Latrobe Valley Post Combustion Capture (LVPCC) CSIRO-LYP Stream Final Technical Report

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EXECUTIVE MANAGEMENT SUMMARY

Introducing the LVPCC project & Objectives, Results of the Economic Assessment, Remark on Water Consumption & Cooperation and Community Engagement.

Brown coal-fired power generation is the source of about half of Victoria's current greenhouse gas emissions [1]. It supplies, however, about 90% of the electricity to Victoria and is the basis for a reliable and cheap electricity system. It is therefore clear that CO_2-emission reduction strategies aimed at the existing power stations are urgently needed to provide a path towards environmental sustainability of the Victorian brown coal industry. The use of carbon capture and sequestration (CCS) is essential to move in this direction and Victoria is well placed due to the vicinity of vast storage capacity in the Gippsland basin, which equals to more than 500 years of CO_2 produced in Victoria at current emission rates [2]. Post-combustion carbon capture (PCC), the focus of this project, is an important first part of the carbon capture, transport and storage (CCS) chain. Amongst the technologies that can capture CO_2, reactive liquid absorption processes are the most advanced, both in commercial and technological terms. Still the technology has never been operated at the industrial scale necessary (Millions of tons of CO_2 per year) and integrated into a power plant at that scale. Main issues involved are:

- There is no business case without a form of carbon regulation in place;
- The high cost of investment results in high risk of investment;
- Public perception of sustainable or clean coal and CCS in particular is underdeveloped;
- The energy penalty of the PCC process is significant;
- There are few trained personnel in the operation of chemical plants in the Latrobe Valley.

In Victoria, between 2008 and 2011, the Latrobe Valley Post Combustion Capture (LVPCC) project has been addressing the issues of investment costs and parasitic load. Loy Yang Power and the CSIRO focussed on assessing PCC improvements by benchmarking CO_2 scrubbing solvents based on amines, while International Power and CO_2CRC focussed on salt based absorption solvents, membrane and adsorption technology. Furthermore, both streams worked on integration of Power Station and Capture Plant processes while public perception has been addressed by presentations and publications in (non-)academic media. This executive summary further focuses on the results by CSIRO and Loy Yang Power (LYP).

CSIRO has installed, commissioned and operated a PCC pilot plant at Loy Yang Power station, the first of its kind in the Southern Hemisphere. In total 9 campaigns were completed between May 2008 and March 2011. As part of the research program CSIRO has experimentally evaluated 5 solvent mixtures in the project. The baseline of the PCC pilot plant was developed by the use of MEA (mono-ethanolamine) solvent. Further solvents based on amines were chosen with an outlook to improved performance towards parasitic load and towards the kinetics leading to lower investments. The trials have confirmed the technical feasibility of the amine based capture processes. That is, 80-90% of CO_2 could be removed from the flue gas, while the product purity is in excess 96% (rest is predominantly water) and the regeneration energy of 4-4.5 MJ/kgCO_2 is obtained for MEA while the blended solvents resulted in values between 3 and 4 MJ/kgCO_2.

The economic assessment has been carried out based on a 539 MW plant and PCC based on the standard MEA solvent with optimal heat integration based on realistic conservative assumptions. The outcome is that for brown-coal fired power stations in Victoria the long run marginal cost of generation (COG) with 90% CO_2 capture can be as low as $83/MWh ($75/ton avoided CO_2), where a new PCC plant is retrofit to a fully amortised Power Station. In contrast, a greenfield brown coal-fired power plant and PCC plant costs as much as $190/MWh ($136/ton avoided CO_2). At much lower investment costs and without affecting the boiler cycle too much, 29% of CO_2 can be captured at a COG of $42/MWh. As a reference, the COG for a fully amortised plant without CO_2 capture is $11/MWh. One option involving the installation of an air cooled unit, instead of a natural draft cooling tower, leads to a decrease of the water consumption of 40% to 1.2 m^3/MWh.

In addition to savings by integration of the power plant and the PCC plant, the LVPCC project has shown that solvents can establish further reduction in COG of 20-30% of which 10-15% is based on decrease of parasitic load and 10-15% through investment cuts. Therefore, the currently projected outlook is that RD&D can result in a most optimistic COG as low as $50/MWh. The impact though of the best solvents on the environment has to be further addressed and it might be that extra investments are necessary and thereby partly counter balance the primary improvements.

The CSIRO has been closely co-operating with Research Institute of Innovative Technology for the Earth (RITE), a Japanese research institute, and Chiyoda, a Japanese vendor of flue gas desulphurisation systems. Within the LVPCC framework their Japanese proprietary solvent has been tested for the brown coal flue gas. It proved to be the most promising of all solvents evaluated with regards to energy consumption and kinetics. The co-operation has been a success as stated by all parties involved and follow-up funding is sought by RITE/Chiyoda to finance long term assessment of the solvent. Also engineers of the Huaneng group in China were trained at the facility at Loy Yang Power in 2008 as part of an APP-funded project, and they are now considered world leading with regards to size (PCC at 120.000 tpa per January 2010). Further to that 3 plant operators from the Latrobe Valley have been operating the pilot plant safe and effective.

The project and the vision upon which the development of PCC is built has been widely communicated to a variety of Company, Government & Research leaders and communities through (invited) presentations, (peer-reviewed) papers, international conference papers and discussions, newspapers, magazines, national and regional media and interactively at community meetings in Latrobe City and Melbourne metropolitan.

Direct impact of the project to LYP was as follows:

- It gave firsthand experience of the technology;
- It demonstrated to LYP that the technology can be adapted to brown coal;
- It gave LYP confidence to engage in further demonstrations with CSIRO and Worley Parson/Mitsubishi Heavy Industry (WP/MHI);
- It provide practical insight into PCC technology and processes for LY's scientific group to the process technology and how to operate the plant at the best practice;
- To provide practical insight into PCC technology and processes Engineering Group on the design and functionality of the plant;
- Facilitated collaborative work between industry and a leading research body (CSIRO) in order to demonstrate the real-world capabilities of CO_2 capture.

The assessment studies have identified that further detailed insight on the investment side of the technology needs to be developed and opportunities addressed. Also the realisation of a (near) zero emissions PCC plant and permitting regulations are becoming of major interest. These and other developments of the PCC technology need to line-up with and support demonstration project(s), such as CarbonNet.

TECHNICAL SUMMARY

Introduction: Post-combustion Carbon capture for flue gases from brown coal-fired Power stations

Post-combustion capture (PCC) is an important first part of the CCS chain. Amongst the technologies that can capture CO_2, reactive liquid absorption processes are the most advanced, both in commercial and technological terms. Still the technology has never been operated at the industrial scale necessary (Millions of tons of CO_2 per year). Main issues involved are:

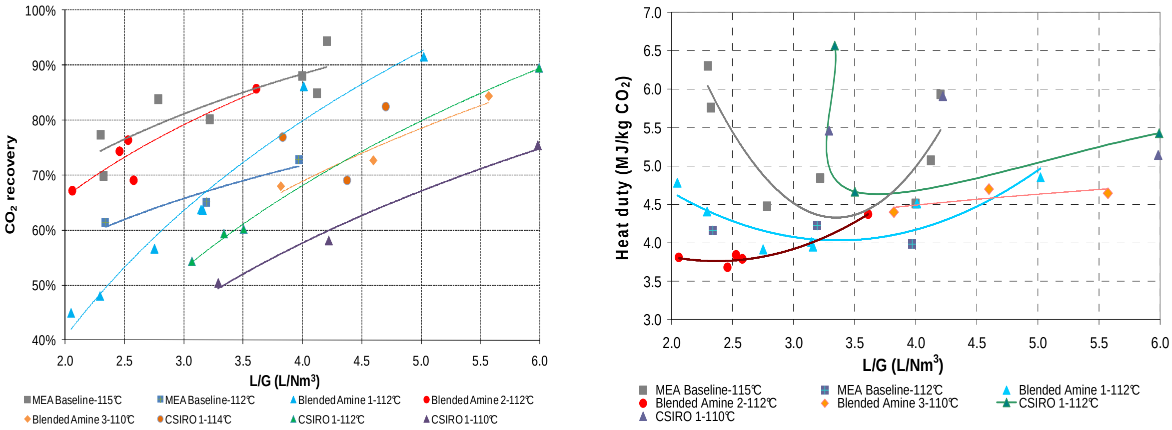
- High cost and therefore risk of investment;
- Parasitic load of the PCC process is significant;
- Integration of a retro-fitted PCC plant will have a significant impact on the steam cycle;
- Environmental impact, corrosion.

In Victoria, between 2008 and 2011, the Latrobe Valley Post Combustion Capture (LVPCC) project has mainly been addressing the issues of investment costs and parasitic load. Loy Yang Power and the CSIRO focussed on assessing PCC improvements by benchmarking CO_2 scrubbing solvents based on amines, while International Power and CO_2CRC focussed on membrane and adsorption technology and on absorption with salt solutions. Furthermore, both streams worked on integration of the Power Generation with the Carbon Capture processes while public perception has been addressed by presentations and publications in (non-)academic media. This technical summary focuses on the results by CSIRO and Loy Yang Power.

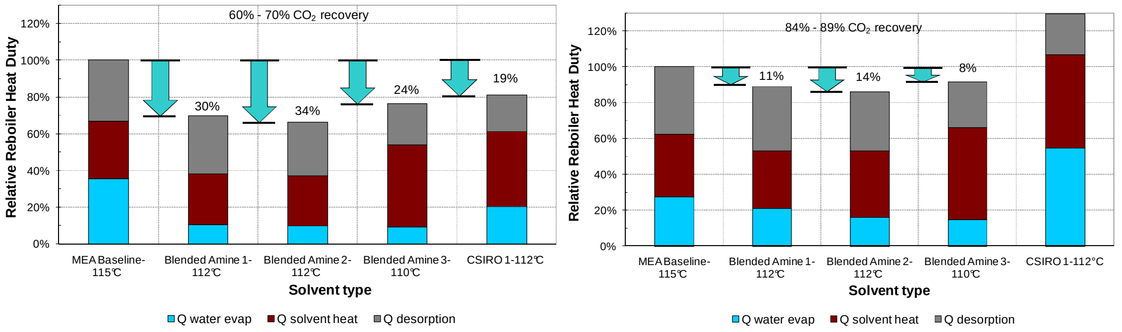
Results of benchmarking solvents

As part of its ongoing PCC-program the CSIRO had screened more than 100 amines in the laboratory in relation to solvent loading, kinetics and theoretical energy use. In this project 5 solvent mixtures were evaluated. A 30 wt-% aqueous MEA (mono-ethanolamine) was used to set a baseline for CSIRO's PCC pilot plant at Loy Yang Power. MEA has been described well in literature and is generally regarded as a world standard. The major parameters investigated include solvent concentration (25-34 wt%), CO_2 loading in the solvent (0-0.4), solvent flowrate (3-10 L/min), gas flowrate (60-180 Nm^3/hr), absorption temperature (30-50 ℃), and stripp er bottom liquid temperature (108-118 ℃).

Further solvents were chosen to decrease the parasitic load by lower binding energy of the CO_2 to the solvent MEA/AMP (2-amino-2-methyl-1-propanol) and CSIRO-1 (proprietary blended amines). Aiming for lower investment costs high reactive solvents (PZ/AMP (piperazine) and RITE) were chosen. This is expected to result in smaller size columns and consequent lower investment costs.



CO_2 recovery (left) and Heat Duty (right) versus the solvent flue gas ratio (L/G) for blended amines as tested in CSIRO's PCC pilot plant at LYP. Blended Amine 1, 2 and 3 are MEA/AMP, RITE-solvent and AMP/PZ, respectively. AMP is aminomethylpropanol and PZ is piperazine. The CSIRO-1 solvent has not yet been operated at optimal plant settings.



Heat Duty as a function of CO_2 recovery and solvent. The high contribution of water evaporation of the CSIRO-1 shows that the operation has room for much optimisation.

In our plant MEA uses about 4.2 MJ/kgCO_2. Up to 34% of the heat duty can be saved compared to this MEA base-case. The RITE solvent shows the strongest improvement regarding heat duty, followed by the other blends. In relation to kinetics none of the solvents seems faster than MEA, on the contrary, all solvents except for RITE's solvent, show lower kinetics.

Discussion on solvent benchmarking

From the graphs it may also be concluded that the plant has a too low packing height to optimally operate the 'slower' solvents. With more packing these solvents would be loaded more per cycle and as a result use less energy per captured kgCO_2 for the high capacity solvents (that is all, but MEA). This is supported by the observation that upon comparing the solvents at lower CO_2 recoveries (~70% CO_2) the energy benefits are much more favourable than at 90% capture. During the project, however, it was reasoned and supported by the economic assessment that the brown coal case needs fast kinetics to end-up with smaller columns and less investment costs, which impacted strongly on the cost of electricity generation. As a result it was chosen to not increase the height of the column packing, but to aim for testing ‘fast’ solvents. On the other side, the option of structured packing should be considered. Another important remark is that the solvents were operated suboptimal when compared to suggested composition based on lab results. Two considerations led to deciding working at lower concentrations than suggested: 1. during operation flooding occurred due to high viscosity, and 2. some solvents are known to accelerate corrosion rate above a certain concentration. For both issues diluting the solution is an obvious solution. CSIRO-1 has only been operated for just over 2 weeks and an optimal operating setting has not been reached yet. This is clearly indicated by the high contribution of water evaporation to the total heat duty. Furthermore, the CSIRO-1 solvent was trialled after installing insulation to the absorbers, which prevent unintended but beneficial inter-cooling.

Improvements of pilot plant during the LVPCC project

Within the CSIRO PCC programme the pilot plants programme was at the beginning based on the philosophy: “Learning by doing.” The pilot plant at Loy Yang Power was modified over the course of the project based on learnings from the pilot plant and lab-research in Newcastle. The purpose of each upgrade may be to automate operation, improve research results or enhance safety and operability. Here the most relevant to scaling up PCC are discussed.

An important feature of the PCC plant is the use of *density meters* on amine solvent lines to monitor CO_2 concentration as the amine solvent density is directly proportional to the level of CO_2 loading of the solvent. The CO_2 concentration readings will indicate the efficiency of CO_2 the absorption and regeneration for a particular solvent under certain operating conditions. *Mist elimination equipment* was installed in absorber column 1 to prevent the entrainment of amine solvent mist, significantly reducing amine solvent loss and increasing campaign duration. The flue gas flow is measured using differential pressure readings from the *blower flow meter*, to ensure optimal accuracy measurements need to be taken in fully established flow. After redesign, the pipe length was increased as a U shape with 1.5 meters on either side of the two pressure measurement points, increasing accuracy of results. Additionally, the new U-shape design prevents the blower flow meter from collecting water, the source of offset errors. A plate and frame *heat exchanger* (STR-HX02) is used for the heat transfer from the hot lean amine from the stripper to the cooler rich amine from the absorber. To improve heat transfer efficiency and acquire a higher temperature for the stream of rich amine entering the stripper, the plate and frame heat exchanger size was increased. However, the heat transfer efficiency did not improve after the installation of a larger STR-HX02. Further investigation revealed that at low flow rate and pressure, the CO_2 in the rich amine solvent converts to vapour, significantly decreasing the heat transfer efficiency. To resolve the issue, a *throttling valve* has been installed on the rich amine stream exiting the heat exchanger. The throttling valve will increase the pressure of the rich amine stream, suppress CO_2 vapour formation and improve heat transfer efficiency. Corrosion can result in low temperature regions of the plant when the flue gas cools below the condensation temperature of acids. The gas in the line before flue gas pre-treatment (FPT) is highly corrosive due to the presence of sulphur dioxide (SO_2). The acidic environment resulted from the dissolution of SO_2 and NOX in condensed water vapour to form sulphuric acid and nitric acid. Within the first year of LYPP operation, acid pinhole corrosion was evident on the blower and on the grade 304 stainless steel piping and knock out box. Subsequently, to prevent further corrosion damage the blower (FPT-BLO1) was relocated and is now positioned after the pre-treatment process. During the blower relocation, *flue gas inlet piping and the knock-out box* was replaced with grade 316 stainless steel for its corrosion resistance in an acidic environment, while the cheaper 304SS is proven reliable for the base side of the process. Before insulation, condensation on the sides of the flue gas inlet pipe caused flue gas particulates to adhere and build up at the pipe wall, eventually completely blocking flow. Thermal insulation proved to solve the problem.

Results of detailed heat integration and economic assessment

The economic assessment has been carried out based on a power plant (539 MW gross) and PCC based on MEA with optimal heat integration based on realistic conservative assumptions, such as 85% availability, 10% interest rate and 10 K approach temperature for the heat exchangers. The outcome is that for existing natural draft water cooled brown-coal fired power stations in Victoria the cost of generation (COG) with 90% CO_2 capture can be as low as \$83/MWh (\$75/ton avoided CO_2), where a new PCC plant is retrofit to a fully amortised power station. In contrast, a greenfield brown coal-fired power station with a PCC plant costs as much as \$190/MWh (\$136/ton avoided CO_2). At much lower investment costs and without affecting the boiler cycle too much, 29% of CO_2 can be captured at a COG of \$42/MWh. One option involving the investment of a gas cooling unit leads to a decrease of the water consumption of 40% to 1.2 m^3/MWh.

In addition to savings by integration of the PCC plant with the power plant, the LVPCC project has shown that solvents can establish a further reduction in COG of 20-30%. The reduction in COG composes of 10-15% as a parasitic load reduction and another 10-15% as a result of investment cost reductions. This is realised through investment cuts of up to 50% based on preliminary calculative effects of improved kinetics, dual phase absorption, cheaper contactors, lined concrete and integrated flue gas cooling, pre-treatment and CO_2 capture. Therefore, the currently projected outlook is that RD&D can result in a most optimistic COG as low as \$50/MWh where 90% CO_2 is captured.

Concerns of sustainability of the PCC technology

Capturing CO_2 to delay or soften climate change should not impose the introduction of other (larger) risks. Hardly any separation process is perfect and as a result some of the CO_2 capture solvents will be emitted from the PCC pilot plant. To what amount will depend on the solvent characteristics, process conditions and maintenance. Optimal solvents in relation to kinetics and heat duty consist of PZ-derivates and secondary amines. The impact of these solvents on the environment has to be further addressed and it might be that extra investments are necessary and thereby partly counter balance the primary improvements.

Solvent samples from the pilot plant were regularly tested for the presence of nitroso-compounds, which analysis procedure has been developed by CSIRO Newcastle and North Ryde in parallel projects. NDELA, which is the nitroso-compound form of diethanolamine DEA, wasn't detected in any MEA sample from our plant; NDELA's detection limit is 230 ppb in an MEA-matrix for the instrument. DEA is commonly present in industrial grade MEA. For solvents containing PZ that were used in the pilot plant, however, N-nitroso-PZ has been detected. Current analysis techniques cannot quantitively determine this concentration.

Conclusion & Recommendations

Flue gas from a brown coal-fired power station was pre-treated and SO_x and NO_2 were depleted to below detection limit by a caustic wash. In the absorbers with random packing CO_2 was captured by amine based solvents. The solvent was regenerated in a stripper which produced more than 96% CO_2, mainly balanced by water. Costs for avoided CO_2 can be $75 per tonne, based on a fully amortised power plant with a retrofitted PCC plant. There is an outlook to possibly $50 per tonne upon improvements of the solvent system on both the operational side and the investment side.

Main issues to be further addressed are the investment costs and environmental impact, i.e., emission or permitting regulations. In the area of diverting or preventing environmental impact a fundamental research approach is necessary and can be further built on the expertise being developed at the Monash University in the Latrobe Valley.

A new project is initiated where investment costs reduction is aimed for by integrating flue gas pre-treatment with CO_2 absorption. .

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1. POST COMBUSTION CO_2 CAPTURE IN VICTORIA

Brown coal-fired power generation is the source of about half of Victoria's current greenhouse gas emissions [1]. It is therefore clear that CO_2-emission reduction strategies aimed at the existing power stations are urgently needed to provide a path towards environmental sustainability for the Victorian brown coal industry. The use of carbon capture and sequestration (CCS) is essential for this direction and Victoria is well placed due to the vicinity of vast storage capacity in the Gippsland basin, which equals to more than 500 years of CO_2 produced in Victoria at current rates [2]. Post-combustion capture (PCC) is an important first part of the CCS chain. The implementation of PCC in the Victorian case requires specific focus towards its technological development in regard of three following issues:

1. Brown coal is not sold into a world market due to its high moisture content in contrast to black coal, oil or natural gas. Therefore, it is expected that brown coal prices will remain at low price levels thus continuing to provide the basis for low cost electricity for Victoria. The capture of CO_2 will result in a large increase in the cost of electricity generation, which needs to be addressed;
2. Brown coal flue gases are available at high temperature, have high water content and contain alkaline ash. This provides a challenging environment for chemical absorption processes;
3. The combined process of coal mining, power generation and PCC should use less water than current power generation as the retreating ground water levels result inan unsustainable situation.

Several CO_2 separation techniques such as absorption into a liquid, adsorption onto a solid and membrane permeation processes [3] have the potential to capture CO_2 from flue gases. Due to high volume flow rate and low CO_2 partial pressure of the gas stream from a coal-fired power plant [4], chemical absorption into a liquid is currently the most suitable option for capturing CO_2 from flue gases [3, 5, 6]. The use of mono-ethanolamine (MEA) as the liquid absorbent or solvent is a commercial activity in a small scale (< 30 ton CO_2/h) and it may soon be used in full-scale for the CO_2 separation from flue gases in coal fired power stations [3]. This is due to its low chemical cost, ability to capture CO_2 from low pressure flue gas and fast reaction kinetics with CO_2. The PCC unit can also be retrofitted to an existing and integrated to a new power station [7-9]. A large amount of energy is required for solvent regeneration resulting in a considerable drop in power station efficiency [6, 8, 9]. Degradation and solvent losses are also identified as important environmental and cost factors, particularly in full-scale applications. Furthermore, in a financial cost analysis of an MEA-based PCC plant, Veawab *et al*. [10] concluded that the absorption and desorption (solvent regeneration) equipment sections have the largest contribution to capital cost investment. They also specified that up to 70% of the total operating costs will be needed to provide the heat duty for the solvent regeneration (desorption section) [10].

1.1 CSIRO – LYP Research Activities and CSIRO’s PCC Program

Post-combustion Carbon Capture is a key technology in a complete CO_2 capture and storage chain. Amongst the technologies that can capture CO_2, reactive liquid absorption processes are the most advanced, both in commercial and technological terms. This report provides an overview of the CSIRO programme on PCC but focuses on results from comparison of several solvents trialled in the CSIRO PCC pilot plant at Loy Yang Power.

Loy Yang Power – since ’08 Brown coal-fired power station

Beijing – since ‘08
Supporting TPRI and Huaneng

Munmorah – since ‘09
Black coal-fired power station

Tarong – since ‘10
Black coal-fired power station

Figure 1: Photographs of pilot plants in Loy Yang Power, Beijing (Huaneng), Munmorah and Tarong.

The following pilot plants have been commissioned by CSIRO at three power plant locations in Australia (as seen in Figure 1):

- Loy Yang Power focusing on application of amines for CO_2 capture in brown coal operations;
- Delta Electricity Munmorah power station focusing on the application of cooled ammonia for CO_2 capture in black coal operations;
- Tarong Energy power station has completed a MEA evaluation for CO_2 capture in black coal power station. The plant is currently investigating new solvents performance.

The pilot plant project at the Huaneng Beijing Cogeneration Plant was supported by CSIRO through the provision of design documents, a hands-on training programme for the future Chinese operators and practical assistance during start-up. This pilot plant uses conventional amine technology on a flue gas from a black coal fired power station, which has flue gas desulphurisation (FGD) installed.

2. OBJECTIVES OF THE CSIRO-LYP PROJECT

The chemical absorption technique is considered to be the most advanced post-combustion capture technology [11]. CSIRO has devised a transportable pilot plant based on MEA. For the Latrobe Valley Post-combustion Capture project (LV-PCC), CSIRO has operated this amine pilot plant using real flue gases from a Victorian brown coal-fired power station at Loy Yang Power (2.2 GW).

The objective of the PCC pilot plant trial program was as follows:

- To obtain practical experience of PCC with real flue gases from a lignite fired power plant;
- To test the performance of PCC LY pilot plant under nominal conditions;
- To assess the effect of operational parameters alteration on the performance of CO_2 absorption.

The performance of the PCC LY pilot plant has been measured against CO_2 removal efficiency, CO_2 production rate and energy requirement for solvent regeneration.

Seven campaigns were carried out with the aim of evaluating a set of different solvents and their results were compared to the benchmark 30 wt-% MEA.

2.1 Blended Amine Solvents

Despite having the benefit of a relatively high rate of CO_2 absorption, in comparison to other alkanolamines, MEA requires a relatively high energy for solvent regeneration in stripper column resulting in high operating costs.

Many PCC researchers have shown interest in examining blended-amines for PCC [6, 14-18]. The blended-alkanolamines generally have the combined capabilities of the two original solvents resulting in a lower energy for solvent regeneration [4, 6, 14]. In this project, a new mixture solvent is investigated. Our work has examined four different solvents, i.e., Blended Amine 1, which is a mixture of MEA and AMP solvent; Blended Amine 2, which is a proprietary solvent from RITE, Japan; Blended Amine 3, which is a blend of AMP and Piperazine; and CSIRO 1, which is a blend of AMP and 3-PM. The pilot plant results obtained with these blended solvents are compared to the MEA baseline results in terms of CO_2 recovery and reboiler heat duty required.

3. PCC PILOT PLANT AT LOY YANG POWER

3.1 Process Description

The transportable PCC pilot plant at Loy Yang Power was designed to capture CO_2 from real flue gases using 30 wt-% MEA. This generic solvent is a suitable baseline case due to the availability of public domain information on its physico-chemical properties and operation in pilot plants. The PCC pilot plant is able to receive 50 kg/h real flue gas from unit 2. The pilot plant consists of one flue gas pre-treatment unit, two absorber columns to capture the CO_2, a stripper column for stripping off the CO_2 from the solvent and a 120 kW electric-boiler unit to generate steam for heating the media in the stripper's reboiler. The pilot plant has been operated with two absorbers in series (*cf.* Figure 2). The plant design incorporates the use of two short absorbers providing a compact plant which can be transported easily.

Water and solvent vapour released through the top of the stripper column is recovered in a 60 kW condenser. The vapour and condensed-liquid are separated in a flash drum situated near the solvent-feed tank. The liquid phase is returned to the solvent feed tank after mixing with hot lean solvent from the stripper's bottom product. The vapour phase, which contains about 98 vol-% CO_2, is delivered back to the flue gas duct. The mass flow of the concentrated-CO_2 product is measured with a coriolis flow meter.

Figure 2 describes a simplified flow diagram of the pilot plant. A portion of flue gases is taking-off by a blower before reaching to chimney. The flue gas is cooled and then flows into the knock-out drum where condensates and particulates are separated. The pilot plant consists of a flue gas pre-treatment unit, which uses a caustic solution (32% NaOH), before the flue gas enters the absorber column 2. The average SO_2 concentration in the flue gas from the power station is around 200 ppmv and up to 98% is removed in the pre-treatment column.

In series operation mode, the treated flue gas initially flows to the absorber column 2, where it is counter-currently contacted with a CO_2-rich solvent from the bottom of absorber 1 at around 35-55 °C under atmospheric pre ssure. Then, the gas containing less CO_2 exits the top of absorber 2 to the bottom section of absorber 1, where it also counter-currently contacts with fresh CO_2-lean solvent pumped from the solvent feed-tank. Absorption and chemical reactions between CO_2, a weak acid, and aqueous amine based solvent, a weak base, occurs in these two absorber columns. The CO_2-lean flue gas, so-called gas out, is emitted from the top of absorber column 1 and it is subsequently returned to the power plant's flue gas duct.

The cold CO_2-rich solvent stream out of the bottom of absorber column 2 is preheated to 90-100 °C (depend on ΔT approach) before entering the stripper column, in which the stream is called hot rich solvent, in a cross-solvent heat exchanger by utilizing the heat from the hot lean solvent (typically 112-115 °C) out of the stripper's bottom. Temperature of the hot lean solvent drops after releasing the heat into the cold rich solvent and is then further cooled with cooling water until reach desired temperature before going into the solvent-feed tank. From the solvent-feed tank, the solvent is then pumped into the absorber column 1. In the stripper column, water vapour and CO_2 separation from the solvent (through the endothermic desorption process) are generated as a result of heat supplied from the reboiler (typically 112-115 ℃). The reboiler heat is obtained from the condensing steam (at a steam pressures range of 135-150 kPa).

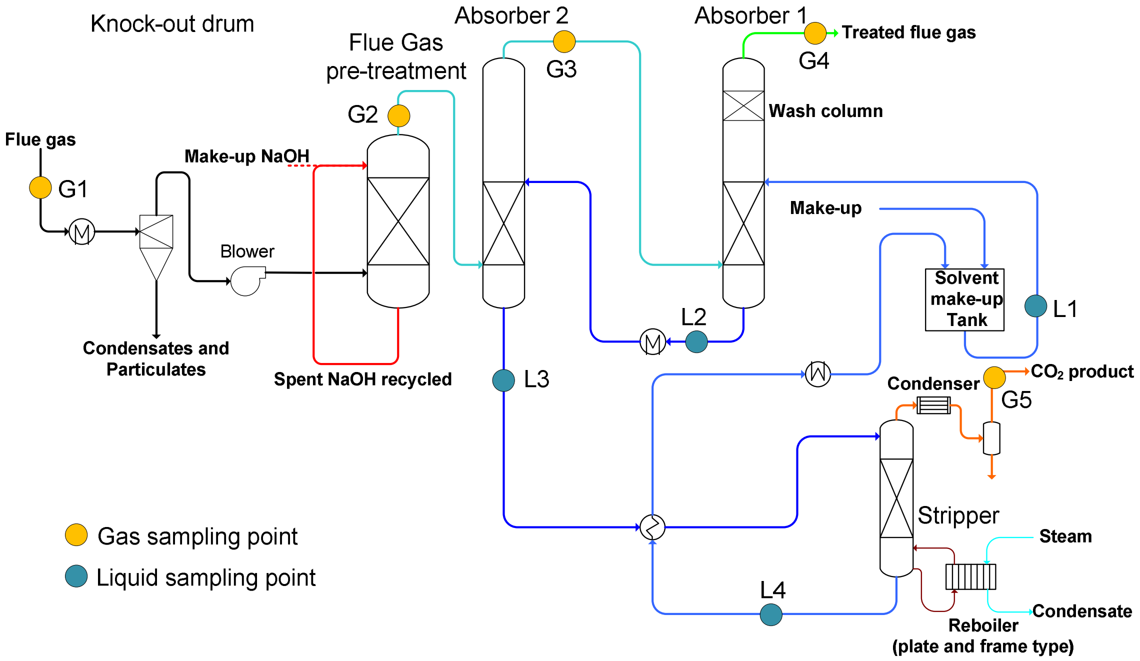


Figure 2: Typical Flow Diagram of PCC Pilot Plant at Loy Yang Power

In order to protect the blower from corrosion due to acid condensate and dust/particle matter entrained with the stream of flue gas, the blower was relocated downstream of flue gas pre-treatment since December 2010.

3.2 Design Basis

Table 1 shows the main constituents and its concentration in the flue gas from Loy Yang Power that was fed to the CSIRO PCC pilot plant. Furthermore, the flue gas contains a significant amount of SO_2 and NO_x. The SO_2 is scrubbed in the pre-treatment column using a 32 wt-% NaOH make-up solution.

Table 1: Typical flue gas composition at LY power station

Element	Composition
H_2O (vol-% - wet)	20 – 23
CO_2 (vol-% - wet)	10 – 11
O_2 (vol-% - wet)	4.0 – 5
Impurities (*wet ppm volume*)	
SO_2	120-200
NO_x (~99% NO, balance NO_2 and N_2O)	150-250
Temperature	160 - 175 ^oC

General information on the PCC pilot plant design is described in Table 2. The mobile pilot plant was transported to Loy Yang at the end of 2007. The plant commissioning started in May 2008. Initially the plant has no insulation assembled onto the pipelines or columns other than the stripper. . Insulation was installed on lean and rich solvent pipelines and the absorber columns in October 2010.

Table 2: Design PCC pilot plant at Loy Yang.

Parameter	Design value
Flue gas flow rate	Max. 160 m^3/h
Blower	Positive displacement (Hibon type PD blower). Include 4 kW motor.
Inlet temp for blower	Max. 70 ℃
Absorption degree	85% - 95%
Max solvent flow rate	15 L/min
Max stripper pressure	1.7 barg
Gas Pre-treatment column	
- Material	304L SS 300DN SHD 10
- Inner diameter	313 mm
- Column height	520 cm
- Packing height	100 cm
- Packing type	Pall ring
- Size	16 mm
- Specific area	338 m^2/m^3
- Packing factor	306 l/m
Absorber column (1 and 2):	
- Material	304L SS 200DN stainless steel
- Inner diameter	211 mm
- Column height	940 cm
- Packing height	135 cm (x 2 beds)
- Packing type	Pall ring
- Size	16 mm
- Specific area	338 m^2/m^3
- Packing factor	306 1/m
Stripper column:	
- Material	304L SS 150DN stainless steel
- Inner diameter	161 mm
- Column height	690 cm
- Packing height	390 cm
- Packing type	Pall ring
- Size	16 mm
- Specific area	338 m^2/m^3
- Packing factor	306 1/m

3.3 Insulation of pipelines

There are currently four major pipelines that are covered with insulation FR Armaflex Black foam with a thermal conductivity of 0.038 W m-1 K-1).

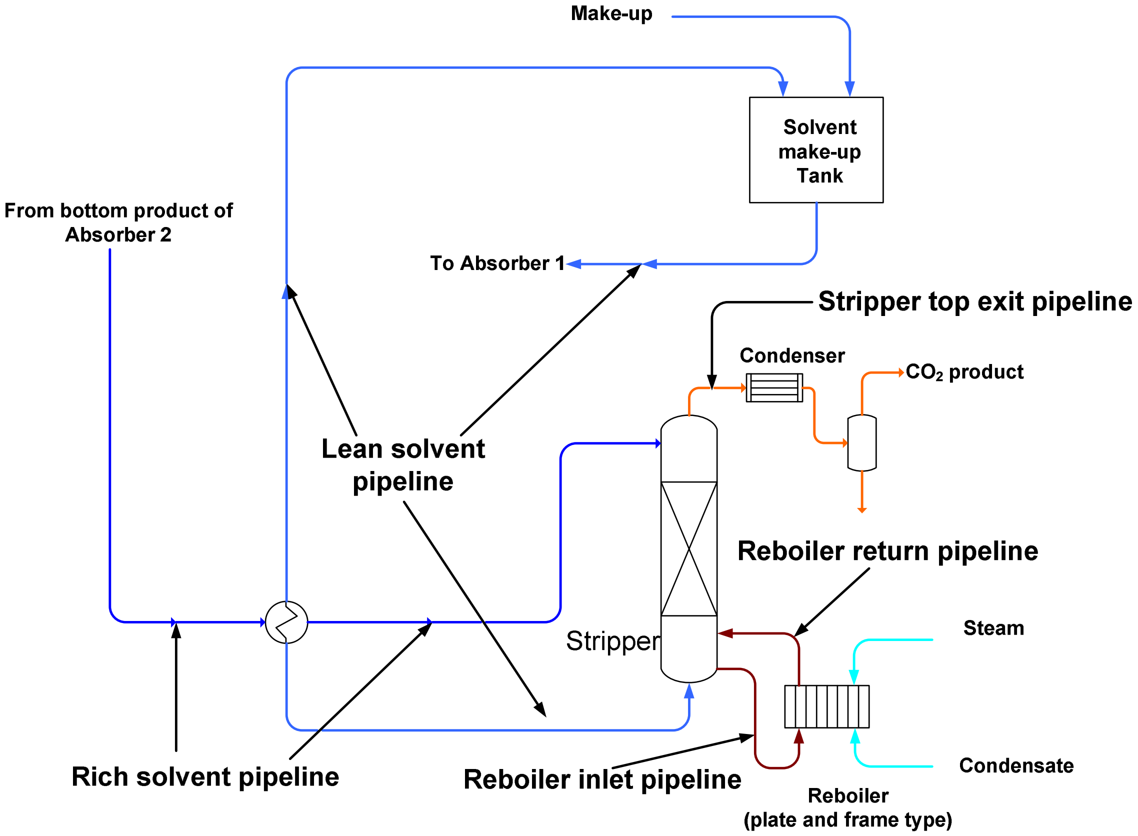


Figure 3. Locations of insulation has been installed in the pilot plant

1. Rich solvent pipeline

The pipeline between the heat exchanger and the stripper inlet is the longest pipe, consisting of three segments; curved pipe in the downwards section (flexible hose), vertical pipe towards the top of regeneration column (304 stainless steel) and followed by a curved pipe to the stripper inlet (flexible hose). The 304 Stainless Steel has 254 mm ID and 2.77 mm wall thickness. Its total length is 14.9 m. An “FR Armaflex” Black foam insulation with an ID of 32 mm and a thickness of 13 mm insulates the 304 stainless steel. The same foam with an ID of 25 mm and a thickness of 9 mm insulates the flexible hose..

2. Stripper top exit pipeline

This pipe is located at the top of the stripper column and directs CO_2 and water vapour to the condenser. This pipe continues towards the knock out drum, after which there is a temperature measurement point. The total pipeline consists of three segments: outlet from the stripper, pipe between condenser and knock out drum and one before temperature sensor. All three are made from 304 Stainless Steel, 254 mm ID and 2.77

mm wall thickness with a total length of 3.3 m. Like the previous pipe, it is also equipped with “FR Armaflex” Black foam insulation with 25 mm ID and wall thickness of 13 mm.

3. Reboiler return pipeline

Through this pipe, a hot gaseous water and carbon dioxide mixture, next to solvent flow, is leaving the steam operated reboiler towards the bottom of the stripper column. Due to high stream temperature, this pipe (length +/- 1.8 m) is made of 38.1 mm ID and 11.8 mm thickness Blue Thunder hose, Clear Ultra High Molecular Weight Polyethylene insulated with FR Armaflex” Black foam insulation with 25 mm ID and wall thickness of 9 mm.

4. Reboiler inlet pipeline

One of the two bottom streams of the stripper is connected to the reboiler to transport the recirculating hot liquid exiting the stripper column. It is also made of 38.1 mm ID and 11.8 mm thickness Blue Thunder hose, Clear Ultra High Molecular Weight Polyethylene insulated with FR Armaflex” Black foam insulation with 25 mm ID and wall thickness of 9 mm.

5. Lean solvent pipeline

The second bottom stream out of the stripper recycles lean amine solution to the absorber. This stream preheats the rich solvent stream by a cross heat exchanger. The Initial solution has a temperature of 115 ºC, where after it firstly flows through a 1.5 meter PARKER SERIES 7093 GST II pipe made of ethylene propylenediene monomer with 19.05 mm ID and 9.1 mm wall thickness.

4. CSIRO-LYP PROJECT - EXPERIMENTAL CAMPAIGN RATIONALE AND METHODOLOGY

4.1 Overview of Campaigns

Campaign 1 examined nominal conditions for a 30% MEA solution in order to get a steady plant operation and to obtain the mass balance of CO_2 and water and heat balance correctly. This campaign was aimed to obtain experience with the analysis techniques for gases and liquids. Also the efficiency of the pre-treatment column was assessed. These initial results were also used to fine-tune or if necessary redefine campaigns 2 and 3.

Campaigns 2 and 3 evaluated several operational parameters using a 30% MEA solution, i.e. flue gas flow rate (at constant gas to solvent ratio), solvent flow rate and stripper bottom's temperature. For each parameter change, other variables were applied according to the nominal conditions.

Table 3 illustrates a range of processing conditions applied in the pilot plant. The performance of solvent is evaluated based on its ability to capture CO_2 and its lowest reboiler duty for solvent regeneration.

Table 3: Process conditions of the pilot plant campaigns using MEA.

Process Parameters	Process conditions	
	MEA baseline	MEA 112 ℃
Solvent flow rate (m^3/h)	0.24, 0.33, 0.42	0.24, 0.33, 0.42
Actual flue gas flow rate (m^3/h)	100, 125, 140	100, 125, 140
Bottom Stripper temperature (^oC)	115	112

Experiments with amine-based blended solvents are conducted in campaigns 4 to 7. In campaign 4, the effect of blending MEA with AMP (called Blended Amine 1) was investigated. The total wt% of Blended Amine 1 comprises of 20 wt-% MEA and 10 wt-% AMP. Campaign 5 examined RITE solvent which is called Blended Amine 2 and also examined a mixture of 25 wt-% AMP and 5 wt-% Piperazine (called Blended Amine 3).

The processing parameters for campaigns 4 and 5 are presented in Table 4.

Table 4: Process conditions of the pilot plant trial using Blended Amine solvents.

Process Parameters		Process conditions	
	Blended Amine 1	Blended Amine 2/RITE	Blended Amine 3
Solvent flow rate (m^3/h)	0.24, 0.33, 0.42	0.23 and 0.29	0.33, 0.42, 0.54
Actual flue gas flow rate (m^3/h)	100, 125, 140	140	100, 125, 130
Bottom Stripper temperature (^oC)	115 and 112	115 and 112	115, 112 and 110

Campaigns 6 examined CO_2 capture using MEA with single absorber column only. This campaign is aimed to see the performance of CO_2 recovery using single column. Campaign 7 provided a first evaluation of a product from the CSIRO solvent development, called CSIRO-1. The CSIRO 1 is a mixture of AMP and 3-PM solvents. The proposed optimal composition of CSIRO-1 was comprised AMP 26 wt% and 3-PM 23 wt%. At this composition, the CSIRO-1 appeared to be too viscous to be used in the pilot plant as such. To enable a first evaluation of this new solvent composition the following measures were taken:

1. Reduce the concentration of AMP to 16 wt-% and 3-PM to 14 wt-%
2. Increase the temperature of solvent inlet to absorber column 1 to 60℃
3. Elevate flue gas temperature enter absorber column 2 to ~50℃.

Table 5: Process conditions of pilot plant trial using MEA at single absorber mode and CSIRO-1.

	Process conditions	
Process Parameters	MEA	CSIRO-1
Solvent flow rate (m^3/h)	0.3, 0.6	0.24, 0.30, 0.42
Flue gas flow rate (m^3/h)	55, 60, 80, 135	80, 100, 125
Bottom Stripper temperature (^oC)	115	114, 112 and 110

For MEA based-trials, concentrated MEA and NaOH 32 wt-% were obtained from Water Treatment Services (Aus) Pty Ltd. Different solvents used for making Blended Amines 1, 2 and CSIRO-1 is also supplied by the Water Treatment Services (Aus) Pty Ltd. These solvents (except NaOH 32 wt-%) were diluted with mains water prior to use.

4.2 Gas and Liquid Analysis

The PCC LY pilot plant is well equipped with instrumental analyses in order to assist with the pilot plant experimental work. The instrumental analyses comprise a gas analyser and a liquid (solvent) analyser. The gas analysis is conducted on-site and the liquid analysis is not carried out on-site but it sends to Energy Technology lab at CSIRO Clayton. The delivery time takes about overnight or 1 day.

Gas sampling points (indicated by G1 to G5) and liquid sampling points (indicated by L1 to L4) are placed at several points in the pilot plant as shown in Figure 2 in order to determine species composition in gas streams and CO_2 loading in liquid streams respectively. Flue gas flow-rate at the blower inlet and solvent flow-rate are monitored.

Gas analysis is conducted on-line with a GASMET Continuous Emissions Monitoring System (CEMS). The instrument incorporates a Fourier Transform Infrared (FTIR) spectrometer, a temperature controlled sample cell, and signal processing electronics. The gas analyser is designed for continuous emission monitoring. Gas components that can been detected are H_2O, CO_2, CO, N_2O, NO, NO_2, SO_2, NH_3, HCl, CH_4, C_2H_4, C_2H_6, C_3H_8, C_6H_{14}, Formaldehyde, Acetaldehyde, Ethanol, Ethanol amine andHF. The instrument is also equipped with a built-in ZrO_2 cell for oxygen measurements. The pH of lean (liquid enters absorber column 1) and rich (liquid enters stripper column) solvents are monitored continuously.

Liquid/solvent analysis is carried out in order to determine total/free amine and CO_2 concentrations. Figure 2 also shows the four liquid sampling points which comprise of liquid enter the absorber 1, rich solvent from absorbers 1 and 2 and finally lean solvent as bottom product of stripper column. A sophisticated sampling system takes 250 mL samples of each sampling point into a bottle. Liquid samples are collected when the absorption process is considered to have reached an equilibrium state. The collected liquid sample is then delivered to Clayton, where analysis is performed at CSIRO, Energy Technology Division, and it arrives within overnight or one day.

The method of analysis is using volumetric titration in order to determine the amount of CO_2 and amine in the solvent. The procedure is described below:

CO_2 determination:
A sample of absorber solution (~2.5 g) is weighed accurately into a vial. The pH of a methanol solution (~50 ml) is adjusted to pH 11 using NaOH (0.5 M). The MEA sample is added to the methanol solution and the mixture is titrated back to pH 11 with NaOH (0.5 M). The second volume of NaOH is used to calculate the amount of CO_2.
.

Amine determination:
Free MEA:
A sample of MEA solution (~0.25 g) is weighed accurately and diluted with water to ~50 ml. The diluted sample is titrated against HCl (0.1 M) until the equivalence point is reached at ~ pH 4-5.

Total MEA:
A sample of MEA solution (~0.25 g) is weighed accurately and diluted with water to ~50 ml. A known excess of HCl (20 ml, 0.1 M) is added to the mixture. The mixture is titrated against NaOH (0.5 M) until the equivalence point is reached. The volume of NaOH used gives the amount of HCl in excess, hence the amount of HCl that reacted with the MEA can be calculated to determine the total MEA in solution.

For mixed amine samples, the CO_2 concentration is determined by the method above.
We have two methods for the determination of the amine concentrations:
by titration (to determine RNH_2 molar concentration) and ^1H NMR to determine the ratio of amines ~ error 3 %
GC ~ error 4%

The instrument name of the analyser is Agilent 6850 series with auto sampler (8 samples), FID detector; 1 µL injection, 200 ml/min flow-rate, 100:1 split; oven 110 °C for 2 min, ramp at 20 °C/min to 250 °C then hold fo r 5 min

4.3 Error Determination

The absolute error or proportional error of each instrumentation/equipment is listed in Table 6 and the instrumental error for specific gas components is listed in Table 7.

Table 6: Absolute error or proportional error of each instrumentation/equipment

Instrument	Error
Flue gas blower	1% of flue gas rate
Solvent flow meter : 7, 5.5 and 4.0 L/min	0.00, 0.2 and 1 L/min respectively
Coriolis flow meter	0.125% of reading value
Temperature and pressure	1℃ and 1 atm./p

Table 7: Combined error of GASMET instrument for different gas components

Component	Measurement range (ppm)	Zero point drift (ppm)	Linearity deviation (ppm)	Temp drift (ppm) ± 1℃	Pressure influence (ppm)	Combined error (ppm)
		<2%	<2%	<0.2%	<0.2%	
NH_3	0-500	10	10	1	1	0-22
CH_4	0-50	1	1	0.1	0.1	0-2.2
C_2H_6	0-50	1	1	0.1	0.1	0-2.2
C_2H_4	0-50	1	1	0.1	0.1	0-2.2
C_3H_8	0-50	1	1	0.1	0.1	0-2.2
C_6H_{14}	0-50	1	1	0.1	0.1	0-2.2
Formaldehyde	0-50	1	1	0.1	0.1	0-2.2
Acetaldehyde	0-50	1	1	0.1	0.1	0-2.2
Ethanolamine	0-500	10	10	1	1	0-2.2

Errors for CO_2- lean loading and CO_2-rich loading were obtained from triplicate measurements. The error for both CO_2- lean loading and CO_2-rich loading are 0.02 mol CO_2/mol Amine. The error for CO_2 recovery is varied between 1% to 2%. The error of reboiler heat duty is varied between 0.3 to 0.4 MJ/kg CO_2. The errors for Q_{cond}, Q_{sh} and Q_{des} are 0.2, 0.2 and 0.3 MJ/kg CO_2.

Calculation Method to Determine CO_2 Recovery

The pilot plant employs three different approaches to determine CO_2 recovery as follows:

1. By using GASMET, we calculate the mass of CO_2 going into the absorber 2 and going out from the absorber 1. The CO_2 recovery is then calculated according equation 1.1

$$100\,\text{x}\,\frac{CO2_{\text{after pretreatment (toABS column 2)}} - CO2_{\text{in treated fluegas}}}{CO2_{\text{after pretreatment (toABS column 2)}}} \qquad 1.1$$

2. By using GASMET, we calculate the mass of CO_2 produced from the stripper. The CO_2 recovery is determined according equation 1.2.

$$100\,\text{x}\,\frac{CO2_{\text{produced from stripper}}}{CO2_{\text{after pretreatment (toABS column 2)}}} \qquad 1.2$$

3. By using liquid/solvent analysis. By this method, we can calculate CO_2 absorbed in two absorber column and also to calculate CO_2 produced from the stripper by the difference of rich solvent entering the stripper column and lean solvent leaving the stripper column.

   The CO_2 recovery can be either calculated by equation 1.3 or 1.4.

$$100\,\text{x}\,\frac{CO2_{\text{produced from stripper}}}{CO2_{\text{after pretreatment (toABS column 2)}}} \qquad 1.3$$

$$100\,\text{x}\,\frac{CO2_{\text{in rich solvent from ABS column 2}} - CO2_{\text{in lean solvent enter ABS column 1}}}{CO2_{\text{after pretreatment (toABS column 2)}}} \qquad 1.4$$

4.4 CO_2 Recovery and the Reboiler Duty for Solvent Regeneration

CO_2 recovery is determined based on analysing the gas of the inlet to absorber column 2 (G2), outlet of absorber column 1 (G4) and CO_2 product from the top of the stripper column (G5). During experimental runs CO_2 produced from the top of stripper column showed large variations. The average CO_2 recovery was calculated based on gas analysis (G2 and G4) and liquid analysis.

Reboiler duty for the regeneration of CO_2-loaded solvent was determined by making an energy balance around the reboiler and/or the stripper column. The energy supplied by the reboiler can be defined into three contributors [8, 12-15]: the heat required evaporating the water, the sensible heat to heat up the solvent to reboiler temperature and the heat of CO_2 desorption. The heat required to evaporate the water is actually equivalent to the latent heat of water condensation which can be measured directly around the condenser. The equation can be represented as follows;

$$\begin{aligned} Q_{reboiler} &= Q_{condenser} + Q_{solvent\ heat} + Q_{desorption} \\ &= m_w \Delta H_w + m_s c_p (T_{bottom} - T_{top}) - m_{CO_2} \Delta H_{CO_2} \end{aligned} \qquad 1.5$$

where $Q_{reboiler}$ is the reboiler duty; m_w is the amount of water flowing into the condenser; ΔH_w is the latent heat of water condensation; m_s is the solvent flow rate; c_p is the heat capacity of the solvent; T_{bottom} is the temperature of hot lean solvent going out from the bottom of stripper column; T_{top} is the temperature of hot rich solvent entering the top of stripper column; m_{CO_2} is the amount of CO_2 produced from the stripper column and ΔH_{CO_2} is the enthalpy of CO_2 desorption. For MEA, the value is obtained from literature [3].

4.5 CO_2 Balance for MEA Base Case

In every trial, CO_2 balance has been used to measure the performance of MEA test. The pilot plant operation could achieve CO_2 balance during the course of experiment. The CO_2 balance shown in Figure 4 indicates the difference between mass of CO_2 enter absorber column 2 and mass of CO_2 leaving the absorber column 1 should be equal to the mass of CO_2 release from the stripper column. Our trials throughout the campaigns confirm that adequate CO_2 mass balance within +/- 10% can be obtained and maintained.

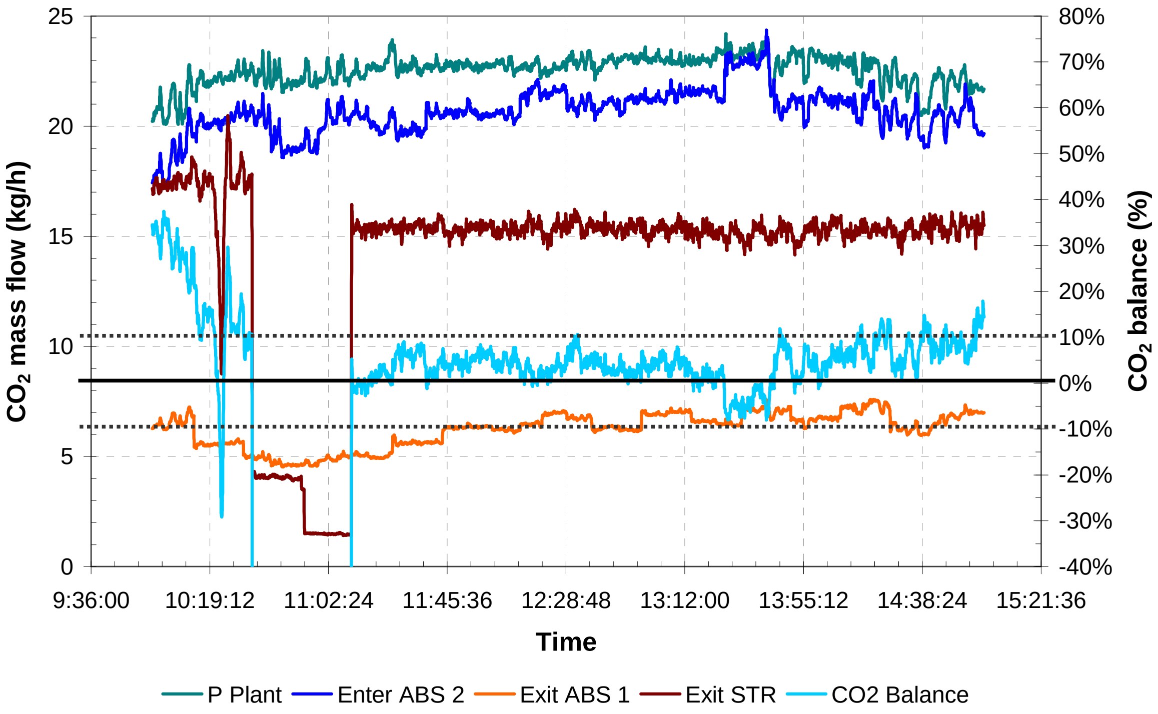


Figure 4: **CO_2 balance in pilot plant trial (determined as the difference between CO_2 mass flow enter absorber column 2 and CO_2 mass flow emits from absorber column 1 and stripper column).**

4.6 Effect of L/G Ratio and Lean Loading on CO_2 recovery

The relationship of varying the L/G ratio on CO_2 recovery using MEA at different stripper's bottom temperatures, is illustrated in Figure 5. The graph implies that for both temperatures, an increase of L/G results in an increase of available solvent to capture CO_2 from the same amount of flue gas.

Figure 5 also shows that an increase of stripper's bottom temperature from 112 ℃ to 115 ℃ causes to raise CO_2 recovery over the range of L/G ratios. This is because increasing the temperature results in a leaner solvent, and therefore improves the CO_2 recovery. This occurrence is illustrated in Figure 6, which shows the CO_2-recovery as a function of lean loading.

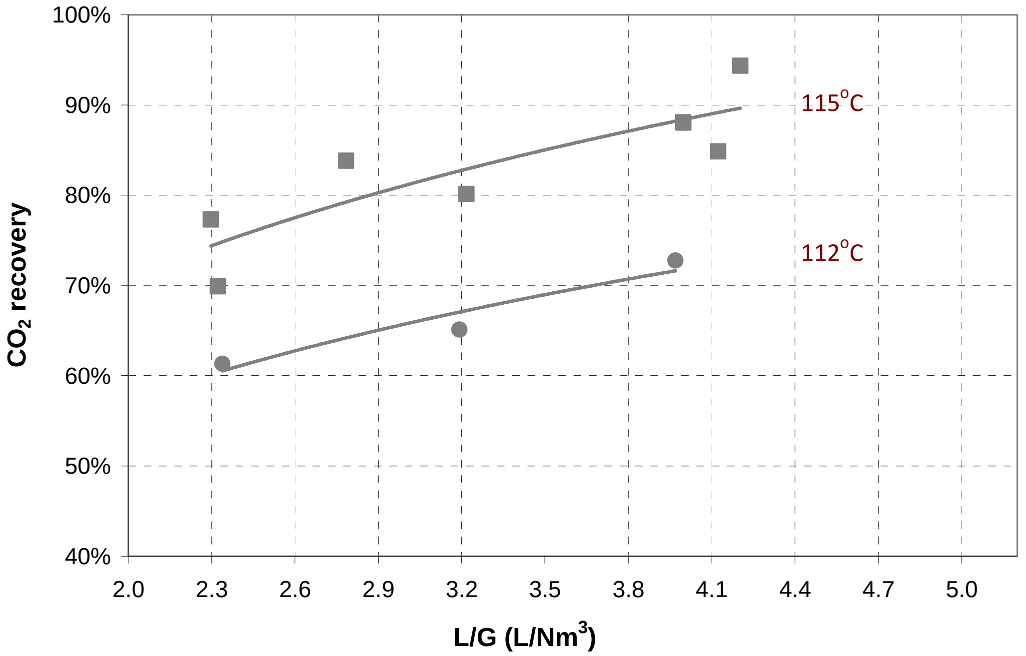


Figure 5: Correlation between L/G and CO_2 recovery using MEA for two different stripper's bottom temperatures.

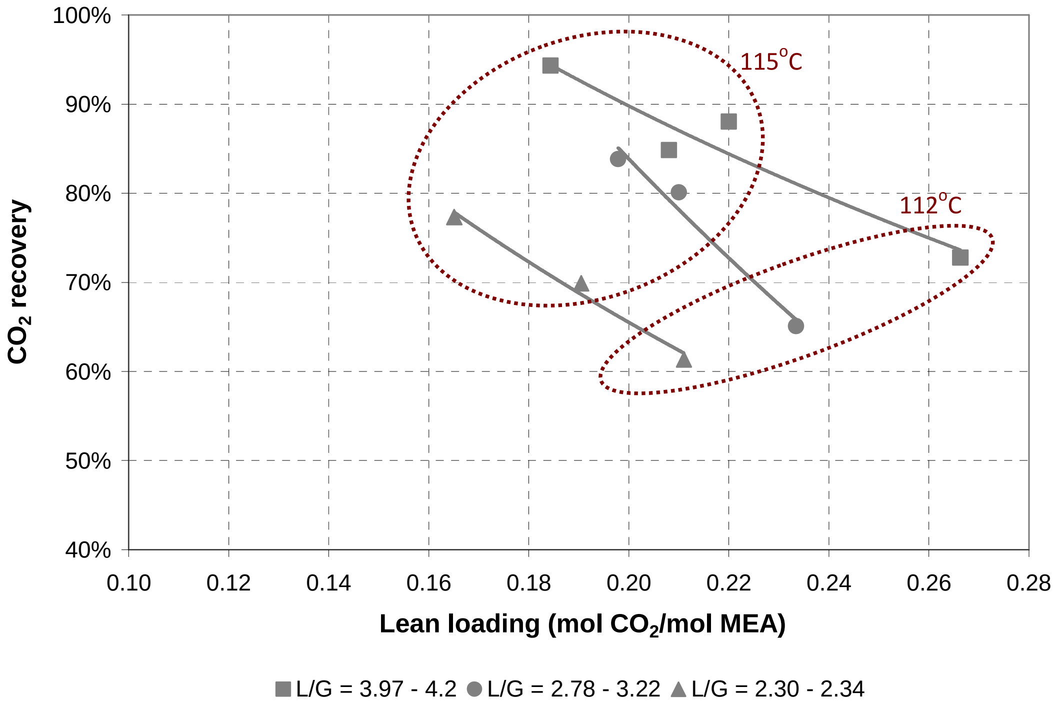


Figure 6: Correlation between lean MEA solvent loading at similar L/G on CO_2 recovery

4.7 Effect of L/G ratio and Lean Loading on Reboiler Heat Duty

The dependency of CO_2 recovery upon L/G ratio and lean loading should also translate into relationship between specific reboiler duty upon the L/G ratio and the lean loading. Figure 7 shows the impact of L/G ratio on the reboiler duty. The reboiler duty of the MEA baseline examined under a stripper's bottom temperature of 115 ℃ shows a parabolic trend as a function of L/G ratio. This finding was also reported by Mangalapally *et al*. [13] and Cifre *et al.* [8] where they presented reboiler duty as a function of solvent mass flow rate.The increase in the reboiler duty below and above the L/G ratio of 3.2 can be explained in Figure 8 by considering three components of reboiler duty. The increasing of reboiler duty at low L/G ratio can be attributed to the increase in stripping steam needed to regenerate the solvent. This is confirmed by the increase in the cooling water for the condenser (Q condenser) under those conditions (*cf.* Figure 9). The increase in reboiler duty for high L/G is due to the increase in the sensible heat requirement caused by the increase in solvent flow.

Figure 7 also indicates that, by regression of the datapoints, the reboiler duty shows a minimum value at L/G around 3.2. Figure 7 also implies that, for the stripper's bottom temperature of 112 ℃, the changes of reboiler duty are less sensitive with increasing the L/G ratio. This observation can be explained by considering a correlation between the reboiler duty and solvent lean loading in Figure 9.

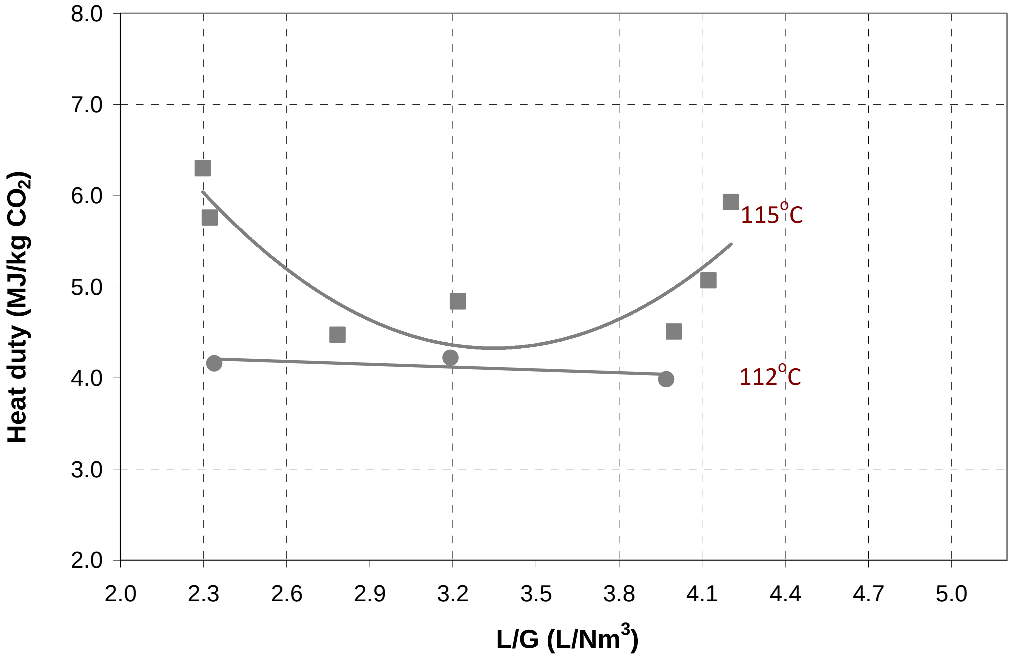


Figure 7: Correlation between L/G on reboiler duty for MEA at two different stripper's bottom temperatures.

As seen in the Figure 8, the condenser heat contribution at the minimum reboiler heat duty is only minor compared to the sensible heat associated to heating up the solvent and the heat of desorption. The amount of desorption heat also leveled-off throughout the L/G ranges. This is because the heat of desorption for CO_2-loading below 0.5 is relatively constant and not very much influenced by temperature changes [13]. In the baseline trials for this current pilot plant setting, the CO_2-loading is within the range of 0.15 – 0.48.

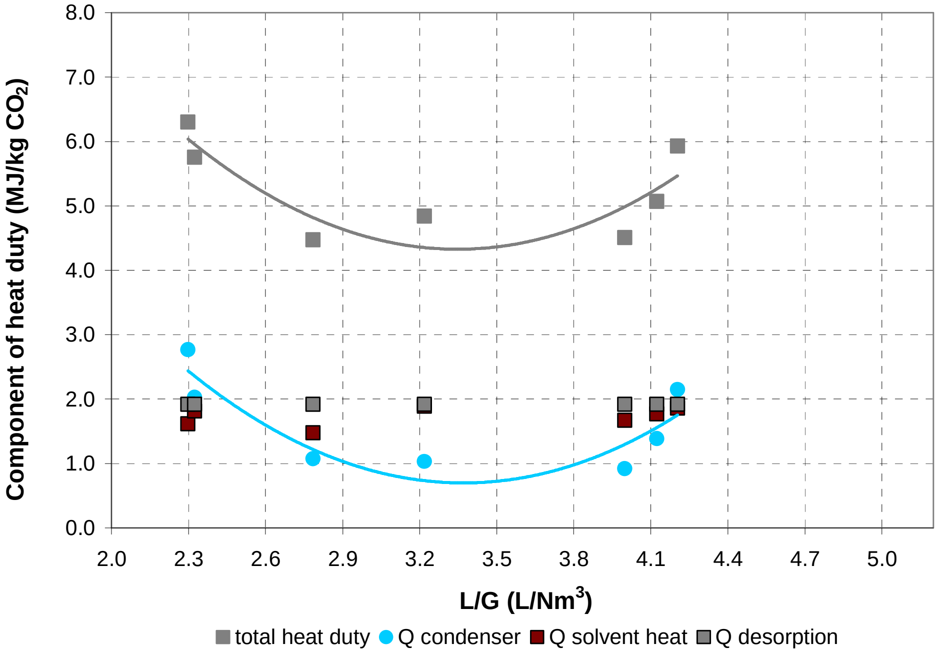


Figure 8: Reboiler duty distribution as a function of L/G ratio for MEA baseline at stripper bottom temperature of 115 °C.

Figure 9 shows that the reboiler heat duty increases when the lean loading reduces below 0.21. The increase of reboiler heat duty is due to the large amount of stripping steam needed to remove the CO_2 from the solvent. However, increasing solvent lean loading > 0.21 (L/G = 2.32) does not seem to affect the reboiler duty. This is due to the relatively small amount of water vapor leaving the stripper column.

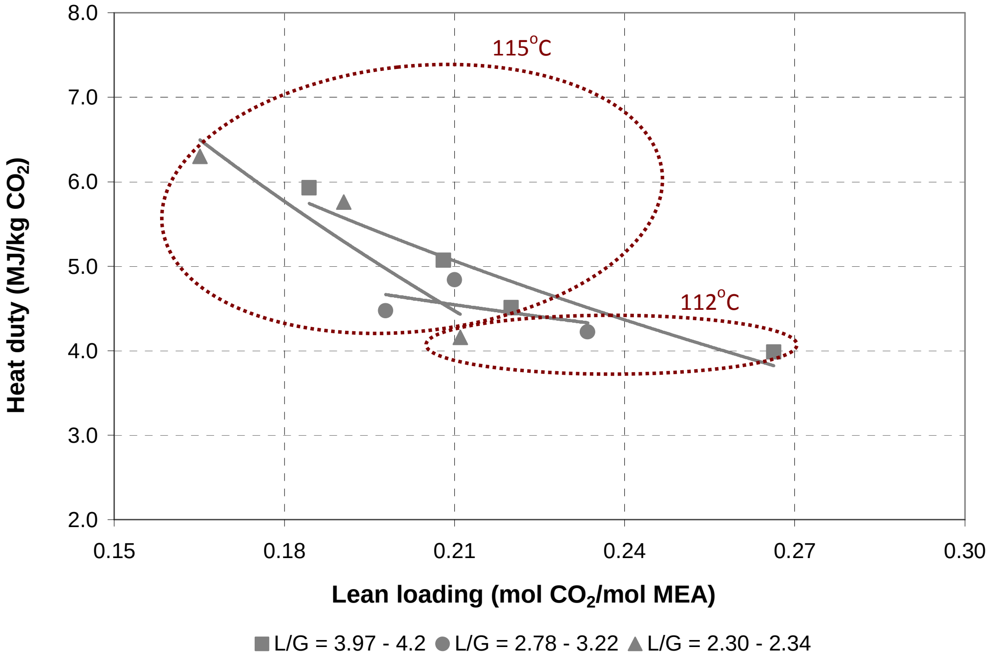


Figure 9: Reboiler duty as a function of lean solvent loading at different stripper bottom temperatures and L/G ratios

4.8 MEA Trials Using Single Absorber

Single absorber MEA trials were conducted in order to investigate its performance in terms of CO_2 recovery and reboiler heat duty required.

Modifications of the plant were implemented in order to accommodate these trials. Figure 10 shows the comparison between MEA trials for double absorbers (112 ℃ and 115 ℃) and single absorber at stripper bottom's temperature of 115 ℃.

Figure 9 indicates that CO_2 recovery obtained by using single absorber column gives lower values compared to MEA base case, which was run using double absorber column. This is obviously to be expected as double columns mean have more number of contact-packing than a single column does. Similar CO_2 recovery can possibly be achieved with single absorber if the process employs a much higher L/G ratio or by increasing the surface area by making column diameter larger. However, this may not be efficient in term of large scale.

The energy duty required, if the plant is operated using single absorber column, also relatively higher compared to that of MEA base case for the L/G ratio above 4.0. At the lowest L/G ratio, it is noticed that MEA trials using single absorber require similar energy duty as MEA trials with double absorber column.

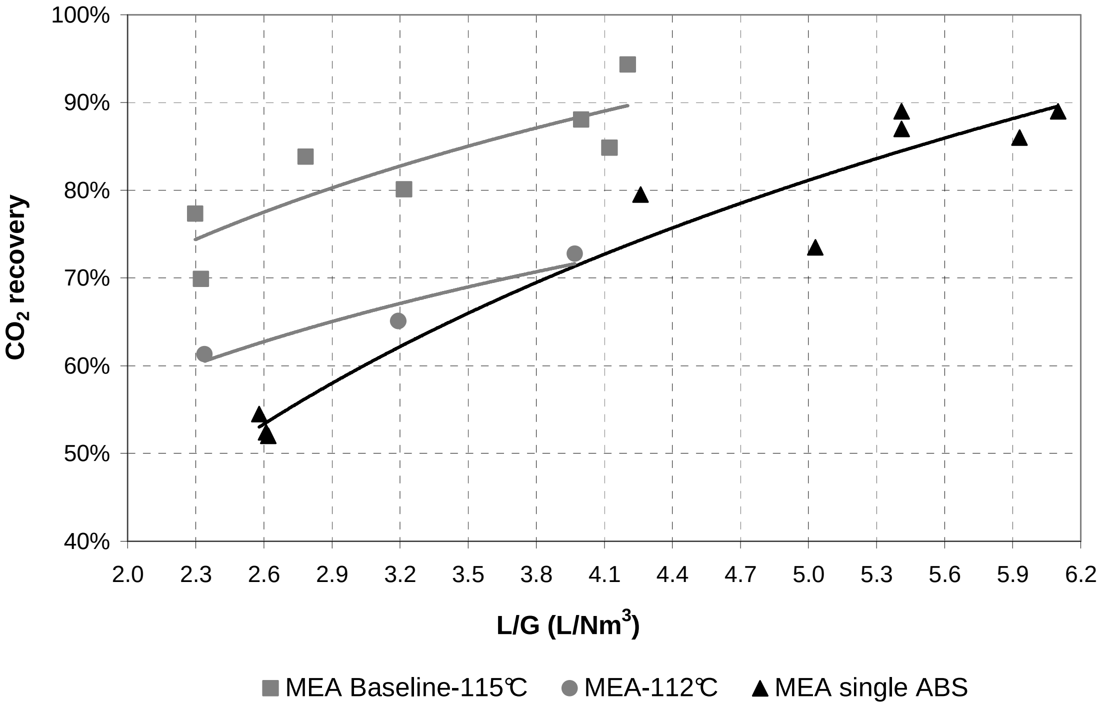


Figure 10: The effect of increasing L/G ratio on CO_2 recovery for MEA examined using single absorber column

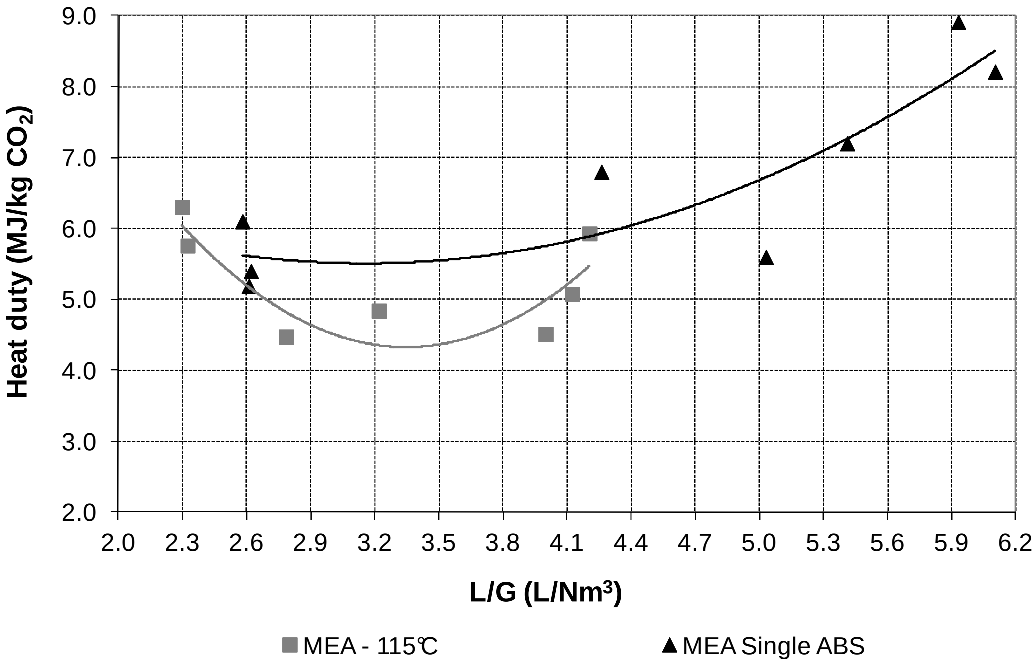


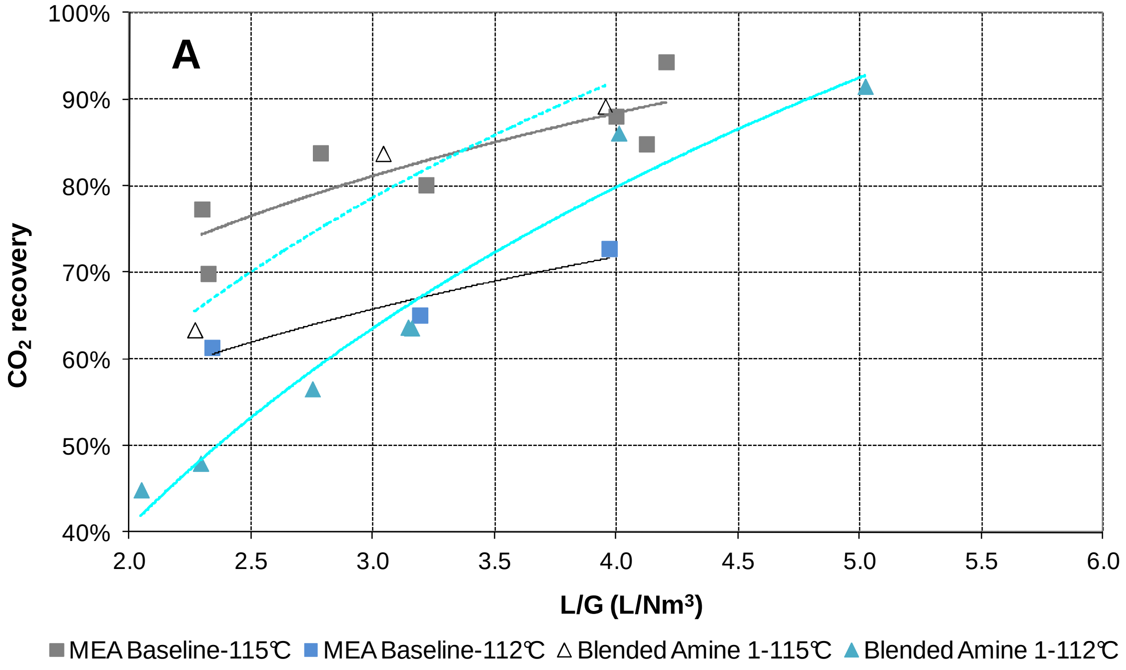
Figure 11: Reboiler heat duty required for MEA trial using single absorber column

4.9 Blended Amines

An important draw-back of the amine based PCC process, in particular for MEA, is the energy requirement for solvent regeneration. One way to remedy this to formulate solvents blends which have a lower energy requirement for solvent regeneration [5, 16]. Ideally this needs to be done while maintaining or improving the solvent capacity and absorption rates.
In this study, Blended Amines 1, 2, 3 and CSIRO-1 were examined as a function of L/G ratio and of the stripper's bottom temperature. The effect of changing the stripper's bottom temperature on solvent lean loading was also discussed. The performance of blended solvents is expressed by the CO_2 recovery and the reboiler duty. They are then compared with the MEA baseline. The amine concentration of the blended solvent was maintained constant throughout the campaign.

4.10 Performance Comparison of MEA with Blended Amines

Figure 12 shows the variation of CO_2 recovery with L/G ratio at different stripper's bottom temperatures for both Blended Amine solvents (Top graph for Blended Amine 1 (A) and bottom figure for Blended Amines 2 and 3 (B)). An increase in the L/G ratio at any stripper bottom's temperature results in an increase of the CO_2 recovery. This is expected, because more solvent is available to react with the CO_2 and this improves the CO_2 mass-transfer from gas phase into liquid phase [17].



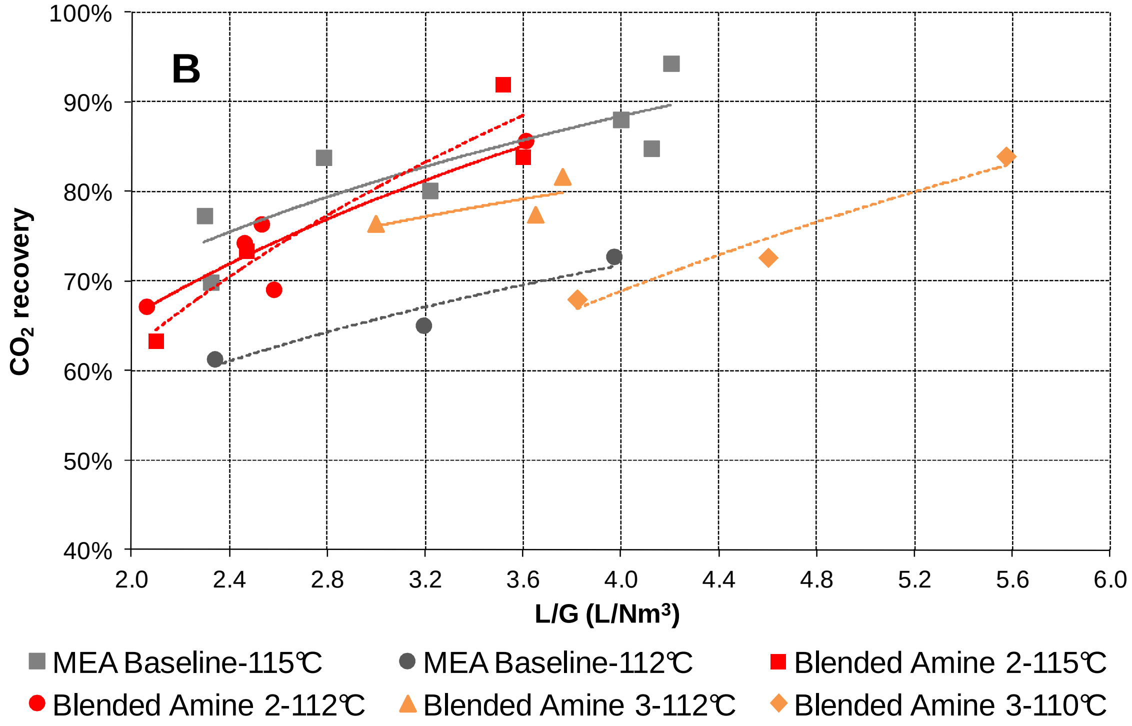


Figure 12: The effect of increasing L/G ratio on CO_2 recovery for different solvents (Top Figure for Blended Amine 1 and bottom Figure for Blended Amines 2 and 3. The CO_2 recovery of MEA is also shown in the graph for comparison).

At 115 °C, Blended Amine 1 shows comparable magnitude of CO_2 recovery to that of MEA baseline. This is also for the Blended Amine 2 examined at both temperatures of 112 °C and 115 °C. This result suggests that Blended Amine 2 does not necessarily require a high stripper bottom temperature. It is also found that Blended Amine 3 gives slightly higher CO_2 recovery than that of MEA at 112 °C. Even the CO_2 recovery of Blended Amine 3 at 110 °C is similar to that of MEA at 112 °C.

The effect of reducing stripper bottom's temperature for both Blended Amines 1 and 3 are apparent. For Blended Amine 1, reducing the stripper's bottom temperature to 112 °C the CO_2 recovery is decreased significantly compared to MEA and the Blended Amine 2. In order to attain a CO_2 recovery similar to that of MEA-115 °C or Blended Amine 2-112 °C, Blended Amine 1 has to use a higher L/G ratio with stripper's bottom temperature of 112°C. This case is also observed for Blended Amine 3 when the stripper bottom's temperature dropped to 110 °C.

The effect of lowering the stripper bottom temperature on the CO_2 recovery reductions of Blended Amine 1 may be associated with increasing the solvent lean loading. Figure 13 shows that a reduction of stripper bottom temperature raises the lean loading. For all temperatures examined, at a relatively constant lean loading, increasing the L/G ratio improves the CO_2 recovery. The figure also shows that operating the stripper bottom temperature at 115 °C for Blended Amine 1 resulted in an increase of reboiler heat duty, which in turn produced a much leaner solvent compared to that of MEA at 115 °C (*cf*. Appendix A). This suggests that 115 °C is an unfavourable operating condition for Blended Amine 1. The graph also indicates that operating the stripper bottom temperature at 112 °C for this solvent gave a comparable lean loading to that of MEA at 115 °C (*cf.* Appendix A***Error! Reference source not found.***) and also significantly lowered the reboiler heat duty compared to that of operating at 115 °C.

For 115 °C, as L/G ratio increased, the reboiler heat duty decreased significantly. The reboiler heat duty might be expected to increase if the L/G ratio increases. Nevertheless, the magnitude of reboiler heat duty shows a large difference across the L/G ratio compared to that of MEA at 115 °C. The reboiler heat duty as a function of L/G ratio for Blended Amine 1 at 112 °C did not change significantly within the limits of error. The reboiler heat duty for Blended Amine 1 at 112 °C is comparable to that for MEA at the same temperature.

Further reduction of temperature to 109 °C did not lower the reboiler heat duty significantly even though the CO_2 recovery was significantly reduced. It is also observed that the effect of L/G changes is not sensitive to the changes of reboiler heat duty at 109 °C, as all L/G values generated similar lean loadings within the limit of error.

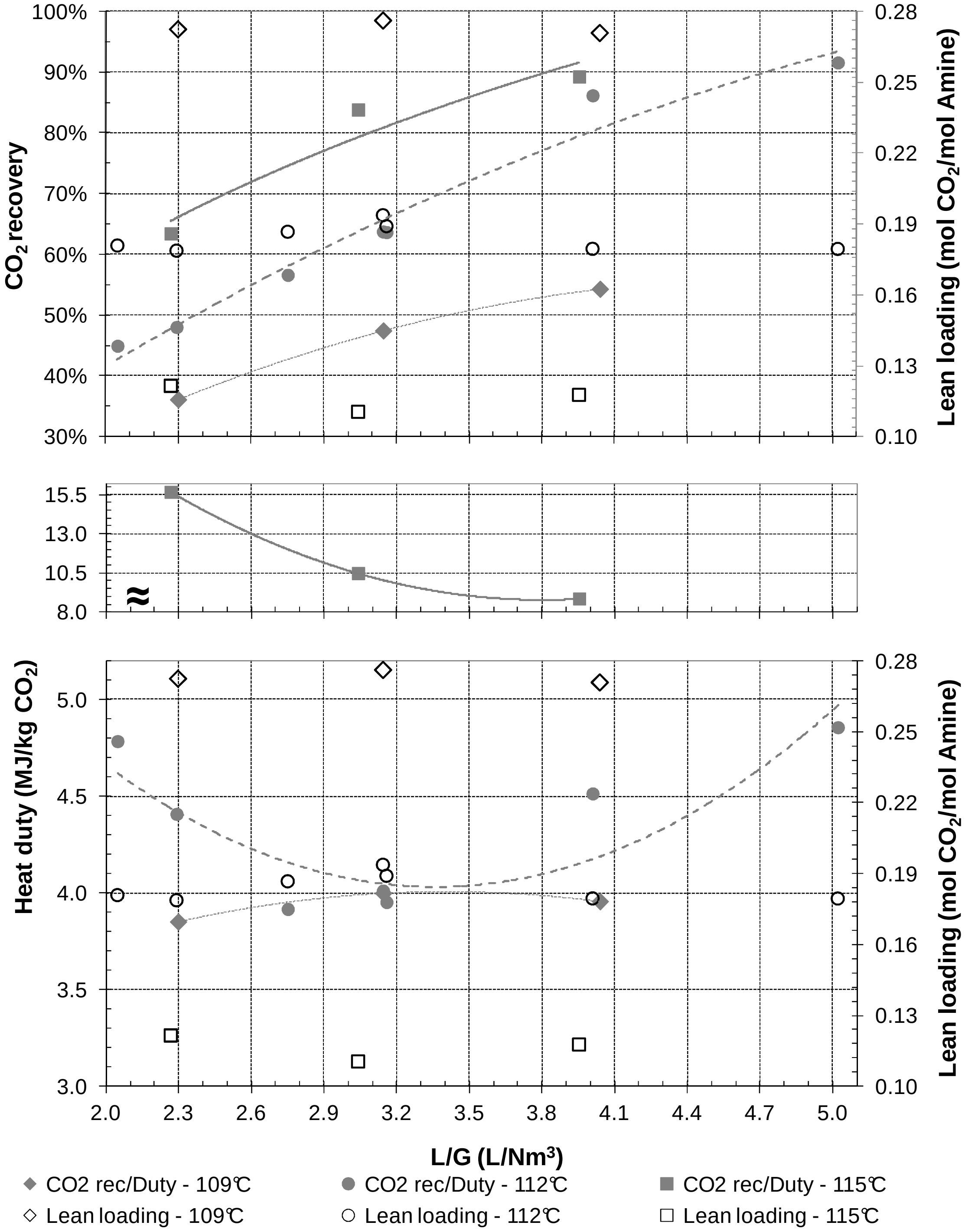


Figure 13. The effect of L/G ratio and lean solvent loading on CO_2 recovery and reboiler heat duty for Blended Amine 1 at stripper bottom temperatures of 109 ℃, 112 ℃ and 115 ℃

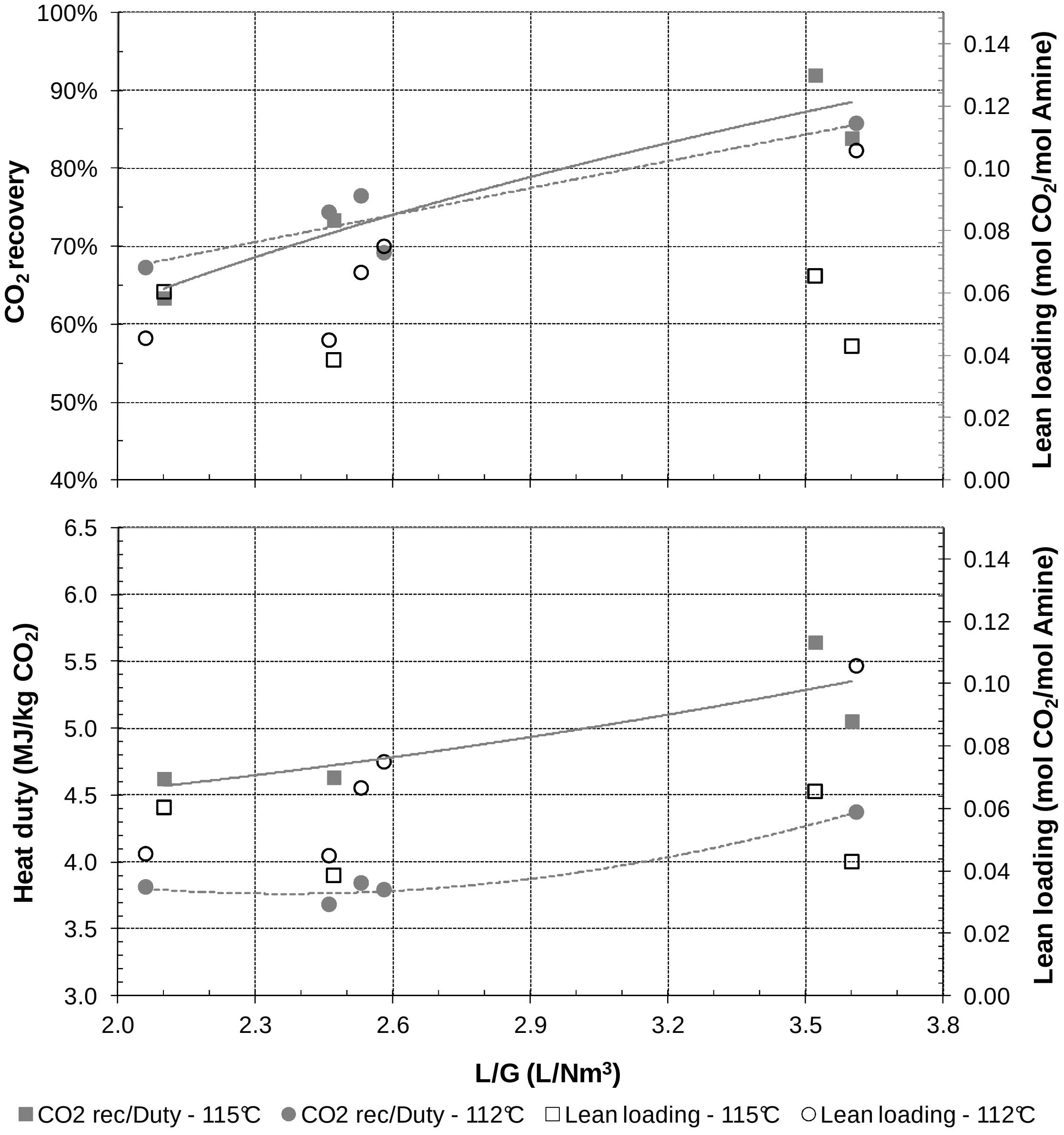


Figure 14. The effect of L/G ratio and lean solvent loading on CO_2 recovery and reboiler heat duty for Blended Amine 2 at stripper bottom temperatures of 112 ℃ and 115 ℃

Figure 14 also shows that the reduction of stripper bottom temperature for Blended Amine 2 led to a decrease in the reboiler heat duty regardless of L/G ratio value even though the change in temperatures had little effect on the lean loading within the limits of error (except for lean loading at 112 ℃ and L/G ratio 3.56, (*cf*. Appendix). Both temperatures show similar trends in the increase of reboiler heat duty as a function of increasing the L/G ratio. Further trials could be conducted at lower L/G ratio in order to investigate whether the reboiler heat duty at low L/G ratio increases as in the case of MEA at 115 ℃ and Blended Amine 1 at 112 ℃. Operating at the L/G ratio lower than 2.0, however, will not benefit CO_2 recovery so that such trials would not have any practical value.

Figure 15 shows the three different components of heat duty for MEA, Blended Amines 1 and 2 as a function of L/G ratio at different stripper bottom temperatures and CO_2 recovery. The Q_{con} for Blended Amine 1 at 115 °C is higher than any other component energy. Q_{con} for Blended Amine 1 at 115 °C possibly slightly increases at L/G ratios higher than 3.95. This trend is also noticed for the reboiler heat duty for MEA at 115 °C and Blended Amine 1 at 112 °C, suggesting that the heat of water vaporization for CO_2 stripping, which is equivalent to Q_{con}, is a major factor in increasing the reboiler heat duty. Figure 15 also shows that the Q_{con} for Blended Amine 1 at all L/G ratios are higher than others when they are trialled at 115 °C. MEA at 115 °C and Blended Amine 1 at 112 °C also reached minimum reboiler heat duty at L/G ratios around 3.20.

Thus the Q_{con} for MEA at 115°C and Blended Amine 1 at 112 °C has a similar pattern to their total reboiler heat duty. The Blended Amine 1 at 112 °C has slightly lower Q_{con} than MEA at 115 °C, suggesting that relatively less heat of water vaporization is required for Blended Amine 1 to obtain similar lean loading to that of MEA at 115 °C (*cf.* Appendix). This is also indicated in Figure 16. The chart reveals that MEA at 115°C generated more steam compared to Blended Amine 1 at 112°C in order to achieve similar CO_2 lean loading (0.18~0.19). The greater amount of steam generated results in the raising of Q_{con}.

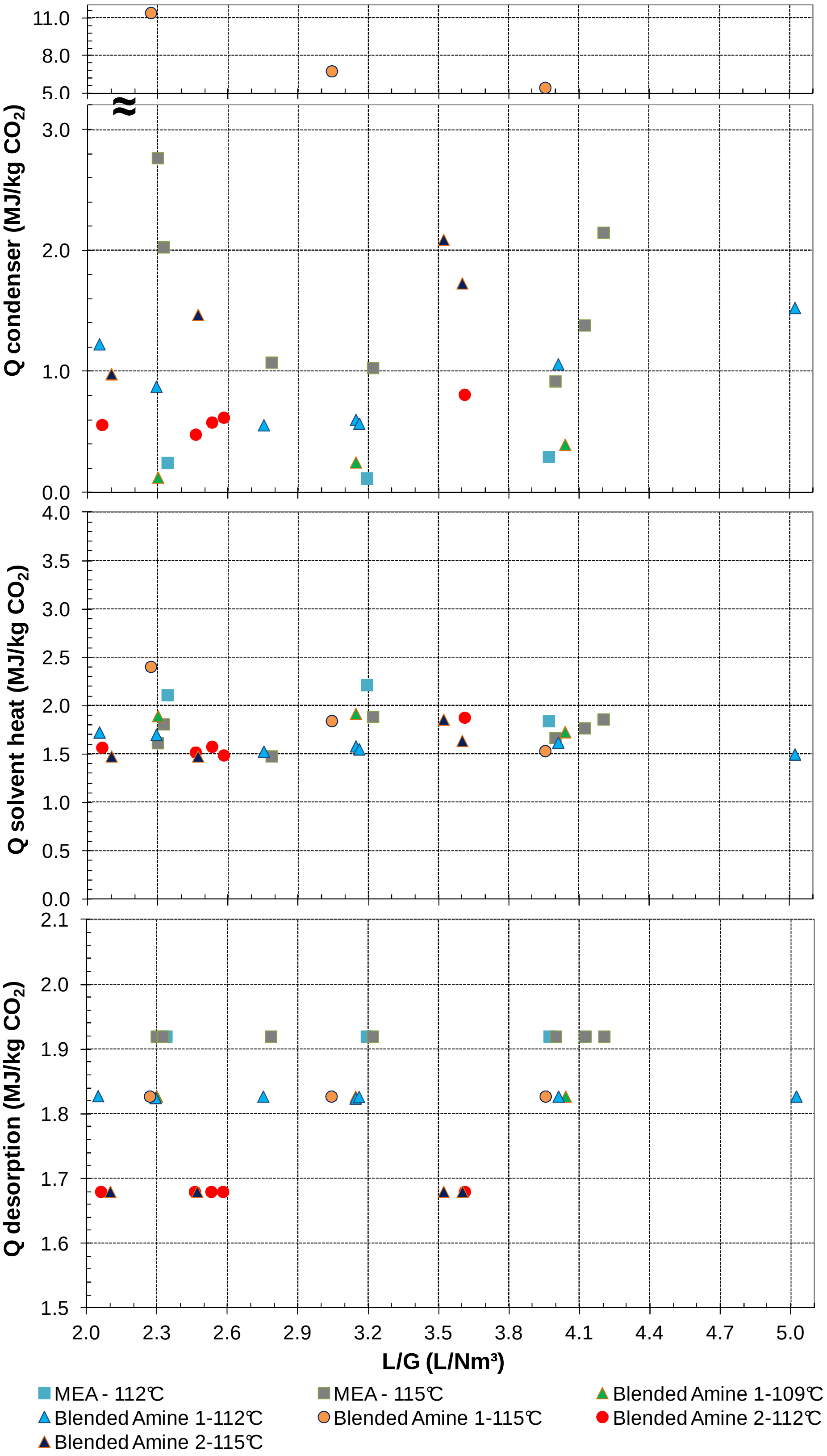


Figure 15. A comparison of heat duty components for MEA, Blended Amines 1 and 2 at different temperatures and CO_2 recovery

As a consequence of increasing the steam flows to the top of the stripper column, the temperature at the top packing in the stripper column also rises. Thus, at the same CO_2-lean loading (0.18~0.19), MEA at 115 ℃ gave higher Q_{con} than Blended Amine 1 at 112℃ as can be noted from Figure 17. Both Q_{con} for MEA at 112 ℃ and Blended Amine 1 at 109 ℃ are relatively constant at different L/G ratios. The magnitude of the Q_{con} for both of them are also lower compared to others.

Nevertheless, for Blended Amine 1 across the operating L/G ratio range up to 4.10, the proportions of condenser heat in the reboiler duty is generally less than those of the individual sensible heat and desorption heat. Yet, for the highest L/G ratio, the three component energies are similar.

For Blended Amine 2 at 112 ℃ and 115 ℃, in general they have similar pattern of Q_{con} to their reboiler heat duty. The Q_{con} for both temperatures are initially constant and then steadily increase at a higher L/G ratio. It is noticed that Q_{con} at 112 ℃ is lower than that of at 115 ℃, as expected. The Q_{con} of Blended Amine 2 at 115 is comparable to the value of Q_{con} from MEA at 115 ℃ (at lower L/G ratio) and Blended Amine 1 at 112 ℃ at lower and higher L/G ratios. The magnitude of Q_{con} for Blended Amine 2 at 112 ℃ is also similar within the limits of error compared to that of Blended Amine 1 at 112 ℃.

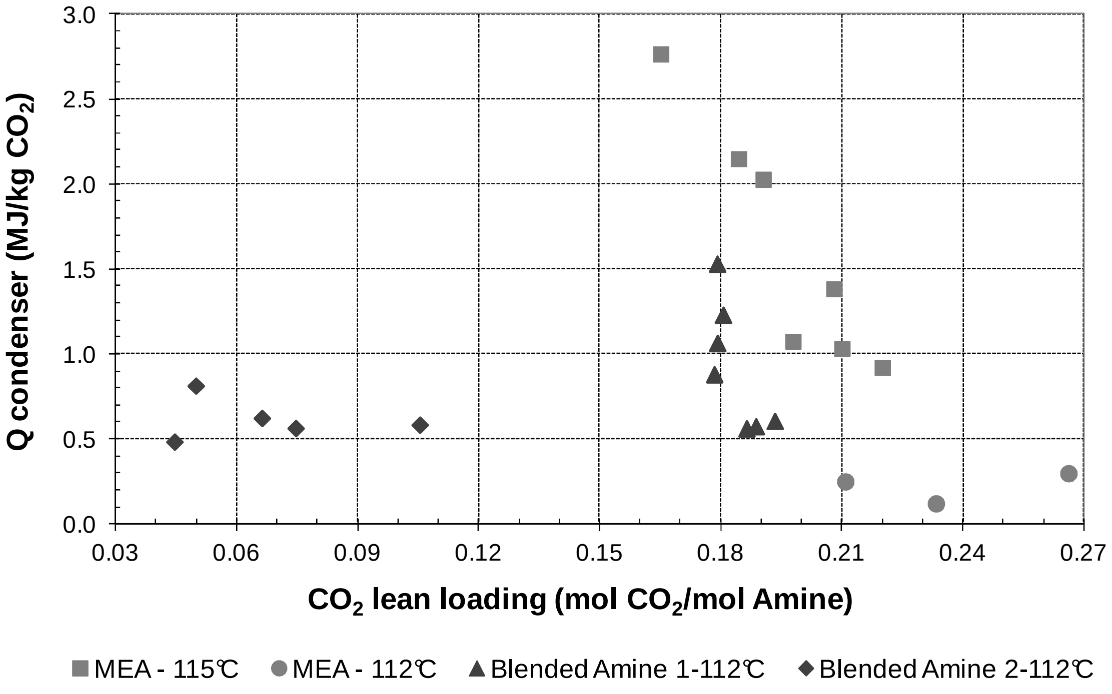


Figure 16. Relationship between CO_2 lean loading and condensing duty

For Blended Amine 2 at 112 ℃ and 115 ℃, it is noticed that the sensible heat and the heat of desorption are nearly constant from the lowest L/G ratio up to an L/G ratio of 2.6. In general, the heat of water vaporization is much lower than the other components of reboiler heat duty. The Q_{con} does steadily increase as the L/G ratio increases. For Blended Amine 2, the sensible heat also rises after L/G ratio 0.26, which is attributed to the increasing of solvent flow rate. The heat of desorption is apparently levells-off regardless of L/G ratio values. Blended Amines 1 and 2 are similar in that the magnitude of desorption heat is slightly higher than that of sensible heat. The Figure also shows that for Blended Amine 2, the three energy components make similar contributions to the reboiler heat duty.

The sensible heat (Q_{sh}) for all solvents at different conditions is similar within the limits of error, except for Blended Amine 1 at 115 ℃, where the Q_{sh} steadily decreases as L/G ratio increases and then starts to level-off above a L/G ratio of 3.0 (within the limits of error). This may be attributed to the temperature difference between the cold-rich solvent entering the stripper column and the hot-lean solvent leaving the stripper bottom not being constant.

Figure 15 also shows that MEA at both temperatures has the highest heat of CO_2 desorption (Q_{des}) compared to the other solvents, suggesting that the Q_{des} has contributed to increase reboiler heat duty for the MEA at both 112 ℃ and 115 ℃. In this study, the magnitude of desorption heat decreases in the following order: MEA > Blended Amine 1 > Blended Amine 2. For Blended Amine 2, the Q_{des} has more contribution than other component energy to reduce the reboiler heat duty.

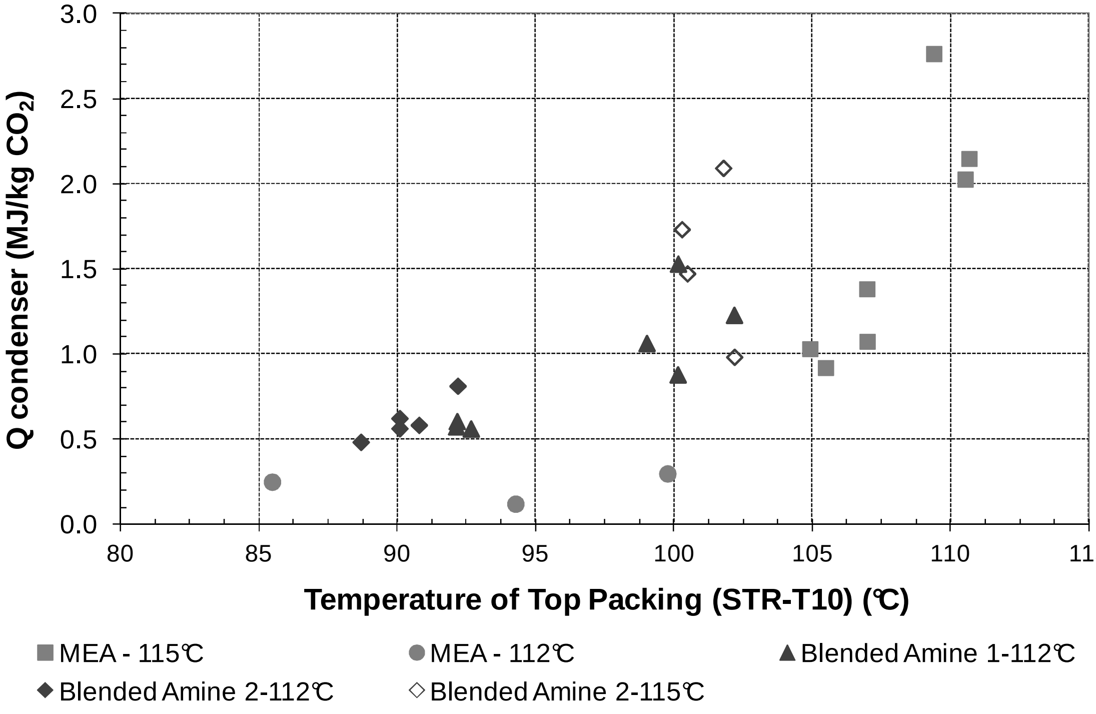


Figure 17.Relationship between condensing duty and temperature at the top packing of stripper column

Figure 18 describes the variation in reboiler heat duty, which represents the energy required for solvent regeneration, with L/G ratio and CO_2-lean loading of Blended Amine 3 in the pilot plant. It can be seen that for MEA, a reduction of CO_2-lean loading from 0.27 to 0.19 mol CO_2/mol amine did not significantly affect on the reboiler heat duty changes. However, an increase of the reboiler heat duty was significantly observed (from around 5 MJ/kg CO_2 to 6.4 MJ/kg CO_2) with a small reduction in the

CO_2-lean loading from 0.19 to 0.17 mol CO_2/mol amine. For Blended Amine 3, the reboiler heat duty changes did not notably observed as the CO_2-lean loading dropped from 0.14 to 0.08 mol CO_2/mol amine. The reboiler heat duty considerably enhanced from around 4.6 MJ/kg CO_2 to 6.6 MJ/kg CO_2 when the CO_2-lean loading slightly reduced from 0.08 to 0.03 mol CO_2/mol amine. It is also noticed that for Blended Amine 3, the reboiler heat duty at an L/G ratio of 3.7 was also much lower than that for two other trials at L/G ratios of 3.0 and 3.8, even though they were carried out at a similar stripper bottom temperature of 112 ℃. The results suggest that the CO_2-lean loading of 0.17 mol CO_2/mol amine for MEA and 0.03 mol CO_2/mol amine for Blended Amine 3 may approach an equilibrium CO_2-lean loading end for each solvent, where qualitatively a small decrease of CO_2-lean loading close to the equilibrium CO_2-lean loading end will require an excessive energy to regenerate the solvent [16]. As the pilot plant does not equip with gas and liquid samplings along the stripper column, representative CO_2 concentration in gas phase and CO_2 loading in liquid phase could not be obtained. Hence, an operating line in the stripper column cannot be provided.

It is also found that the reboiler heat duty of MEA for the CO_2-lean loading range between 0.20 and 0.27 mol CO_2/mol amine were comparable within the limit of error to the reboiler heat duty of Blended Amine 3 for the CO_2-lean loading of 0.08 to 0.14 mol CO_2/mol amine, yet the CO_2 recovery of Blended Amine 3 were higher than that of MEA.

In comparison with MEA, Figure 18 also shows that the reboiler heat duty of Blended Amine 3 at 110 ℃ across a range of L/G ratios is comparable, within the limits of error, to those of MEA at 112 ℃ (all L/G ratios) and 115 ℃ (L/G ratios of 2.8–4.0); even though Blended Amine 3 and MEA have different CO_2-lean loadings and CO_2 recoveries. However, the reboiler heat duties of Blended Amine 3 at higher temperatures (112 ℃ and 115 ℃) were notably higher than that of MEA at the same temperatures. An exception was observed for Blended Amine 3 at an L/G ratio of 3.7, when the reboiler heat duty was similar to that of Blended Amine 3 examined at 110 ℃.

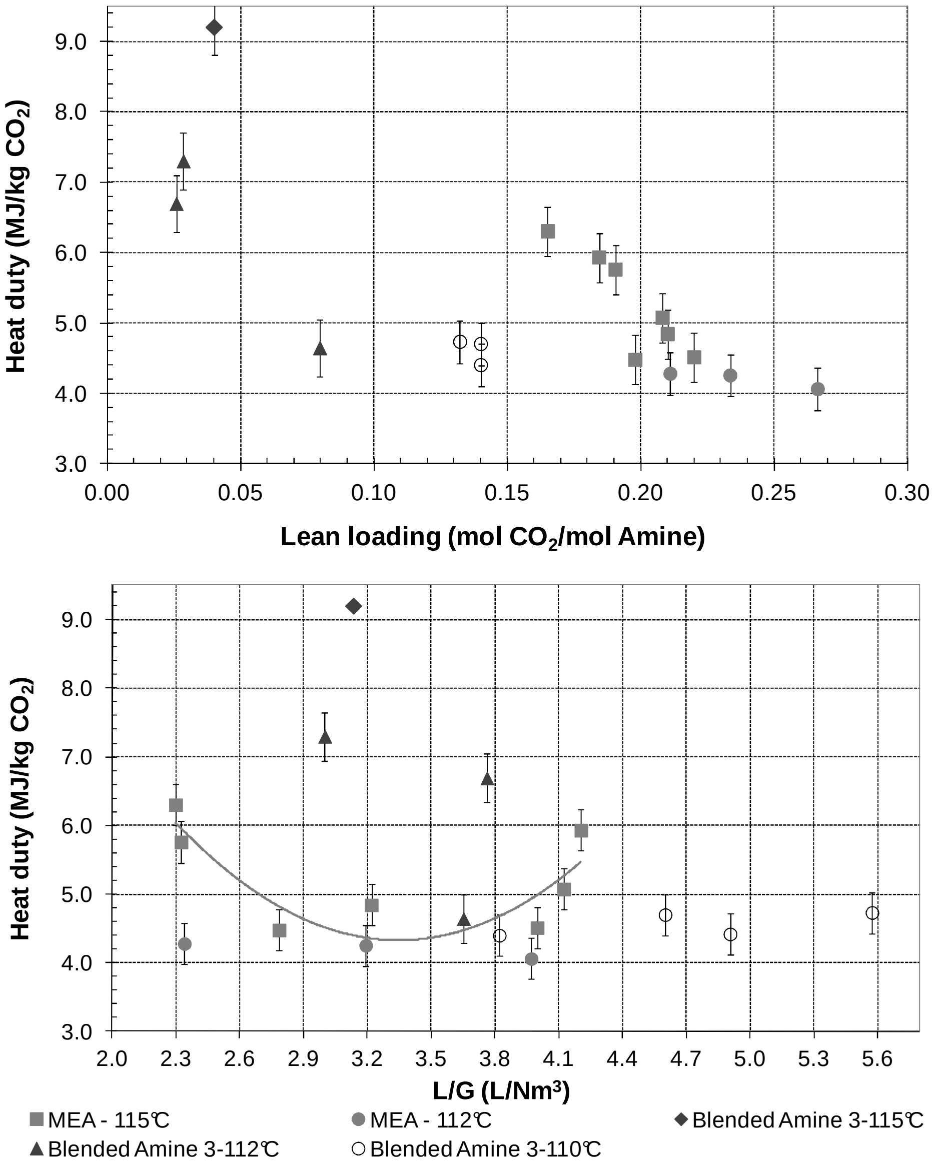


Figure 18. The variation of reboiler heat duty with L/G and CO_2-lean loading for Blended Amine 3.

To understand behavior of the reboiler heat duty, it should consider three energy components contributing to CO_2 stripping in the stripper column [17]. The heat duty which must be supplied in the reboiler is the sum of three components: (1) Heat of vaporization (Q_{con}) to generate steam for stripping-off CO_2 (2) sensible heat (Q_{sh}) to increase the temperature of the solution at the stripper inlet to the boiling point in the reboiler, and (3) heat of desorption (Q_{des}) of CO_2 from solution.

Error! Reference source not found. compares the Q_{con} values of MEA and Blended Amine 3 as a function of L/G ratio for different stripper bottom temperatures. It should be noted that the Q_{con} is related to the CO_2 partial pressure, which corresponds to the generating steam for CO_2 stripping. It is noticed that superfluous reboiler heat duty in the case of Blended Amine 3 at 112 ℃ and 115 ℃ (except for an L/G ratio of 3.7 at

112 ℃) could therefore be associated with an increase in Q_{con}. This indicates that Q_{con} for Blended Amine 3 at 112 ℃ or 115 ℃ was significantly higher than that of MEA at the same temperatures. The magnitude of Q_{con} of MEA at 115 ℃ (for an L/G ratio <2.7 and >4.0) is comparable to that of Blended Amine 3 at 112 ℃. The exception is for the experiment using Blended Amine 3 at 112 ℃, which resulted in a CO_2-lean loading of 0.08 as explained earlier in this section.

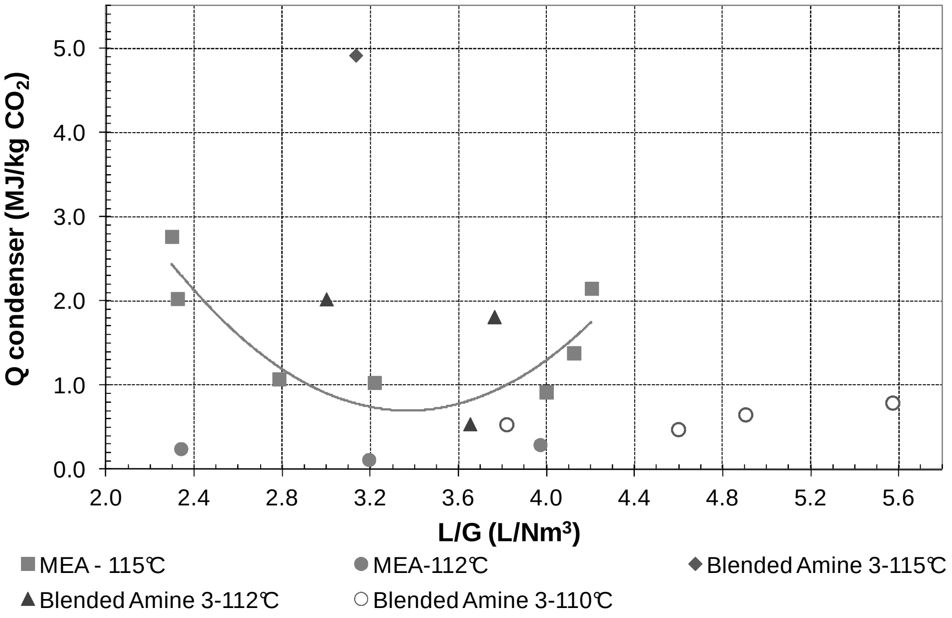


Figure 19. Q_{cond} profile as a function of L/G ratio for MEA and Blended Amine 3

It is also observed that reducing the stripper bottom temperature to 110 ℃ for Blended Amine 3 indicates CO_2 desorption from the Blended Amine 3 solution readily occurred at 110 ℃. This suggests that heating the Blended Amine 3 to above 110 ℃ will cause an excessive supply of reboiler heat duty and hence increased the Q_{con}. The Q_{con} of MEA at 112 ℃ is slightly lower than that of Blended Amine 3 at 110 ℃. This indicates that less energy is required for evaporating the water to obtain a CO_2-lean loading in the range 0.21–0.27 than for Blended Amine 3 to obtain a CO_2-lean loading of 0.14 (*cf.* Appendix A).

Error! Reference source not found. shows that the sensible heat value (Q_{sh}) for Blended Amine 3 at 110 ℃ is higher than those of Blended Amine 3 and of MEA at 112 and 115 ℃. This suggests that an increase of Q_{sh} relates to raising the solvent flow rate or L/G ratio.

For an L/G ratio of 3.6–3.8 at 112 ℃, the Q_{sh} values are significantly higher than at 115 ℃ and another test at 112 ℃ (L/G ratio of 3.0). This may be attributed to the temperature difference between the solvent entering the stripper column and the solvent leaving the stripper bottom being higher than that for a test with low Q_{sh} values.

The Q_{des} of MEA is also significantly higher than that of Blended Amine 3. A lower desorption energy, which is assumed to be similar to the solvent heat of absorption, may also contribute to the different behaviour of reboiler heat duty for different solvents. It is perhaps the increase in Q_{des} with increasing CO_2 capture can be compensated for by using a lower heat of absorption solvent.

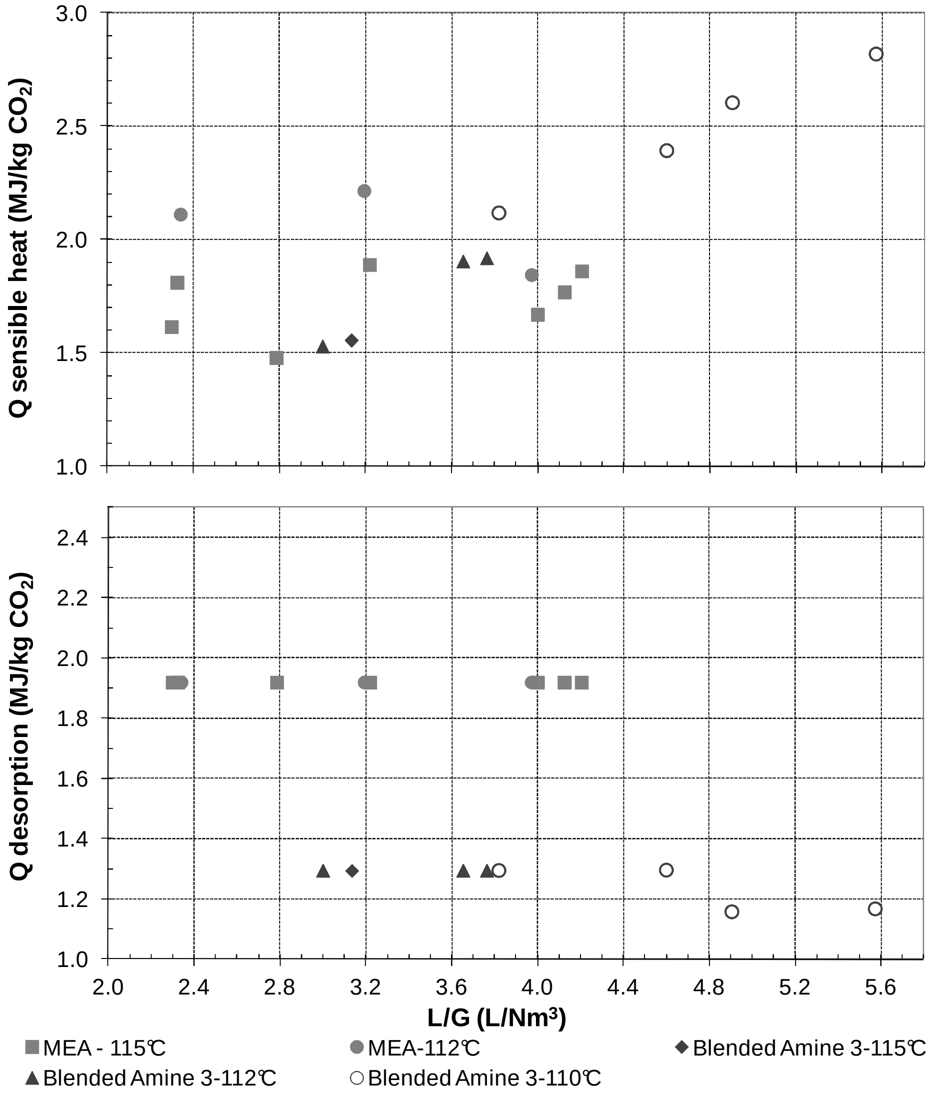


Figure 20. Q_{cond}, Q_{sh} and Q_{des} of MEA and Blended Amine 3 systems at a range of L/G ratios and stripper bottom temperatures

Figure 21 and Figure 22 provide some insight into the performance of the CSIRO-1 solvent as used in the pilot plant.Figure 21 shows that CSIRO-1 gives lower CO_2 recovery compared to MEA baseline-115 ℃. The CO_2 recovery of CSIRO-1 at 114 ℃ with medium L/G ratio is comparable to MEA baseline-115 ℃. It is also found that CSIRO-1 at 112 ℃ with medium L/G ratio is also comparable to that of MEA at 112 ℃ with a lower L/G ratio. CSIRO-1 trialled at lower reboiler temperature can reach a CO_2 recovery similar to CSIRO-1 at 112 ℃ and MEA at 112 ℃, if the L/G ratio is very high.

It can be noted from Figure 22 that further reduction in lean loading for CSIRO-1 from 0.22 to 0.10 does not significantly improve the CO_2 recovery. However, further minor reduction in lean loading (0.10 to 0.08) does remarkably raise the CO_2 recovery to MEA baseline-115 ℃ with relatively lower L/G ratio . Figure 21 and Figure 22 also shows that CSIRO-1 at 110 ℃ can achieve a CO_2 recovery similar to that of CSIRO-1 at 112 ℃ and also to that of MEA at 112 ℃. As the lower regeneration temperatures leads to an increased rich loading the L/G ratio needs to be higher to maintain the CO_2-recovery. Figure 22 also shows that the lean loadings for the CSIRO-1 solvent at regeneration temperatures of 112 ^{o}C and 114 ^{o}C are much lower than for MEA, illustrating the potential to achieve better performance in terms of recovery. Further lab-based optimisation work is needed to improve the performance of the CSIRO-1 solvent.

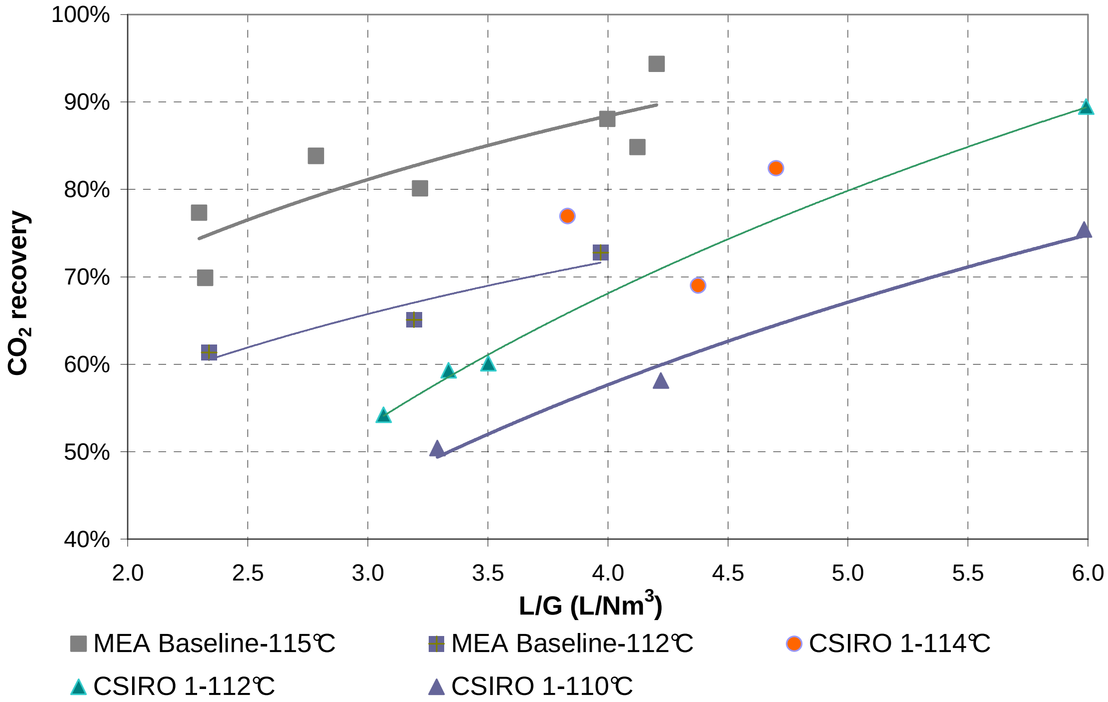


Figure 21: The effect of increasing L/G ratio on CO_2 recovery for CSIRO-1 at different stripper's bottom temperatures. The CO_2 recovery of MEA is also presented in the graph for comparison).

Figure 23 compares the reboiler duty as a function of L/G ratios for difference solvents, i.e. MEA baseline and both selected Blended Amines (1, 2 and 3) and CSIRO-1. In general, the blended solvents also show reduction in the reboiler duty required compared to that of the MEA baseline for a given value of L/G ratio. For blended solvent 1, it shows a parabolic manner as shown for MEA baseline. Nevertheless, the magnitude of reboiler duty for Blended Amine 1 shows a little difference across the L/G ratio compared with the case of MEA baseline at 115 ℃.

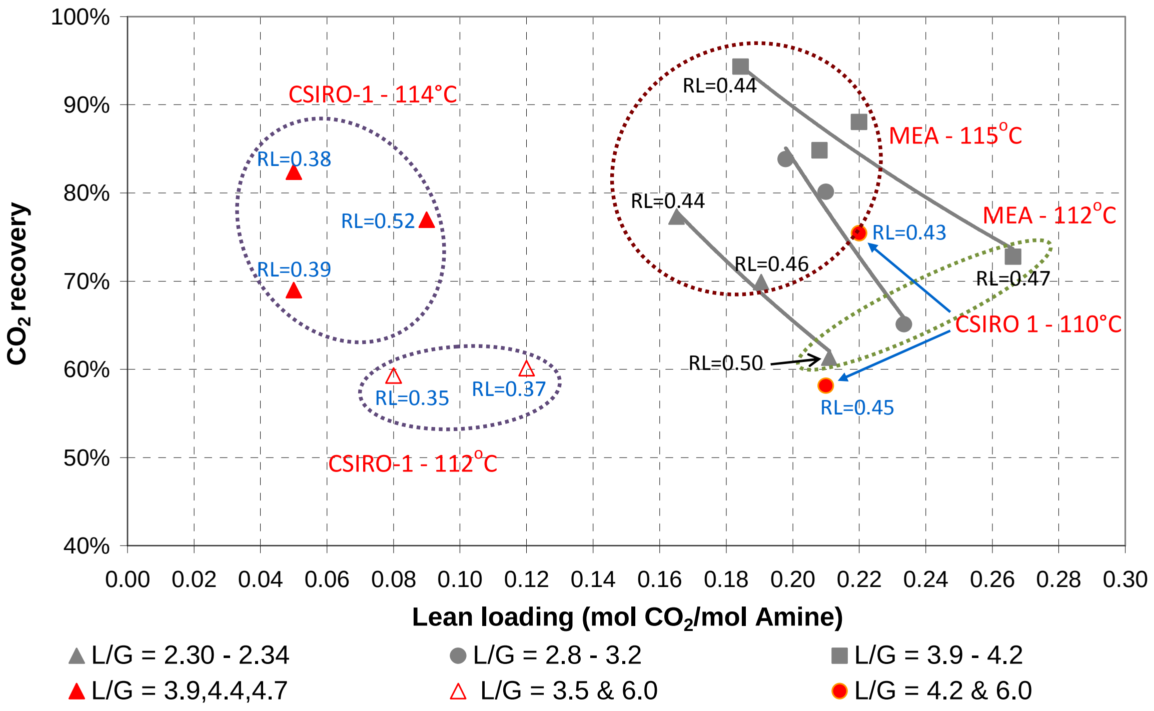


Figure 22: The correlation between lean loading and CO_2 recovery for CSIRO-1 and MEA baseline (RL =Rich Loading).

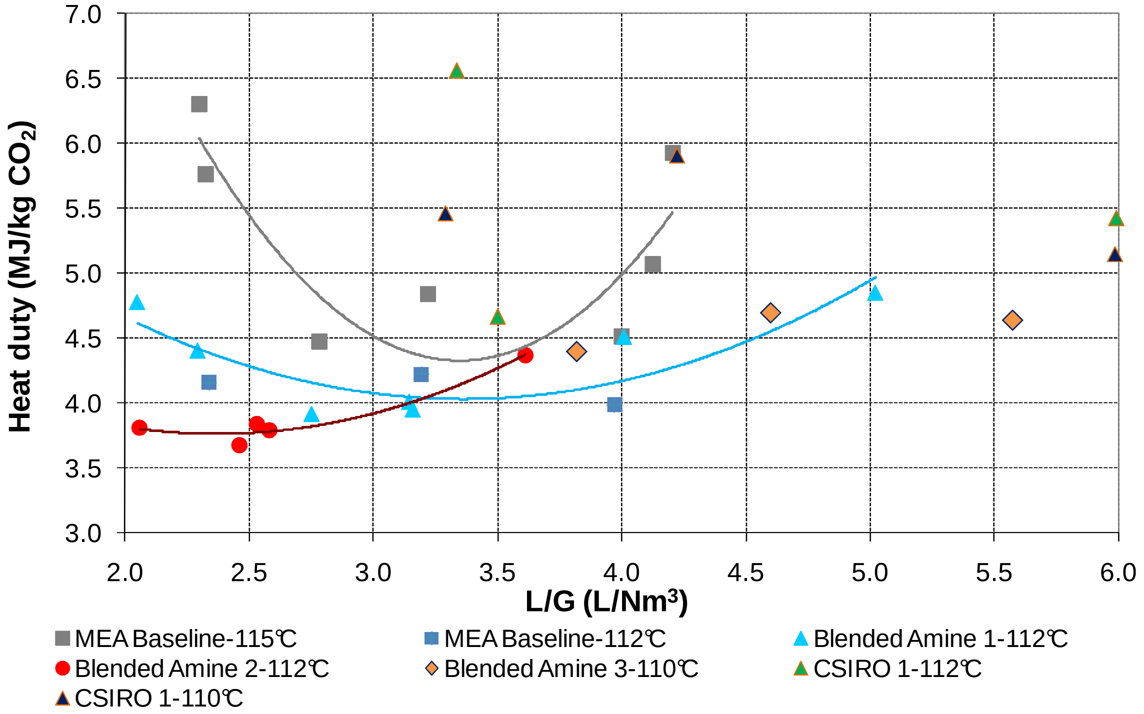


Figure 23: A relationship of reboiler duty and L/G ratio for different solvents tested in CSIRO's pilot plant.

However, for Blended Amine 2, the reboiler heat duty is the lowest and it has a different trend. The reboiler duty has initially levelled-off until reaching L/G ratio 2.6 and it then steadily increases until reaching the value of reboiler duty comparable to the MEA baseline for the L/G ratio above 3.2. This indicates that the effect of increasing L/G ratio is observed for Blended Amine 2. Blended Amine 3 shows that the reboiler heat duty is levelled-off from L/G ratio 3.8 to 5.6. This result suggests that a minimum energy required for Blended Amine 3 even though the plant has to use a higher L/G or solvent rate. For CSIRO-1 at 114 ℃, it has relatively higher reboiler heat duty (at L/G ratios 3.8, 4.4 and 4.7, the reboiler heat duty obtained were 9.2, 14.2 and 10.1 MJ/kg CO_2 respectively) compared to other solvents in this study. Such small lean loading obtained under the conditions used for this solvent may cause the higher requirement of energy for solvent regeneration. However, this should be investigated further by assessing its reboiler heat duty distribution.

Figure 24 describes the distribution of reboiler duty components from all solvents tested in order to get a comparable CO_2 recovery of 84%-89% and of 60% - 70%. For a CO_2 recovery of 84%-85%, the total reboiler duty (summation of Q condenser, Q solvent heat and Q desorption) for Blended Amines -1, -2 and -3 decrease by 11%. 14% and 8%, respectively, relative to that of MEA. However, the reboiler heat duty of CSIRO-1 is higher than that of MEA baseline and all Blended Amines. From figure 16 and 17 that it can be seen that although CSIRO-1 has the lowest energy requirement for CO_2 desorption the higher water evaporation and higher sensible heat requirement result in overall less efficient process. Further work in optimisation of the solvent formulation and process conditions is still needed.

For lower CO_2 recovery, the reboiler heat duty of all Blended Amines 1, 2 and 3 remarkably decreases by 30%, 34% and 24% respectively compared to that of the MEA baseline at 115 ℃. The CSIRO-1 solvent is also down by 19% compared to that of MEA baseline. The relative reduction at the lower CO_2 recovery increases due to the MEA baseline having a higher water evaporation compared to that of both Blended Amine solvents. At this lower CO_2 recovery, a similar magnitude for the sensible heat requirement for both Blended Amine 3 and CSIRO-1 also occurs.

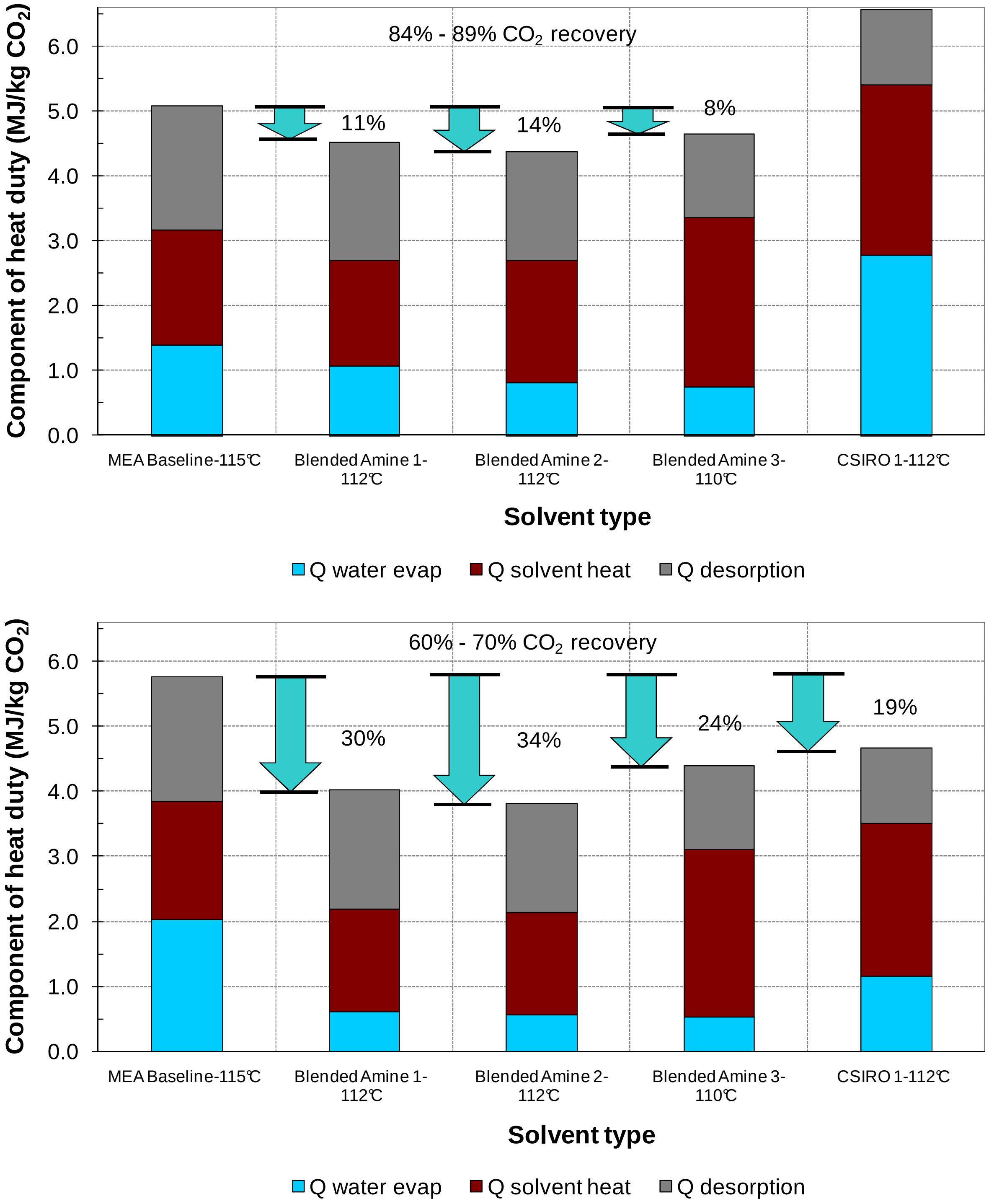


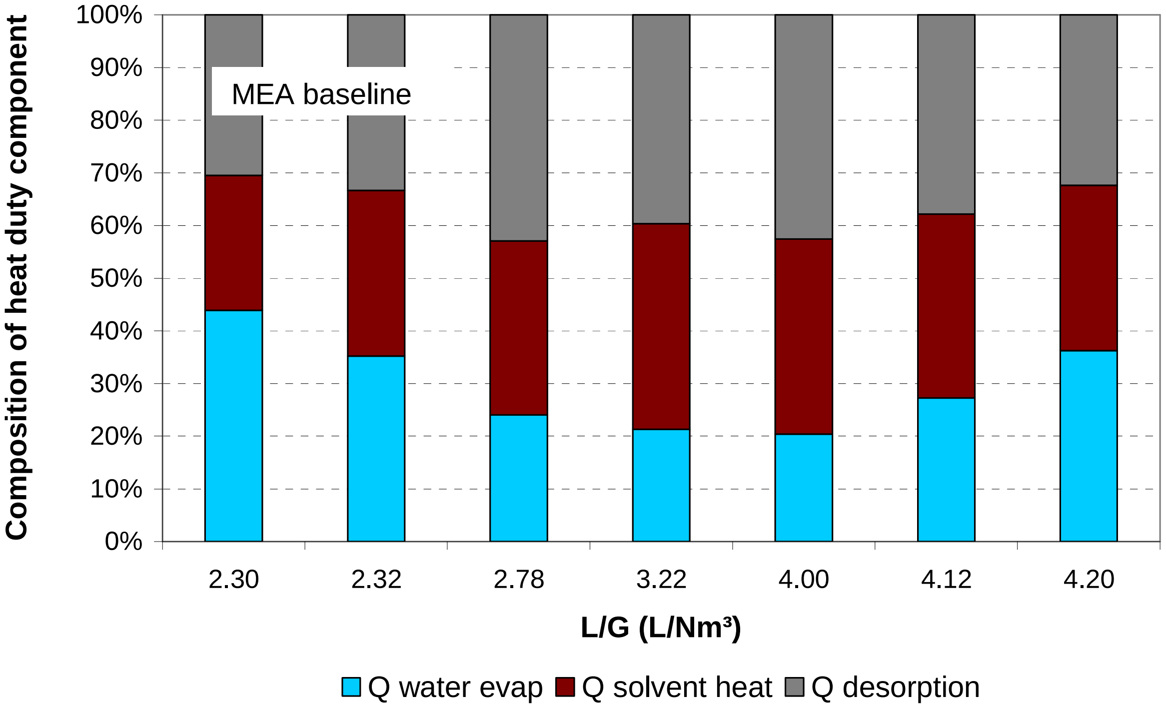
Figure 24: Comparison on component reboiler duty values of MEA baseline-115 ℃ and the Blended Amines 1, 2, 3 and CSIRO-1 at similar range of CO_2 recovery.

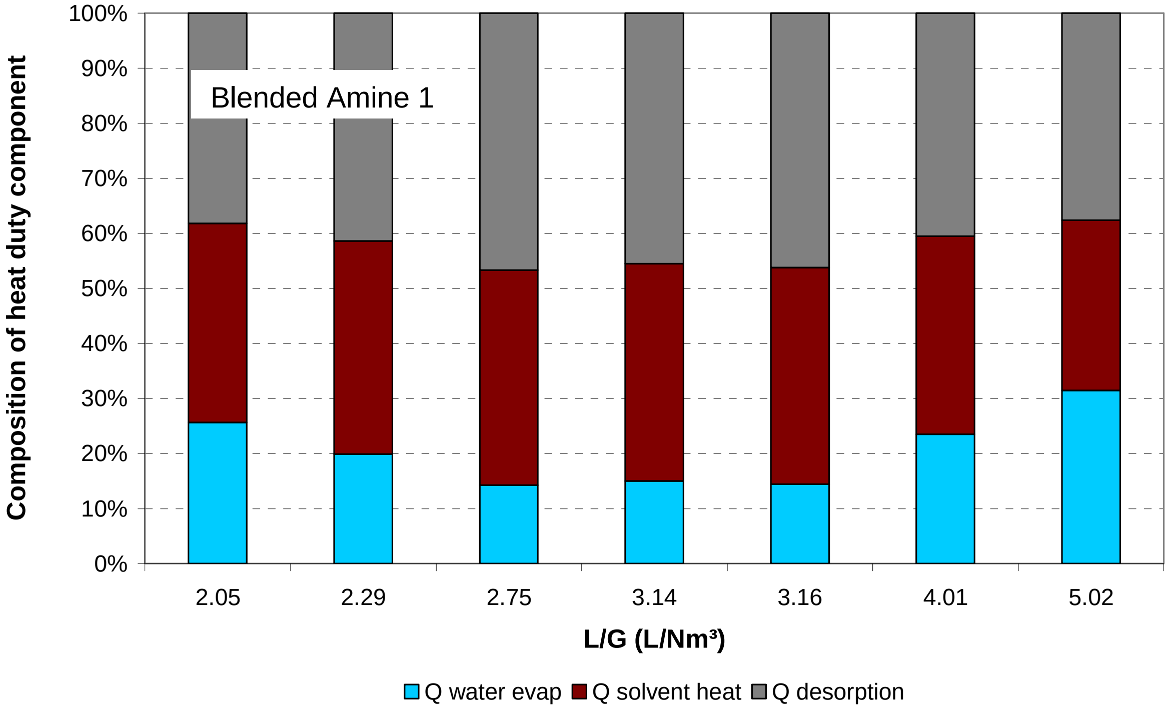
4.11 Analysis for Reboiler Duty for Different Solvents

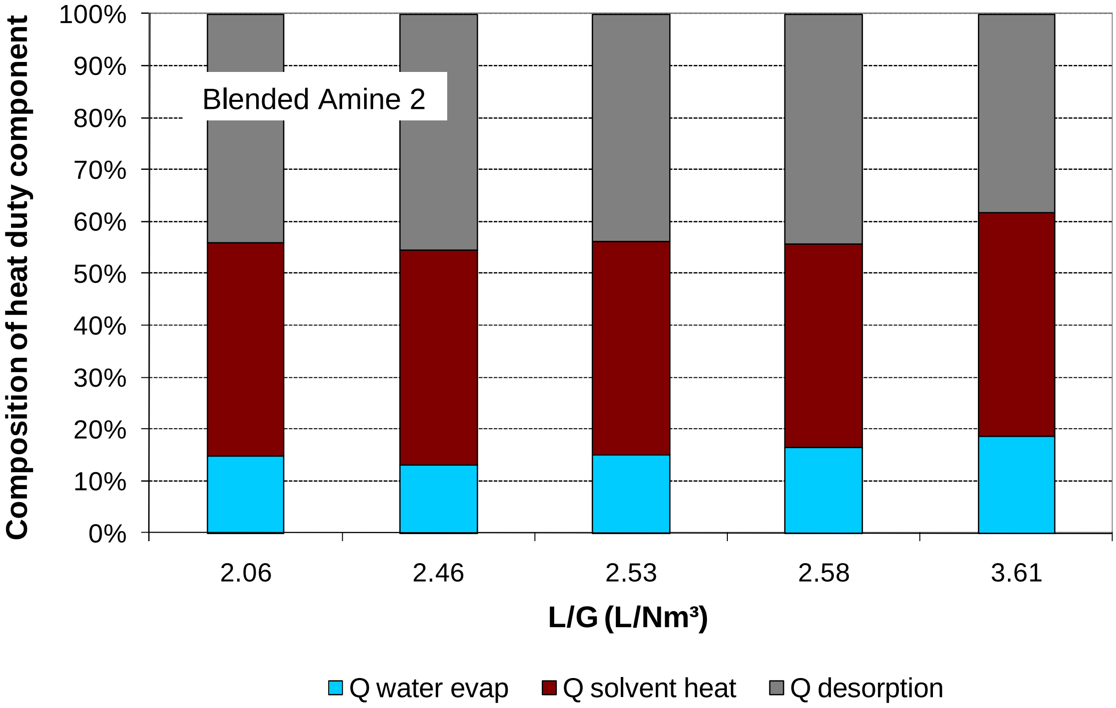
While the experimental conditions for all solvents, such as recovery and L/G ratio, have varied throughout the campaigns, one can distill information by analysing the reboiler duty for the different solvents. The proportions of three energy components to the reboiler duty (water evaporation, sensible heat and CO_2 desorption) for all solvents are illustrated in Figure 25 as a function of L/G ratio.

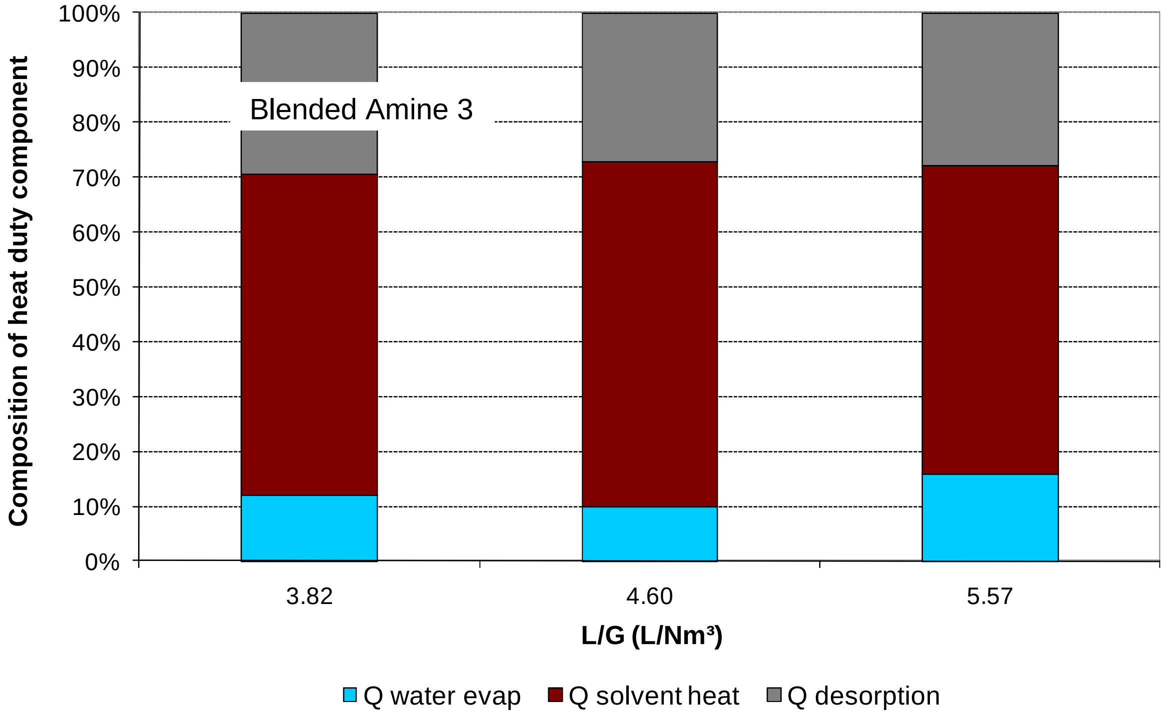
For MEA, at the lowest L/G ratio, the heat of water evaporation, as determined by the condenser duty, does predominantly contribute to the reboiler duty required. This contribution is reduced as the reboiler duty approaches a minimum value and the involvement of sensible heat and heat of desorption become more pronounced. At the highest L/G ratio, the role of all the three components contributing to the total reboiler duty is comparable.

For Blended Amine 1 across the range of operating L/G ratio’s, the contribution of water evaporation on the total reboiler duty is less than those of the individual sensible heat and desorption heat. For the regeneration conditions and solvent rich loadings, the solvent has a relatively higher CO_2 partial pressure than that of MEA solvent, and therefore it requires less energy to evaporate the water to strip-off the CO_2. A similar trend was also observed for Blended Amine 2.




Blended Amine 1
Composition of heat duty component
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
2.05
2.29
2.75
3.14
3.16
4.01
5.02
L/G (L/Nm³)
Q water evap
Q solvent heat
Q desorption


Blended Amine 2
Composition of heat duty component
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
2.06
2.46
2.53
2.58
3.61
L/G (L/Nm³)
Q water evap
Q solvent heat
Q desorption



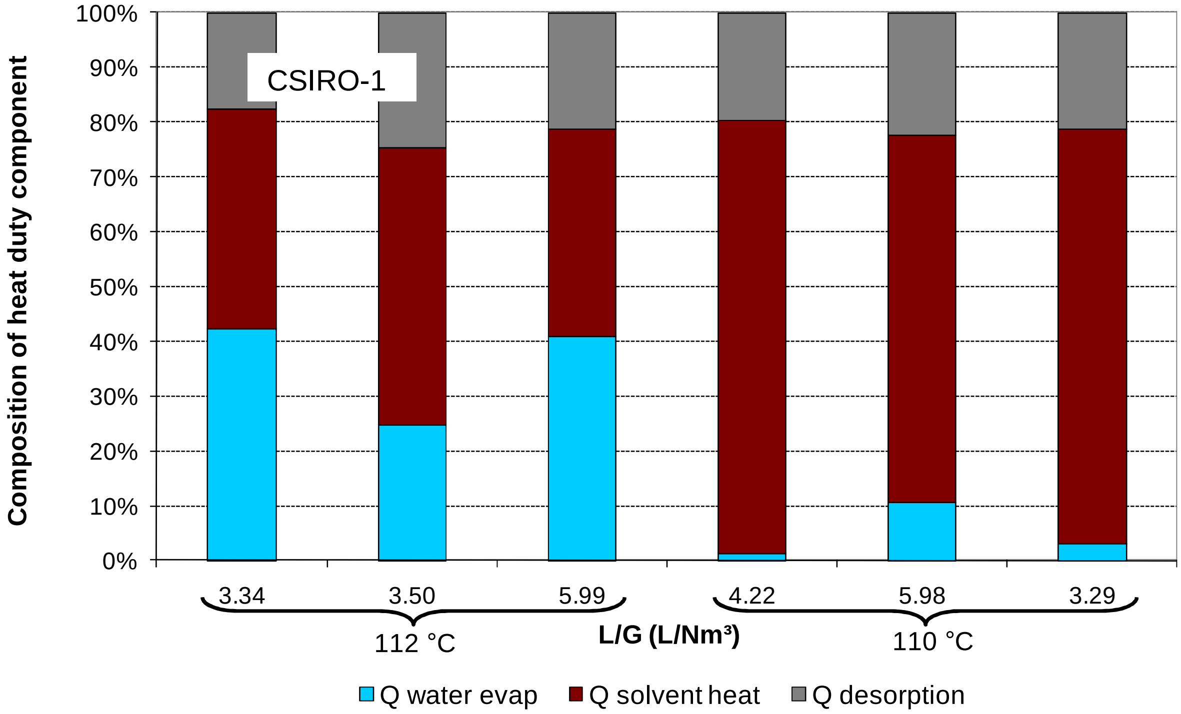
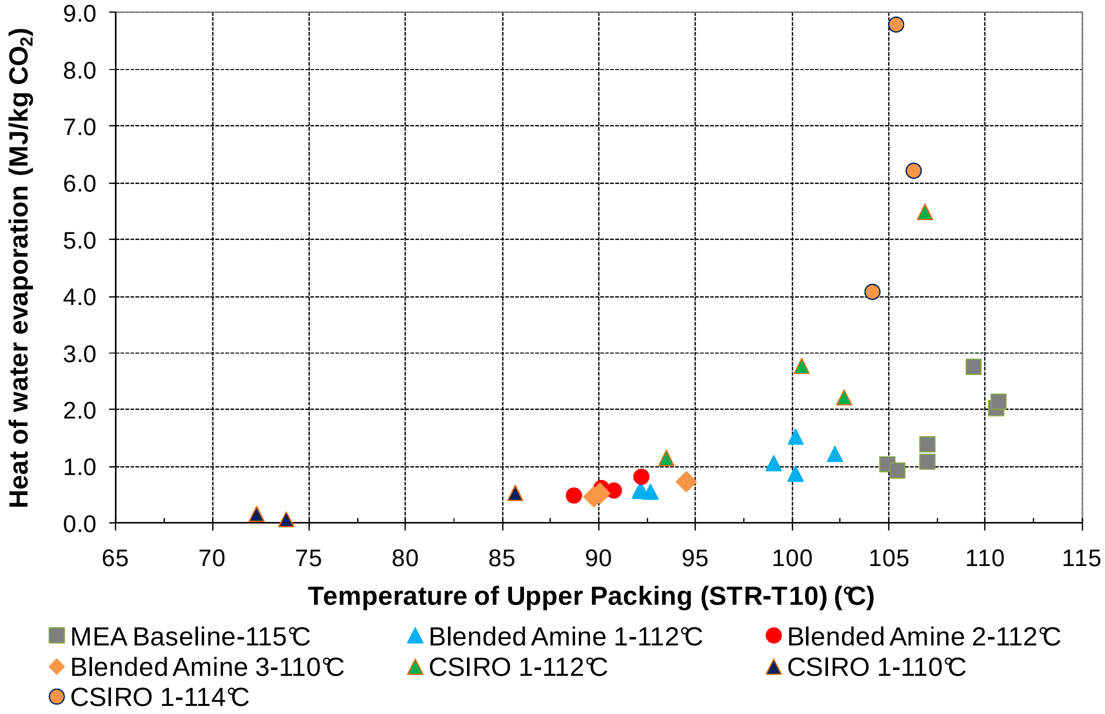


Figure 25: The proportions of reboiler duty components for different solvents tested in LY PCC Pilot plant as a function of L/G ratio.

For Blended Amine 3 and CSIRO-1, the behaviour is not the same as found for the other solvents. It is noticed that the heat of desorption changes is less sensitive with variation in L/G ratio. In general, the heat of water evaporation for Blended Amine 3 is much lower than the other component of reboiler duty and the sensible heat takes the largest portion in the total reboiler heat duty. The higher of sensible heat is attributed to the increase of L/G ratio used and also big difference in temperature between the solvent inlet to stripper column and the stripper's bottom temperature. Such indication is also observed for CSIRO-1, especially at 110 ℃. The higher portion of heat for water evaporation is due to more water is evaporated for stripping-off the CO_2. To overcome this issue, process optimisation resulting in suggestions for process improvements and an accurate process control around the stripper column should be implemented.

The heat of desorption of Blended Amines 1 and 3 is shown to be apparently similar regardless of L/G ratio values. CSIRO-1 is relatively lower than those of all solvents. In addition, the magnitude of desorption heat for CSIRO-1 and Blended Amines 1, 2 and 3 are lower than that of MEA.

Overall, the finding indicates that different mechanisms of CO_2 stripping between blending amine solvents and MEA baseline during the regeneration in the stripper column occur as they have different properties and processing parameters. The measurement of single solvent, such as MEA in this study, and blended solvent should be useful to the guidance of improving the efficiency and the reliability of the PCC process. Kvamsdal *et al.* [14] also pointed out that there are many dependent variables to optimize the design of PCC plant by considering stripper operation conditions, variation of solvent rate and load from the power station, which is useful from a practical point of view.



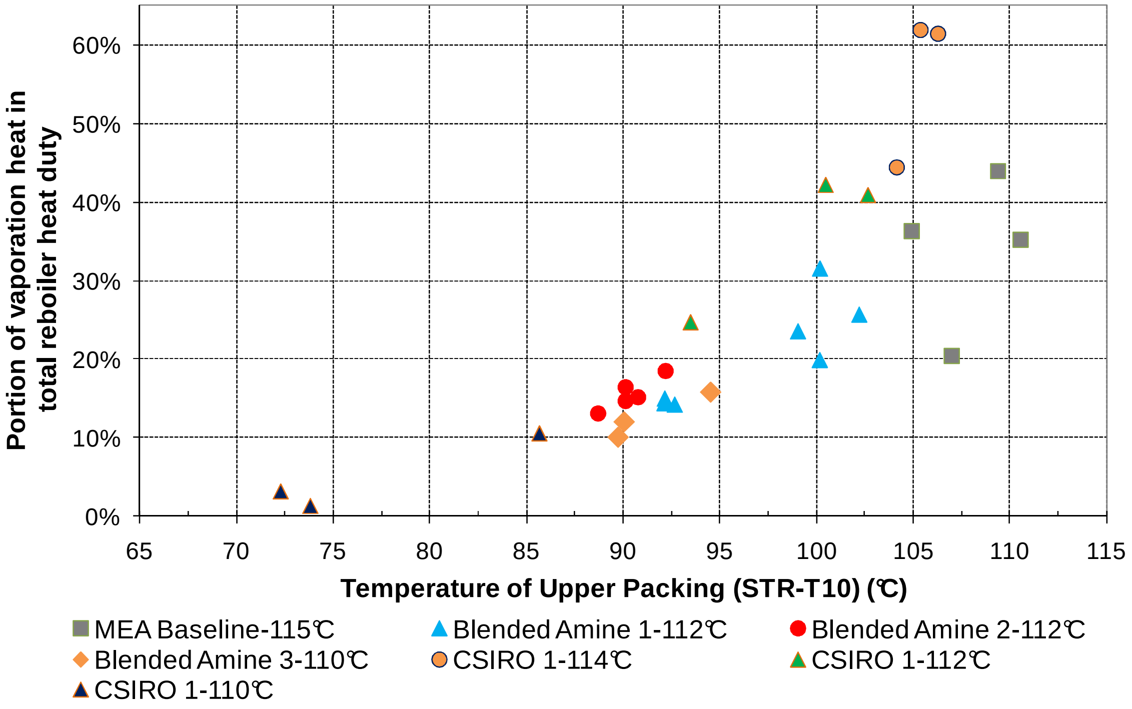


Figure 26: Correlation between contribution of water evaporation heat to the total reboiler heat duty and upper packing temperature in stripper column for all solvents tested.

Figure 26 indicates that CSIRO-1 at 114 ℃ and 112 ℃ and MEA show relatively high in the heat of water evaporation. The figure confirms that an increase of upper packing temperature in the stripper column enhances the heat required to evaporate the water.

5. CONCLUSION ON BENCHMARKING OF SOLVENTS

In general, the magnitude of CO_2 recovery for all sets of solvents tested in the pilot plant is dependent on the L/G ratio and solvent lean loading. It is shown that a solvent with a higher lean loading requires a greater solvent (recycle) flow rate, or vice versa, in order to capture a given amount of CO_2. The effect of reducing the stripper's bottom temperature from 112 to 110℃, except for Blended A mine 2, is found to be significant in decreasing the CO_2 recovery for all solvents.

The reboiler duty is significantly dependent upon the L/G ratio and solvent lean loading. For MEA, the relationship between reboiler duty and L/G ratio shows a parabolic profile, which has a minimum reboiler duty of 4.3 MJ/kg CO_2 removed at L/G ratio of around 3.2. A similar pattern occurs for the Blended Amine 1, but not for the Blended Amine 2. For Blended Amine 2, an increase of L/G ratio steadily increase the reboiler heat duty after L/G ratio of 2.6. For Blended Amine 3, the reboiler duty seems constant at a range of L/G tested. For the relation with the lean loading, the reboiler duty of both MEA and Blended Amine 1 is inversely dependent on the solvent lean loading. Yet, at a higher lean loading the reduction of the reboiler duty is minor. The effect of increasing reboiler duty was not observed for Blended Amine 3 as it is observed that the lean loading does not change much. However, for CSIRO-1, at higher temperature (114 ℃ not shown), less reduction in lean loading resulted in an excessive reboiler heat duty and at relatively lower temperature (112 and 110 ℃), a remarkable decrease in lean loading slightly increase in energy duty. As a result, in future work, it may be expected that at even lower stripper bottom temperature less reboiler duty per unit of removed CO_2 might be found for this solvent system.

It is indicated that the higher reboiler duty of MEA is primarily related to a higher heat of desorption and heat of water vaporization compared to the Blended Amines. Analysis of the three contributions to the reboiler heat duty may also explain the discrepancy between the trend in reboiler duty of MEA and that of both Blended Amines and CSIRO-1. At the lowest L/G ratio, MEA requires more condenser cooling than the other two solvents. On the other hand, due to having a higher CO_2 partial pressure, the blended solvents tend to require less energy to evaporate the water necessary to strip-off CO_2 than that of MEA. However, in case of CSIRO-1, the implementation of higher temperature (114 ℃) seems not necessary. The high temperature at the upper packing in the stripper column results in a high water evaporation. In short, different mechanisms of CO_2 stripping between blended solvents and MEA baseline will prevail in the stripper column and more detailed process analysis is required.

The results in general invite further works to explore novel mixture solvents and process conditions in order to improve the CO_2 absorption capacity and minimizing the reboiler duty. It should be noted that maintaining solvent chemical stability, changes of rich solvent and solvent's susceptibility upon loss must also be investigated in further studies.

6. CSIRO PILOT PLANT EMISSIONS MONITORING

The GASMET CEMS (continuous emissions monitoring system) is currently used at PCC pilot plant at Loy Yang Power to measure an extensive range of compounds in flue gas. The emission compounds that are of interest include MEA as a measure of solvent loss, NH_3 as a degradation product and the acid gasses NO_X, SO_2, HCl and HF to measure removal rates. The error in gas concentration measurements from the GASMET CEMS as given by the vendor was previously shown in Table 7.

Figure 27: The GASMET CEMS used at LYPP to measure various compounds and emissions

Since the commissioning of the GASMET gas analyser, the reliability of these detection limits for various components has been investigated. Generally, the measurements from the GASMET CEMS are reliable with adequate calibration of the system. The GASMET CO_2 concentration measurements in particular, have been comparable to results attained from the previously used mobile gas chromatography unit. The accuracy, however, of other measured components has been of concern with data exhibiting interference and scattering. The anomalies observed in data have hindered efforts to appropriately analyse data. The scattering of data may arise from the calibration drifts due to the variances in ambient temperature, presence of vibration or interference components such as water. Significant fluctuations in ambient temperature can cause calibration drift and affect the components in the GASMET gas analyser. The recommended temperature range for use of the GASMET CEMS is 22 ± 2 ℃ and the maximum temperature is 35 ℃.

Although the apparatus is designed for industrial use, vibration potentially causes the misalignment of optical components in the system resulting in scattering of data and drifts in calibration. The GASMET CEMS is subjected to a continuous vibration source originating from a nearby induced draft fan at Loy Yang Power. To ensure optimal correction for data interference from water and other components with reference peaks similar to water, the vendor recommends that water calibrations should be conducted every 6 months on the GASMET gas analyser.
The data for MEA emissions is relatively accurate despite having some fluctuations during the MEA trial. In contrast, unexpected measurements for concentration of HF, SO_2, NO_2 and NH_3 were acquired using the GASMET system.

The emission of MEA from Absorber 1 and 2 was expected to be influenced by temperature and loading while exhibiting some relationship with flow rate, L/G ratio, pressure or campaign duration. During the analysis of MEA trial data, it was postulated that MEA emissions may be dependent on differences in loading. However, due to small differences in loading and potential inaccuracy of GASMET measurements, the correlation between loading and MEA emissions is not conclusive.

The MEA trial results demonstrated significant differences between emissions for Absorber 1 and 2. The loading in Absorber 2 was greater and most emissions were below the detection limit, thus emission rate from Absorber 2 either was unmeasurable or had high measurement errors. In contrast, Absorber 1 with a lower loading had significant emissions rates. Thus, the main source of MEA emissions was from Absorber 1. The emission rate and loading differences between the two absorbers may provide evidence for the dependency of emission on loading. Alternatively, the difference between the absorber may have caused other issues such as the problems with the GASMET system or the wash section.

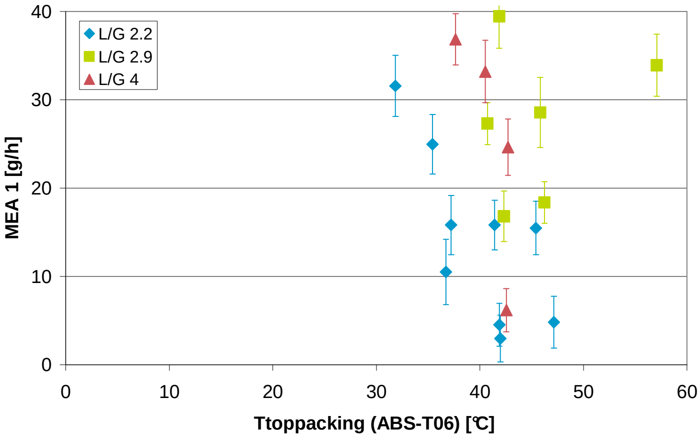


Figure 28: Plot of MEA emission against temperature at top of packing in Absorber 1 with error bars

There is evidence from the MEA trial to suggest that an increase of gas flow rate has the potential to decrease MEA emissions. It has been postulated that the increase of gas flow rate is related to an increase in the amount of CO_2 extracted by the amine, thus reducing amine emissions.

In contrast, emissions of MEA were expected to be higher with increased temperature due to increases in volatility and reaction rate. Similarly, high liquid flow rates with lower loading (increased concentration of free MEA) were expected to increase rates of MEA emissions due to an increase in solvent evaporation. However, as seen in Figure 28,

Figure 29 and Figure 30, no such relationships were observed between MEA emission and other process parameters such as temperature, flow rate and L/G. Pressure drop is not a useful parameter in MEA emission analysis as pressure drop in the Absorber 1 is dependent on the loading and L/G ratio. Furthermore, it was concluded that the water calibration did not improve MEA measurements from the GASMET system due to the presence of vibration; instead water calibrations may introduce inaccuracies in MEA measurements.

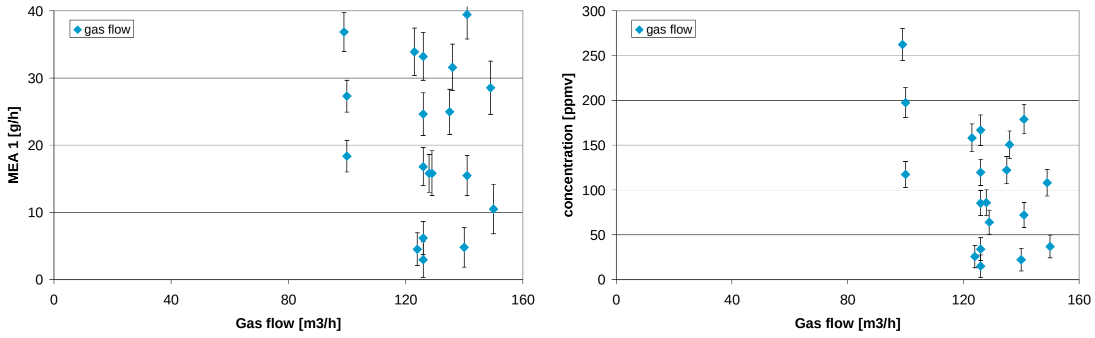


Figure 29: Plot of MEA emission (left) and MEA concentration (right) against gas flow rate with error bars

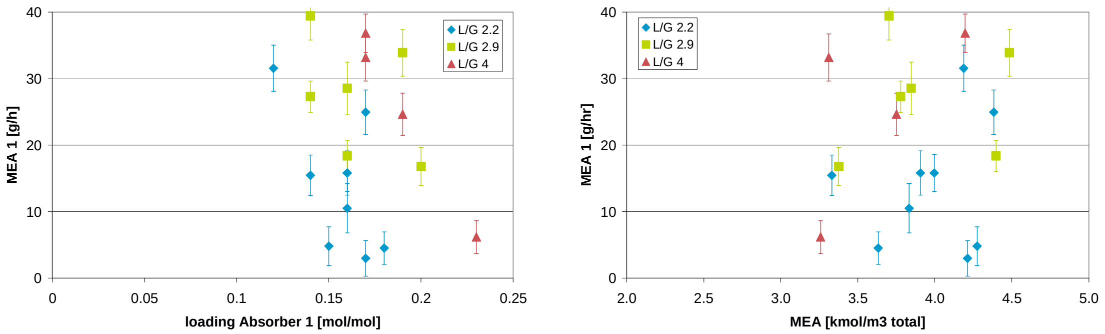


Figure 30: Plot of MEA emissions against Absorber 1 loading (left) and against free MEA (right) with error bars

The emission rate of MEA is proportional to MEA flow rate and assumed to be in liquid-vapour equilibrium. With this information, the measured GASMET MEA emission results can be theoretically validated with a liquid-vapour equilibrium calculation to predict MEA vapour emission.

The accurate measurement of NH_3 is important as it is a degradation product and is associated with solvent loss. The flue gas NO_X is mainly composed of NO and is a product from the power station. Monitoring the emission of both NH_3 and NO_X is necessary as these components have a degree of toxicity and environmental impact. Figure 31 shows that during the MEA trial, the emission data for NH_3 was not stable and readings were close to the detection threshold causing high measurement errors. The instability in NH_3 data may be due to changes in the solvent, problems with the GASMET system or wash section. In contrast, the Munmorah PCC pilot plant has experienced high NH_3 measurements but further investigation indicated that the problem was due to a fault with the O_2 sensor. Thus, this issue has emphasised the importance of regular sensor servicing, maintenance and calibration requirements at LYPP to ensure GASMET accuracy.

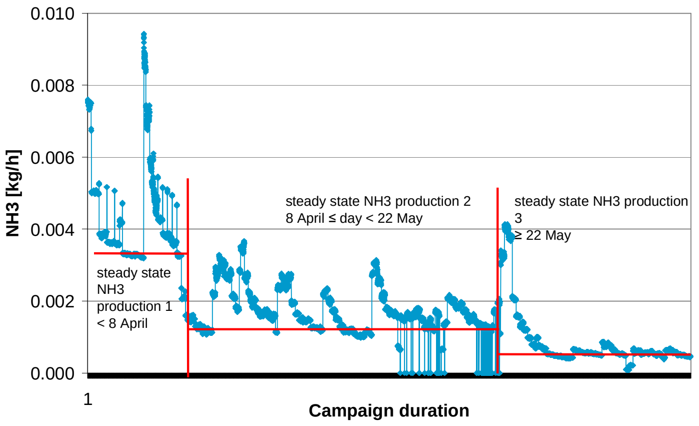


Figure 31: NH_3 emission during trials in MEA campaign

Figure 32 demonstrates that mass flow of NO decreases in Absorber 1 during the MEA trial. The data for NO emissions during this trial were stable and accurate. However, two NO_X instruments at the inlet and outlet of Absorber 1 are recommended to individually measure NO and NO_2 concentration. This will be necessary for the validation of the GASMET reading and provide further information on potential pollutant secondary products.

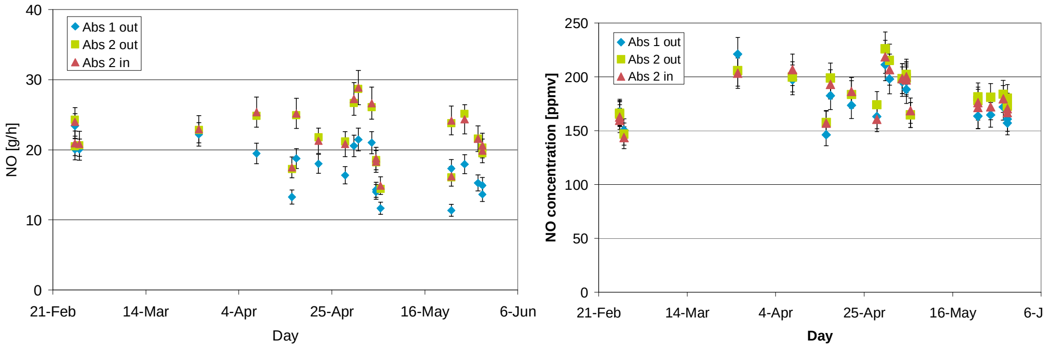


Figure 32: NO mass flow (left) and concentration (right) in the absorbers during the MEA campaign

The measurement of impurities such as NO_X, SO_2, HCl and HF in the stream from the power station is usually accurate. The concentration of SO_2, HCl and HF exiting the pre-treatment process are close or below detection limits as the removal rates of these are large. Measurements near or below the detection threshold are unmeasurable or associated with increased measurement error. Thus, the accuracy of SO_2, HCl and HF are questionable. The measurement of SO_2 has inconsistencies and may be due to changes in solvent or lignite composition. However, other unexpected data for acid gas measurements includes a higher HF concentration compared to HCl and an increase in HF mass flow rate in Absorber 1. This indicates issues with the GASMET and not associated with changes in solvent.

Using suitable sampling techniques from the plant will provide additional validation information about emission rates of major pollutants. Also, sampling for gas and droplets at the plant would provide input information about L/G ratios of streams for a plant simulation model. This emission rate and L/G ratio data will be required in the future to observe the impact of emission in an air quality model and used for an environmental impact assessment study.

7. CSIRO PILOT PLANT MODIFICATIONS

Since the commissioning of the post combustion capture (PCC) pilot plant at Loy Yang Power, a number of upgrades and modifications have been implemented to automate operation, improve research results or enhance safety and operability.

One important feature of the PCC plant is the use of density meters on the amine solvent lines to assist in determining the instantaneous CO_2 concentration in the liquid. Experimental studies have confirmed that that amine solvent density is directly proportional to the level of CO_2 loading of the solvent. The CO_2 concentration readings will indicate the efficiency of CO_2 the absorption and regeneration for a particular solvent under certain operating conditions.

Campaign duration is dependent on the amount of solvent in the feed tank. Thus, minimisation and prevention of solvent loss extend campaign duration and is particularly important when the solvent is expensive or availability is low. Mist elimination equipment was installed in absorber column 1 to prevent the entrainment of amine solvent mist, significantly reducing amine solvent loss and increasing campaign duration.

The flue gas flow was found to be unstable. The flow is measured using differential pressure readings from the blower flow meter. In order to obtain optimal accuracy, the flow need to be in fully established condition. It is found that the blower flow meter pipe length was too short and a stable flow pattern wasn't established and hence, led to incorrect reading. The upstream pipeline of the blower was then redesigned. The new pipe spool has a U shape with 1.5 meters on either side of the two pressure measurement points after which the stability and accuracy of results improved. . Furthermore, the new U-shape design prevents the blower flow meter from collecting condensate water, which is one of the sources of offset errors.

A plate and frame heat exchanger (STR-HX02) is used for the transfer of heat from the hot lean amine from the stripper to the cooler rich amine from the absorber. To improve heat transfer efficiency and acquire a higher temperature for the stream of rich amine entering the stripper, the plate and frame heat exchanger size was increased. However, the heat transfer efficiency did not improve after the installation of a larger STR-HX02. Further investigation revealed that the lower flow rate in the larger heat exchanger lead to decreased pressure. At low flow rate and pressure, the CO_2 in the rich amine solvent converts to vapour, significantly decreasing the heat transfer efficiency. To resolve the issue, a throttling valve has been installed on the rich amine stream exiting the heat exchanger. Theoretically, the throttling valve will increase the pressure of the rich amine stream to prevent CO_2 vapour formation and improve heat transfer efficiency. To monitor the pressure, a pressure gauge will be installed on the stream after the throttling valve.

Corrosion can result in low temperature regions of the plant when the flue gas cools below the condensation temperature of acids. The gas in the line before flue gas pre-treatment (FPT) is highly corrosive due to the presence of sulphur dioxide (SO_2). The acidic environment resulted from the dissolution of SO_2 and NO_X in condensed water vapour to form sulphuric acid and nitric acid. Within the first year of LYPP operation, acid pinhole corrosion was evident on the blower and on the grade 304 stainless steel piping and knock out box. Subsequently, to prevent further corrosion damage the blower (FPT-BLO1) was relocated and is now positioned after the pre-treatment process. During the blower relocation, flue gas inlet piping and the knock out box was replaced with grade 316 stainless steel due to its superior corrosion resistance in an acidic environment.

Before insulation, condensation on the sides of the flue gas inlet pipe caused flue gas particulates to adhere and build up at the pipe wall, eventually completely blocking flow. Thermal insulation proved to solve the problem by preventing heat loss.

Figure 33: CSIRO's PCC pilot plant at Loy Yang Power (2008 left and 2011 right).

8. HEAT INTEGRATION AND TECHNO-ECONOMIC ASSESSMENT

8.1 Evaluation of Baseline PCC Process with Heat Integration

The heat integration and techno-economic analysis of a standard PCC process, particularly one operating in Victoria, aims to provide a baseline process with the associated costs. The techno-economic analysis is based on capturing CO2 from the flue gas of a brown coal-fired power plant with 539 MW gross output and a standard PCC process using an aqueous 30% mono-ethanolamine (MEA) solution. The heat integration and optimisation study was performed with Steam Pro, Steam Master and ASPEN-Plus Rate-Sep software. Costs were determined for the power plant configurations shown in Table 8.

Table 8 Power plant configurations used in the techno-economic evaluation of an existing and new power station

Existing Subcritical Power Station	New Subcritical Power Station
- Natural draft cooled brown coal-fired power station - Capital costs fully amortised - Without CO_2 capture - Maximum CO_2 capture avoiding any modifications in the existing steam cycle - With a throttle valve in the steam cycle enabling 90% CO_2 capture	- Natural draft cooled brown coal fired power station (design based on existing power station without CO_2 capture) - With 90% CO_2 capture where the PCC plant is air-cooled - Throttle valve was used to provide steam from the power plant at the right pressure to the reboiler in the capture plant

In the case of 90% capture the steam turbine design was such that the power plant still had the ability to extract full power from the steam cycle when the capture plant was not required to operate.

The analysis for each plant was based on a constant fuel flow of 1690 MW (HHV). The standard fuel costs used in the study were 0.5 $/GJ and the interest rate used was 10% with an amortisation period of 30 years. A flue gas desulphurisation plant was incorporated to reduce the SO_2 content in the flue gas to the level which the capture process could tolerate. All costs are those of March 2008 and the overall cost accuracy is estimated to be +/- 30%.

Table 9 Overview of performances and costs of the baseline PCC process with a natural draft cooled brown coal-fired power plants – 539 MW gross power output

Case	Existing power station No CO_2 capture (fully amortised)	Existing power station With maximum CO_2 capture – no steam cycle modification	Existing power station 90 % CO_2 capture – throttle valve	New power station No CO_2 capture	New power station 90 % CO_2 capture – throttle valve
Efficiency [HHV%]	28.9	22.8	17.1	28.9	17.1
Specific emission [tons/MWh]	1.2	1.1 29% CO_2 capture	0.2	1.2	0.2
Cooling water [m^3/MWh]	2.0	2.2	TBD	2.0	1.17 air cooling
Steam [m^3/MWh]	0.087	0.11	0.15	0.087	0.15
Capital costs [k\$/$kW_{e,net}$]	N.A.	1.2	2.5	2.9	7.4
Cost of generation [\$/MWh]	11	42	83	61	190
CO_2 Avoided Cost [\$/ton CO_2]	N.A.	264	75	n.a.	136

TBD = to be determined; N.A. = not applicable; MWh = MWh Nett

An overview of the results of the analysis is shown in Table 9. The following conclusions can be drawn from the analysis:

- For the standard PCC process, steam cycle modifications (installation of throttle valve to maintain pressure in low pressure turbines) result in the lowest costs per tonne avoided.
- 90% CO_2 capture from a fully amortised power plant will add \$72 per MWh to the cost of generation resulting in a cost of \$75 per tonne CO_2 avoided.
- 90% CO_2 capture from a new power plant will add \$130 per MWh to the cost of generation resulting in a \$136 per tonne CO_2 avoided.
- The generation efficiency at 90% CO_2 capture from a typical brown coal fired power station will be reduced by just over 40%, i.e., from 28.9 to 17.1%.
- The cooling water consumption drops by 22% when 29% CO_2 is captured from an existing power plant. Due to a decrease of the net power output, however, the cooling water consumption per MWh increases by 10%.

Results from this economic evaluation have potential applications onto a future new or retrofit Post-combustion Capture of CO_2 (PCC) process in a natural draft cooled brown coal-fired power plant.

8.2 Effects of Economic Parameters

The effects of the following economic parameters were investigated:

1. CO_2 capture capital cost

2. Capacity Factor
3. Amortisation period
4. Interest rate
5. Emissions Trading Scheme Tax or Credit

Figure 34 shows the effects of each parameter on the cost per CO_2 avoided with respect to a new subcritical power station. The effects of each parameter on the cost per CO_2 avoided with respect to an amortised subcritical power station can be seen in Figure 35. The effect of each parameter on the total long run marginal cost is demonstrated in Figure 36. Lastly, the effect of an emissions trading scheme in the economics of a PCC plant was also investigated in Figure 37.

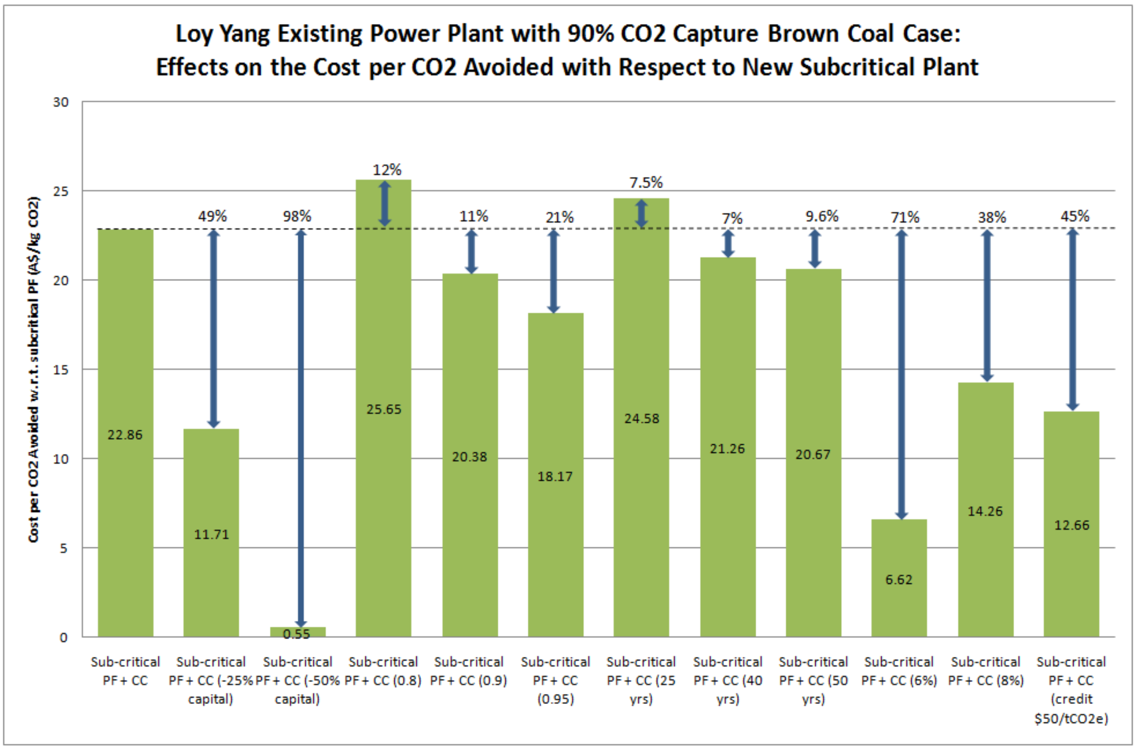


Figure 34: The effects on cost per CO2 avoided with respect to a new subcritical power plant of various parameters, CO_2 capture capital cost, capacity factor, amortisation period, interest rate and a $50 /tonne CO_2 credit for implementation of a capture technology.

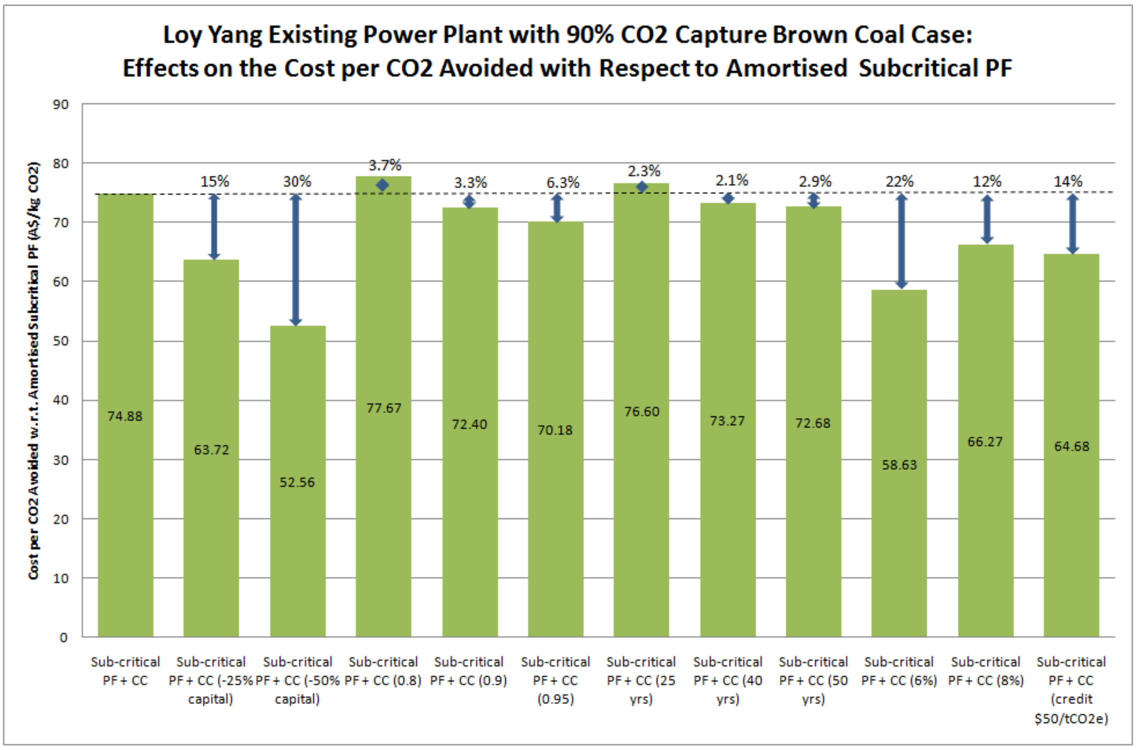


Figure 35: The effects on cost per CO2 avoided with respect to an amortised subcritical power plant of various parameters, CO_2 capture capital cost, capacity factor, amortisation period, interest rate and a $50 /tonne CO_2 credit for implementation of a capture technology.

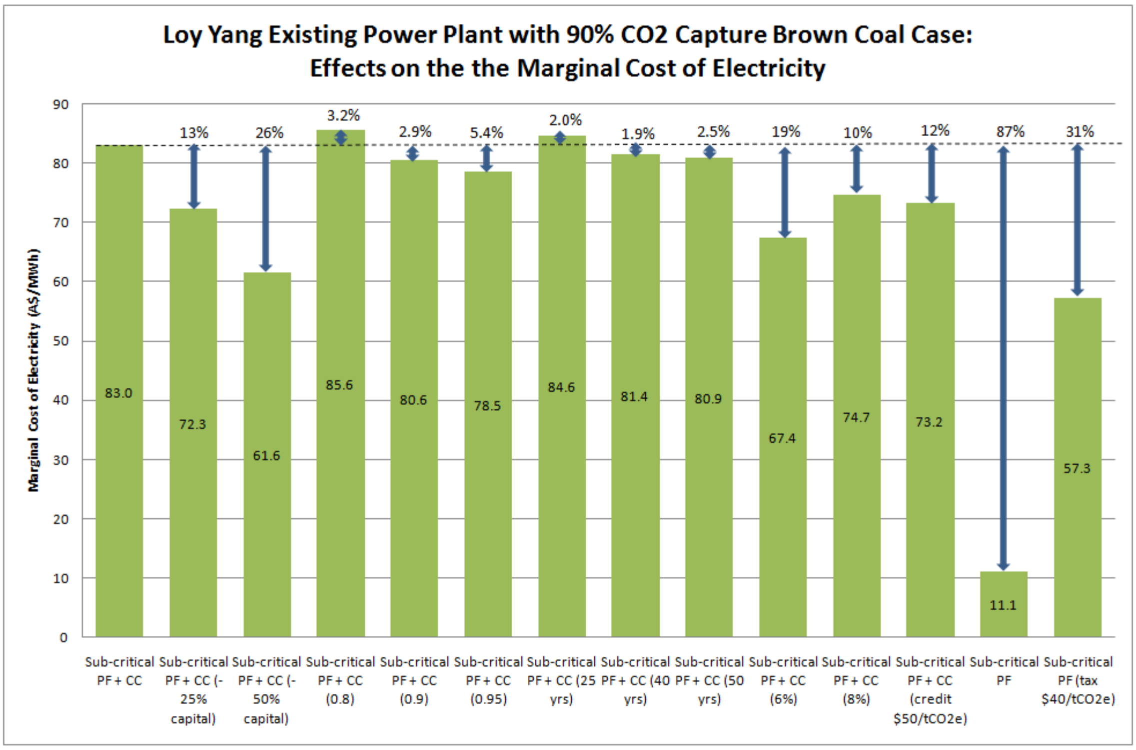


Figure 36: The effects on marginal cost of various parameters, CO_2 capture capital cost, capacity factor, amortisation period, interest rate and the emission trading scheme.

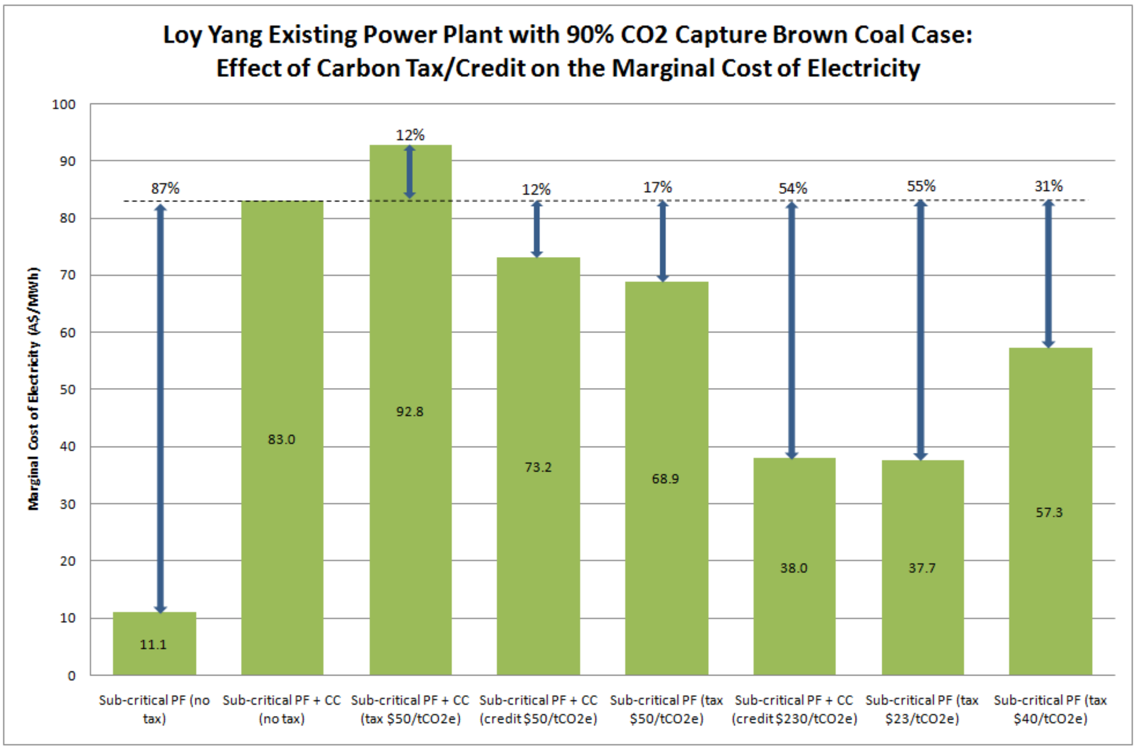


Figure 37: The effects on marginal cost of the emissions trading scheme, either tax for CO_2 emission or credit for implementation of capture technology.

8.2.1 Effect of CO_2 Capture Capital Cost

As seen in Figure 34, Figure 35 and Figure 36, the CO_2 capture plant capital cost variable has the most significant effect on cost of electricity generation compared to the other parameters. The CO_2 capital cost was reduced by 25% and 50% and the general effect on cost was observed as follows:

- Total marginal costs decreases considerably with a decrease in CO_2 capture capital cost;
- Cost per CO_2 avoided with respect to a new subcritical power station without capture significantly reduces with decreasing in CO_2 capture capital cost;
- Cost per CO_2 avoided with respect to an amortised subcritical power station without capture reduces with decreasing in CO_2 capture capital cost.

8.2.2 Effect of Capacity Factor and Amortisation Period

The capacity factor and amortisation period had the least influence on cost of electricity generation compared to other parameters. The industry standard for capacity factor of 0.85 is used for comparison against factors of 0.8, 0.9 and 0.95. The amortisation periods of 25 years, 40 years and 50 years is compared against the maximum amortisation period of 30 years given by the Australian Tax Office. Summary of the effects of capacity factor on costs are, same effects seen for amortisation period:

- Increasing capacity factor or amortisation period above the standard generally decreased the cost of electricity (for both marginal and cost of CO_2 avoided) by a smaller percentage compared to the other parameters;

- Decreasing the capacity factor or amortisation period below the standard resulted in a small increase of cost of electricity (for both marginal and cost of CO_2 avoided);

8.2.3 Effect of Interest Rate

The interest rate has a significant influence (almost as much as CO_2 capture capital cost) on the cost of electricity generation. The standard interest rate of 10% is used in the economic evaluation of a power plant is and 3% interest lost during the construction period is also taken into account. As seen in Figure 34, Figure 35 and Figure 36, reducing the interest rate to 6% or 8% decrease the cost of electricity, with a greater decrease seen in cost of CO_2 avoided compared to total long run marginal cost.

8.2.4 Effects of the Emissions Trading Scheme

The introduction of an emissions trading scheme will have a major effect on the economics of a power plant, refer to Figure 37. A rough non-expert estimate of a tax or credit of $50 per tonne of CO_2 emission (A/tCO_2$e) was used to observe a qualitative effects of the emissions trading scheme.

- A power plant with CO_2 capture may obtain a credit of $50/t$CO_2$e under the emission trading scheme. The effect of such on a subcritical PF power plant with CO_2 capture is a decrease in marginal cost by 11.8% compared to one without emissions credit.
- With an introduction of a $50/t$CO_2$e tax for a subcritical PF power plant with no CO_2 capture technology, the total marginal cost for the generation of electricity is still 17% smaller than that for a power plant with CO2.

Using a tax rate of $23 per tonne of CO_2 emission as recommended by the Australian Greens Party Leader Bob Brown [19]: capture

- With a $23/tCO2e tax for a subcritical PF power plant with no CO_2 capture technology, the total marginal cost for the generation of electricity is 54.6% smaller than that for a power plant with CO_2 capture
- With the introduction of the tax of $23/t$CO_2$e, the marginal cost will increase from 11.1 to 37.7 A$/MWh, increases by a factor of 3.4
- Thus, more rewards such as increased emission credits will need to be provided to give power plants more incentive to retrofit carbon capture technologies.

Using a tax rate of $40 per tonne of CO_2 emissions, the revised 2011 figure given as the amount industry groups were prepared to pay by the Australian Greens Party Leader Bob Brown [20].

- With a $40/t$CO_2$e tax for a subcritical PF power plant with no CO_2 capture technology, the total marginal cost for the generation of electricity is 30.9% smaller than that for a power plant with CO_2 capture
- With the introduction of the tax of $40/t$CO_2$e, the marginal cost will increase from 11.1 to 57.3 A$/MWh, increases by a factor of 5.1

Similar effects of a CO_2 tax on cost are observed with the cost of CO_2 avoided:

- For a subcritical PF power plant with CO_2 capture and $50/t$CO_2$e credit, the cost per CO_2 avoided with respect to a new subcritical PF without capture is reduced by 44.6%

- For a subcritical PF power plant with CO_2 capture and \$50/tCO_2e credit, the cost per CO_2 avoided with respect to an amortised subcritical PF without capture is reduced by 13.6%

8.2.5 Conclusion on sensitivity

The carbon capture capital cost and the interest rate are the two variables that have the greatest influence on the marginal cost and cost per CO_2 avoided for this case study. The capacity factor and the amortisation period have the least effect on the marginal cost and the cost per CO_2 avoided.

The effect of implementing an emissions trading scheme will vary depending on the amount of carbon tax to be charged and the credit received. Generally, a carbon tax will increase the marginal cost and cost per CO_2 avoided and carbon credits will reduce cost.

9. CO_2 CAPTURE PLANT CORROSION

One of the most severe operational issues observed in amine absorption processes for CO_2 capture is corrosion [21-23]. Corrosion of process equipment can cause a significant economical burden on the project by reducing productivity and reliability of the plant [21]. Thus, preventing corrosion of plant equipment is a major driver in choosing the optimal combination of amines and steel. Various grades of steel are available where cost tends to increase with corrosion resistance.

In laboratory conditions, an electrochemical method is under development at CSIRO to determine the optimal combination of amine solvent and steel type. The electrochemical corrosion rates for various solvent-steel combinations over a time period of days are measured and analysed.

To acquire a greater understanding of the mechanism, corrosion can be simulated under conditions similar to operating conditions in an amine treatment plant. Interpretation of experimental results from laboratory simulations of metal corrosion are limited as they do not take into account all of the system dynamics of an operating CO_2 capture amine plant [24].

Pilot plant studies are ideal for corrosion data and are more accurate for simulating the actual amine plant conditions [24]. The approaches to corrosion data collection from pilot plants include the use of probes or coupons installed at various locations throughout the plant [25, 26]. The corrosometer probes or electrode probes are used to test the instantaneous corrosion rate providing information of the short and long term effects of corrosion [24]. Corrosion coupons, commonly steel, are used to measure long-term weight loss measurements of the material and provide long term, time averaged corrosion behaviour under plant conditions over days or months [24, 26]. Examples of pilot plant corrosion data collection are discussed below.

9.1 Castor Pilot Plant

The Castor CO_2 capture pilot plant was built adjacent to a coal fired power station in Denmark [25]. The capacity of the plant is approximately 1 tonne CO_2 per hour [25]. Various solvents have been tested during the operation of the plant since 2006 [25]. In a study by Kittel *et al.*, weight loss was measured from the corrosion coupons located at six different locations, inlet and outlet of absorber for solvent streams, inlet and outlet of stripper for solvent, absorber flue gas outlet and stripper CO_2 gas outlet [25]. The solvent used was MEA 30% and corrosion was monitored over a 500 hour exposure time on two grades of steel, AISI 1018 carbon steel and AISI 316 or AISI 304 stainless steel [25].

The points of greatest temperature and fluid velocity are the most prone to corrosion, the highest corrosion rate was found at the outlet of the stripper [25]. For both grades of stainless steel used, there was full passivity resistance to corrosion and corrosion rates were within the acceptable range in all locations of the pilot plant [25]. Carbon steel unexpectedly exhibited corrosion resistance in high temperature rich solvent at the stripper inlet [25].

9.2 International Testing Centre (ITC) Regina Pilot Plant

In Canada, an ITC CO_2 capture pilot plant had the capacity to capture 1 tonne CO_2 per day from a natural gas burner [25]. The corrosion monitoring system used nine corrosometer probes that are able to withstand the typical operational conditions for a conventional CO_2 extraction plant [25]. The location of the nine probes include stripper overhead, rich amine to stripper, reflux and vapour, CO_2 product, stripper bottom, absorber bottom, lean amine to storage, absorber overhead and absorber off-gas [25]. The readings from the probes were measured as current density and converted into thickness reduction for analysis of corrosion effects [25].

From this CO_2 capture pilot plant investigation, the sections of the plant that are most susceptible to corrosion are the stripper inlet and outlet of solvent streams [25]. The data suggests that there is a strong correlation between high temperature and corrosion rate [25]. It appears that MEA concentration has a significant effect on increasing corrosion rate, small MEA and CO_2 concentration yielded low corrosion rate whereas high MEA and rich CO_2 streams had high corrosivity [25].

9.3 ITC Boundary Dam Pilot Plant

A CO_2 sequestration pilot plant constructed near SaskPower's boundary dam power station has the capacity to extract up to 4 tonnes of CO_2 per day [26]. The Boundary Dam pilot plant is considered to be of an adequate size to obtain appropriate data required from design of commercially sized plants [27]. This pilot plant is a semi-commercial demonstration ITC unit used to test the viability of potential CO_2 extraction technologies [26].

Instantaneous corrosion rate is monitored with corrosometer probes installed at various locations within the pilot plant including downstream SO_2 scrubber, amine absorber bottom, downstream of feed gas cooler, hot rich amine solvent to stripper, amine reboiler, stripper overhead, amine reclaimer and stripper bottom [26]. Corrosion coupons installed at various point in the pilot plant monitor the effects of long term corrosion [26]. Iron concentration in amine solvent during operation can also be measured to indirectly monitor corrosion in the entire unit [26]. During industrial operational conditions, corrosion of equipment in the Boundary Dam pilot plant is minimised by the addition of corrosion inhibitor [26].

The pilot plant investigations confirmed that corrosive environments within an amine CO_2 capture plant arise from both high temperature and high CO_2 loading [25, 26].

9.4 Electrochemical Method to Determine Corrosion Rates

The majority of the collected data was on the corrosion behaviour of stainless steel grade 304 in a MEA-H_2O-CO_2 system and AMP-PZ-H_2O-CO_2 system at 40℃ under lean and saturated CO_2 loaded conditions.

Corrosion of the materials and equipment is one of the most severe operational problems experienced in the amine-treating facilities. Corrosion causes considerable economic impact on an industrial scale, causing unplanned downtime, production losses and reduced equipment life [28], resulting in significant expenditure in addition to process costs. Furthermore, corrosion may have an adverse effect on the health and safety of personnel working at the amine-treating plant. The most noteworthy example is the incident that occurred at the amine-treating plant, owned and operated by the Union Oil Co., in Romeoville, Illinois, on the 23rd of July, 1984. Severe corrosion caused the rupture of an amine absorber pressure vessel, leading to an explosion, fire, morbidity and mortality and a cost of more than US$100 million in damages [29].

The search for novel amine solvents, which not only have increased kinetics or absorption/desorption capacity compared to conventional solvents, but also with reduced corrosivity has therefore become a top priority.

The objective of this work is to investigate the relative corrosivity of various amine solvents/solvent blends by measuring the corrosion rates of three steels; mild steel, stainless steel grade 304 and stainless steel grade 316 under the CO_2 loading conditions typically experienced in an amine-treating plant. The composition of the solvents, system temperatures and CO_2 loading concentrations to be used in the corrosion tests are summarised in Table 10: Amine solvent/solvent blend compositions for corrosion experiments0.

Table 10: Amine solvent/solvent blend compositions for corrosion experiments

Parameter	Conditions
System Temperature	Room temperature (22℃ ± 1℃), 40℃, 80℃
CO_2 Loading (mol CO_2/mol amine)	Purged (0.0 mol/mol), Lean (0.2-0.25 mol/mol),
	Saturated (0.5-0.75 mol/mol)
Solvent/Solvent Blend (w/w%)	MEA (30%)
	Blended Amine 3 (AMP/PZ) (25%/5%)

The results indicate that the relative corrosivity of the MEA-H_2O-CO_2 system versus the AMP-PZ-H_2O-CO_2 system on stainless steel grade 304 is dependent on the CO_2 loading of the system. Under purged CO_2 conditions (0.00 mol CO_2/mol amine), at room temperature, both systems were similarly corrosive. Under lean CO_2 loading conditions (0.2-0.25 mol CO_2/mol amine), the Blended Amine 3 system was significantly more corrosive than the MEA system. Under saturated CO_2 loading conditions (0.5-0.75 mol CO_2/mol amine), no definitive conclusion about the relative corrosivity of the systems can be made, due to lack of reproducibility in the Blended Amine 3 system measurement. However, the corrosion rate is similar in magnitude between the two systems, suggesting similar corrosivity under saturated conditions.

10. PUBLICATION LIST

- Artanto, Y., Jansen, J., Osborn, M., Pearson, P., Thong, Do, Cottrell, A.J, Meuleman, E., Feron, P.H.M. Performance of MEA and MEA-blends in the CSIRO PCC Pilot Plant at Loy Yang Power in Australia. *Paper accepted for publication by FUEL Journal 2012.*
- Artanto, Y., Jansen, J., Pearson, P., Puxty, G., Cottrell, A., Meuleman, E. and Feron, P., Pilot scale evaluation of AMP/PZ to capture CO_2 from flue gas of an Australian brown coal-fired power station. *Paper to be submitted to International Journal of Greenhouse Gas Control 2012/2013*.
- Artanto, Y., Jansen, J., Meuleman, E. and Feron, P.H.M. Behaviour of the Mass-Transfer Coefficient of CO_2 absorption in Different Solvents at the PCC Pilot Plant at Loy Yang Power. *Paper orally presented in the 5th International Conference on Clean Coal Technologies (CCT2011)*, Zaragoza, Spain, 8-12 May 2011.
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APPENDIX A

CO_2-lean loading and CO_2-rich loading of different solvents tested in LY pilot plant at various stripper bottom temperatures

Solvent name	L/G (L/Nm^3)	STR bottom temperature (℃)	CO_2-lean loading (mol CO_2/mol Amine)	CO_2-rich loading (mol CO_2/mol Amine)	
				Column 1	Column 2
			± 0.02	± 0.02	± 0.02
MEA	2.30	115	0.17	0.39	0.44
	2.32		0.19	0.38	0.46
	2.78		0.20	0.36	0.46
	3.22		0.21	0.35	0.44
	4.00		0.22	0.29	0.45
	4.12		0.21	0.34	0.46
	4.2		0.18	0.27	0.44
	2.34	112	0.21	N/A	N/A
	3.19		0.23	N/A	N/A
	3.97		0.27	N/A	N/A
Blended Amine 1	2.27	115	0.12	0.48	0.56
	3.04		0.11	0.37	0.51
	3.95		0.12	0.27	0.49
	2.05	112	0.18	0.52	0.58
	2.29		0.18	0.52	0.58
	2.75		0.19	0.49	0.57
	3.14		0.19	0.47	0.58
	3.16		0.19	0.34	0.46
	4.01		0.18	0.46	0.59
	5.02		0.19	0.51	0.59
Blended Amine 2	2.10	115	0.06	0.27	0.36
	2.47		0.04	0.24	0.34
	3.52		0.07	0.21	N/A
	3.60		0.04	0.18	0.30
	2.06	112	0.05	0.23	0.31
	2.46		0.04	0.25	0.33
	2.53		0.07	0.25	0.33
	2.58		0.07	0.23	0.34
	3.61		0.07	0.24	0.31
Blended Amine 3	3.1	115	0.04	-	0.26
	3.0	112	0.03	N/A	0.29

	3.7		0.08	N/A	0.27
	3.8		0.03	N/A	0.28
	3.8	110	0.14	N/A	0.28
	4.6		0.14	N/A	0.31
	4.9		N/A	N/A	N/A
	5.6		0.13	N/A	0.28

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