1.

In Figure 4-6(d), the model consistently under-predicts the treated gas CO₂ concentration, though the trend of the model response is in agreement with the pilot plant data logs. This indicates that the model overestimates the amount of CO₂ captured, but it is sensitive enough to respond to disturbances in inlet CO₂ concentration and the other two changes. The overestimation of the capture level can be attributed to one of the following two reasons. First, absorber performance depends primarily on the effective wetted area (Kvamsdal and Rochelle, 2008), and it has been estimated by the Onda correlation in this work, an empirical formulation known to often provide values different from experimental results (Wang et al., 2006). An overestimated value of wetted area would result in more area available for mass transfer in the model, leading to a prediction of greater amount of CO₂ absorbed than is observed in the pilot plant. Second, the assumption that chemical equilibrium is achieved in the model implies that reactions are instantaneous. CO₂ absorption in MEA is a fast reaction, but it is not instantaneous, which may explain the overestimation of the amount of CO₂ captured by the model. The likely culprit between the two

options depends on the phenomenon that dominates between mass transfer and chemical reaction. This would be investigated in Section 4.5.2.

Furthermore in light of Figure 4-6(e), where the model overestimates the reboiler duty required for solvent regeneration but also tracks very well with the trend of the pilot plant data log, it is logical to attribute this to the over-estimation of CO₂ absorbed in the solvent which indicates that a higher duty would be required to regenerate the solvent, as the reboiler temperature reading from the pilot plant is imposed on the reboiler in the model.

Finally, as previously mentioned in Section 4.3.3, the implementation of a control scheme for lean solvent composition in the model is different from the one in the pilot plant. This may introduce some deviation in model prediction from pilot plant measurements. However, the model satisfactorily predicts the rate of change from one steady-state to another

4.4.2 Case 2 – Process with Intercooler: Falling flue gas flow rate

4.4.2.1 Pilot plant data logs and comparison

Data logs from the same facility at the University of Texas at Austin were made available for some dynamic runs performed in 2010, where the absorber has been configured with an intercooler. The absorber has two packed beds of Raschig-Jaeger RSP250 of 3.05m length. A redistributor section containing a chimney tray/collector and a liquid distributor is located between the two beds. The solvent is collected below the top packed bed, cooled using a plate frame heat exchanger, and then reintroduced into the absorber through a liquid distributor above the bottom packed bed. Other column specifications are provided in Table 7.

Just as in the first case, there are no dynamic step tests available in the data logs, so the same criteria outlined in Section 4.4.1.1 of this work was used to select the Run 5 performed on 30th of August 2010. The positions of the Resistance Temperature Detectors (RTD) attached to the absorber are given in Figure 4-7.

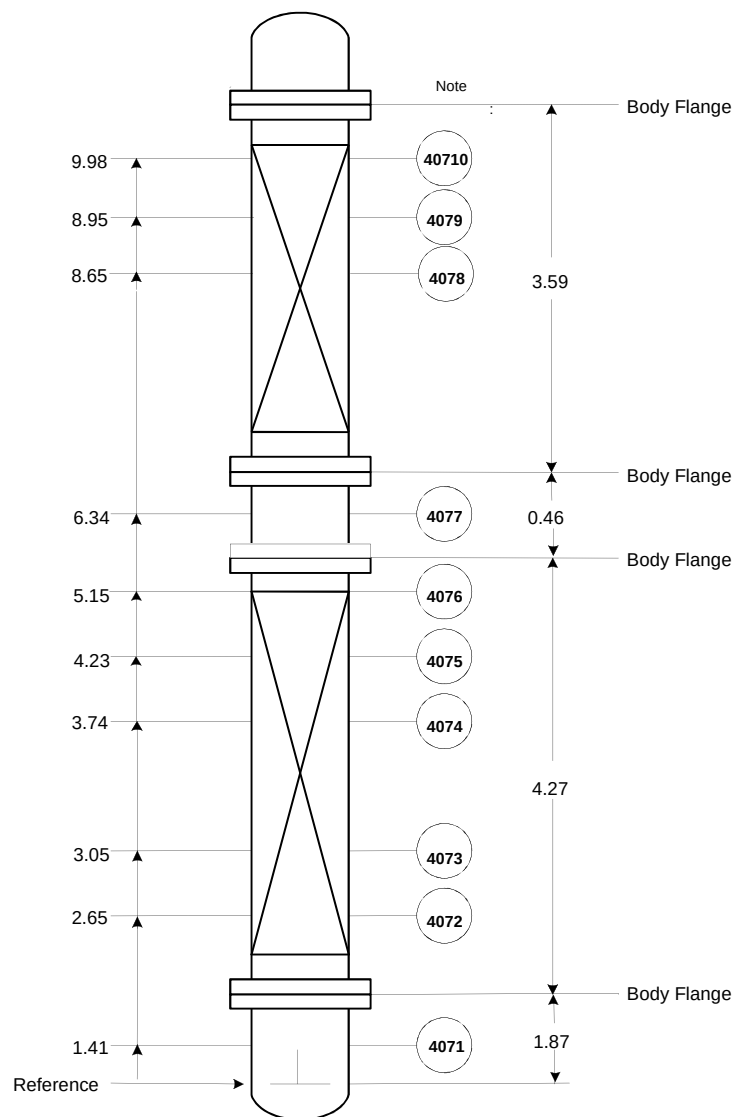


Figure 4-7: Absorber Resistance Temperature Detector (RTD) Elevations

Table 4-7: Columns specifications

Description	Absorber	Regenerator
Column inside diameter (m)	0.427	0.427
Height of packing (m)	6.1	6.1
Nominal packing size (m)	0.0381	0.0381
Specific area (m ² /m ³)	500	200

4.4.2.2 Model topology in gPROMS[®] and Process Inputs/Disturbances

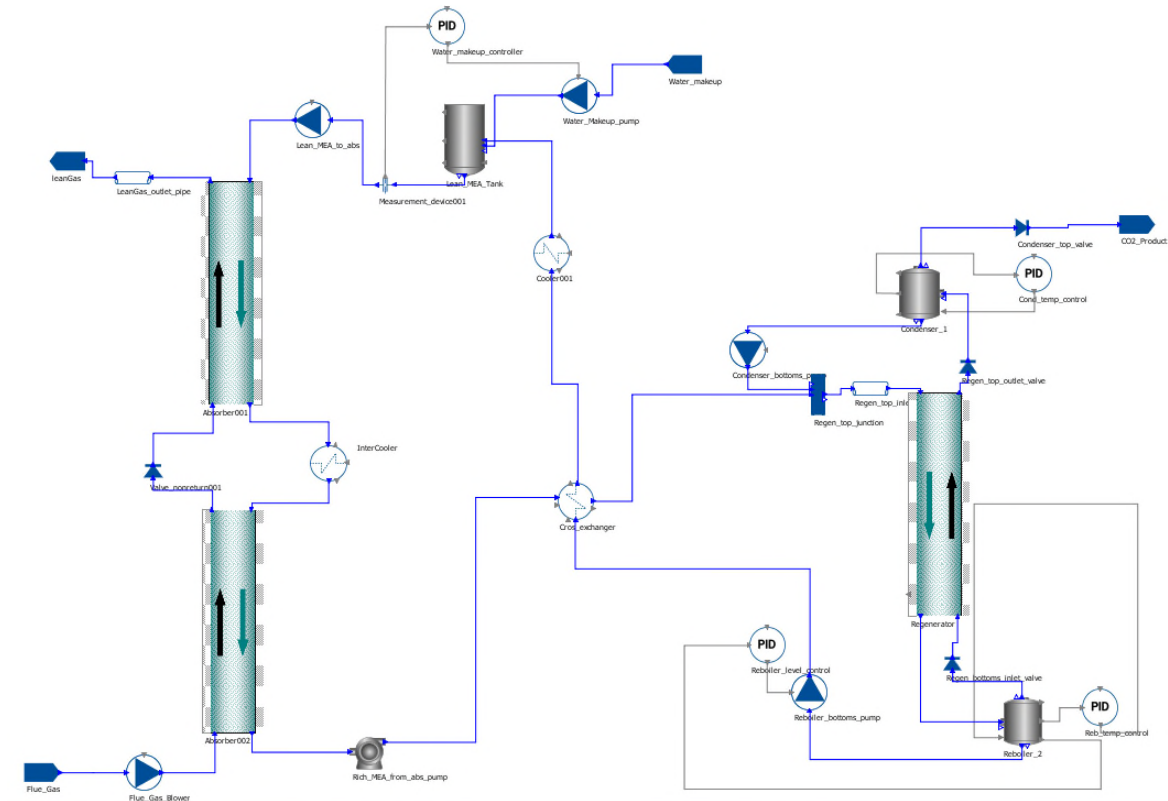


Figure 4-8: Amine Capture Plant Model with Intercooling in gPROMS

In this case, the three main inputs /disturbances identified and introduced to the model are:

- Decreasing flue gas flow rate into the absorber
- Increasing intercooler solvent return temperature
- Fluctuating inlet flue gas CO₂ concentration

The initial conditions of the process are given in Table 4-8. The data log is presented in Figure 4-9.

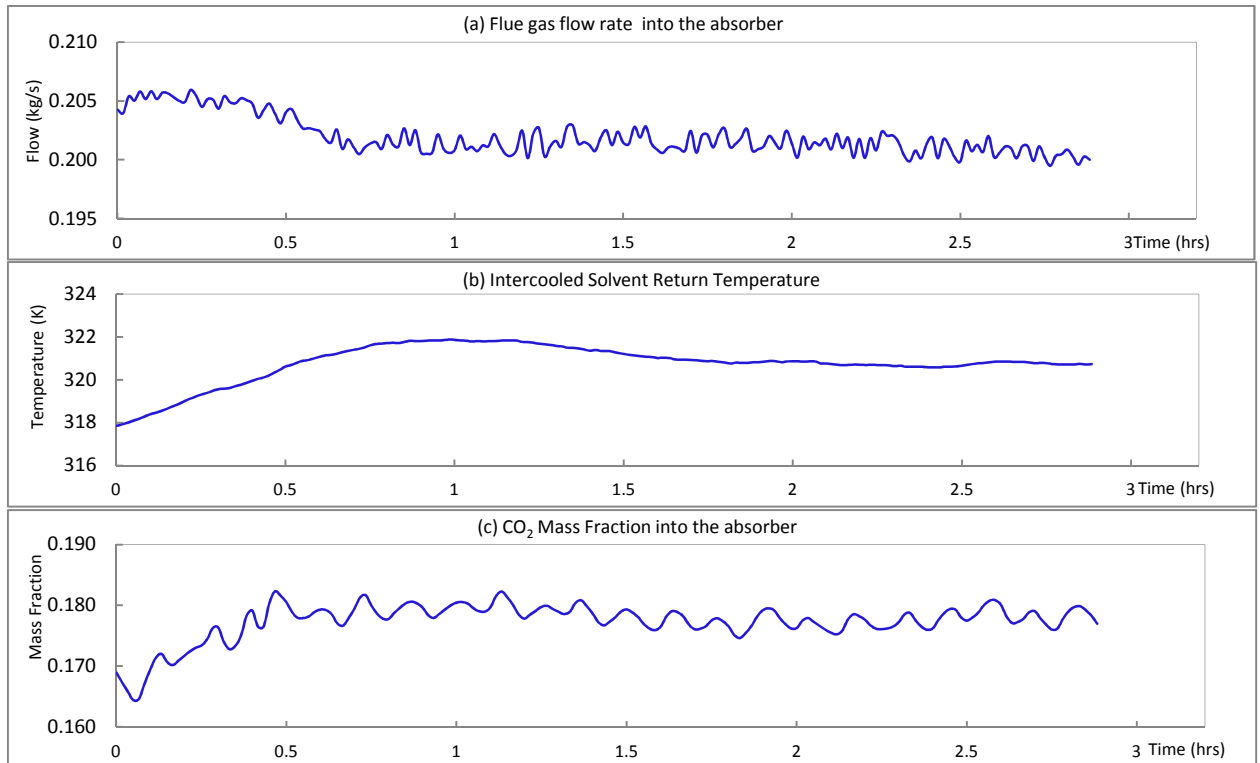


Figure 4-9: Process Inputs/Disturbances Applied to Case 4.2

Table 4-8: Initial Process Conditions for Dynamic Test Run 5

Stream ID	Flue	Lean MEA
Temperature (K)	313	314
Pressure (10^5 Pa)	1.05	1.05
Total flow (kg/s)	0.204	1.157
Mass fraction		
H ₂ O	0.025	0.633
CO ₂	0.173	0.059
MEA	0.000	0.308
N ₂	0.803	0.000

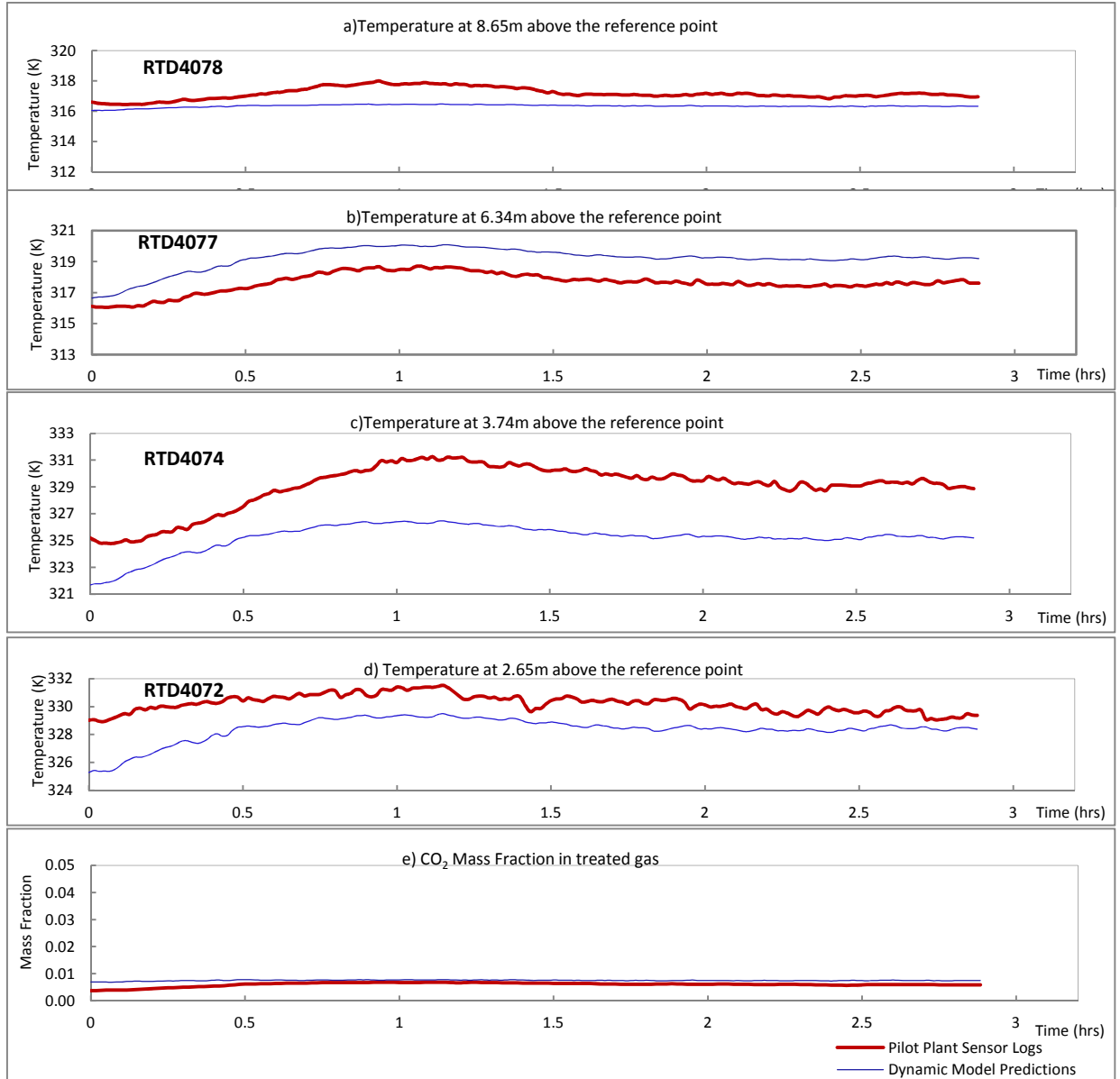


Figure 4-10: Comparison of Pilot Logs and Model Response for Case 4.2

4.4.2.3 Discussion of Results

Considering Figure 4-9(a)-(c), it can be deduced that the falling flue gas flow rate causes an increase in CO₂ concentration. From the subsequent model response recorded in Figure 4-10(a)-(e), it is the increasing intercooler return temperature that appears to correspond to the biggest response in the model, highlighting the impact of intercooler on the absorber performance.

In Figure 4-10(a)-(d), the profile of the model response to the inputs and disturbance introduced is in agreement with the pilot plant data logs, though

there is some deviation in the compared temperature profiles from less than 1K at RTD4078 to a maximum of about 5K at RTD4074. As the absorber is being operated at relatively high L/G ratio, this discrepancy would have then been caused by the implementation of Onda correlation for wetted area estimation in the model, which as earlier stated is an empirical expression known to often underperform by providing values quite different from experimental results. The estimated wetted area defines the mass transfer area in the absorber, which impacts the amount of CO₂ absorbed, which then dictates the heat of absorption calculated, hence influencing the temperature profile predicted in the model. A wetted area estimate, lower than what is obtained in the pilot plant would result in the trend observed in Figure 4-10(a)-(d), where the model under-predicts the temperatures, implying that less CO₂ is absorbed into the solvent, which is also confirmed in Figure 4-10(e). Only at the point corresponding to sensor RTD4077 is the prediction different, because it is the point of intercooling where pilot plant measurements are temperature measurements of the vapour in the absorber, while the model prediction is driven by the temperature imposed on the cooled solvent returned to the lower half of the column.

Another reason for the discrepancy is the necessary approximation of the nearest model discretization points to pilot plant measurement points along the absorber length, as model variables are only calculated at such points, which do not exactly correspond to the measurement points in the plant, and can therefore introduce a deviation in the comparison. However, irrespective of the observed deviation, there is a clear model agreement with the plant data logs.

In Figure 4-10 13(e), the model prediction is very close to the pilot plant data logs, although it consistently overestimates the CO₂ concentration in the treated gas. This means that model slightly underestimates the amount of CO₂ captured but is sensitive to disturbances in CO₂ concentration in the inlet flue gas. As explained earlier, the reason for this can be attributed to the estimated wetted area that influences both the material and energy continuity in the model (Equations (4-1)&(4-2).

Another potential culprit for the deviations observed is the different control scheme implemented for lean solvent composition in the model, which has been covered in Section 4.3.3. As before, its impact is negligible as the model satisfactorily predicts the pilot plant response to the imposed process inputs and disturbances.

4.4.3 Case 3 – Process with Intercooling: Decreasing intercooled solvent temperature process

4.4.3.1 Pilot plant data logs and comparison

The process details are the same as given in Section 4.4.2, with column specifications provided in Table 7 and the positions of the RTDs attached to the absorber given in Figure 10. The data logs for Run 6 performed on the 30th of August 2010 was chosen based on the selection criteria described in Section 4.4.1.1.

4.4.3.2 Process Inputs and Disturbances

The process flow diagram is given in Figure 4-8. The input and disturbances that are tracked are:

- A step decrease in intercooled solvent return temperature
- Fluctuating CO₂ concentration in the flue gas
- Falling lean amine inlet temperature
- Falling flue gas inlet temperature

The initial conditions of the process are given in Table 4-9. The data log is presented in Figure 4-11.

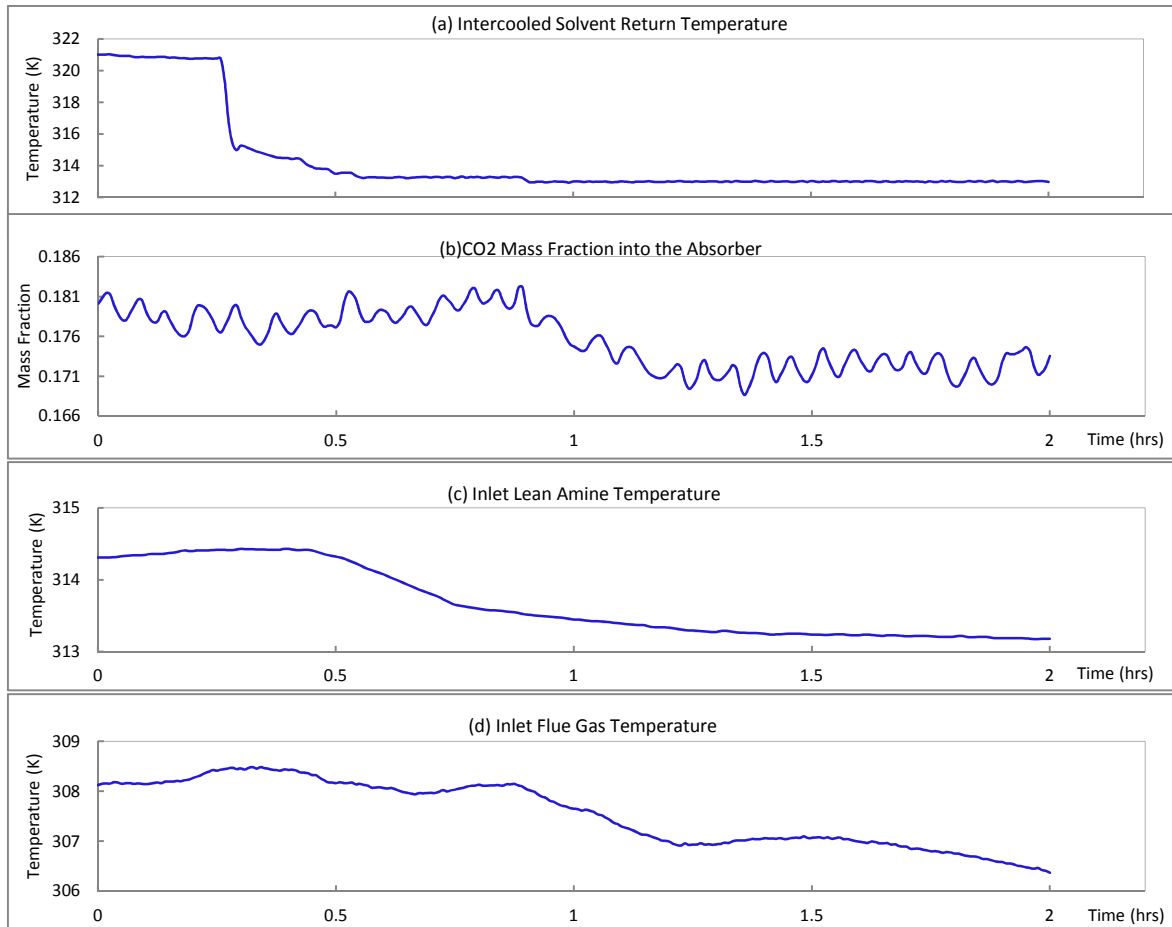


Figure 4-11: Process Inputs/Disturbances Applied to Case 4.3

Table 4-9: Initial Process Conditions for Dynamic Test Run 6

Stream ID	Flue	Lean MEA
Temperature (K)	308	314
Pressure (10^5 Pa)	1.05	1.05
Total flow (kg/s)	0.201	1.158
Mass fraction		
H ₂ O	0.025	0.633
CO ₂	0.180	0.059
MEA	0.000	0.308
N ₂	0.796	0.000

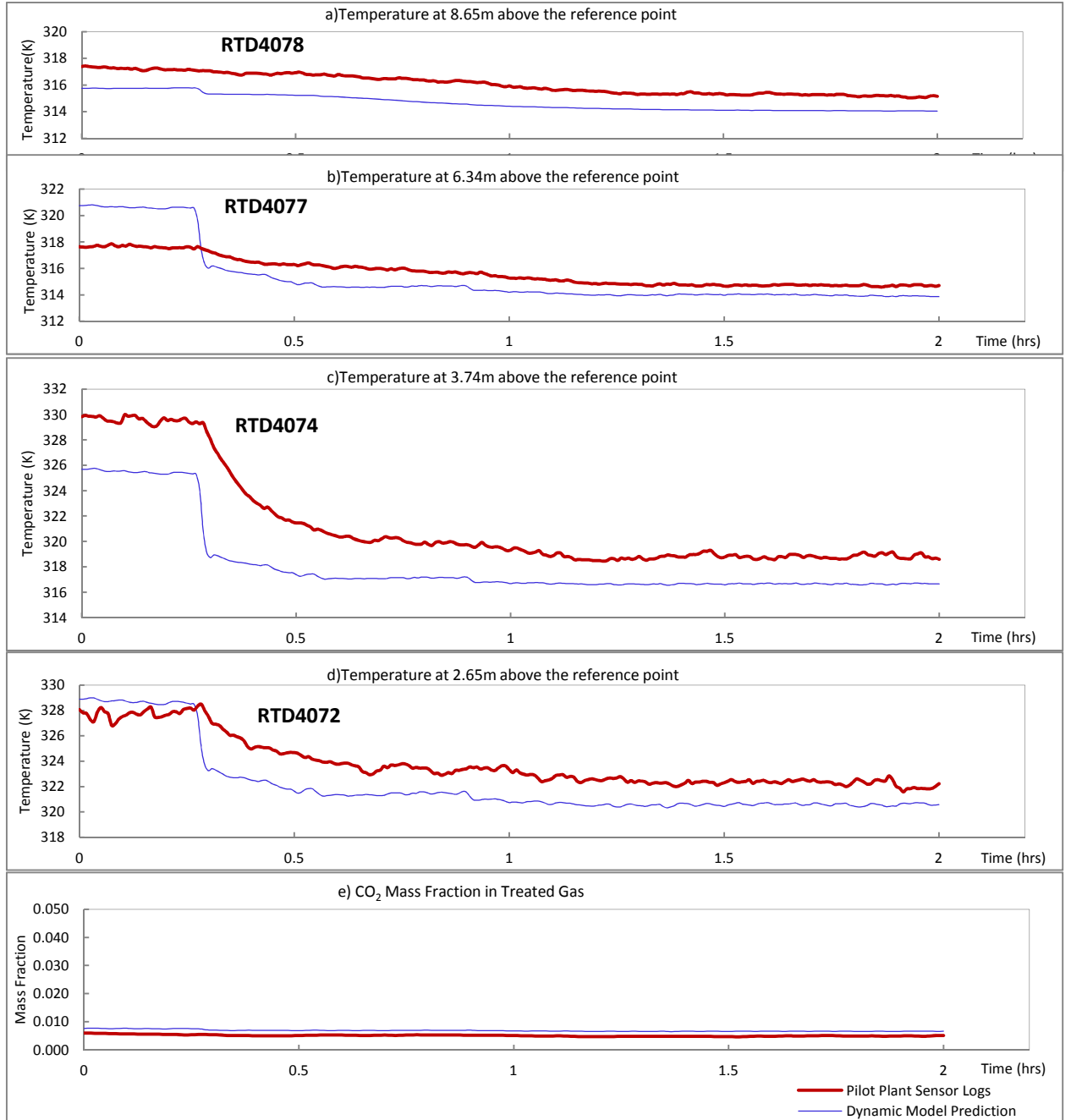


Figure 4-12: Comparison of Pilot Logs and Model Response for Case 4.3

4.4.3.3 Discussion of Results

Considering Figure 4-11(a)-(d) and the model response recorded in Figure 4-12(a)-(e), the step change input of intercooler solvent return temperature from 321 K to 313 K and the three other disturbances appear to have a marginal effect on the capture level, as the CO₂ mass fraction of the treated gas only decreases slightly.

In Figure 4-12(a)-(d), just as observed in Figure 4-6 and Figure 4-10, the profile of the model response to the inputs and disturbance is in agreement with the pilot plant data log. But as with Case 4.2, there are some deviations in the compared temperature profiles with a maximum of about 4 K at RTD4074. In Figure 4-12(e), the model consistently over-predicts the treated gas CO₂ concentration slightly. The reasons for both are covered in detail in Section 4.4.2.3.

In this case, however, the step change input of a fall in return temperature for the intercooled solvent (Figure 4-11(a)) is of particularly interest because a proportional improvement on the absorber capture level is the expected result, but only a marginal change is observed.

This implies that either the absorber is being operated in a manner that makes intercooling inconsequential or that the intercooler has been placed at a position where its impact on absorber performance is negligible. Depending on the L/G ratio, a temperature bulge can be observed along the length of the absorber, shifting from top to bottom with increasing L/G ratio (Kvamsdal and Rochelle, 2008). The intercooler is expected to be most effective if it is placed just before the temperature bulge. The L/G ratio in this case is about 5.7, which is moderately low when compared with the runs made by Dugas (Dugas, 2006). This means that the temperature bulge occurs at the top of the absorber, making an intercooler at the middle of the absorber length ineffective. The absorber should be operated with an L/G ratio that ensures the bulge occurs around the middle of its length for the intercooling to provide benefits.

On further analysis of the disturbances and the response of the pilot plant and model response, the fluctuating CO₂ concentration of the inlet flue gas (Figure 4-11(b)), which is on a downward trajectory, in addition to the falling temperatures of inlet lean solvent (Figure 4-11(c)) and flue gas (Figure 4-11(d)) can all contribute to the marginal fall in CO₂ concentration of the treated gas. Therefore, further model analysis would be performed to determine the impact of intercooling.

4.5 Process Analysis

4.5.1 Flue Gas Moisture Content

4.5.1.1 Justification for case study

The flue gas moisture content is highly dependent on the fuel from which the flue gas was produced (via combustion), as well as the flue gas temperature and pressure, and can amount to about 25wt% of the gas (Levy et al., 2008). It plays a major role in the water balance in the absorber (Kvamsdal et al., 2010), and therefore influences the performance of the absorber. It also has an impact on the temperature profile of the absorber since the exothermic nature of the absorption of CO₂ into the solvent results in water evaporation from the solvent. Water also condenses from vapour in the absorber when it comes in contact with fresh and cooler solvent. These competing processes define the temperature bulge observed in the absorber (Kvamsdal and Rochelle, 2008).

For a 585 MW coal fired power plant, moisture flow rates in the flue gas can range from 25 kg/s for units firing bituminous coals to 75 kg/s for those firing high moisture lignites (Levy et al., 2008). The flue gas from the plant is passed through the flue gas desulphurisation systems before it is sent to a CO₂ Capture unit. Upstream to the absorber, a direct contact cooler (DCC) is usually provided to reduce the flue gas temperature, using recirculating cool water (Kvamsdal et al., 2010; NETL, 2007). In the DCC, water condenses from the flue gas if it is cooled below its dew point, reducing the moisture content before it is fed into the absorber by a blower. So a study is carried out to analyse the impact of an increasing flue gas moisture content on the absorber performance. This scenario can be caused by the failure of the DCC water pump.

4.5.1.2 Setup of the case study

Although the moisture content is greatly dependent on flue gas temperature, the temperature is kept constant while the moisture content is increased, so as to get a model response due to the moisture content increase only, not one that is also influenced by temperature increases. For the purpose for this analysis, it is assumed that the flue gas can hold more moisture at its current conditions.

The case described in Section 4.4.1 is used. The same run is performed, however at the 1 hour mark of the run all inputs in the model are kept constant and disturbances are eliminated, while the moisture content is ramped up from 1.5 wt% to a modest 15 wt% over the 2 hours, increasing the moisture flow rate from 4g/s to 45g/s (Figure 4-13), with the nitrogen concentration reduced to maintain the same total flow rate. The flue gas composition is then held steady for another hour to observe the model responses.

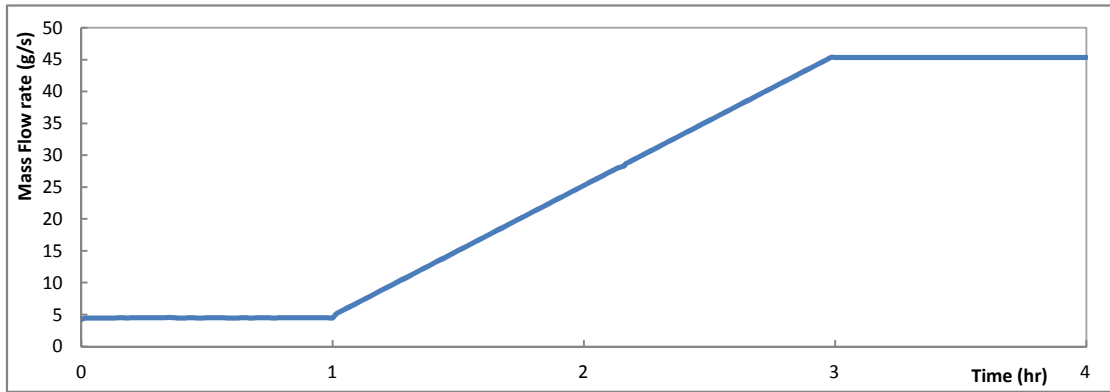


Figure 4-13: Inlet Flue Gas Moisture Flow rate as Process Input

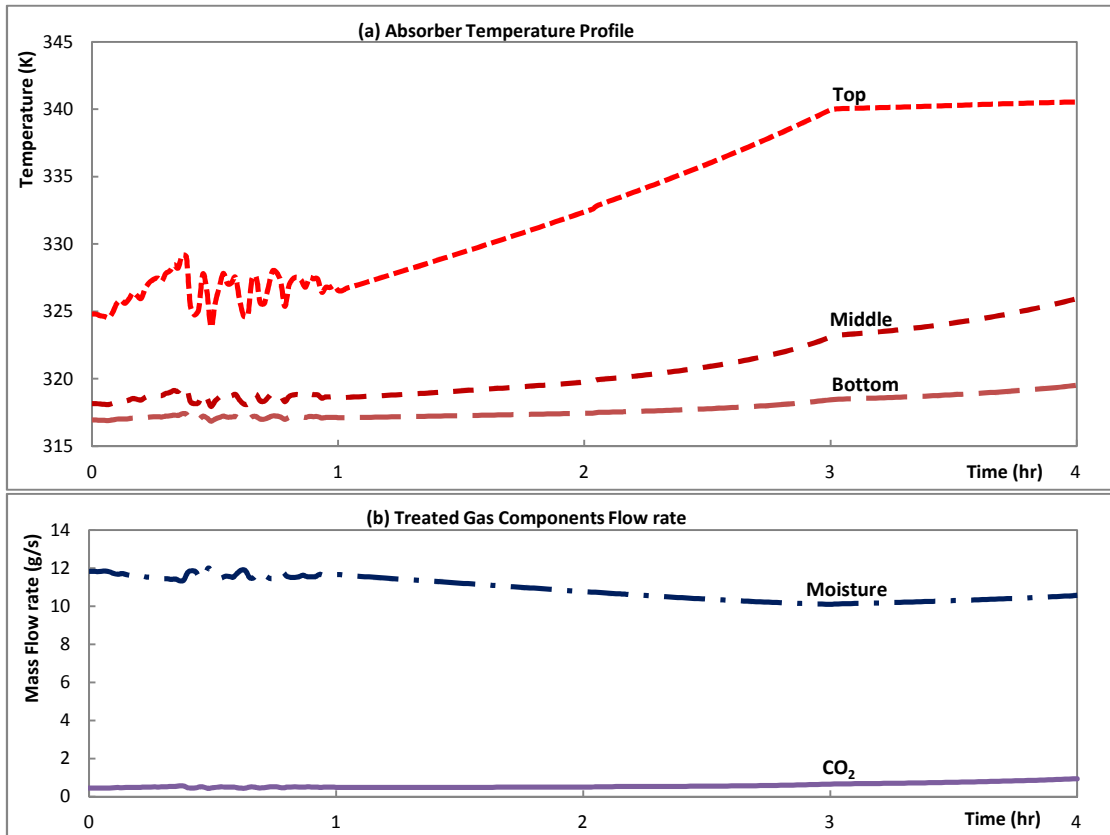


Figure 4-14: Effect of Moisture Content Increase on Model Performance

4.5.1.3 Discussion of Results

The results are displayed in Figure 4-14. The CO₂ flow rate in the treated gas is observed to increase slightly as the flue gas moisture content increases, indicating a decrease in capture level. However, the moisture flow rate in the treated gas decreases slightly before attempting to stabilise at a new steady-state, signifying that most of the additional water in the inlet flue gas condenses into the solvent, which should increase the reboiler duty required. However such a response is not observed, as the temperatures were maintained at 387 K with minimal change in reboiler duty, most likely caused by the slow dynamic response of the system (Lawal et al., 2010). A new steady-state is not arrived at within the hour of observation.

The temperature profile on the other hand, reveals significant changes. The temperatures in the absorber increase with moisture content, and the biggest change of 15 K occurs at the top of the absorber, indicating that it is the region of water condensation as the flue gas comes in contact with fresh and cooler solvent. This is in agreement with the findings of Kvamsdal et al. (2010), who proposed controlling the temperature at the top of the absorber as the optimal setup to maintain absorber water balance. The temperature control is achieved by keeping the inlet flue gas temperature below the gas dew point, which controls the moisture content of the inlet flue gas.

Therefore, in assessing the impact of inlet flue gas moisture content on the performance of the model, an inference can be drawn that it is an important measurement for model validation. A further conclusion can be made that the dynamic validation runs covered in Section 4.4 could have produced better temperature profile predictions if measurements for inlet flue gas moisture content (which would fluctuate along with the concentrations of the other components) were imposed on the model, instead of the constant value estimated as a function of the air humidity.

4.5.2 Inter-cooler Impact on Temperature Bulge in the Absorber

4.5.2.1 Justification for case study

A study is performed to investigate the benefits of effective intercooling on the absorber performance. As mass transfer in the absorber decreases with increasing temperature while chemical reaction increases with temperature (Kvamsdal et al., 2010), it is possible to infer the dominant phenomenon between the two by reducing the temperature in the absorber via intercooling and analysing the impact on the absorber performance.

Although reactions are assumed to be in equilibrium in the model, the equilibrium constants are a function of temperature (Equation (4-11)), and would therefore respond to temperature changes. An increased capture level resulting from intercooling would suggest that mass transfer is dominant, while a reduced capture level will reveal that chemical reaction controls absorption. In Section 4.4.3.3, the cause of the marginal increase in capture level of the absorber has not been categorically identified since there are four distinct disturbances on the process, therefore further analysis was proposed.

4.5.2.2 Setup of the case study

As stated earlier, the impact of intercooling is likely to be more pronounced if the temperature bulge occurs along the middle of the absorber length. This occurs around an L/G ratio of 6.2 (Kvamsdal and Rochelle, 2008), as a result the flue gas flow rate is reduced in the case described in Section 4.4.3 from 0.201 kg/s to 0.187 kg/s, reaching this ratio. This is done before the period of study so as to eliminate the model dynamic response that will result from the fall in flue gas flow rate, which would cloud primary subject of study i.e. the effect of intercooling.

All other inputs are kept constant and the disturbances are eliminated to ensure that the impact of intercooling is correctly analysed. The same points of measurements used in Case 4.2 & 4.3 were retained in the model analysis for consistency. The model is run for a quarter of an hour without an intercooling duty for it to attain steady-state, a steady temperature drop of 10K over 15

minutes is introduced to the intercooled solvent (Figure 4-15), then the model prediction is observed over the following hour. The results are given in Figure 4-16.

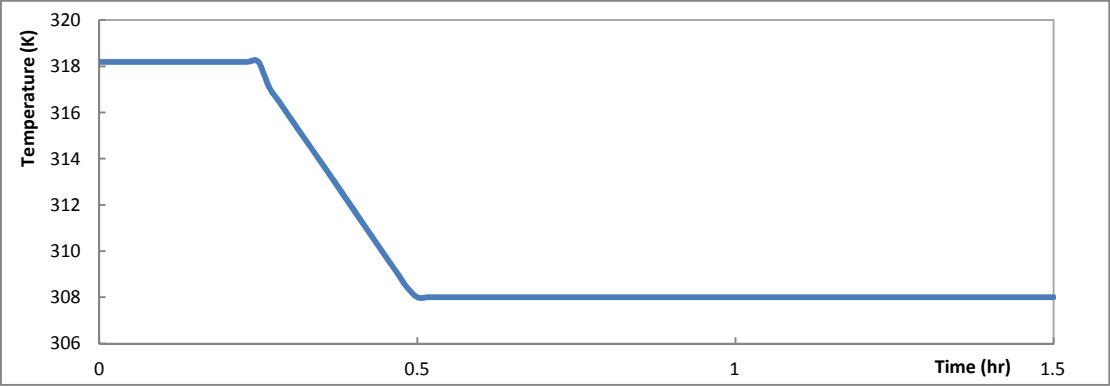


Figure 4-15: Intercooler Return Temperature Process Input

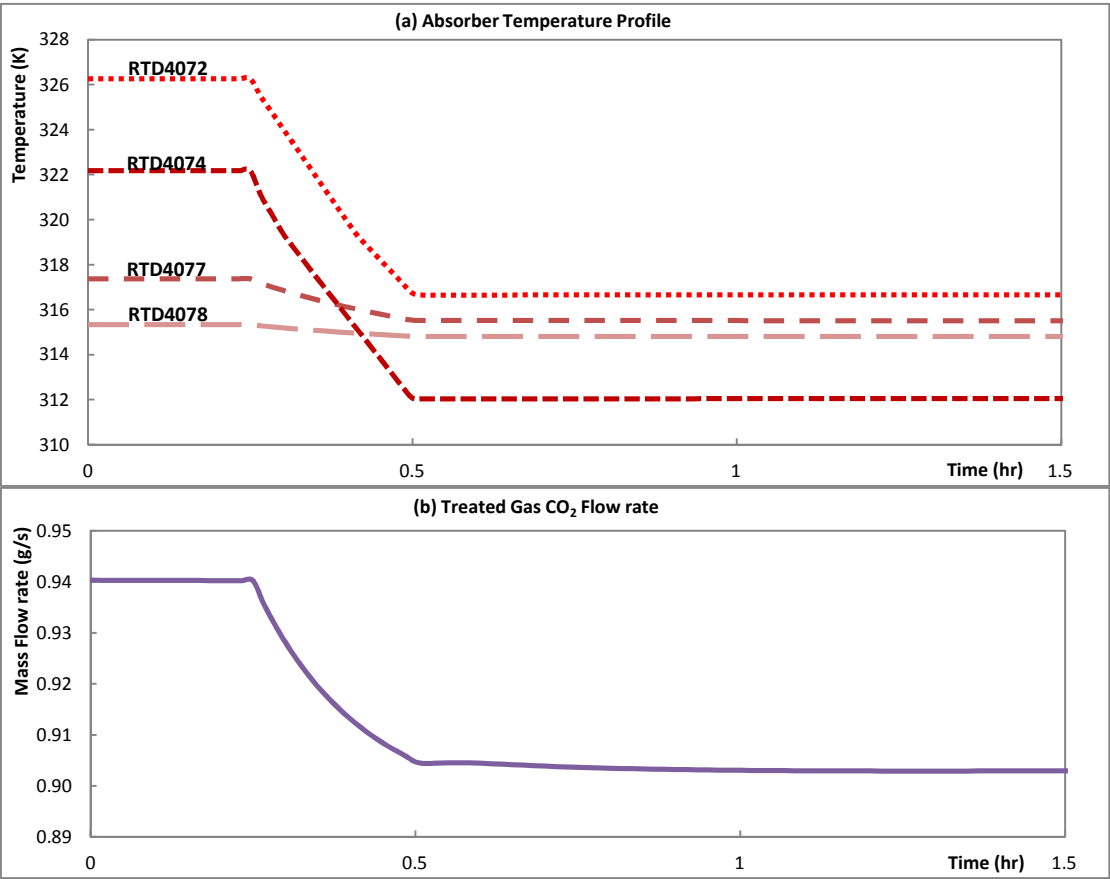


Figure 4-16: Effect of Absorber Intercooling on Model Performance

4.5.2.3 Discussion of Results

It is observed that the falling intercooled solvent temperature has a pronounced impact on the temperature profile, as already seen in Section 4.4.3.3, especially in the bottom half of the column. More significantly, the intercooling has a modest impact on capture level, as the CO₂ flow rate in the treated gas falls by 4% before attaining a new steady-state. This effect is all the more remarkable considering the already low concentration of CO₂ at the onset of the run. This suggests that absorption of CO₂ in MEA solvent is limited by mass transfer at the conditions in the absorber. The primary implication of this is that the model prediction can be significantly improved by a better estimation of wetted area.

5 MODEL IMPROVEMENT

5.1 Motivation

After the model described by Lawal et al. (2009a, b, 2010) was successfully implemented in gPROMS[®] and subsequently analysed in Section 4.5, the limitations identified prompted the improvement of the rate-based model, by eliminating the assumption of a chemical equilibrium and updating the mass transfer calculations.

Rate-based models built on the two-film approach have been developed that avoided an assumption of chemical equilibrium. Kvamsdal et al. (2009), Simon et al. (2011), Ziaii et al. (2009), Gaspar and Cormos (2011, 2012), Posch and Haider (2013) and Harun et al. (2012) have developed dynamic models for CO₂ absorption in MEA by adding enhancement factors to account for the chemical reactions. Kale et al. (2013) avoided enhancements factors, and considered the reaction contribution via a source term in the liquid-side continuity in a steady-state model of the absorber. Zhang et al. (2009) also developed an absorber model that included mass transfer and chemical reactions within the model continuity, and Plaza et al. (2010) presented a similar model used to simulate the full capture plant, yet both are only steady-state models.

The models described above are semi-mechanistic models, as first principles have been used to develop these models, with mass transfer parameters determined using correlations. Jayarathna et al. (2013) however, chose a simpler modelling approach by using the Kent-Eisenberg method, which involves empirical correlations, to build a dynamic model. However, such a model can hardly be extended to other solvents, nor relied upon to predict behaviour beyond the correlation's empirical range. Therefore, a rate-based dynamic model that explicitly employs mass transfer and chemical reactions within its continuity equations is required for prediction of PCC plant operations.

The primary benefit of such a model is that it would provide a robust prediction of the process. It can also be applied to the comparisons of different solvent performance as long as the kinetic data of CO₂ absorption in the solvents are

available. In addition, a better analysis of the diverse PCC plant configurations can be made. Potentially, new operational problems could be identified, as the inclusion of reaction rates in model continuity brings the dynamic simulations close to reality.

5.2 Model Implementation

5.2.1 Reaction Kinetics

The two film theory is used to describe the model, along with the continuity equations and accompanying assumptions already covered in Section 4.2.1. The key change here is that the assumption of a chemical equilibrium at the vapour-liquid interface in the previous model is replaced with an assumption that reactions occur in the liquid film.

The kinetic models, described in Section 3.4 of this report, have been considered. CO₂ diffuses from the vapour film into the liquid film, and then reacts with the MEA in the solvent, which is why reactions are only considered in the liquid film. As a result, the material continuity expression of the liquid film becomes:

$$\frac{\partial^2 C_i}{\partial z^2} - r_i = 0 \quad (5-1)$$

The reaction rate r of each component i is determined from the kinetic models.

5.2.2 Mass Transfer

Correlations by Onda et al. (1968) were used to estimate the mass transfer coefficient in both films and the wetted area on the column packing in the model described in Section 4. As it has been shown in Section 4.4 that the performance of an absorber is primarily dependent on the interfacial or wetted area, it is important that other methods of estimating it be considered. Therefore, the Billet and Schultes (1999) correlations, described in Section 3.3, are also implemented. This is vital because the Onda correlations are empirically derived for columns with random packing, while the Billet-Schultes correlations have been semi-theoretically derived and can be applied to a

column with structured packing. This implies that they are more robust (Wang et al., 2006), as confirmed by Cosmos and Gaspar (2012; Gaspar and Cormos, 2012)

A linear pressure profile is assumed, while liquid holdup for both cases is estimated using the correlation given by Billet and Schultes (1999). Fuller et al. (1966) method is still used to calculate the vapour diffusivity for the vapour components, while the method provided by Versteeg and Van Swaaij (1988) diffusivity of liquid diffusivity CO₂ in water and MEA solution.

Finally, in determining the molar flux of species through both the vapour and the liquid film, the Maxwell-Stefan expression was previously used. This is still maintained in the vapour film. However, to ensure material balance convergence in the liquid film due to the introduction of reaction kinetics in the continuity, the Ficks Law of diffusion is used:

$$N_i = -D_i \frac{\partial C_i}{\partial z} \quad (5-2)$$

5.2.3 Thermodynamic and Physical Properties

In the model proposed by Aboudheir et al. (2003), solubility of CO₂ in MEA solution at the vapour liquid interface is described using expressions provided by Versteeg and Van Swaaij (1988). For other components that attain VLE at the interface, retaining the property calculation methods used in Section 4 is sufficient, as the Electrolyte NRTL activity coefficient model in Aspen Properties satisfactorily describes the non-ideality of the vapour-liquid interaction in the system. However, since reaction kinetics have been introduced in the liquid film, the equilibrium chemical reactions defined in the interface are eliminated. With the assumption of VLE at the interface implies equal vapour and liquid fugacities. Vapour fugacity for each component *i* is given as:

$$f_i^v = \varphi_i^v x_i^v P \quad (5-3)$$

Where φ^v is calculated from an equation-of-state model, y^v is the vapour fraction and P is the component partial pressure. Liquid fugacity is then determined as:

$$f_i^l = \alpha_i x_i^l P^L \quad (5-4)$$

Where α is the activity coefficient, x^l is the liquid fraction and P^L is the Saturation pressure (usually calculated from Antoine equation). Therefore:

$$\varphi_i^v y_i^v P = \alpha_i x_i^l P^L \quad (5-5)$$

The activity coefficient is an important kinetic parameter in the models proposed by Zhang et al. (2009)/Plaza et al. (2010) and AspenTech (2008). In addition, an activity coefficient model in Aspen Properties® incorporates Henry's law in describing the solubility of non-condensable gases (such as CO₂ and N₂) in the liquid phase (AspenTech, 2010). If Henry's Law is ignored, gas solubility for such components tends to be under-predicted. Therefore, specifying the components as Henry components in Aspen Properties introduces the Henry constant update to the activity coefficient of each individual component.

The heat of CO₂ absorption into MEA solution is determined from expressions given in Equations (4-3) and (4-4). Finally, all other VLE parameters are retrieved from Aspen Properties database via CAPE OPEN, while physical properties were accessed from both Aspen Properties and Multiflash.

5.2.4 Other Considerations

To implement reaction rates into the continuity of the column models, it is important to appropriately account for the composition of all components taking part in the reactions. As seen in the previous section, the solvent streams are specified in terms of three components – CO₂, MEA, H₂O – an apparent approach to composition, where ionic components such as the carbonate and carbamate are reduced to their corresponding stable states of CO₂, MEA and H₂O. The assumption of chemical equilibrium in Section 4.2 ensured that no difficulty was encountered with this apparent approach. However, as the assumption is eliminated, this has become inadequate.

Therefore, it is essential all components involved in chemical reactions – CO₂, MEA, H₂O, H₃O⁺, OH⁻, HCO₃⁻, CO₃²⁻, MEAH⁺ and MEACOO⁻ – are considered

in the lean solvent as it is introduced into the absorber column. This is achieved by using equilibrium reactions to split up the apparent component composition into the true component composition of the lean solvent. When the kinetic model proposed by Aboudheir et al. (2003) is used, equilibrium reactions and constants described in the same reference are used. While the models provided by Zhang et al. (2009)/Plaza et al. (2010) and AspenTech (2008) are implemented with equilibrium reactions described by Equations (4-6) – (4-10), whose constants are derived from Equation (4-11) using coefficients provided in Table 4-1. Due to the difficulty of handling ionic components in simulations, the true composition of the absorber liquid outlet, i.e. the rich solvent, is reduced to its apparent composition containing only CO₂, MEA, H₂O and perhaps N₂.

Solving the model column model in gPROMS requires discretisation of partial differential along the axial length of the column and across the thickness of vapour and liquid films. Similar discretisation parameters used in Section 4.2 are also used here for the column axial length and the vapour film thickness. However, due to the chemical reactions that have been implemented, it is vital that sufficient discretisation points are used in the liquid film to ensure good solution precision. Yet, the higher the number of discretisation points specified, the greater the computation required.

During model implementation, it was observed that reaction rates in the liquid film were greater at regions closer to interface with the vapour film, than at regions closer to the bulk liquid. Therefore, a logarithmic approach to discretisation is implemented, reducing the number of discretisation points and hence computation requirement. An illustration of the anticipated model changes compared to the model described in Section 4.2 is shown Figure 5-1.

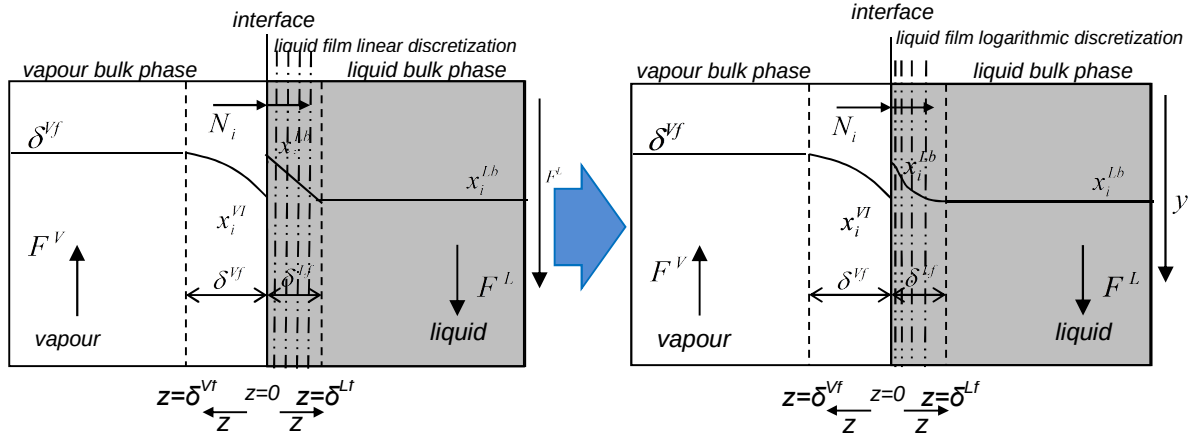


Figure 5-1: Model 3 ► Model 5 Implementation

5.3 Model Validation

5.3.1 Pilot Plant Data and Considerations

The absorber of the PCC plant was used to validate the model, using data logs of the at the SRP pilot plant at the University of Texas at Austin (Dugas, 2006). Cases 25, 32 and 47, at different L/G ratios, are selected and validated against the model results. Process conditions of Cases 25, 32 and 47 are given in Table 4-2 and Table 4-6, and absorber specifications are given in Table 4-3.

Although the three kinetic models described in Section 3.4 were implemented in gPROMS, successful model convergence was only attained for the kinetic model described by Aboudheir et al. (2003). This “Model 5” is then validated at steady state, with two different sets of mass transfer coefficients, Onda and Billet-Schultes, considered. The results are compared to those of the previous model, which will be identified as “Model 3”, without the adjusted flue gas flow rate described in Section 4.3.3, with focus on the rich solvent loading, the capture level and the temperature profile.

Table 5-1: Steady-State Validation

Case	Variable	Pilot Plant Data	Model 3	Model 5 Onda	Model 5 Billet
25	Lean loading	0.278	0.278	0.278	0.278
	Rich loading	0.386	0.351	0.347	0.354
	Capture level (%)	93	99	89	96
32	Lean loading	0.281	0.281	0.281	0.281
	Rich loading	0.428	0.449	0.475	0.474
	Capture level (%)	95	81	93	93
47	Lean loading	0.279	0.279	0.279	0.279
	Rich loading	0.539	0.459	0.493	0.490
	Capture level (%)	69	65	78	77

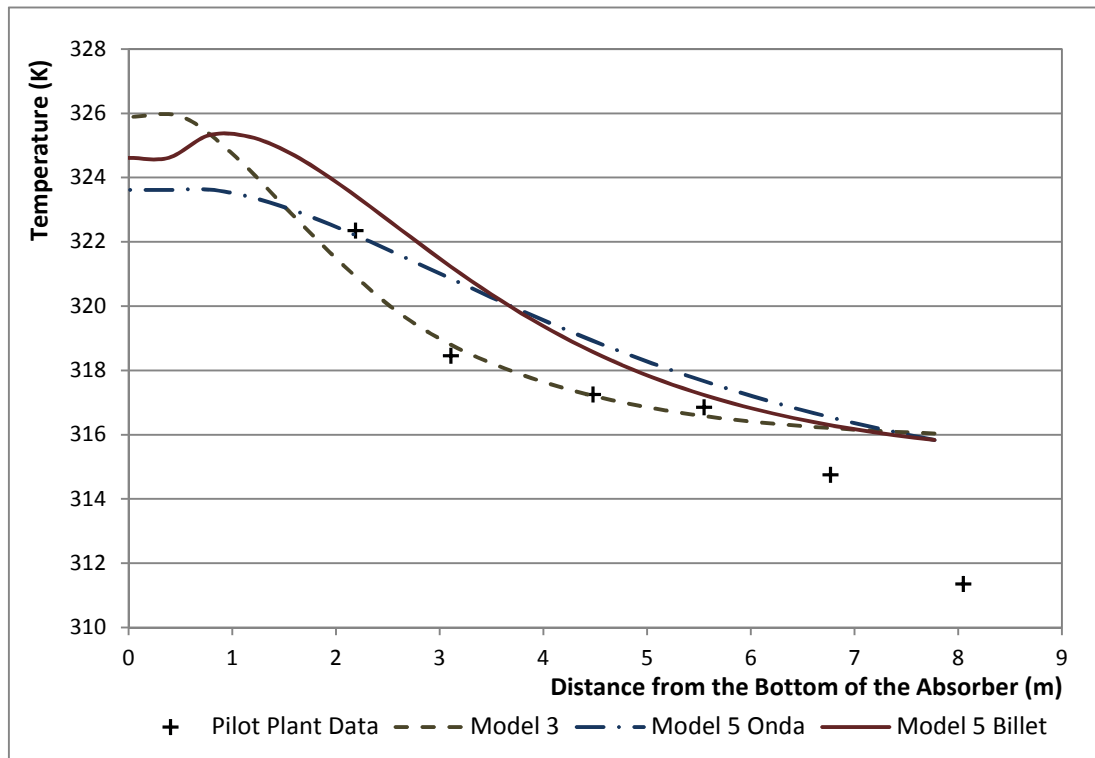


Figure 5-2: Temperature Profile Comparison for Case 25

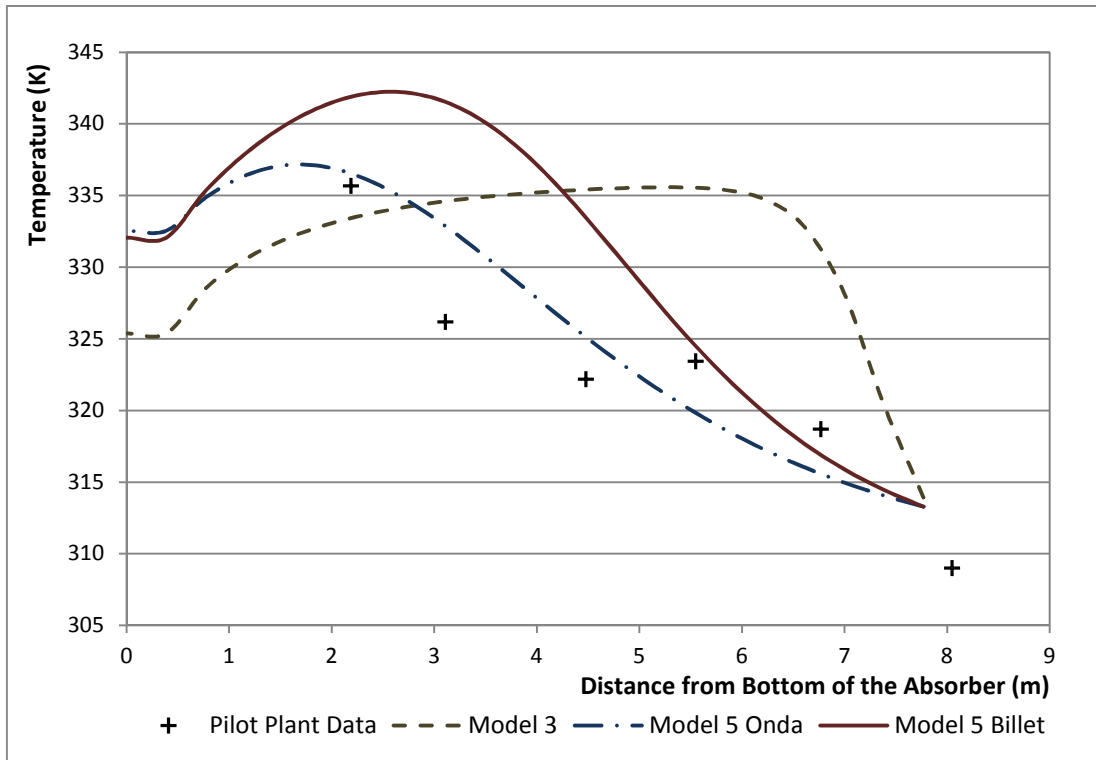


Figure 5-3: Temperature Profile Comparison for Case 32

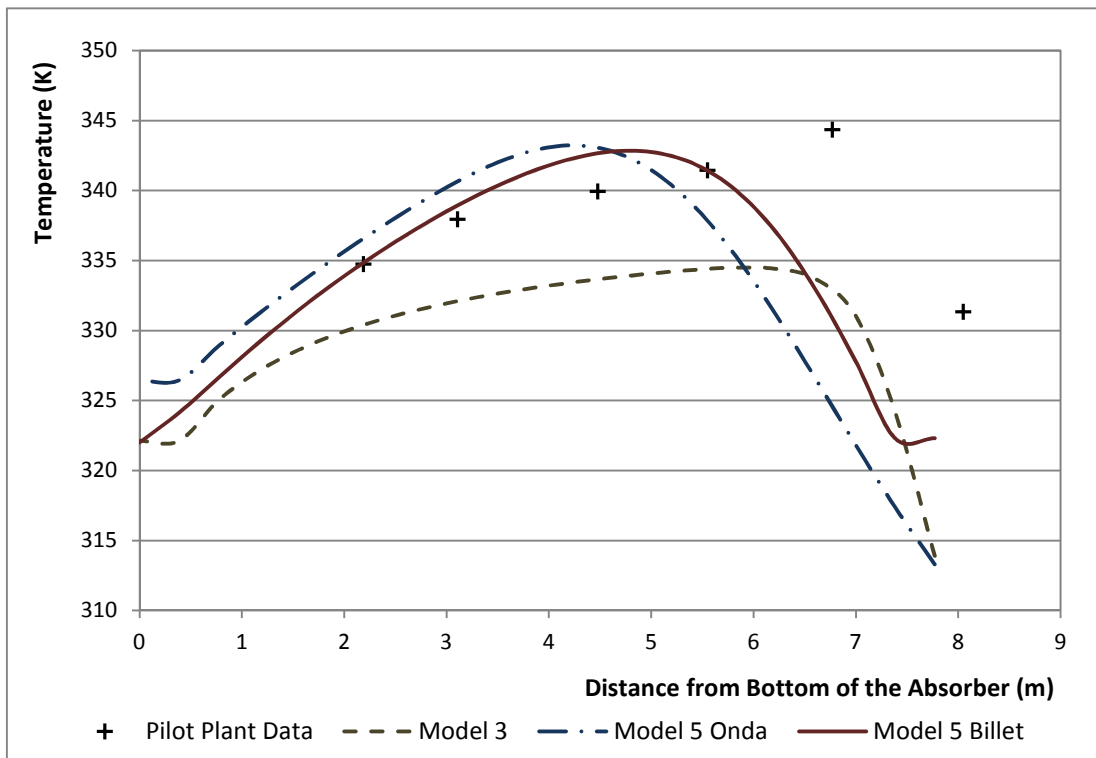


Figure 5-4: Temperature Profile Comparison for Case 47

5.3.2 Validation Discussion

From the cases considered (Table 5-1), there is better prediction of the capture level when reaction kinetics is implemented, irrespective of the mass transfer correlations used, with close predictions attained for Cases 25 and 32. Capture level is overestimated for Case 47, and there seems to be little improvement in rich loading predictions of the solvent exiting the absorber. Yet from Figure 5-2, Figure 5-3 and Figure 5-4, it is clear that Model 5 offers a better prediction of temperature profiles, regardless of the mass transfer correlations utilised. The largest difference is observed in Case 32, where the previous model (Model 3) struggles at the flow rates reported. Also in Case 32, using the Onda correlations in Model 5 provide a better temperature profile prediction, as the Billet-Schultes correlations predict higher absorber temperatures. This is likely due to the fact that random packing was used in the absorber column, as the Onda correlations were formulated for random packing.

Predictions for rich loading are reasonable, but could be improved. The material balance can point to the factor influencing this in the plant. Hence, it is clear that one or a combination of the following is the cause of the slight discrepancies:

- Pilot plant was not at steady state when the measurements were taken.
- Solvent has been carried out of the absorber by the vapour.
- Liquid holdup in the impacts absorber performance significantly.

During the pilot campaign, Dugas (2006) describes sampling to have been done an hour after an operating condition is set, and then repeated an hour later. Solvent losses were not reported, but discrepancies were identified for measurements of inlet gas rates into the column and temperature at the top. Therefore, the likely culprit for the observed differences between the pilot plant data and model prediction is either due to errors in inlet gas rate measurement or the absorber liquid holdup and how it is estimated in the model.

According to Razi et al. (2012), liquid holdup is often split into a static part and a dynamic part. The static part remains when gas and liquid flow is turned off and constitutes pockets of liquid that can actively participate in mass transfer. The

dynamic holdup is the difference between the total and the static holdup. As stated in Section 5.2.2, liquid holdup in this model is estimated via expressions given by Billet and Schultes. The model reported by Zhang et al. (2009), which provides reasonable predictions for rich loading, uses the Stichlmair correlation for liquid-up. Liquid hold-up estimation may be the reason for non-convergence of the model when kinetic models by Zhang, Plaza or AspenTech are utilised. Thus other liquid hold up methods ought to be explored.

Ultimately, adding chemical reactions to the model continuity ensures that plant performance is better predicted by the model. More validation cases of varied PCC plant dimensions/configurations are required to confirm its efficacy.

5.4 Dynamic Analysis

5.4.1 Approach

Case 32 is selected as a base case to investigate the dynamic behaviour of the absorber model. Process conditions were held constant for 2 minutes, before flue gas flow rate into the absorber was ramped up by 50% over 10 minutes, while all other process inputs remained constant. The system was then allowed to return to steady state. The procedure is repeated for a 50% ramp down of flue gas flow rate (Figure 5-5).

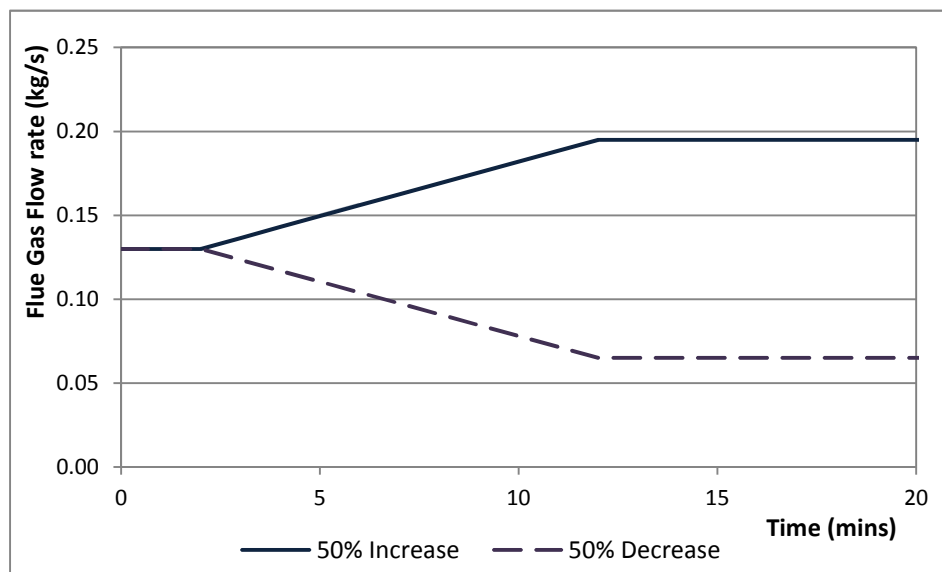


Figure 5-5: Absorber Model Dynamic Analysis Inputs

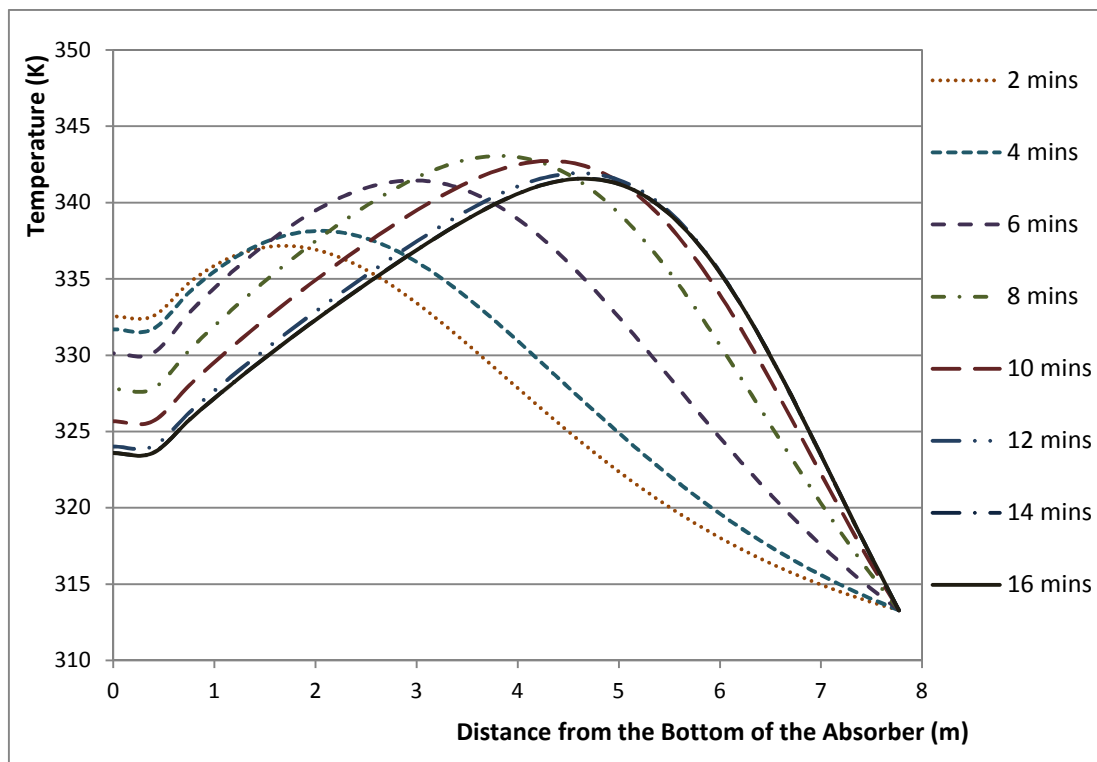


Figure 5-6: Temperature Profile Due to Flue Gas Flow Increase (Onda)

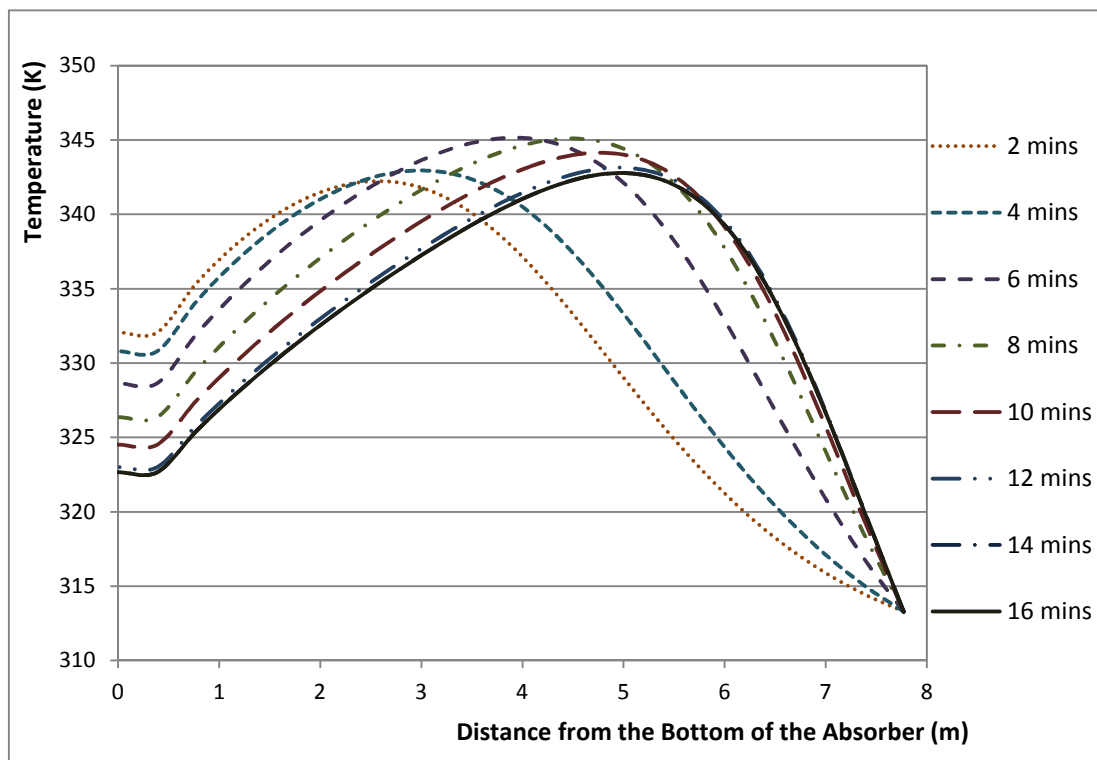


Figure 5-7: Temperature Profile Due to Flue Gas Flow Increase (Billet-Schultes)

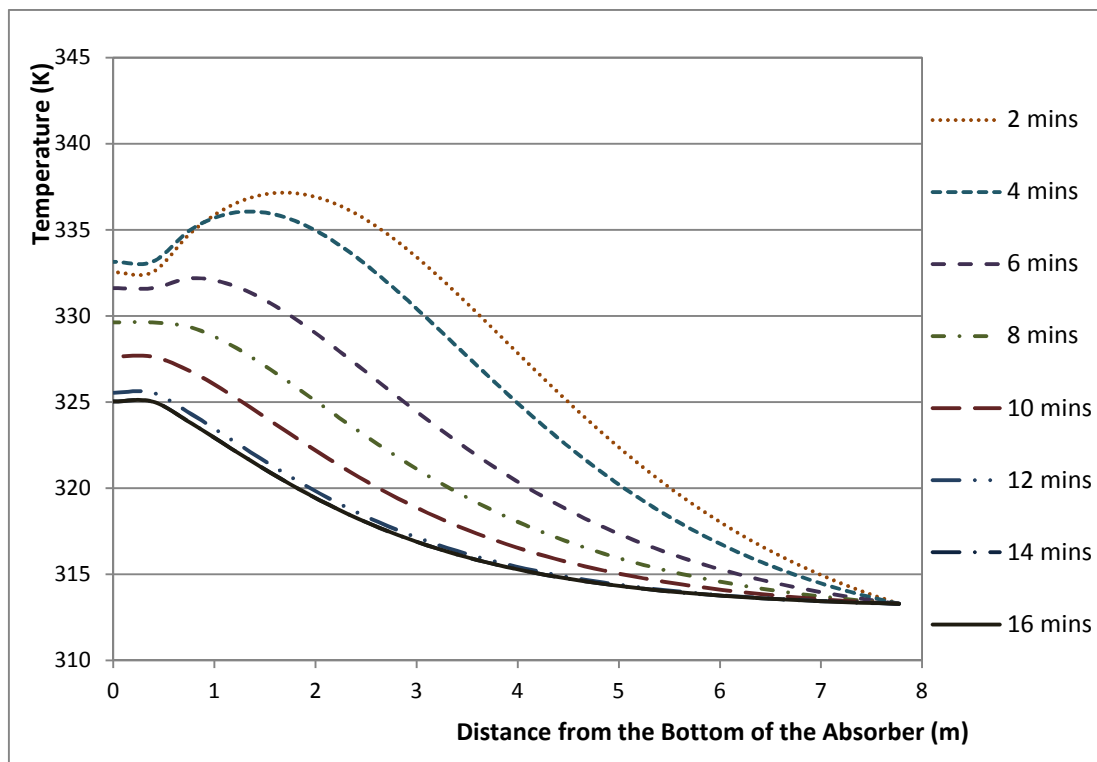


Figure 5-8: Temperature Profile Due to Flue Gas Flow Decrease (Onda)

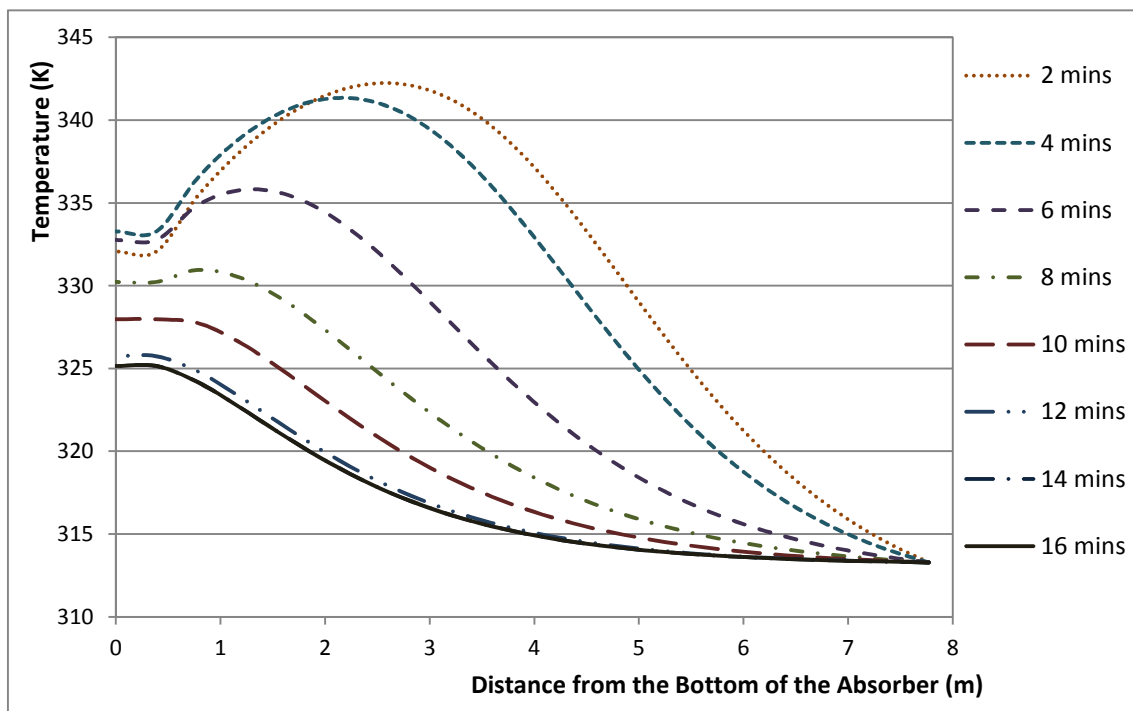


Figure 5-9: Temperature Profile Due to Flue Gas Flow Decrease (Billet-Schultes)

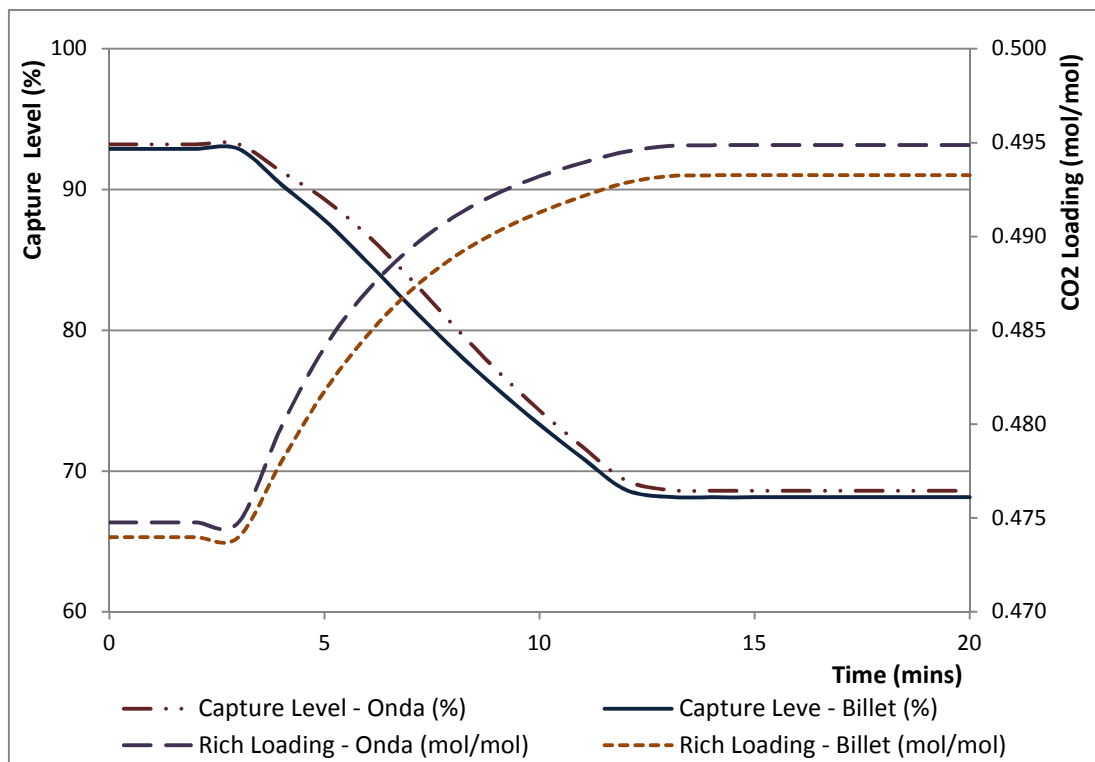


Figure 5-10: Model Response Due to Flue Gas Flow Increase

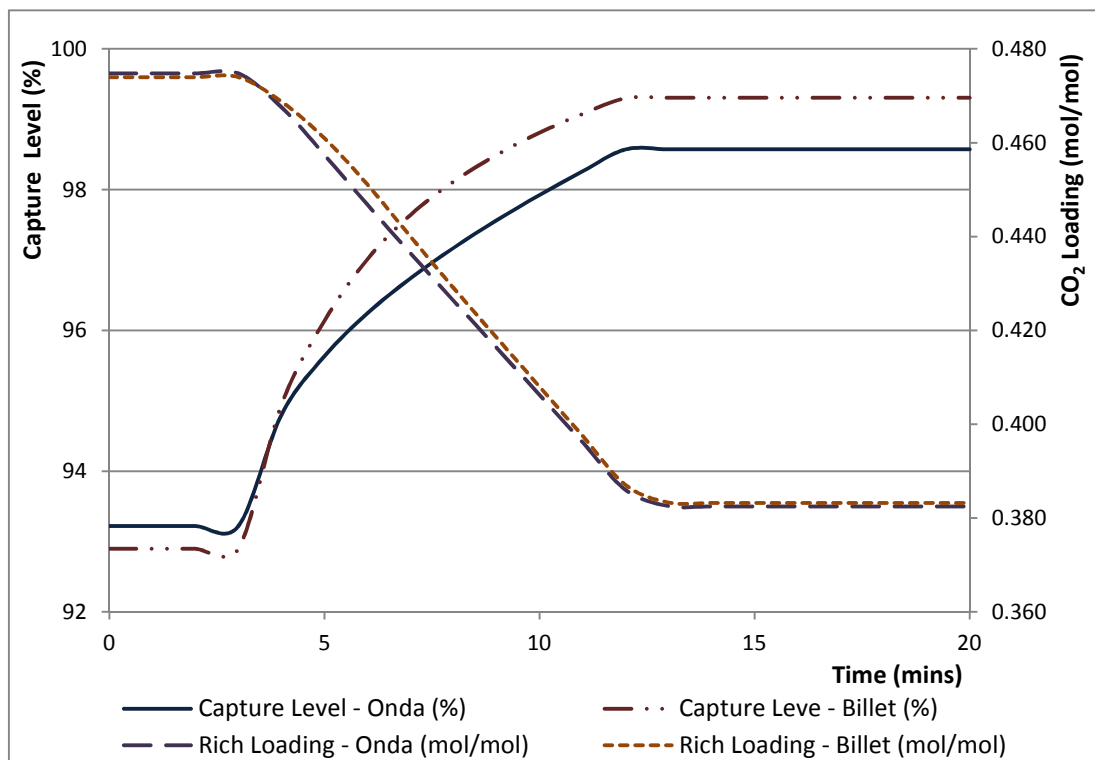


Figure 5-11: Model Response Due to Flue Gas Flow Decrease

5.4.2 Discussion of Results

Figure 5-6, Figure 5-7, Figure 5-8 and Figure 5-9 show snapshots of temperature profiles of the absorber during the period of dynamic study, clearly revealing a shifting temperature bulge as L/G ratio changes. In Figure 5-6 and Figure 5-7, where the flue gas inlet rate is ramped up, dropping L/G ratio from 5.5 to 3.7, temperature bulge moves from the lower section to the upper section of the absorber. In fact, the system is able to attain a new steady-state within 4 minutes after the ramp up ended. At this point, the temperature profile is similar to what is observed in the pilot plant for Case 47, whose L/G ratio is 4.0. On comparing Figure 5-6 and Figure 5-7, though it is revealed that the Billet-Schultes correlations consistently predict higher temperatures than the Onda correlations, the trends produced by the two sets of mass transfer correlations are very similar.

A parallel outcome is observed in Figures Figure 5-8 and Figure 5-9, where flue gas inlet rate is ramped down, doubling L/G ratio, and pushing the temperature bulge further down the bottom of the absorber. Again, steady-state is reached within 4 minutes after ramp down and similar trends are provided by the two mass transfer correlations, with Billet-Schultes predict higher temperatures. The final temperature now resembles that of Case 25 from the pilot plant, which was initially operated at an L/G ratio of 7.8.

Finally, Figure 5-10 and Figure 5-11 reveal changes in capture level and rich loading as gas flow rate increases and decreases respectively. Predictions by the two sets of mass transfer correlations are almost indistinguishable from one another. From Figure 5-10, capture level falls from 93% to 68% as expected and rich loading increases significantly as L/G ratio falls. Figure 5-11 then shows that as capture level rises to 99%, rich loading drops markedly with rising L/G ratio.

The next step is to use this high fidelity model to build a full PCC plant for operability analysis.

6 INTEGRATION OF CAPTURE PLANT IN POWER PLANT

6.1 Motivation

The most pressing challenges of CCS is that it is estimated to reduce the plant efficiency by 15% and increase the cost of electricity by 60% when integrated with an NGCC power plant (Ciferno et al., 2010). Recent literature highlights efforts targeted at these issues, however doubts remain about the accuracy of many of these studies, as the models used have not been validated (Berstad et al., 2011; Peeters et al., 2007; Li et al., 2011a). Where models have been validated, some questions remain. For instance, in the analysis performed by Sipöcz and Tobiesen (2012), it is reported that a 440MW NGCC Plant would only require a single 9.13m diameter absorber with 26.9m Mellapak 250X packing for its PCC plant. This result is arrived at after a PCC plant model, which was validated at pilot plant scale, was scaled up. However, this is a very optimistic estimate, and is at odds with the design of a PCC plant for a similar capacity NGCC plant, which Hetland et al. (2009) reported to require four 9.6m diameter absorbers with 30m Mellapak 250X packing.

Various authors (Berstad et al., 2011; Botero et al., 2009; Sipöcz and Tobiesen, 2012; Li et al., 2011a, b; Jonshagen et al., 2011) have also analysed the impact of EGR on the performance of the integrated process. It has been found that EGR is mostly beneficial to an integrated plant due to a concomitant fall in exhaust gas flow rate, an increase in exhaust gas CO₂ concentration, and a reduced solvent pumping requirement. However, the impact of EGR on the thermodynamic performance on the PCC plant has not been explored in detail, especially in regards to its role in solvent regeneration. This is important, as it may uncover potential avenues to enhance the impact of EGR.

As a result, high fidelity models of a NGCC power plant and a PCC plant, which have been validated, are required for rigorous analysis of the integration of the two plants. Chemical engineering principles need to be applied in scaling up the PCC plant model that has been validated at pilot scale. An appropriately sized

compression train is also desirable to determine the additional energy required to deliver the CO₂ to a nearby storage site via a pipeline. In this manner, the integrated plant performance can be fully explored, along with estimated water requirements in the whole process. Furthermore, as a performance improvement scheme, the impact of EGR on the PCC plant can also be thermodynamically investigated. In addition, the supplementary firing of turbine exhaust gas can be analysed in the integrated plant.

The implication here is that economic analysis performed with such models would inspire confidence. Previous reported efforts are mainly based on cost factors and employ several technical and economic assumptions that dramatically influence results (Sipöcz and Tobiesen, 2012; Rubin et al., 2007). In addition, the plant location, which is an influential economic factor, is another parameter that is routinely neglected. Therefore, rigour in this analysis is ensured by eliminating assumptions and providing a suitable location for the facility. The location would provide a basis for generating construction costs for the plant through a bottom-up approach, using material and labour costs in the region.

6.2 Model Development

6.2.1 NGCC Power Plant

A 440MW NGCC power plant is modelled in GE's GateCycle™ turbine library software, an application that uses the turbine data to determine the corresponding "as-built" performance. GateCycle™ models are used detailed engineering, design, retrofitting, repowering and acceptance testing (GE Energy, 2013). The plant consists of an Ansaldo V94.3A gas turbine and a three pressure level steam cycle with reheat. Important model input and design data is given in Table 6-1. The model is replicated in Aspen HYSYS V8.0 by incorporating the gas turbine performance and design parameters from GateCycle™. The thermodynamic properties of the Brayton cycle described by Peng Robinson equation of state, while that Rankine cycle is represented by steam tables. There are sixteen heat transfer stages in the heat recovery steam generator (HRSG), and each one is modelled individually as a heat exchanger.

Table 6-1: NGCC Plant Input and Design data

Description	Values
Fuel gas flow rate (kg/s)	15.69
Fuel lower heat value (kJ/mol)	974.5
Air to gas combustion ratio (wt)	43.76
Turbine inlet temperature (°C)	1425
Gas turbine inlet pressure (bar)	20.68
HP turbine inlet pressure (bar)	124.00
IP turbine inlet pressure (bar)	28.65
LP turbine inlet pressure (bar)	4.45
Condensate pressure (bar)	0.04
Superheated steam temperature (°C)	565
Reheated steam temperature (°C)	558
HRSG minimum approach (°C)	11
Ambient temperature (°C)	15
Cooling water exit temperature (°C)	25

In benchmarking the model from GateCycle™ to Aspen HYSYS, the effects of turbine blade cooling on the gas turbine performance introduced some challenges. These have been handled using techniques described by Jonsson et al. (2005), which enables the Brayton cycle in Aspen HYSYS to be tuned to be the exact representation of the one in GateCycle™. On the other hand, Rankine cycle calculations of both models are identical.

6.2.2 PCC Plant

The rate-based column in Aspen HYSYS is used to develop a PCC plant model with MEA solution as solvent. This model is underpinned by the two-film theory, which describes diffusion of components across the vapour and liquid films of minuscule thickness, with a phase equilibrium existing in the interface between the films. Chemical reaction is also accounted for and is assumed to occur in the liquid film. The kinetic expressions for reactions and electrolytic interactions imposed on this model are provided by AspenTech (2008) and described in Section 0. Globally, Electrolyte NRTL activity coefficient is used to describe the system.

Such a model is the highest level of modelling packed columns (Kenig et al., 2001), as both the physical and the chemical behaviour of all components in the system are explicitly represented, without using enhancement factors. The “True Species” simulation approach is utilised, where all components – CO₂, MEA, H₂O, H₃O⁺, OH⁻, HCO₃⁻, CO₃²⁻, MEAH⁺ and MEACOO⁻ – are accounted for, as opposed to the “Apparent Species” approach, where ionic components are reduced to their corresponding stable states of CO₂, MEA and H₂O.

This model has been validated previously with pilot plant data (AspenTech, 2008). The model is scaled up to handle the exhaust gas from the NGCC power plant. Scale-up techniques described by Lawal et al. (2012) were utilized, with Mellapak 250X packing. The lean solvent recycle to the absorber was closed, ensuring that the model remains a good representation of the PCC plant (Lawal et al., 2010). Preliminary design and operations data is provided in Table 6-2.

6.2.3 Compression Train

A CO₂ compression train is sized and modelled to appropriately account for its energy demands required to compress the captured CO₂. A final compression stage discharge pressure of 110bar is specified according to KEPCO/MHI application (IPCC, 2005), where CO₂ is at its supercritical or dense phase, for efficient pipeline transport. Pure CO₂ becomes supercritical at a pressure of 96bar, and remains so at all temperatures (IPCC, 2005), however the higher pressure of 110 bar provides allowance for impurities present. A molecular sieve is added to the model to remove water and ensure a 99.5% final CO₂ concentration.

Table 6-2: PCC Plant Design and Operations

Preliminary Design		Operations	
Absorber column number	4	Capture level (wt%)	90.00
Absorber diameter (m)	10	Lean loading (mol CO ₂ /mol MEA)	0.2340
Absorber packing height (m)	15	Rich loading (mol CO ₂ /mol MEA)	0.4945
Regenerator column number	1	Flue gas inlet temp (oC)	40.00
Regenerator diameter (m)	9	Absorber pressure (bar)	1.013
Regenerator packing height (m)	15	Regenerator Pressure (bar)	1.500

A pump is provided that is capable of increasing CO₂ pressure to 175 bar, to account for an increasing reservoir pressure, as more and more CO₂ is stored underground. The model is described by REFPROP database.

The compression train comprises of centrifugal compressors, aftercoolers and scrubbers. A maximum fluid head (polytropic) of 3050m is enforced at each compression stage/impeller, due to equipment mechanical limitations (Brown, 2005). As this is a CO₂ compression application, a maximum compressor discharge temperature of 120°C is imposed, which in turn limits the number of impellers in a single compressor without intercooling to two. Compressor maps/curves, which are compressor manufacturer (OEM) proprietary data, have also been used. These provide a relationship between actual volume flow rate at the suction, compression efficiency and fluid head. In this case, data for a natural gas compression application, manufactured by the Elliot Group has been appropriately scaled (considering gas molecular weight differences) and used. The design and performance is given in Table 6-3.

6.3 Process Integration

6.3.1 Considerations

There are four main integration points (Figure 6-1):

- [A] exhaust gas fed to the PCC plant,
- [B] steam extracted from the NGCC plant to the reboiler at PCC plant,
- [C] condensate returned to the NGCC plant from the reboiler, and
- [D] captured CO₂ from the regenerator to the CO₂ compression train.

Pre-treatment of the exhaust gas is performed before it is fed into the PCC absorber. It passes through a desulphurisation unit to remove SO_x gases and an electrostatic precipitation unit to remove NO_x gases. It is assumed that oxygen inhibitors are used to limit MEA solvent degradation. A direct contact cooler (DCC) then cools the gas to around 40°C for favorable absorption conditions in the absorber, and condenses water out of the gas.

Table 6-3: Compression Train Design and Operation data

Description	Value
Number of compressors	5
Compressor efficiency range (%)	78.0 – 83.5
Aftercoolers exit temperature (°C)	40
Compressor Speed (rpm)	6000

Steam is drawn from the cross-over of the IP and LP turbines through a throttle valve, which limits pressure losses, and then used to regenerate the solvent in the PCC plant. The condensate from the reboiler is returned to the condenser of the NGCC plant. This position is chosen due to the steam quality of 4.5bar, which is saturated at 148°C. Pressure losses occur over the cross-over line and the reboiler tubes, so a reasonable pressure drop is assumed and the steam condenses at 3bar, with a saturation temperature of 134°C. At this temperature, an appropriate minimum approach can be maintained in the reboiler, where the solvent temperature is constrained to a maximum of 120 – 125°C to avoid thermal degradation. An attenuator is used to control the temperature of the steam draw, spraying condensate to ensure the temperature remains just above saturation. For this study, it is assumed that the LP turbine can handle large flow rate variations with negligible fall in efficiency.

6.3.2 Exhaust Gas Recirculation

Part of the exhaust gas from the HRSG exit is cooled to around ambient conditions using a DCC, and then sent back to the inlet of the air compressor. EGR has the following advantages:

- a fall in exhaust gas flow rate, reducing the required PCC plant capacity;
- an increase in exhaust gas CO₂ concentration, leading to a more efficient CO₂ capture; and
- a reduced solvent circulation in the PCC plant, resulting in less pumping required.

Table 6-4: Process Performance Comparison

	NGCC Plant only	Integrated Plant	Integrated Plant + EGR
Power plant net output (MW)	440.6	376.0	386.1
Power loss due to PCC & comp. (%)	-	14.66	12.37
Plant net efficiency (%)	59.62	49.38	50.71
Total cooling water demand (tonne/s)	7.72	10.29	10.62
Cooling water increase (%)	-	33.34	37.62
Net Specific Emission (kg CO₂/MWh)	354.5	40.1	39.5
Gas turbine net output (MW)	287.7	287.7	287.6
Exhaust gas flow rate (kg/s)	693.6	693.6	416.1
Exhaust gas CO ₂ content (mol%)	3.996	3.996	6.610
Exhaust gas outlet temp. (°C)	99.5	125.0	120.7
Steam generated (kg/s)	103.8	106.6	109.0
Steam draw-off flow rate (kg/s)	-	61.87	57.25
Absorber column number	-	4	3
Absorber L/G ratio (mol basis)	-	1.31	2.09
Total Solvent circulation rate (kg/s)	-	721.6	675.3
Duty/CO ₂ captured (kJ/kg)	-	4003	3724
Additional PCC plant demand (MW)	-	6.25	3.74
Compression train inlet rate (kg/s)	-	39.61	39.41
Compression power demand (MW)	-	13.37	13.25

The reduced heat transfer is caused by the condensate that returns to the NGCC plant at a higher temperature, i.e. just below saturation at 3bar, before it is sent to the low pressure economiser section of the HRSG. The implication here is that a redesign of the HRSG, to account for the steam draw, would potentially improve heat transfer with the exhaust gas. In the end, it is determined that for 90% capture, 4003kJ of steam energy is required to strip the solvent of 1kg of captured CO₂ in the integrated plant. The 90% capture level results in a corresponding 90% fall in net specific emission to 40.1 kg CO₂/MWh.

With no change observed in output of the gas turbine in NGCC plant, power demands from equipment like the blower and solvent pumps in the PCC plant,

and the compressors in the compression train all contribute in reducing the net power produced. In addition, cooling water demand is estimated to increase by 33%, as a result of the cooling required in the condenser and DCC in the PCC plant, and the compressor aftercoolers in the compression train.

6.3.3.2 EGR Scenario

From Table 6-4, when a 40% EGR is implemented, the net output improves by 10MW resulting in an efficiency recovery of 1.3% point. Although, the net output of the gas turbine falls by 0.1MW, 2.4kg/s of additional steam is generated in the HRSG at similar minimum approach temperatures, resulting in a 4°C fall in exhaust gas temperature. However, the exhaust gas temperature is still 21°C higher than the stand-alone NGCC plant. As already explained, this implies a compromised heat transfer, which can potentially be rectified with a redesign of the HRSG to account for the steam draw. However, it is noted that less steam is extracted for solvent regeneration when EGR is implemented, as only 53% of generated steam used by the reboiler. The reason for this is explored in detail in Section 3.3.3. It is also observed that cooling water demand increases by 38% compared to the NGCC plant, mainly as a result of the cooling requirements of the DCC used to cool the recycled exhaust gas. However, net specific emission reduces marginally to 39.5 kg CO₂/MWh due to the recovery of 10MW.

As only 60% of the exhaust gas proceeds to the PCC plant, smaller absorber capacity is required. As opposed to resizing the four absorbers, only three are employed. The CO₂ concentration in the exhaust gas increases by 65%, and would require either a lower lean loading or a higher absorber L/G ratio to maintain the capture level of 90%. Among the two options, a higher L/G ratio was selected as it was observed to require less steam extraction from the NGCC plant, leading to a new rich loading of 0.5130. However, the total solvent circulation rate with EGR falls marginally by 6%, as only 3 absorber columns are used.

Considering the solvent regeneration, it is determined that 3724kJ of steam energy is required to strip the solvent of 1kg of captured CO₂, i.e. a drop in steam draw rate and an improvement on the scenario without EGR. Part of the

reason for this is the 6% drop in solvent circulation rate, as less energy is needed to reach the reboiler temperature required for a 0.2340 lean loading. Another contributing factor is elucidated in Section 6.3.3.3 below.

6.3.3.3 Thermodynamic Analysis of EGR on the PCC Plant

According to Fick's law (Equation (5-2)), a higher CO_2 concentration in the exhaust gas results in a higher gradient or potential for diffusion/mass transfer of CO_2 into MEA solvent. In addition, it has been previously shown in Section 4.5.2.3 that CO_2 absorption into the solvent is limited by mass transfer i.e. the rate of mass transfer is much slower than the rate of chemical reactions. Therefore, it is posited that when EGR is implemented, the higher CO_2 concentration in the absorber would lead to a higher rate of mass transfer, which translates to an increased mass transfer in the absorber. This assertion can be confirmed using the rigorous model employed for this study, where both the mass transfer and the chemical reaction in the system are explicitly described.

In the regenerator, the energy required for solvent regeneration achieves four things:

- It provides sensible heat to the rich solvent to increase its temperature to the required temperature in the reboiler.
- It evaporates water in the reboiler, with water vapour acting as a stripping agent as it moves up the regenerator, aiding the CO_2 removal from the solvent.
- It provides heat to reverse the chemical reactions that have occurred in the absorber, and in theory, an energy that is equal to that released due to the exothermic reactions.
- It imparts heat to liberate dissolved CO_2 out of the solvent solution.

For MEA solvent, this heat of reaction with CO_2 is much greater than the heat of dissolution (or in this case, mass transfer) of CO_2 into MEA solvent. The heat of reaction and heat of dissolution are summed up as the heat of absorption. This would mean that as a 90% capture level is maintained for the EGR scenario,

less of the exothermic chemical reaction occurs with the higher CO₂ concentration, leading to an overall reduced heat of absorption.

In the absorber, CO₂ has to diffuse into the solvent before chemical reaction occurs. The chemical reactions, described by Equations (3-16) – (3-19), enhance the mass transfer by consuming CO₂ and maintaining a gradient for more CO₂ diffusion into the solvent. However, a proportion of the diffused CO₂ remains unreacted, which means there is no associated heat of reaction released (which would need to be replaced later during solvent regeneration). To gauge the role played by the unreacted CO₂ in this chemical absorption dominated system, a parameter called the “Free Carbon (FC) Ratio” is defined. The FC ratio is described as the fraction of the total CO₂ (inclusive of ionic species HCO₃⁻, CO₃²⁻ and MEACOO⁻ that are the product of chemical reactions) in the solvent that has been captured in the absorber that is made up of unreacted diffused CO₂. This is calculated as:

$$\text{FC Ratio} = \frac{F_m(\text{Rich Solvent CO}_2(T)) - F_m(\text{Lean Solvent CO}_2(T))}{F_m(\text{Rich Solvent CO}_2(A)) - F_m(\text{Lean Solvent CO}_2(A))} \quad (6-1)$$

Where F_m represents molar flow rate, CO₂(T) is the “True CO₂ content” in the solvent that is made up of unreacted CO₂, and CO₂(A) is the “Apparent CO₂ content” that includes the ionic species – HCO₃⁻, CO₃²⁻ and MEACOO⁻.

This fraction is a measure of the proportion of CO₂ that has been captured in a chemical absorption PCC plant, without chemical reaction. A larger value of FC ratio for a PCC plants indicates a bigger influence of mass transfer in the absorber. Therefore, for the scenarios without and with EGR, the metric is calculated to be 3.71×10^{-4} and 7.81×10^{-4} respectively. The higher value for the EGR scenario provides evidence mass transfer increases when EGR is implemented.

The true CO₂ composition is then compared to the apparent CO₂ composition of solvent along the length of packing in an absorber under both scenarios. Figure 6-2 shows a higher fraction of free CO₂ along the length of an absorber with EGR as the solvent falls down the absorber.

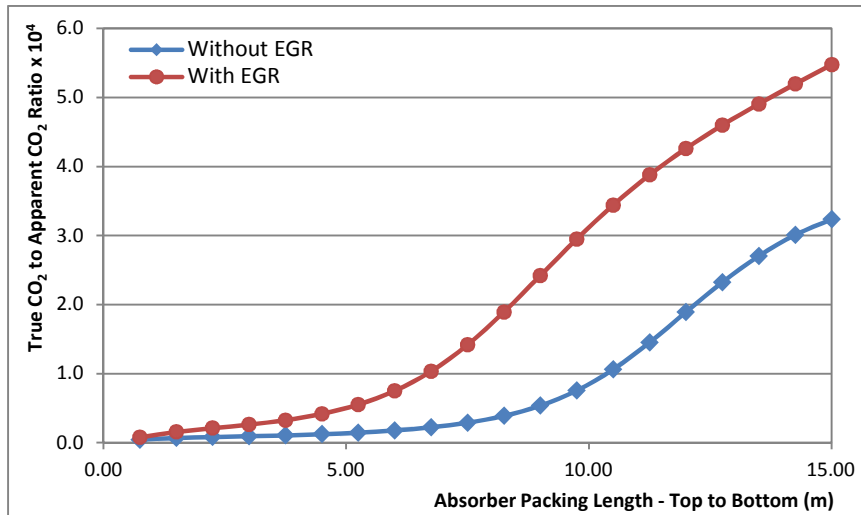


Figure 6-2: True CO₂ to Apparent CO₂ Ratio in Solvent along Absorber Length

In fact, under the same lean loading and capture level, the amount of unreacted CO₂ in the rich solvent that is fed to the regenerator, is calculated to be 3.19kmol/hr and 1.94kmol/hr for the scenarios with and without EGR respectively. These values represent the amount of CO₂ liberated from the solvent in the regeneration without the need of heat to reverse chemical reactions. The greater value for the EGR scenario lends more credence to the assertion that mass transfer plays a greater role. Therefore, this is the reason less steam is required for solvent regeneration, along with drop in solvent circulation rate. The implication of this is that using other means to enhance mass transfer in the absorber would also result in a reduced steam requirement. A good example of this is using a rotating packed bed for the absorber and regenerator columns (Tan and Chen, 2006).

6.4 Supplementary Firing of Gas Turbine Exhaust

6.4.1 Considerations

As a way of increasing the CO₂ concentration in the gas that is fed to the PCC plant, the exhaust gas exiting the gas turbine can be fired using a burner placed in the duct connecting the gas turbine outlet to the HRSG inlet to burn additional natural gas (Li et al., 2011a). Not only does the supplementary firing (SF) of gas turbine exhaust increase the CO₂ concentration, but it also provides more energy for the HRSG to generate additional steam, and reduces the oxygen

content of the gas, which in turn results in decreased oxidative degradation of the solvent.

SF is implemented for the 40% EGR scenario, with the steam cycle redesigned to account for SF. The flow rate of the exhaust gas around the burner is 702 kg/s, with an initial oxygen content of 7.54mol%, equating to an oxygen flow rate of 59 kg/s, which is more than enough for complete combustion of additional gas to be fired. Therefore, to maintain rigour in the analysis, the following assumptions are made:

- Complete combustion of added natural gas is reached due to the excess oxygen available.
- There is negligible energy loss to the surroundings, as the burner is located in the gas turbine-HRSG connecting duct.
- Flame stabilisation is achieved due to the excess oxygen available.
- The configuration and tube placements in the HRSG remain unchanged.
- Superheated steam temperature is limited to 600°C due to turbine design constraints.
- Minimum approach temperature of 11 °C is maintained in evaporators.
- Pressure drops are constant in the HRSG tubes.

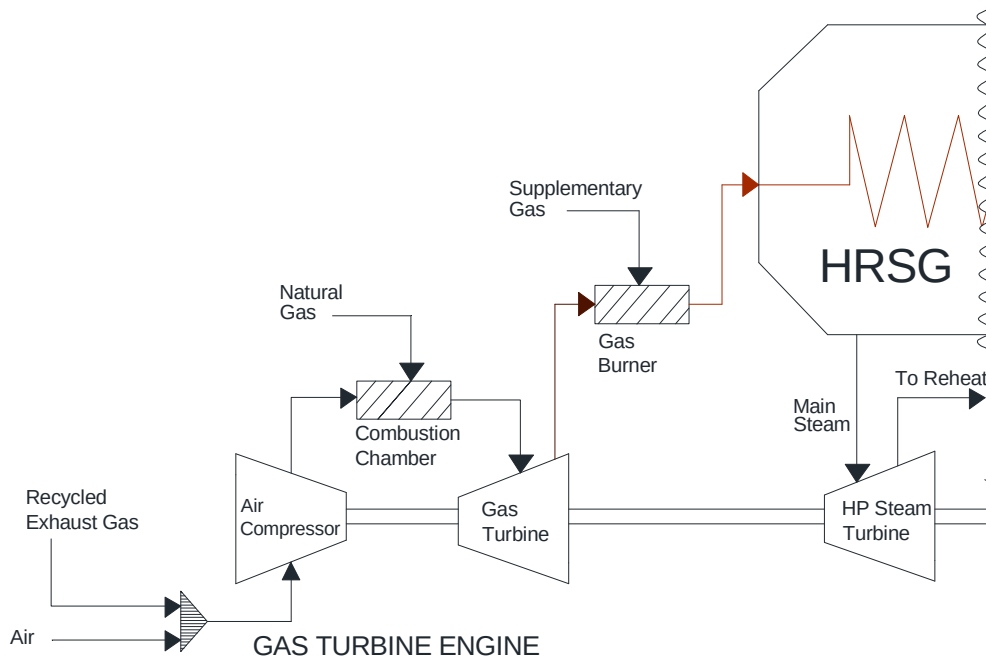


Figure 6-3: Implementation of Supplementary Firing of Exhaust Gas

With no HRSG configuration changes to be made, steam generation is limited to the subcritical region. Therefore, SF is explored for a range of 0.5 – 2.0 kg/s of additional gas. HRSG operational parameters with SF are provided in Table 6-5. The flow rate of the exhaust gas increases marginally, however its composition changes significantly, particularly its CO₂ and O₂ content, as O₂ is consumed in combustion. The impact of this is shown in Figure 6-4.

The increasing CO₂ concentration would require longer packing in both columns in the PCC plant to retain the same capture level for the four SF scenarios with a reasonable reboiler duty. Therefore, to provide a basis for comparison, the same design and operating parameters for the PCC plant is used for all four cases and the updated values are provided in Table 6-6.

Table 6-5: HRSG Operational Parameters with SF

Description	0.5 kg/s	1.0 kg/s	1.5 kg/s	2.0 kg/s
HP turbine inlet pressure (bar)	143.60	176.60	196.60	213.60
IP turbine inlet pressure (bar)	30.71	33.21	38.21	40.21
LP turbine inlet pressure (bar)	4.36	4.36	4.36	4.36
Superheated steam temperature (°C)	596	600	600	600
Reheated steam temperature (°C)	595	600	600	600

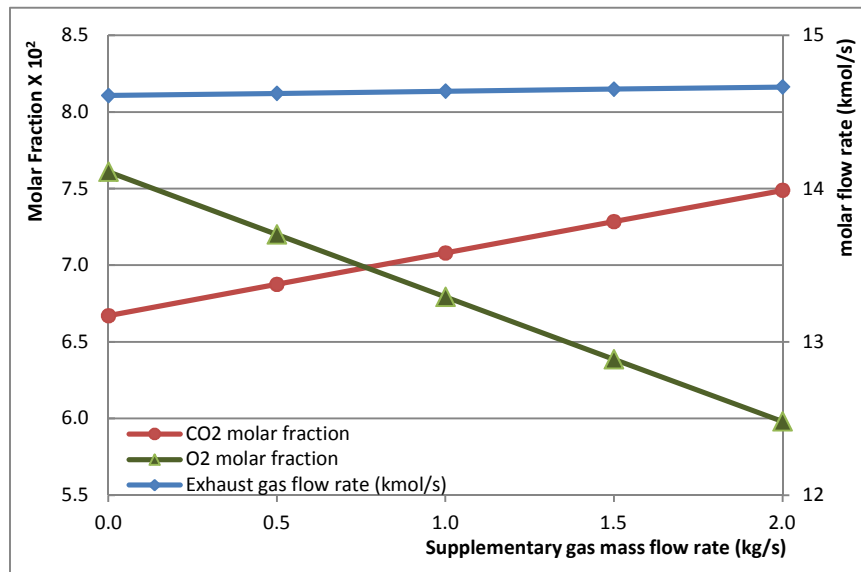


Figure 6-4: Changing Composition of Exhaust Gas with SF

Table 6-6: SF Updated PCC Plant Design and Operations Data

Preliminary Design		Operations	
Absorber column number	3	Capture level (wt%)	90.00
Absorber packing height (m)	25	Steam/CO ₂ captured (kJ/kg)	3700
Regenerator column number	1	Lean loading (mol CO ₂ /mol MEA)	0.3200
Regenerator packing height (m)	25	Rich loading (mol CO ₂ /mol MEA)	0.5300

6.4.2 Discussion of Results

6.4.2.1 Impact of SF on EGR Scenario

It is shown in Figure 6-5 that SF generally improves the performance of the plant. Net power output increases proportionally with the additional gas fired in the burner, reaching a maximum of 435MW with the firing of 2 kg/s of natural gas, while plant net efficiency remains relatively constant at a 50.8%. The implication here is that as long as complete combustion (limited by available oxygen) can be maintained, with minimal environmental heat losses, then as much natural gas as possible can be fired in the gas burner to enhance the output of an NGCC plant integrated with a PCC plant and compression train.

The main driver for this rise in output is the increase in quantity and quality of steam generated in the HRSG, as observed in Figure 6-6, which in turn increases power generation in the steam turbines. Although there is an increase in the absolute value of steam extracted from the Rankine cycle for solvent regeneration, due to the rising CO₂ capture rate displayed in Figure 6-7, the percentage of generated steam that is extracted drops almost linearly to 48% when 2 kg/s of additional gas is fired, leading to a higher proportion of the steam being fed into the LP turbine. This also contributes to the higher integrated plant output. Figure 6-7 also shows that power demands of compression train increases proportionally with the CO₂ capture rate, the additional power generated using SF more than compensates for the increasing compression load. These all contribute to make the net specific emissions stabilise at about 39.5 kg CO₂/MWh, even with increasing SF.

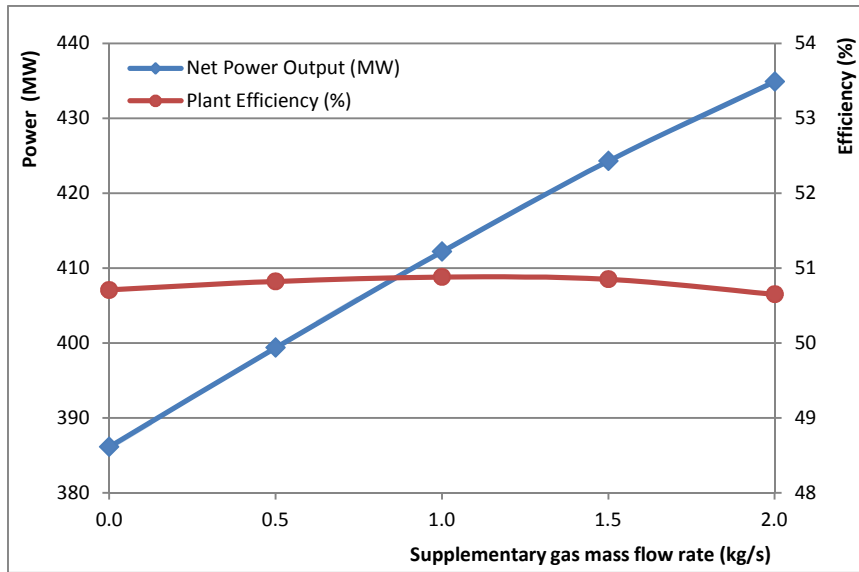


Figure 6-5: SF Power Output and Net Efficiency

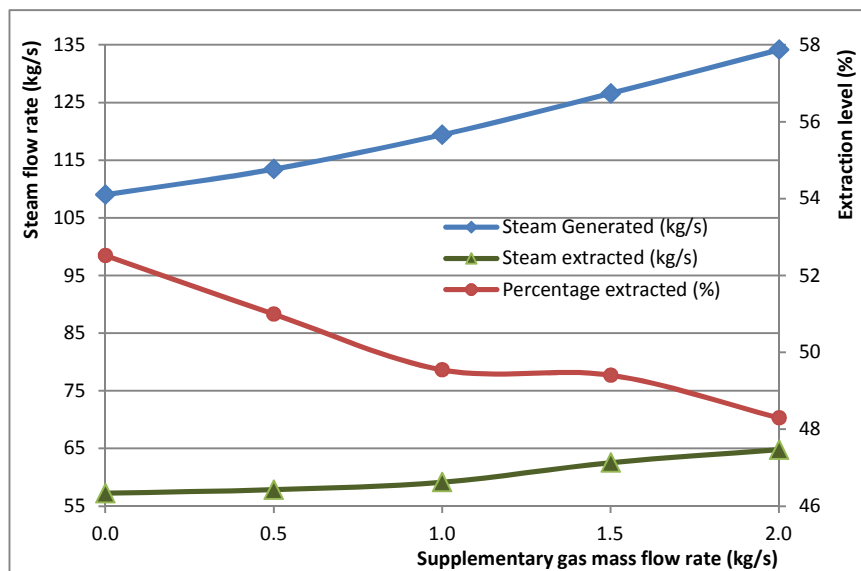


Figure 6-6: SF Steam Generation and Extraction

With the existing HRSG configuration, updating the operation parameters with SF also provides an opportunity to maximise heat transfer in the HRSG. As a result, it is observed in Figure 6-8 that HRSG exhaust gas temperature, which is an indication of heat transfer, drops with from 121°C when only EGR is implemented to 109°C with SF of 2 kg/s of additional gas. The impact of this improved heat transfer is reflected in the additional steam generated, which is of higher quality. On the other hand, the cooling water requirements for plant increase with increasing SF to a maximum of 12106kg/s. This is driven by the

DCCs for exhaust gas, the condenser in the PCC plant and the aftercoolers in the compression train, which are dealing with increasing flue gas flow rates.

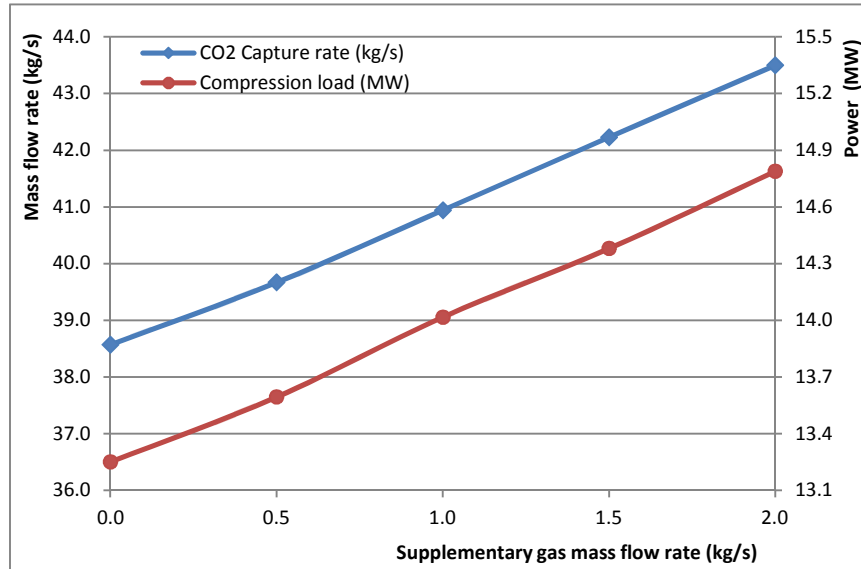


Figure 6-7: SF CO₂ Capture rate and Compression Load

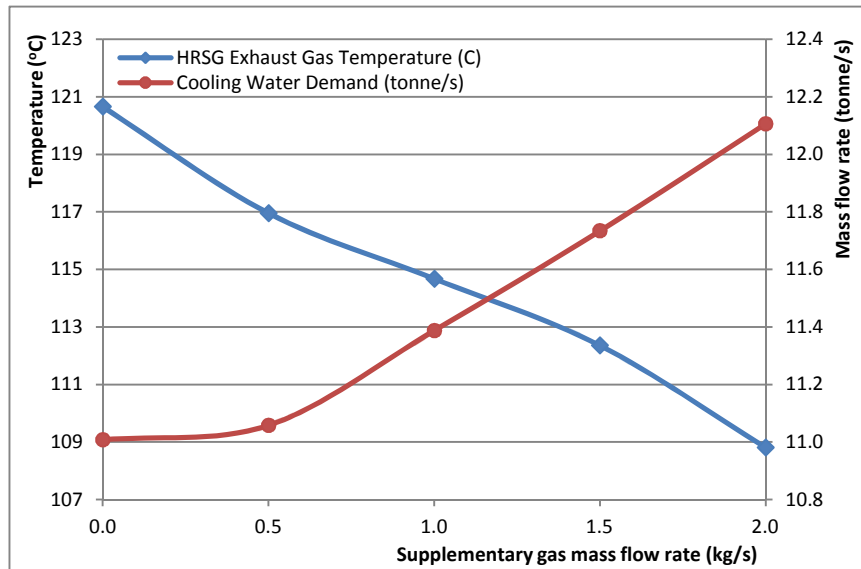


Figure 6-8: SF HRSG Exhaust Gas Temperature and Cooling Water Demand

6.4.2.2 Thermodynamic Analysis of Supplementary Firing on PCC Plant

With an increasing SF of natural gas, there is an increasing CO₂ concentration in the exhaust gas that is fed to the PCC plant (Figure 6-4). To maintain the 90% capture level, solvent circulation rate is increased, as opposed to reducing the lean loading of 0.3200.

The amount of steam energy required to strip the solvent of 1kg of captured CO₂ is preserved at a value of 3700kJ. This is notwithstanding the fact that more CO₂ is being captured with increasing SF (Figure 6-7) and therefore being stripped from the solvent. As covered in Section 6.3.3.3, the rising solvent circulation rate should also bring about an increase in steam energy requirement. However, this is not the case because a change in the absorption mechanism offsets this energy requirement to maintain the value of 3700kJ. It has been shown previously in Section 6.3.3.3 that an increasing CO₂ concentration increases mass transfer in the absorber, which then reduces the overall heat of absorption. The impact of this is explored in Figure 6-9, which shows how the FC ratio of the PCC plant increases with increasing SF of natural gas in the NGCC plant, confirming the improved mass transfer.

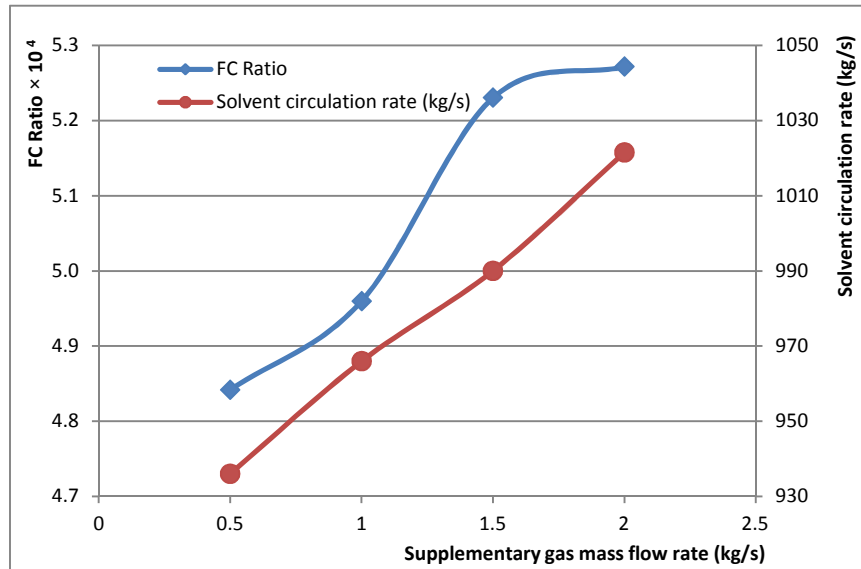


Figure 6-9: PCC Plant FC Ratio and Solvent Circulation Rate due to SF

Compared to the analysis in Section 6.3.3.3, which was tempered by a reduced solvent circulation rate, Figure 6-9 clearly reveals an increasing circulation rate with increasing SF. However, due to the increasing mass transfer of CO₂ diffusing into the solvent in the absorber, accompanied with the decreasing chemical reactions, the reduced heat of absorption compensated for the increased heat required by a rising solvent circulation rate, which lead to the attainment of same amount of energy required to strip the solvent of 1kg of captured CO₂ for all four SF scenarios.

6.5 Economic Analysis

6.5.1 Cost Estimation

Economic analysis is performed in Aspen Process Economic Analyzer[®] (APEA) V8.0, an industry standard tool known to be far more accurate than factor-based costing methods (Whiteside, 2005), and which uses data from the 1st quarter of 2012. APEA generates capital costs via a bottom-up approach, relying on material costs and wage rates to estimate equipment fabrication and installation costs. Simulation unit operations are mapped to appropriate equipment cost models, which are then sized and designed according to relevant design codes. For example, British Standard 5500 pressure vessel design code was specified for this analysis. The equipment costs are then estimated by simulating vendor fabrication procedures. Piping and instrumentation diagrams, attached to process equipment, are used to estimate associated bulk costs of plant piping and instruments. Civil costs are a function of the equipment weight and size.

The cost of a hypothetical plant, located in Northern England, is evaluated using material costs and wage rates from the UK. Indirect project costs, including engineering costs and owner's costs, are accounted for using wage rates and construction equipment rental rates. The following assumptions are made:

- The captured CO₂ has neither economic value nor disposal costs, but is sequestered in a nearby saline aquifer.
- All electricity requirements, including those for equipment motors and control process elements are generated in the plant

- Cooling water is sourced from a nearby body of water at cost of pumping and operation of a cooling tower.

Important cost inputs are provided in Table 6-7, with the costs given in Euro. Three key cost metrics are evaluated for the stand-alone NGCC plant, the integrated plant, the integrated plant with EGR and the 2kg/s SF scenario:

- Overnight cost, which is the capital requirement but assumes the plant can be constructed in a day and excludes interest.
- Levelised cost of electricity (LCOE), which is the unit cost of electricity generation over the life of the power plant, accounting for operating and maintenance cost.
- CO₂ Avoided Cost, which is calculated as:

$$= \frac{[LCOE]_{with\ CCS} - [LCOE]_{without\ CCS}}{[CO_2\ emitted/MW]_{without\ CCS} - [CO_2\ emitted/MW]_{with\ CCS}} \quad (6-2)$$

Table 6-7: Economic Analysis Cost Inputs

Description	Value
Gas price (€/GJ)	8.10
MEA Price (€/ton)	2000
Interest rate (%)	12.0
Contingency (%)	15.0
Project economic life (year)	30
Capital Escalation (%/year)	5.0
Raw Material Escalation (%/year)	3.5

Table 6-8: Economic Performance

	NGCC Plant only	Integrated Plant	Integrated + EGR	Integrated + EGR + SF
Overnight cost (€/kW)	749	1185	1153	1422
Increase in overnight cost (%)	-	58	54	90
LCOE (€/MWh)	54	70	68	67
Increase in LCOE (%)	-	30	26	24
CO ₂ avoided cost (€/ton CO ₂)	-	51	44	43

6.5.2 Discussion of Results

Results are provided in Table 6-8 and it is observed that the overnight cost increases by 58% for the integrated plant compared to the original cost of €749 per kW for the NGCC plant. This is a significant increase in the capital requirement, and must be overcome to encourage the deployment of CCS with NGCC plants. When EGR is implemented, the overnight cost is still 54% greater than the stand-alone NGCC plant cost. Although the number of absorber trains required for the EGR scenario is 3 compared to the 4 for the integrated plant, the DCC required for the recycled exhaust gas and the increased cooling water tower capacity, only translates to a four point reduction from the cost without EGR. This cost reduction is mainly driven by the 10MW output recovered by implementing EGR.

Finally, when SF of 2kg/s of gas is implemented onto the EGR scenario, the overnight costs increase further by 90% compared to the NGCC plant cost. This is partially driven by the higher capacity requirements for the PCC plant, compression train and cooling water tower. However, the crucial cause of this increase is the larger steam cycle capacity in the power plant i.e. larger steam turbines and HRSG. In fact, the higher pressures in the HRSG required thicker heat exchanger tubes that are more expensive. Therefore, with overnight costs almost doubling when SF is implemented, it is unlikely to be considered a viable option in improving the performance of an NGCC plant integrated with CCS.

The LCOE for the integrated plant is 30% greater than the LCOE for the NGCC plant. When EGR is then implemented, this falls to 26%, which is only a modest improvement. Adding an SF of 2kg/s of gas reduces this further by 2%, however such a drop is unlikely to justify the additional capital outlay required. In fact, Figure 6-10 reveals that the largest driver for the LCOE remains the cost of natural gas for all scenarios under consideration, with the fixed operational and maintenance (O&M) costs (made up of running labour cost) estimated to be a greater proportion of the LCOE than the capital requirements.

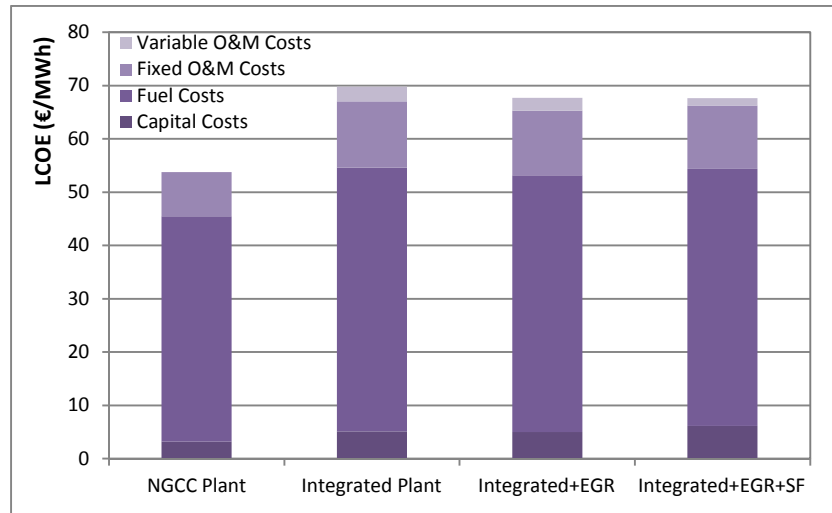


Figure 6-10: Distribution of Costs in LCOE

Only the variable O&M costs, which is made of solvent make up costs, is less than the capital proportion of the LCOE, but it is likely to also be greater in scenarios where CO₂ disposal costs are also considered. Therefore, integrating a PCC plant and compression train to an NGCC plant does not change the significance of gas prices on the LCOE.

The CO₂ avoided cost for the integrated plant is estimated to be €51 per ton of CO₂ captured. These are comparable to values in previously published studies, which fall between €45 to €90 (Finkenrath, 2011). However, this value would be greater when CO₂ transport and storage costs are also accounted for. With the implementation of EGR, the CO₂ avoided cost drops to €44 per ton of CO₂ captured, which the SF of 2kg/s of additional gas only improves this marginally to €43 per ton of CO₂ captured.

7 ALTERNATE INTEGRATION ANALYSIS

7.1 Motivation

The integration of a PCC plant in an NGCC power plant has been explored previously (Ciferno et al., 2010; Berstad et al., 2011; Botero et al., 2009; Sipöcz and Tobiesen, 2012; Amrollahi et al., 2012; Peeters et al., 2007) and in the preceding section. In these studies, the steam that is used for solvent regeneration in the PCC plant is extracted from the IP/LP turbine cross-over as shown in Figure 6-1. This approach is mainly informed by studies performed for the integration of PCC plants in coal fired power plants, where this has been proven to be the most energy efficient method of providing steam to the reboiler in the PCC plant (Lucquiaud and Gibbins, 2011). However, the configuration of the steam cycle in an NGCC plant presents the opportunity of extracting steam from alternate locations. This requires rigorous analysis, along with the option of using a dedicated boiler to generate steam for solvent regeneration.

It is imperative that the advantages of investing in an NGCC power plant as opposed to a coal-fired, which are listed in Section 2.7.1, are maintained when a PCC plant is integrated with it. One such benefit is the operational flexibility of NGCC plants, i.e. the ease at which cyclic loads are handled, with fast ramp ups and reduction in the power generated. The IP/LP cross-over location for steam extraction introduces significant operational challenges in the power plant due to the downstream impact on LP turbine, as well as the slow response of the PCC plant compared to power plants (Lawal et al., 2012). The location also causes plant layout complications, as piping arrangement for the extracted steam may be convoluted, requiring numerous bends, which in turn introduces pressure drop that results in steam of a lower quality arriving at the reboiler. As reboiler duty requirements remain unchanged, a higher quantity of steam would be needed to satisfy it, leading to a greater overall parasitic load on the power plant. Furthermore, integrating the PCC plant to the power plant increases complexity, which erodes plant reliability significantly.

With future energy mix expected to include an ample proportion of intermittent renewable energy like wind and solar, the ability to load-balance huge amounts of unpredictable supply with unpredictable demand via NGCC plants is vital. Therefore, utilising a PCC integration approach that maintains such an operational advantage at minimum efficiency losses, with easy accessibility and reduced complexity, is highly desirable. Two options are analysed – using a boiler to generate steam solely for solvent regeneration and extracting steam from the LP drum in the HRSG for the same purpose.

7.2 Model Development

A high fidelity 440MW NGCC power plant model, which consists of an Ansaldo V94.3A gas turbine and a three pressure level steam cycle with reheat, is built in Aspen HYSYS V8.0 and used in this analysis. The model development is described in detail in Section 6.2.1. Important model input and design data is given in Table 6-1.

The PCC plant model, using MEA solvent, is developed using the rate-based column to model the absorber and regenerator, with chemical reactions also accounted for. This model has been validated previously with pilot plant data (AspenTech, 2008). The model is described in Section 0. The scaled up capture plant details are provided in Table 7-1.

A compression train, of the same configuration as the one described in Section 6.2.3 is also sized and used to compress the captured CO₂ to 110bar, where it is at a supercritical state.

Table 7-1: Alternate PCC Plant Design and Operations

Design Data		Operations/Performance	
Absorber column number	3	Capture level (wt%)	90.00
Absorber diameter (m)	10	Lean loading (mol CO ₂ /mol MEA)	0.2700
Absorber packing height (m)	25	Rich loading (mol CO ₂ /mol MEA)	0.5075
Regenerator column number	1	Flue gas inlet temp (°C)	40.00
Regenerator diameter (m)	9	Absorber pressure (bar)	1.013
Regenerator packing height (m)	15	Regenerator Pressure (bar)	1.500

7.3 Process Integration

7.3.1 Conventional Integration Approach

The integration procedure described in Section 6.3.1 is implemented with the updated PCC plant design and operating conditions, and is used as a reference for comparison. The exhaust gas is pre-treated to remove SO_x and NO_x gases and its temperature is reduced to 40°C, before it is fed into the PCC absorber. It is assumed that oxygen inhibitors are used to limit MEA solvent degradation. The solvent is regenerated at a pressure of 1.5bar and CO₂ is sent to the compression train where it is compressed to its supercritical state. Importantly, steam for solvent regeneration is extracted from the IP/LP cross-over location.

7.3.2 Dedicated Boiler

As opposed to extracting steam from the power plant for solvent regeneration in the PCC plant, a gas-fired steam boiler is introduced to generate steam to meet the reboiler requirements, eliminating one integration point and leaving steam flow rates in power plant unchanged. Gas of the same composition, and hence LHV that is fired in the gas turbine, is used in the boiler. Boiler specifications and performance are given in Table 7-2. Saturated LP steam is produced for solvent regeneration. The hot exhaust gas exiting the boiler is used to preheat the boiler feed water to a temperature just below saturation, boosting thermal efficiency to about 90%. Finally, the exhaust from the boiler feed water preheater is combined with the HRSG exhaust, and sent to the desulphurisation unit, and eventually to PCC plant.

Table 7-2: Boiler Specifications & Performance

Description	Values
Fuel gas flow rate (kg/s)	5.51
Boiler efficiency (%)	82.0
Excess air (%)	10.0
Boiler exhaust gas temperature (°C)	247.6
Boiler exhaust gas CO ₂ content (mol%)	9.01
Steam pressure (bar)	4.5

7.3.3 Alternate Steam Cycle Integration

Similar to the conventional approach, there are four key integration points for this alternate approach proposed. The difference is that steam for solvent regeneration is drawn from the LP drum of the HRSG, as opposed to the cross-over of the IP and LP turbines (Figure 7-1). The steam is saturated at a pressure of 4.5bar, and is extracted via a throttle valve to limit pressure losses, with an attenuator used to control the temperature by spraying condensate to ensure the temperature remains just above saturation.

To generate sufficient LP steam in the HRSG for solvent regeneration, less HP and IP steam is produced to allow ample thermal energy in the exhaust gas to reach LP section of the HRSG. The implication of this is that there is less HP and IP steam entering the steam turbines, which results in less power being generated from the plant. The change in efficiency that results from large flow rate variation in the turbines is assumed to be negligible in this study.

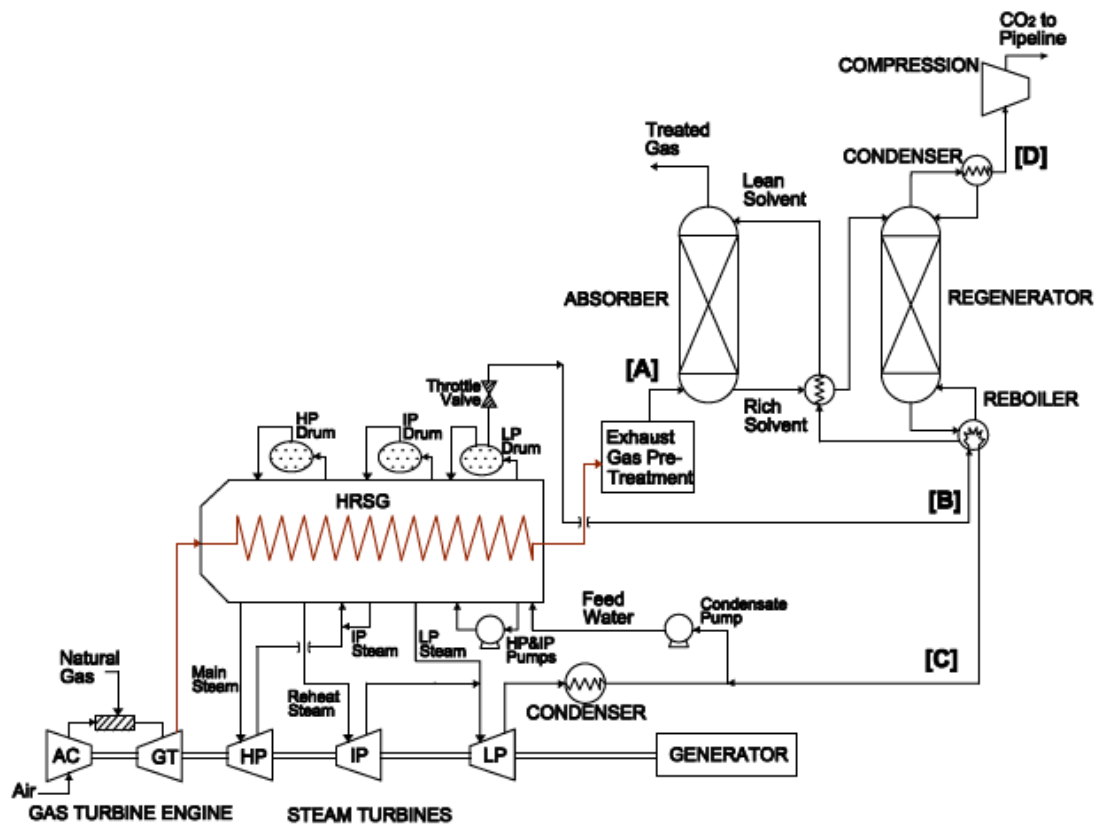


Figure 7-1: Flow Diagram of Alternate Integrated NGCC, PCC and Comp. Plant

In modifying the steam cycle to generate more LP steam, the minimum approach temperature is maintained, while the tube arrangement in the HRSG remains unchanged. However, additional economizer tubes for the LP section are added to the end of the HRSG (a common practice), since more heat exchange area is needed, along with a larger/an additional LP steam drum to meet the requirements of the PCC plant reboiler. With pressure losses occurring over the transfer line and the reboiler tubes, it is assumed that the steam condenses at 3bar, at a temperature of 134°C, which ensures that solvent thermal degradation is avoided. The condensate is returned to the condenser of the NGCC plant.

Table 7-3: Process Performance Comparison

	NGCC Plant only	Dedicated Boiler	Conventional Integration	Alternate Integration
Plant net output (MW)	440.6	415.7	370.4	343.7
Power loss (%)	-	5.65	15.93	21.99
Plant net efficiency (%)	59.62	40.40	48.64	45.14
Cooling water (tonne/s)	7.72	15.01	10.04	10.67
Cooling water rise (%)	-	94.43	30.10	38.32
Exhaust gas flow rate (kg/s)	693.6	800.8	693.6	693.6
Exhaust gas CO ₂ content (%)	3.99	4.67	3.99	3.99
HRSG gas outlet temp. (°C)	99.5	107.2	123.7	120.8
Total steam (kg/s)	103.8	213.2	108.1	132.1
HP steam produced (kg/s)	76.22	76.22	76.22	39.10
Reboiler steam rate (kg/s)	-	109.4	72.72	83.49
LP turbine steam rate (kg/s)	103.8	103.8	35.42	48.61
Absorber L/G ratio	-	1.72	1.47	1.47
Solvent circulation rate (kg/s)	-	1086	800.9	800.9
Duty/CO ₂ captured (kJ/kg)	-	4599	4705	4705
PCC plant demand (MW)	-	7.16	6.11	6.11
CO ₂ capture rate (kg/s)	-	52.33	38.76	38.76
Compression power (MW)	-	18.04	13.36	13.36
Net Emission (kgCO₂/MWh)	354.5	51.6	41.3	44.7

7.3.4 Results and Discussion

From Table 7-3, it is clear that using a dedicated boiler to generate steam for solvent regeneration introduces the lowest parasite load among the three options considered. For the PCC plant design employed, plant net output drops by 6%, 16% and 22% for the dedicated boiler, conventional integration and alternate integration scenarios, respectively. This is because no steam is taken from the steam cycle when a dedicated boiler is used, unlike in the other two scenarios.

More importantly though is net efficiency of the plant, with respect to gas LHV, which is estimated to be 40, 49 and 45% for the aforementioned scenarios respectively (Figure 7-2). Using the dedicated boiler results in such a low efficiency due to the additional gas burnt in the boiler, which is 35% of the gas consumed by the gas turbine. Although the thermal efficiency (with respect to LHV) of regenerating solvent with steam produced in the boiler approaches 90%, none of this steam is used for power generation. Hence, the plant output remains high at such low efficiencies, as only the compressors, gas blower and solvent pumps power demands accounting for the parasitic load on the power plant.

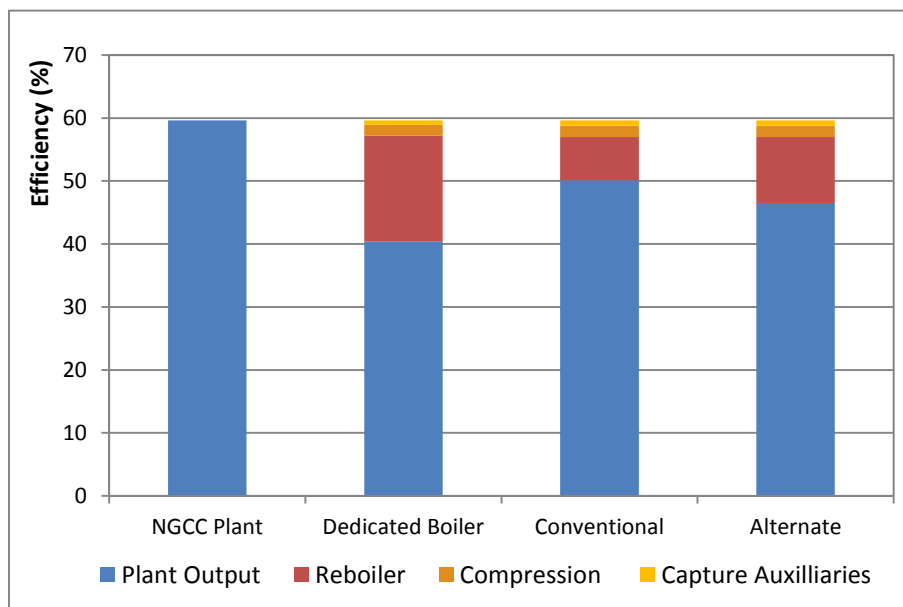


Figure 7-2: Net Plant Efficiency Losses Due to Integration

On the other hand, the conventional and alternate approaches to integration require no additional gas consumption, but the conventional approach performs better in net output and net efficiency. This is a consequence of the amount of HP steam (higher quality) available for power generation in the HP turbine. Only about half the HP steam produced via the conventional approach is generated using the alternate approach, although more steam is generated overall. Redesigning the HRSG to generate more LP steam for solvent regeneration comes at the expense of HP steam that used for power regeneration.

Under the same PCC plant configuration and operating parameters, the reboiler duty requirement is the same for the conventional and alternate integration scenarios, yet more steam is required for solvent regeneration in the alternate integration. This is as a result of the temperatures at which the 4.5 bar steam is extracted, as superheated steam is extracted at 302°C from the IP/LP crossover pipe in the conventional approach, while saturated steam at 148°C from the LP steam drum in the alternate approach. A minor benefit from this alternate steam extraction is a more efficient heat transfer in the HRSG, evidenced by the lower temperature of the exhaust gas.

The dedicated boiler scenario requires a higher L/G ratio to meet a 90% capture level, due to higher CO₂ concentration in the gas, which is a mixture of exhaust gases from the HRSG and the boiler with CO₂ concentrations of 3.99 and 9.01% respectively. This also results in less energy required to liberate 1kg of captured CO₂ from the solvent than in the other two scenarios, the reason for which is explained in Section 6.3.3.3. In addition, a greater CO₂ capture rate is also achieved, with higher concomitant compression and solvent circulation duties. The compression train capacity is sufficient for the increased flow rate of captured CO₂, though it approaches its choke point. Finally, a higher net specific emission of 52kg of CO₂ for each MWh of power generated is achieved, compared to values of 41 and 45kg for the conventional and alternate approaches to integration, respectively.

In conclusion, the cooling water demand when a dedicated boiler is used is almost double the standalone power plant requirement, a summation of the

individual condensation duties of the power, PCC and compression plants. It is only 30 and 38% greater when the conventional and alternate integration approaches are employed, as substantial condensation occurs in PCC plant reboiler. The demand for the alternate approach is greater due to a larger power plant condenser load, as there is more steam exiting the LP turbine.

7.4 Supplementary Firing as an Operational Strategy

7.4.1 Considerations

SF is routinely used in commercial operations of NGCC power plants to boost plant thermal output, especially in cogeneration configurations and during periods of high demands from the grid. To avoid using a dedicated boiler for steam generation that results in low net efficiency, the reduction in output, caused by PCC and compression plant integration, can be offset by SF. If this proves viable, with minimal efficiency losses, such an approach would be particularly attractive for retrofit scenarios, which can also utilize the alternate integration configuration.

In Section 6.4, SF is considered under a design scenario, where the HRSG is redesigned to extract more thermal energy from the exhaust gas. As the amount additional gas being fired is increased, the pressure of the steam being generated could be increased. In this analysis however, the HRSG tube arrangement is unchanged, but as commonly done, more LP economiser tubes are added to the end of the HRSG, with a larger/an additional LP steam drum as described for the alternate integration approach. The objective of the operational SF is to return the steam cycle to its full capacity, while at the same time, providing enough LP steam to meet reboiler duty requirements for solvent regeneration in the PCC plant.

Therefore, SF is implemented (Figure 7-3) under unchanging operating conditions for the conventional and alternate integration approaches, with the additional thermal energy being used to increase steam generation. The gas is fired in a burner located in the gas turbine-HRSG connecting duct, under the following assumptions:

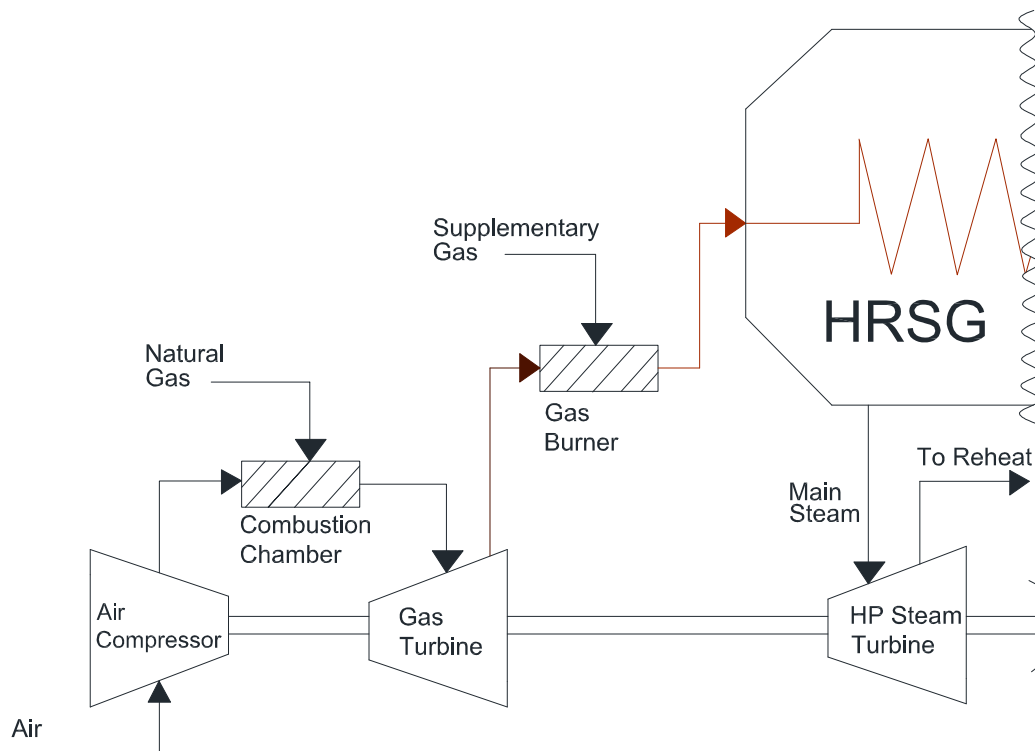


Figure 7-3: Supplementary Firing of Exhaust Gas in Integrated plant operations

- Complete combustion of additional natural gas is reached due to the excess oxygen available.
- There is negligible energy loss to the environment, due to the burner location.
- Flame stabilisation is achieved due to the excess oxygen.
- Minimum approach temperature of 11°C is maintained in evaporators.
- Pressure drops are constant in the HRSG tubes.

Although sufficient oxygen remains in the turbine exhaust gas for higher SF rates, the amount of gas fired in the burner is limited to 4kg/s, about 25% of the gas that is burnt in the gas turbine combustor. This ensures that temperatures at the HRSG inlet remain below 800°C to mitigate thermal stress on HRSG tubes. Exhaust gas oxygen concentration falls from 12.4% to 10.3% at a SF rate of 4kg/s. The flow rate of the exhaust gas exiting the HRSG increases marginally, however its CO₂ concentration increases significantly, as illustrated in Figure 7-4. The compression train is easily able to handle the increased flow rate of captured CO₂.

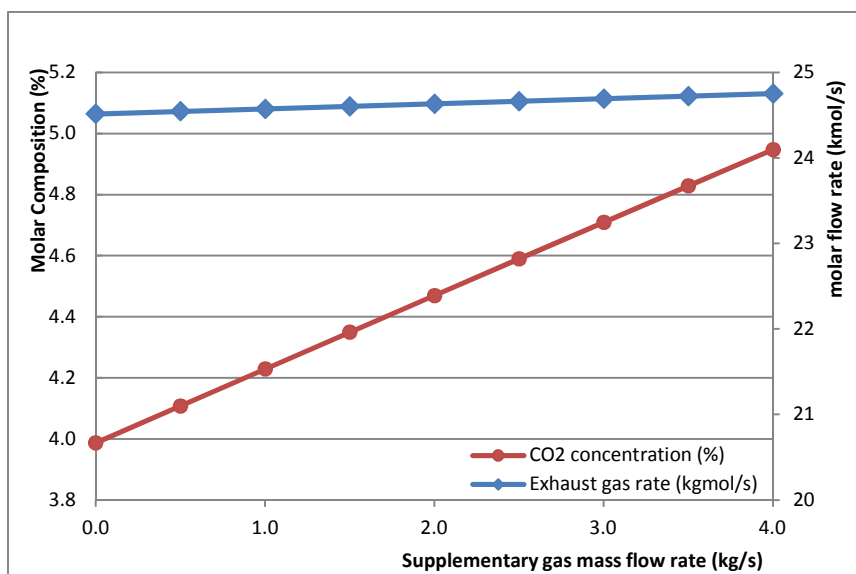


Figure 7-4: CO₂ Concentration in Exhaust Gas Vs. SF Rate

7.4.2 Results and Discussion

In Figure 7-5, as expected it is observed that SF boosts the output of the integrated plant under both approaches of integration, at a rate that is proportional to the SF rate. Figure 7-6 reveals that net plant efficiency falls with increasing SF rate for both approaches. However, SF is more beneficial under the alternate integration approach, as for every kg of additional gas fired in the burner, more power is generated compared to the conventional approach at lesser efficiency losses, resulting in both approaches producing the same output of 412MW and net efficiency of 43.5% at a SF rate 3.8kg/s. This is a consequence of the operational objective of SF – to produce enough steam to simultaneously return the steam cycle at its full capacity and meet reboiler duty requirements for solvent regeneration. And as seen in Figure 7-7, an increasing SF rate results in an increasing HP steam generation in the alternative integration approach while HP steam generation is maintained at the full HP turbine capacity in the conventional approach. It is at a SF rate of about 3.8kg/s that the full HP turbine capacity is attained for the alternate integration approach.

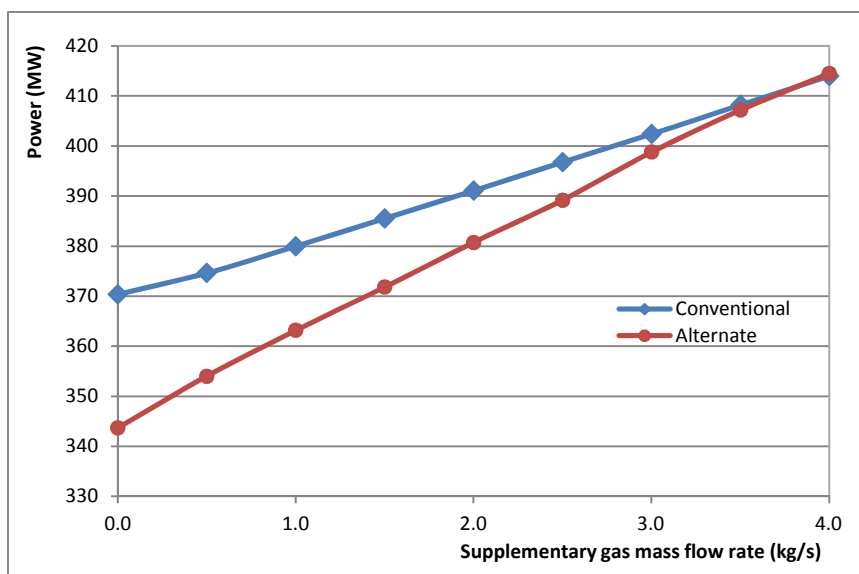


Figure 7-5: Net Power Output vs. SF Rate

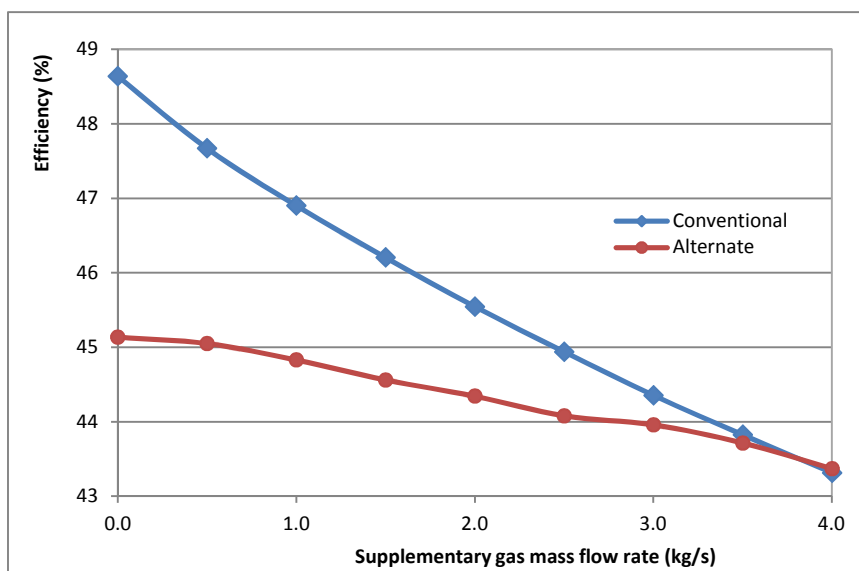


Figure 7-6: Plant Efficiency vs. SF Rate

LP steam generation increases under both approaches, as more steam is required to meet the reboiler duty required to regenerate the solvent from the increasing amount of CO₂ being captured. Also, it is inferred from Figure 7-7 that the rate of increase for LP steam generation is slightly greater for the conventional integration approach, with the additional LP steam is sent to LP turbine to replace what is drawn from the IP/LP crossover pipe. In the end, more steam LP steam is generated in the alternate approach. As explained earlier, this is due to the temperature at which steam is extracted to meet reboiler duty

requirements, with saturated steam drawn from the LP steam drum and superheated steam taken from the IP/LP crossover in the alternative and conventional approaches, respectively.

A similar convergence trend is observed for the net specific emission (Figure 7-8), cooling water demand (Figure 7-9) and exhaust gas temperature (Figure 7-10). The specific emission rises with increasing SF rate at a faster rate for the conventional approach than for alternate one, arriving at a value of 46.5kg CO₂/MWh at a SF rate of 4kg/s.

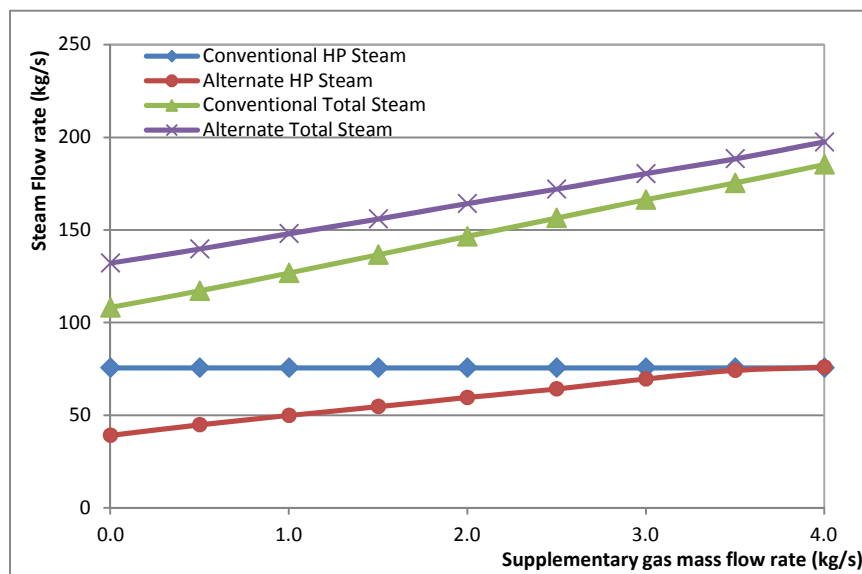


Figure 7-7: Steam Generated vs. SF Rate

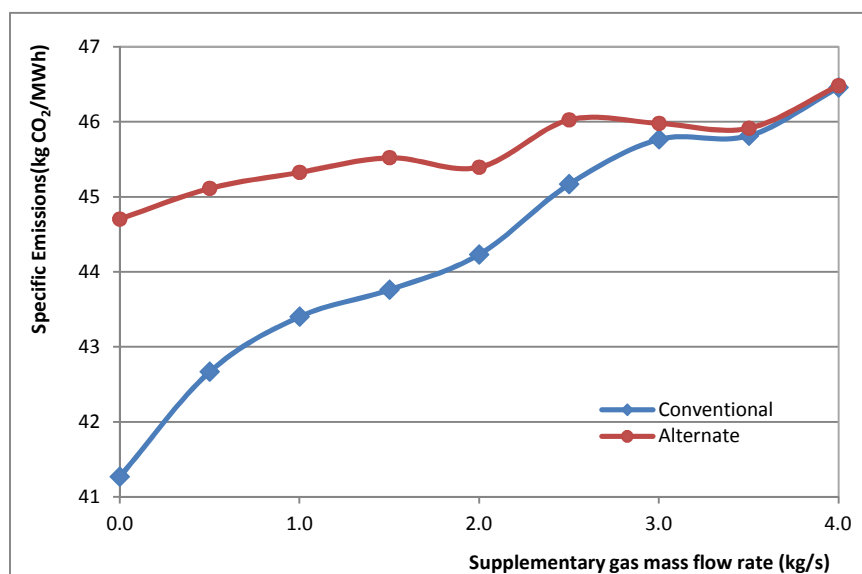


Figure 7-8: Net Specific Emission vs. SF Rate

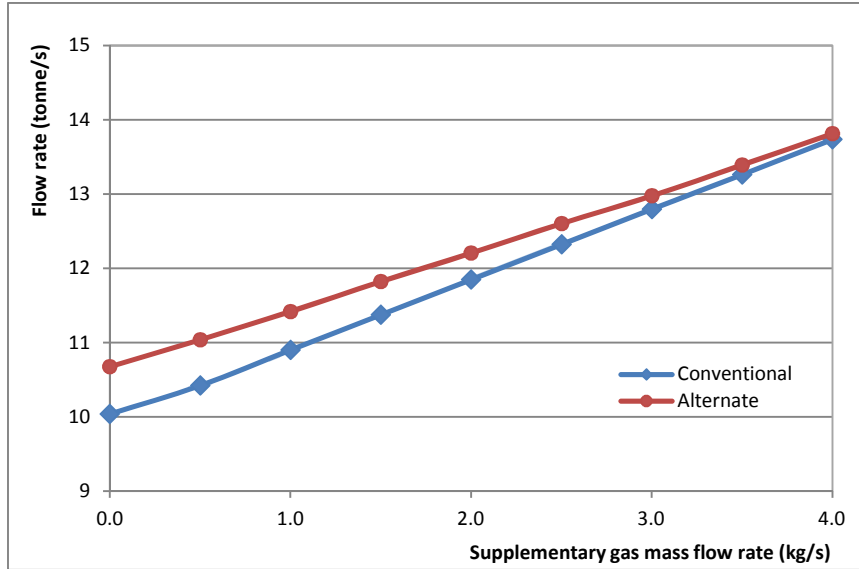


Figure 7-9: Cooling Water Demand vs. SF Rate

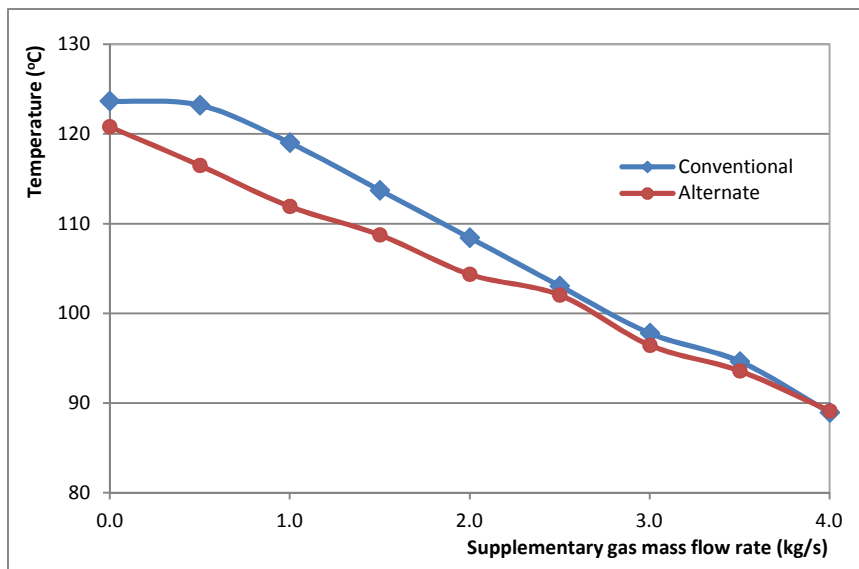


Figure 7-10: Exhaust Gas Temperature vs. SF Rate

Likewise, the difference in cooling water requirements between the two approaches decreases to about 80kg/s from a value of 650kg/s with no SF, due to the narrowing difference in power plant condensation duty. Finally, the same exhaust gas temperature of 89°C is attained in the two integration approaches at a SF rate 4kg/s, a sufficient level to avoid low temperature corrosion, and is a result of comparable heat transfer efficiency from the increased LP steam generation.

To maintain 90% capture level as the CO₂ concentration increases with an increasing SF rate, solvent circulation rate is increased at a constant lean loading, subsequently increasing the L/G ratio as illustrated in Figure 7-11. With increased solvent circulation and CO₂ capture rate, the duty required for solvent regeneration also increases. However, it is observed in Figure 7-12 that as SF rate increases, less steam is required to liberate 1 kg of CO₂ from the solvent. This is due to the increasing CO₂ concentration in the exhaust, which has been previously shown to enhance capture efficiency (Section 6.3.3.3).

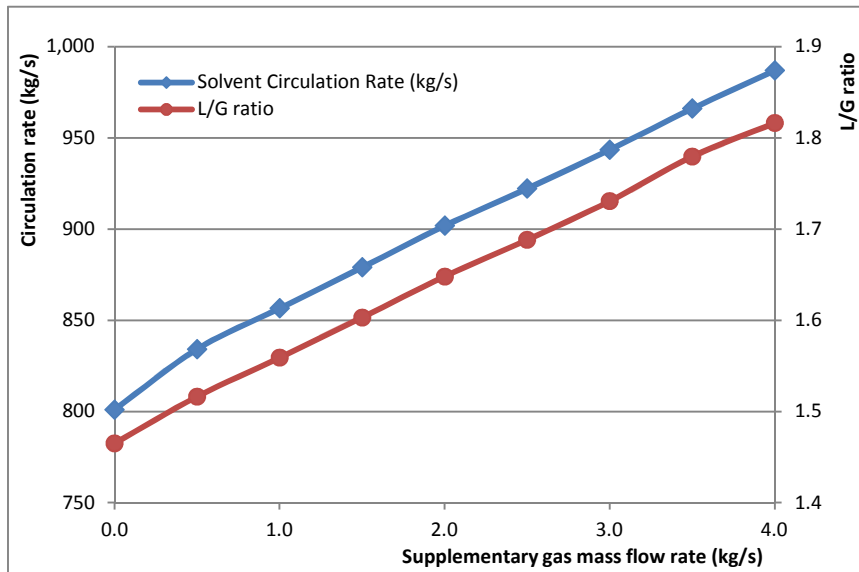


Figure 7-11: Solvent Circulation as a Function of SF Rate

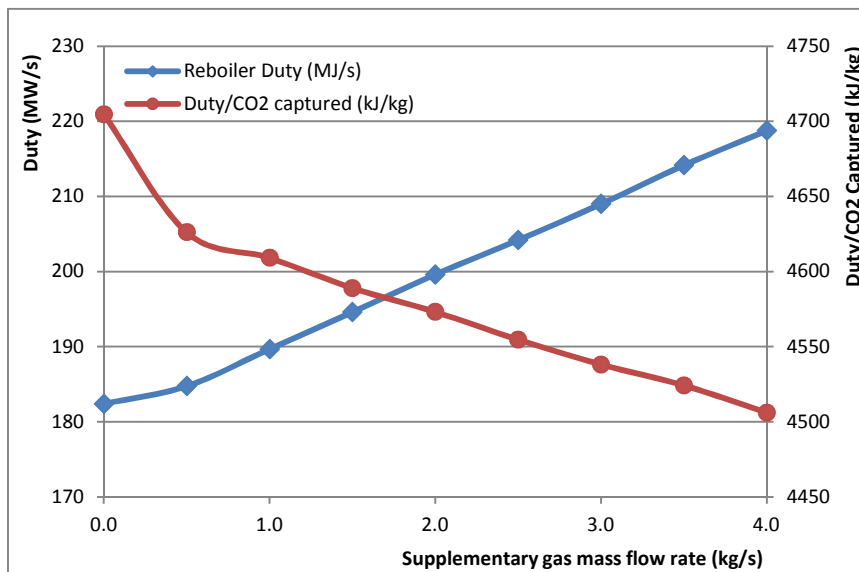


Figure 7-12: Reboiler Duty as a Function of SF Rate

Finally, as the CO₂ capture rate increases with SF rate, the compression duty proportionally increases to compress the higher amount of captured CO₂ (Figure 7-13).

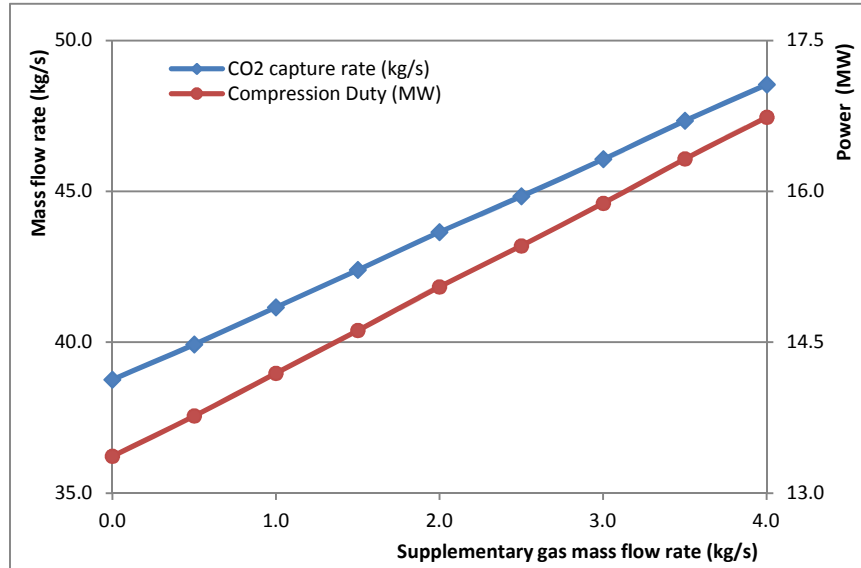


Figure 7-13: Capture Rate and Compression Duty as a Function of SF Rate

8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

This work was embarked on with the aim of analysing the PCC process for integration with gas-fired power plants as a viable approach to CO₂ emission reduction. The following objectives were set:

1. Develop a high-fidelity dynamic model of a PCC plant.
2. Explore the PCC plant operation to identify improvement opportunities.
3. Investigate the integration of a PCC plant to an NGCC power plant and analyse its performance.
4. Perform an economic analysis of CO₂ capture plant integrated with an NGCC plant.
5. Evaluate opportunities for improving integrated plant performance and operation.

These were all met and reported in different sections of the report.

8.1.1 Dynamic Model Validation and Analysis

A dynamic model of a PCC plant with MEA was built using the approach by Lawal et al. (2010). The absorber and regenerator were modelled in gPROMS[®] using a rated-based approach and chemical reactions assumed to be at equilibrium. Plant logs, obtained from the SRP pilot plant at the University of Texas at Austin, were used for validation. The comparison of the model predictions for the standalone columns with the integrated system revealed that the latter provided better predictions.

Dynamic model validation is then carried out, the first successful attempt for such a system. Three cases were considered, a conventional process and two others that incorporated an intercooler in the absorber. Temperature profile of the absorber, CO₂ concentration in the treated gas and the reboiler duty were used as basis for comparison. It was observed that the model satisfactorily predicts the plant behaviour resulting from process inputs and disturbances like changes in flue gas and lean amine flow rate or fluctuating CO₂ concentration in

the flue gas. The model is able to handle multiple process inputs and disturbances, producing trends in close agreement with the plant logs.

The validated model was then used for process analysis, to study the impact of increasing flue gas moisture content and effective intercooling in the absorber. It was observed that moisture content increase has a marginal impact on capture level, but significantly influences the temperature profile, making it an important parameter in the dynamic validation study. Intercooling, on the other hand, was observed to modestly improve the absorber performance when it is targeted at the temperature bulge. This identifies mass transfer, rather than chemical kinetics, as limiting factor in CO₂ capture with chemical absorption using MEA.

Hence, objectives 1 and 2 are fully satisfied under this section.

8.1.2 Model Improvement

Based on identified areas for improvement from preceding study, both mass transfer and chemical reactions rates were explicitly incorporated into the model continuity equations. This is the highest level of modelling packed columns, and is the first such dynamic model to be reported in open literature for the CO₂ capture process. The model is again validated with pilot plant data, and is observed to produce better predictions for capture level and temperature profiles in the absorber, compared to the previous model that has an assumption of chemical equilibrium. Little improvement was observed for rich loading predictions, most likely due to the estimates used for liquid holdup. Thus, the impact of liquid holdup on absorber performance should be explored. The model was then used to analyse transient behaviour in the absorber, which was shown to be highly dependent on L/G ratios, confirming past assessments.

The feats achieved in this section conclude objective 1.

8.1.3 Integration of Capture Plant in Power Plant

High fidelity models of a 440MW NGCC power plant, PCC plant and CO₂ compression train were built in Aspen HYSYS. The power plant model is tuned and validated with data from GE's GateCycle™ gas turbine library, the rate-

based PCC plant model is scaled up from a validated model, and the compression train model is sized to determine the added energy requirement. The three plants are integrated for 90% capture level and it is observed that net power output falls by 15%, while cooling water demand rises by 33%.

A 40% EGR results in a 10MW output recovery, but cooling water demand increases further. The increased exhaust gas CO₂ concentration due to EGR was shown to enhance CO₂ mass transfer in the PCC plant absorber, which led to a reduction in steam demands by the PCC plant reboiler. The implication here is that using other method to enhance mass transfer should also result in reduced steam requirements. SF of gas turbine exhaust was explored, and it was shown to improve power output in proportion to the amount of additional natural gas that is fired.

Economic analysis of the plant located in Northern England is performed via a bottom-up approach and the integrated plant overnight cost is 58% higher than cost of the NGCC plant, discouraging deployment of CO₂ capture. The impact of EGR is marginal, while SF almost doubles the overnight cost. Cost of electricity increases by 30% for the integrated plant, but only by 26% with EGR, and 24% with SF. Yet in all cases, the cost of natural gas is the largest driver for LCOE. Ultimately, the cost of CO₂ avoided is determined to be €51 per ton of CO₂ for the integrated plant, €44 per ton of CO₂ when EGR is considered, and €43 per ton of CO₂ with implementation of SF.

In this Section objective 2 was completed, objectives 3 and 4 were fully satisfied, and objective 5 is partially attained.

8.1.4 Alternative Integration Analysis

The study was carried out to evaluate other options for integrating an NGCC power plant, a PCC plant and a CO₂ compression train. The same 440MW power plant and compression train were integrated with a resized rate-based PPC plant model to achieve a 90% CO₂ capture level, with the aim of exploring operational flexibility and avoiding plant layout problems, which have been identified as difficulties in the conventional approach to integration. Therefore,

as opposed to extracting steam from the IP/LP crossover for solvent regeneration, two other options are explored – using a dedicated boiler to produce steam, and an alternate steam extraction from the LP steam drum.

For the PCC plant design used, integrated plant output is observed to drop by 6%, 16% and 22% for the dedicated boiler, conventional and alternate integration scenarios, respectively. Yet, net efficiency is 40, 49 and 45% for the aforementioned options, a consequence of the additional gas burned in the boiler, which keeps net output high but erodes efficiency. Net output is lowest in the alternate approach due to reduced HP steam generated, as thermal energy is diverted to produce additional LP steam to meet the reboiler duty for PCC solvent regeneration. Furthermore, cooling water demands increases for all 3 options, with net specific emissions of 52, 41 and 45g of CO₂ per MWh.

As opposed to using a dedicated boiler, an operational approach to SF is implemented, with the objective to produce sufficient steam to return the steam cycle of the power plant to its full capacity and meet reboiler duty requirements for solvent regeneration. It is observed that the net output, plant efficiency, net specific emission and cooling water requirements converge to same value for both conventional and alternate integration approaches, with increasing SF rate. At a SF rate of 3.8kg/s gas, which is a 24% increase on the standalone NGCC plant full load, net output converges to 412MW. This proves that the alternate integration strategy is viable strategy, with operational and plant layout benefits, when it is implemented with SF.

Objective 5 was the target of this section, and it was fully achieved.

8.2 Recommendations

After the realisation of the objectives of this research, recommendations are made. In regards steps to take to expand the work that has been reported:

1. The improved absorber model ought to be validated with different absorber specifications and operating ranges to confirm its performance. Also, using the model to simulate and explore PCC plant behaviour and dynamic response is a logical next step.

2. Other mass transfer correlations and reaction kinetic models should be implemented in the column model to identify the combination that best predicts the performance of a PCC plant.
3. An improvement for the model will be adding a pressure drop relationship for packed columns. This is important in a commercial scale PCC model.
4. The role of eddy diffusion in PCC plant columns ought to be investigated, as it is likely to be significant at commercial scale. The column size at which eddy diffusion begins to influence is a useful factor to identify.
5. Pressure losses that occur across the inlets of steam turbine due to reduced steam flow rates ought to be quantified to provide improved estimates of efficiency losses for an integrated plant.
6. The cost of CO₂ transport and storage should also be considered in the economic analysis, to provide a full picture of the systems costs.

Promising areas have been identified for investigation and future research, which may accelerate the deployment of PCC technology on power plants:

1. Solvent substitution of MEA with ammonia, potassium carbonate, other amines and others is vital. MEA can serve as a reference solvent to which the performance of other solvents can be compared. The model developed in this work can easily be expanded to cover other solvents, so long as chemical kinetic data for it is available.
2. Configurations of PCC plant can be explored with high fidelity models to quantify the energy savings that result from their implementation. It would also be prudent to accompany such with economic analysis and operability study to fully assess their feasibility.
3. As NGCC power plants are usually used for load balancing, performance analysis of an integrated plant under part load operation is necessary. However, the availability of performance maps in the turbo-machinery is a prerequisite before such analysis can be credible.
4. Global optimisation of the integrated plant to determine PCC plant design parameters such as column and packing dimensions, and operating conditions such as solvent circulation rate, lean loading and regenerator

- column pressure would be illuminating. In addition, heat integration via pinch analysis of the integrated plant should also provide useful insights.
5. Developing an NGCC plant dynamic model for integration with the PCC plant dynamic model for the operability analysis would be a very useful exercise. Process control schemes for flexible control of the integrated plant can be explored, along with advanced control techniques such as self-optimising control.
 6. It was revealed in this work that enhancing mass transfer in the PCC absorber would result in improved capture efficiency and reduced energy demands for solvent regeneration. Thus, applying process intensification techniques, such as swapping absorber and regenerator columns with rotating packed beds, would result in enormous savings in the PCC process. Other concomitant benefits like smaller equipment sizes and faster process dynamics make this very attractive.
 7. Jet pumps/ejectors can be employed to extract HP steam and combine it (with minimal pressure losses) with LP steam for solvent regeneration in an integrated plant. This reduces the impact of steam extraction on the power plant, resulting in an increased net plant output.
 8. A cogeneration configuration of the HRSG, where the PCC plant reboiler is integrated to it, would be beneficial to integrated plant net output, especially in scenarios where SF is implemented as minimum temperature approach can easily be maintained.
 9. A CO₂ transport pipeline case study via modelling and simulation using a systems approach to evaluate energy requirements would be valuable.

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