

Development of an Aqueous Ammonia Based PCC Technology for Australian Conditions

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1 Executive Summary

This research project focuses on the development of the advanced aqueous ammonia based post combustion capture (PCC) technology for significant reduction of CO₂ emission from coal fired power stations in Australia.

Currently, the commercially available PCC technology is mainly based on alkanol/alkyl amine solutions. This technology will reduce the power plant efficiency by 25-30% and involve significant capital/investment costs including the expensive flue gas desulfurization which is not installed in Australian power plants. As a promising solvent, aqueous ammonia has many advantages over amine-based capture technologies, including no degradation in the presence of O₂, a higher CO₂ absorption capacity than monoethanolamine (MEA), a low regeneration energy. It also has a potential to capture oxides of nitrogen (NO_x) and sulphur dioxide (SO₂) from the flue gas of coal-fired power plants, and to produce value-added chemicals, such as ammonium sulfate and ammonium nitrate, which are commonly used as fertiliser.

This research project is based on CSIRO PCC pilot plant trials with an aqueous ammonia based liquid absorbent under real flue gas conditions in a \$7M AUD pilot plant at Delta Electricity's Munmorah power station and ongoing work in this area. The pilot plant trials have confirmed the technical feasibility of the process and confirmed some of the expected benefits. The pilot plant trials have also highlighted some of the issues when using aqueous ammonia in a PCC process. These include a relatively low CO₂ absorption rate and high ammonia loss. These issues currently limit the economical feasibility of the aqueous ammonia based PCC process.

The strategy of the research proposed here is to extend a number of novel approaches developed previously by CSIRO to address the issues identified and make the process economically favourable. These novel approaches to be further explored in this project include promotion of CO₂ absorption rate through the introduction of additives, in particular those stable and environmentally friendly additives, combined removal of SO₂ and CO₂ and recovery of ammonia, and absorption under pressure to further enhance CO₂ absorption and suppress ammonia loss. In addition, the research project will combine an experimental and modelling approach to develop a rigorous rate based model for the aqueous ammonia based capture process which allows for reliable process simulation, optimisation and scale up. The outcomes of this research project will include the demonstration of the advanced aqueous ammonia based PCC at a CO₂ capture rate of at least 10 kg/h with CSIRO's process development facility in Newcastle. The advanced technology is expected to achieve a CO₂ absorption rate that is comparable with the standard MEA based solution, limit the power plant efficiency loss below 20%, and achieve the combined removal of SO₂ and recovery of ammonia to produce ammonium sulphate and eliminate additional flue gas desulfurization and reduce wash water consumption. The combined outcomes will enable the advanced technology to achieve a significant reduction in incremental levelised cost of electricity compared to state of the art, advanced amine based PCC technology.

This project is planned over a three-year time frame and is divided into 6 stages. This report summaries the progress of the projects and presents the results obtained in stage 3.

Stopped-flow spectrophotometry was used to elucidate the mechanism involved in the reaction of $\text{CO}_2(\text{aq})$ with ammonia/promoter mixture and understand the role of promoters in the reaction. Piperazine (PZ) and proline salt (potassium proline, PRO^-) were selected as the representative promoters in this study.

The fast kinetic reactions of $\text{CO}_2(\text{aq})$ with blended solutions containing ammonia/PZ were investigated using stopped-flow spectrophotometry at 25°C . Global analysis of the kinetic measurements using a chemical model which incorporated the complete reaction sets of the individual amines with CO_2 ($\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ and $\text{PZ-CO}_2\text{-H}_2\text{O}$) resulted in good agreement with experimental data. This confirmed the simple combination of those reactions involved in $\text{PZ-CO}_2\text{-H}_2\text{O}$ and $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ can explain the reaction mechanism between CO_2 and blended NH_3/PZ solutions. The analysis of CO_2 reaction pathways based on the developed kinetic model for $\text{PZ-NH}_3\text{-CO}_2\text{-H}_2\text{O}$ showed that PZ plays a major role in promoting CO_2 reaction in the solution with low CO_2 content, while with an increase in CO_2 loading in the solution, the contribution to CO_2 reaction from reactive amine species (PZCO_2^-) and ammonia become more important.

The fast kinetic reactions of $\text{CO}_2(\text{aq})$ with potassium proline were also investigated using stopped-flow spectrophotometry at 15 and 25°C . A detailed reaction scheme including all the reactions in the proline- CO_2 -water system has been developed and all unknown rate and equilibrium constants were reported at 15 and 25°C .

The milestones of the project for the report period have been achieved and the project is on track to achieve the milestones which are due on 30 September 2014.

2 Introduction

PCC is one of the leading capture technologies for significant reduction of CO₂ emission from coal fired power stations. Currently, the state of the art PCC technology is based on amine solutions, MEA in particular. A report by US Department of Energy (Ramezan, 2007) shows that the advanced amine technology will reduce the power plant efficiency by 30% and involve significant capital investment costs for retrofitting an existing coal fired power station (Conesville unit 5 in Ohio, subcritical, 90% capture). The incremental levelized cost of electricity (LCOE) is estimated to USD \$69/MWh. Recent studies of low CO₂ emission technologies for power generation in the Australian context (EPRI, 2010) show that addition of an advanced amine PCC process (state of the art) and CO₂ transport and storage to a new coal fired power station (pulverised black coal, supercritical, 750 MW sent out) will lead to a decrease in plant efficiency from 38% to 28.4 % (25.3% decrease) and an increase in LCOE from \$77 AUD/MWh to \$167 AUD/MWh (Figure 1 a). As shown in Figure 1b, the significant increase is due to increase in capital (plant cost), fuel, O&M and CO₂ transport and storage. The capital cost increase accounts for almost 60% of the total incremental LCOE. High capital costs are due to the fact that the new plants have to process more than 33% of coal extra to have the same power output and need to remove a large amount of CO₂ from an even larger amount of flue gas and compress it. This involves an increase in the size of the existing equipment and introduction of flue gas desulfurization (FGD) unit and CO₂ capture and compression facilities.

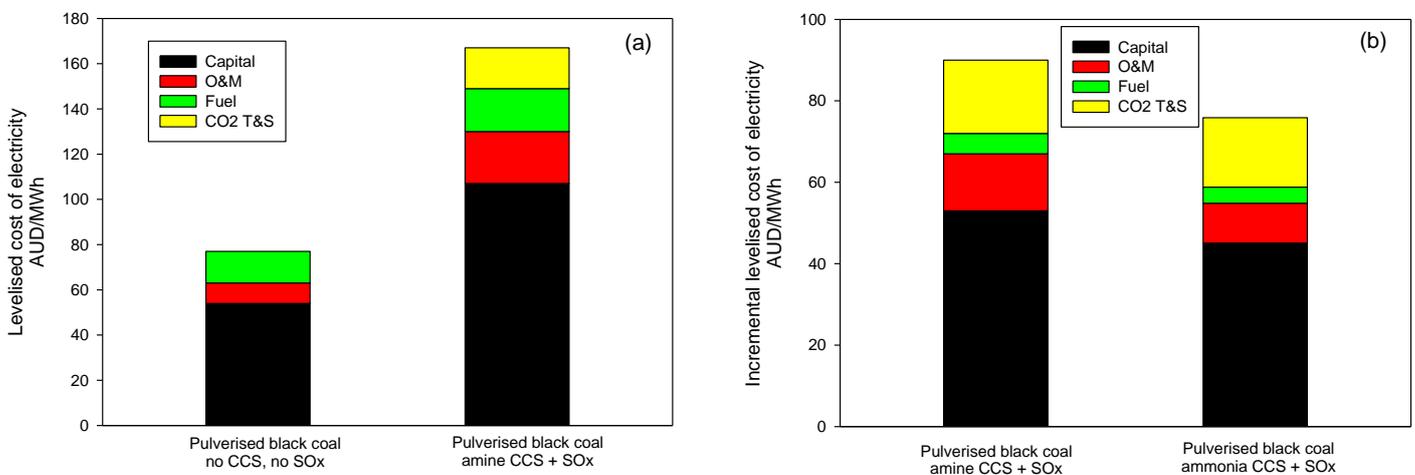


Figure 1 (a) Levelised cost of electricity (LCOE) for a new plant with and without CCS; (b) Incremental LCOE with the amine based CCS. The estimated incremental LCOE with the advanced ammonia based CCS is also included in (b) to demonstrate the potential benefits from using ammonia based CCS

The advanced amine solvent has poor SO_x tolerance which requires a deep cut in SO₂ content to levels below 10 ppm. The cost of building a desulfurization unit is substantial. According to the EPRI report, in a new plant in Australia in which the bare erected capital cost increase due to CO₂ removal and compression

is \$888 M AUD while capital increase due to clean up costs (installation of FGD) is \$90 M AUD (EPRI, 2010). FGD alone will count for more than 9% of the increased capital costs.

It is clear that to make CCS technologies, and in particular PCC, economically more feasible, the research focus will be on the reduction of capital costs by using more efficient, smaller and cheaper units and development of solvents which require low parasitic energy consumption. The low energy consumption means the use of less coal and treatment of less gas, which results in a smaller facility, and has less environmental and health effects. In this context, the current submission is proposed, aiming at the development of advanced aqueous ammonia based PCC to achieve a significant cost reduction and reduce environmental risks.

Advantages of aqueous ammonia based PCC

Aqueous ammonia is a promising emerging solvent for CO₂ capture. Compared to other amines, ammonia, as one of the most widely produced chemicals in the world, is a low cost solvent, does not degrade in the presence of O₂ and other species present in the flue gas, and is less corrosive. The environmental and health effects of ammonia are well studied and are more benign than amines. Ammonia has a high CO₂ removal capacity and a low regeneration energy. It also has the potential of capturing multiple components (NO_x, SO_x, CO₂ and Hg) (Ciferno, 2005) and producing value added products such as ammonium sulphate and ammonium nitrate, which are widely used as fertilisers. This potential is of particular interest to Australian power stations since desulfurization and DeNO_x are not implemented in Australia. It has been estimated by Powerspan (McLarnon, 2009) that the power plant efficiency loss is below 20% for an ammonia based capture process. A scoping study by US Department of Energy (Ciferno, 2005) suggested that the incremental cost of electricity using ammonia is less than half of that using traditional amines. It has to be pointed out that these reports assumed the availability of low temperature cooling water for solvent and flue gas cooling and recovery of ammonia. In Australia where ambient temperature is generally high, the energy consumption for production of low temperature cooling water is expected to be high, thus partially offsetting the energy saving from the solvent regeneration.

CSIRO has identified the aqueous ammonia based technology as a promising low cost technology for significant reduction of multiple components emissions from coal fired power stations in Australia. CSIRO and Delta Electricity completed pilot plant trials of the aqueous ammonia based capture technology under the real flue gas conditions in \$7 M AUD pilot plant scale research facility at Delta's Munmorah Power Station in 2010. The pilot plant trials have confirmed the benefits and technical feasibility of the process and its potential for application in the Australian power sector. The benefits include high CO₂ removal efficiency (more than 85%) and production of high purity of CO₂ (99-100 vol%), and effectiveness of the combined SO₂ removal (more than 95%) and ammonia recovery, high stability of ammonia solvent and low regeneration energy. Part of the results were published in a number of conferences and journal papers (Yu, 2011a and 2011b). It is the first time that results from an actual aqueous ammonia plant operating on real flue gases have been published.

Areas for improvement

The pilot plant trials have identified a number of research opportunities to further develop aqueous ammonia based capture technologies.

- Relatively low CO₂ absorption rate compared to amine based solvent, which results in 2-3 times the number of absorbers compared to monoethanolamine (MEA, the benchmark solvent) and thus higher capital costs.
- Relatively high ammonia loss at high CO₂ absorption rate. The consumption of wash water is high.
- Operating the desorption process in a similar pattern to regular amine processes will result in the formation of ammonium-bicarbonate solids in the condenser, resulting in blockage.
- The available process simulation models were insufficient to support the process optimisation and scale up.

This limits the economical feasibility of the aqueous ammonia based PCC process. In this research project, CSIRO will collaborate with the University of Newcastle and Curtin University of Technology (by way of student exchange or other collaboration), exploring and evaluating novel approaches and concepts to further advance the aqueous ammonia based PCC process in Australian context.

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3 Scope of the Project

This research project will further develop a promising aqueous ammonia (NH₃) based post combustion capture (PCC) process to achieve a significant reduction of investment and running cost in the Australian context and reduce potential environmental risks resulting from the implementation of PCC technologies.

The objectives of the project are:

1. Develop a novel aqueous ammonia based solvent which has fast CO₂ absorption rate equivalent to MEA while maintaining a low regeneration energy requirement.
2. Further advance the combined SO₂ removal and ammonia recovery technology to eliminate additional FGD, reduce the ammonia slip in the exiting flue gas to acceptable levels and produce a value added fertiliser, i.e. ammonium sulphate.
3. Further develop CSIRO technology (patent application no WO/2010/020017) to enhance CO₂ absorption, reduce ammonia loss and cooling water consumption.
4. Develop and validate a rigorous rate based model for the capture process which will guide process modification to achieve further savings on capture costs.

The research proposed here is to extend a number of novel approaches developed previously by CSIRO to address the issues identified, achieve the project objectives and thus make the process economically favourable. The new ideas and approaches include;

Promotion of CO₂ absorption rate through addition of promoters. Ammonia has been confirmed as a high loading capacity solvent and has a theoretically 1:1 ratio with CO₂ on a molar basis. It has been reported in a study by DOE (Ciferno, 2005) that the CO₂ carrying capacity in g CO₂ per g of ammonia solution (8 wt.%) circulated is 0.07 as compared with 0.036 g CO₂ per g MEA solution (20 wt.%). However, the CO₂ absorption rate is much lower in ammonia than in MEA, as identified by our recent pilot plant investigation (Yu, 2011a). This is preventing ammonia of achieving its high loading capacity and low regeneration energy potential.

The CO₂ absorption flux within the column can be correlated by $N_{CO_2} = K_G A (P_{CO_2} - P^*_{CO_2})$, where N_{CO_2} is CO₂ absorption flux, K_G mass transfer coefficient, P_{CO_2} partial pressure of CO₂ in the flue gas, $P^*_{CO_2}$ CO₂ equilibrium partial pressure in the solvent and A , effective interfacial surface area. For a given CO₂ absorption flux to achieve a typically 85-90% CO₂ removal efficiency, K_G and $(P_{CO_2} - P^*_{CO_2})$, need to be high in order to reduce A , which is directly related to the size of column (capital cost).

Recent studies by CSIRO showed that with introduction of a small amount of additive such as an amino acid salt which is environmentally friendly, stable and cheap, the CO₂ mass transfer coefficients increase significantly (Yu, 2012). With the introduction of 0.3 M additive to 3 M ammonia, the mass transfer coefficients increase dramatically compared to ammonia alone. They are comparable with MEA at high CO₂ loadings which are relevant to industrial applications. It is expected that further tests of new additives and optimisation of the solvent will lead to the development of the novel ammonia based solvent with high mass transfer coefficients which match and are even higher than those for MEA while maintaining its low regeneration energy.

The promotion of CO₂ absorption in ammonia is relatively new and the mechanism involved is unknown. Recently CSIRO has developed a new software tool in Matlab® to model CO₂ absorption into aqueous MEA, PZ, ammonia and binary mixtures of PZ with AMP or ammonia (Puxty, 2011). The tool solves partial differential and simultaneous equations describing diffusion and chemical reaction automatically derived from reactions written using chemical notation. It has been demonstrated that by using reactions that are chemically plausible the mass transfer in binary mixtures can be described by combining the chemical reactions and their associated parameters determined for single amines. The observed enhanced mass transfer in binary mixtures can be explained through chemical interactions occurring in the mixture without need to resort to using additional reactions or unusual transport phenomena (e.g. the shuttle mechanism). Such a tool in conjunction with a stopped flow reactor at the University of Newcastle will help elucidate the promotion mechanism (Wang, 2011).

Combined removal of SO₂ and recovery of ammonia. This research project also tests a hypothesis that an integrated approach can be used to achieve the combined removal of SO₂ and recovery of ammonia. In this approach, as described in our publication (Yu, 2011a), the wash water is circulated between the pre-treatment column (before absorber) and wash column (after absorber). Ammonia recovered from the flue gas in the wash column is used to capture SO₂ in the pre-treatment column. The results from the pilot plant trials have demonstrated the effectiveness of the approach. More than 95% SO₂ in the flue gas and more than 80% ammonia which slips to flue gas in the absorber can be removed from the gas phase by the wash water. The removal of SO₂ from flue gas by ammonia is the established technology and its fundamentals have been well documented (Kohl, Nielsen, 1997). Ammonia has a strong affinity for SO₂, thus permitting a compact absorber with a very low liquid-to-gas ratio. The high-purity, high-market value ammonium sulphate crystals were successfully compacted into a premium granular by-product. The combined removal of SO₂ and ammonia has a potential of reducing or offsetting the cost involved for removal of SO₂ and ammonia with production of saleable ammonium sulphate. The focus of the research project is to identify conditions under which SO₂ and ammonia are selectively removed at high efficiencies in preference to CO₂, understand the mechanism involved for oxidation of sulphite to sulphate, and explore more efficient methods for separation of ammonium sulphate from the aqueous ammonia solvent.

Absorption under pressure. This research project will also further develop a new concept developed by CSIRO. The flue gas is pressurised and absorption of CO₂, SO₂ and recovery of ammonia can take place under pressure. The flue gas cooling requirement is provided by the expansion of the flue gas after pressurisation. It is well known that pressurisation of flue gas will lead to high energy penalties but the size of absorption columns and ammonia loss as well as energy consumption for production of cooling water can be reduced significantly. In the Australian context, capital costs are the major contributors to the capture costs while fuel contribution is relatively small. The proposed high pressure absorption experiments and the rigorous process model to be developed will allow an evaluation of the feasibility of the concept and its economic viability.

Development of rate based absorption model. The available process simulation models were insufficient to support the process optimisation and scale up. The project will develop a rigorous rate based model for the advanced aqueous ammonia based capture process and validate the model with results from previous pilot plant trials and from experiments with the CSIRO's processes development facility. The developed model will be used to evaluate novel process concepts such as rich solvent recycle in the absorber and identify approaches to further reduce ammonia loss and energy and water consumption.

The research plan has been developed to carry out the proposed research activities. The project is planned over three year and divided into 6 stages with each stage being approximately 6 months. This report is the progress report of Stage 3 of the project and presents results from the stopped flow kinetic study.

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4 Approaches and Methodologies

The results obtained from the wetted wall column experiments have shown that the ammonia mixed with promoters such as piperazine, potassium sarcosinate and potassium proline can have a mass transfer coefficient more than double of those for ammonia alone at various CO₂ loadings (Yu, 2013). To fully understand the mechanism of CO₂ absorption into the mixture of ammonia and promoters and further improve the solvent formulation, it is necessary to develop the detailed reaction scheme for the reaction of CO₂ with the ammonia mixture in the liquid phase. To this end, stopped-flow spectrophotometric techniques have been used to develop a detailed reaction scheme including all the reactions in the ammonia-promoter-CO₂-water system. Previously we have used the same technique to study the reaction of CO₂ with sarcosine and sarcosine/ammonia respectively (Xiang, 2012 and 2013). The reaction scheme including all the reactions in the sarcosine-CO₂-water system has been developed and all unknown rate and equilibrium constants have been obtained. For the reaction of CO₂ with the blended ammonia/sarcosine, we did not observe any catalytic effects between ammonia and sarcosinate in the blended solution. The mechanism of the reaction of CO₂ with the ammonia/sarcosinate mixture is the simple combination of the individual reactions of ammonia and sarcosinate with CO₂. In this study, we extend the previous study to the reaction of CO₂ with PZ/ammonia and PRO⁻/ammonia, respectively. Since Wang et al. (2011) and Conway et al. (2013) have studied the reaction of CO₂ with ammonia and PZ respectively, our focus is to determine if the mechanism of the reaction of CO₂ with the ammonia/PZ mixture is the simple combination of the individual reactions of ammonia and PZ with CO₂. In case of the reaction of CO₂ with PRO⁻/ammonia, we focus on the reaction of CO₂ with PRO⁻ since the kinetic model for the PRO⁻-CO₂-H₂O is not available.

4.1 CO₂-Amine (NH₃/promoter)-H₂O system

4.1.1 CO₂-NH₃-PZ-H₂O system

The absorption of CO₂ into amine solutions incorporates a series of reversible reactions and protonation equilibria involving carbonate species, amine, and carbamate species. It should be noted in the following that the reaction mechanism of CO₂ absorbed into PZ promoted ammonia solutions is assumed to be the combination of the individual mechanism i.e. no additional reactions are required apart from those in the individual amine reaction sets (no synergistic effects).

In the absence of amine, CO₂(aq) is involved in two reversible reactions: one with water (H₂O), and the other with hydroxide (OH⁻) as described in reactions (R1)-(R2). In addition, a series of protonation equilibria involving CO₃²⁻, HCO₃⁻, and OH⁻, are described in reactions (R3) - (R5). The well determined constants related to reactions (R1)-(R5) were taken from literature (Harned, 1941; Maeda, 1987; Wang, 2009).



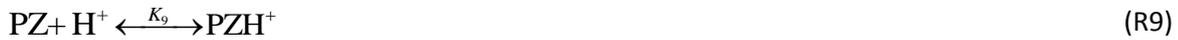


The series of reactions describing the interaction of ammonia with H^+/CO_2 are listed in reactions (R6) – (R8). The protonation of ammonia, K_6 , for reaction (R6), has been extensively investigated and values for this equilibrium constant were taken from the literature (Fernandes, 2012). The formation of ammonium carbamate/carbamic acid from the reaction of ammonia with CO_2 , k_7 , k_{-7} , K_7 , reaction (R8), together with the protonation/deprotonation of ammonia carbamate/carbamic acid, K_8 , reaction (R9), and the constants associated with these reactions, were taken from Wang et al.(2011).



A similar mechanism can be compiled for PZ. However, additional reactions are required to describe the interaction of H^+/CO_2 with PZ ensuing from the presence of the second amine group. The complete reaction set describing the interactions of H^+ and CO_2 with PZ species is shown in reactions (R9) – (R18).

Firstly, PZ can react with a single or two protons to form the singly and di-protonated species, PZH^+ , PZH_2^{2+} , K_9 , K_{10} , reactions (R9) – (R10). The values for those protonation equilibrium constants have been determined previously via potentiometric titration of the free amine and were taken from the literature (Fernandes, 2012).



Secondly, there are several species including PZ and mono-protonated PZ (PZH^+) which can react with CO_2 to form mono- and di- carbamate species, k_{11} , k_{-11} , K_{11} , k_{12} , k_{-12} , K_{12} , PZCO_2^- and mono-protonated PZCO_2^- (PZCO_2H), k_{13} , k_{-13} , K_{13} , k_{14} , k_{-14} , K_{14} , as shown in reactions (R11)-(R14).



The interaction of the mono and di-carbamate species, PZCO_2^- , PZCO_2H , $\text{PZ}(\text{CO}_2^-)_2$, $\text{PZ}(\text{CO}_2^-)\text{CO}_2\text{H}$, with H^+ is described in reactions (R15) – (R18).



The rate and equilibrium constants related to the reactions of $\text{CO}_2(\text{aq})$ with PZ species (PZ, PZH^+ , PZCOO^-), as well as the protonation constant of piperazine carbamates (PZCO_2^- , $\text{PZ}(\text{CO}_2)_2$), were taken from Conway et al. (2013).

The detailed reaction mechanism that describes all the interactions between PZ and ammonia with CO_2 , including all protonation equilibria, is shown graphically in Figure 2.

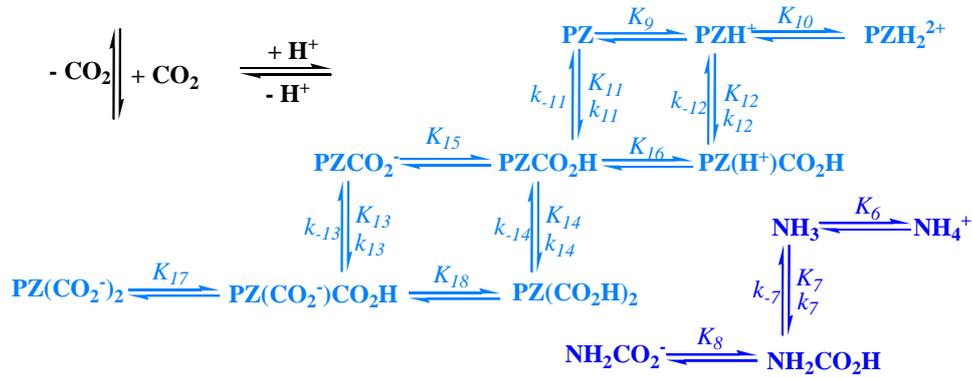


Figure 2 Extended reaction scheme involving a series of reactions between CO_2/H^+ and PZ/NH_3

4.1.2 $\text{CO}_2\text{-NH}_3\text{-PRO}^-\text{-H}_2\text{O}$ system

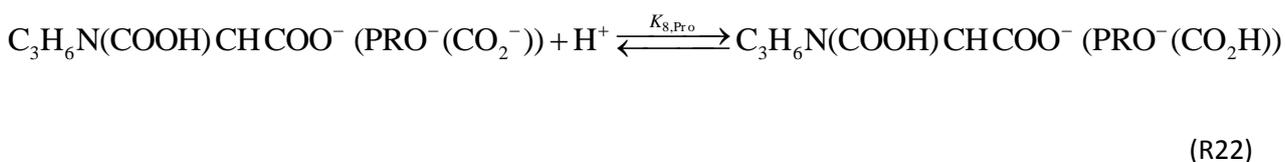
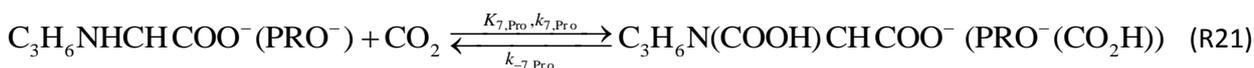
The study of the reaction of CO_2 with sarcosine/ammonia suggests that the reaction of CO_2 with the mixture of ammonia and sarcosine is simple combination of the individual reaction (Xiang, 2013). Considering the similarity between sarcosine and proline, it is reasonable to assume that the reaction of CO_2 with $\text{PRO}^-/\text{ammonia}$ should be a simple combination of the reaction of CO_2/PRO^- and $\text{CO}_2/\text{ammonia}$.

Proline exists in 3 different protonated forms, as shown in (R19) and (R20). Only the completely deprotonated form, PRO^- , has a deprotonated amino group and thus is a Lewis acid which is reactive towards $\text{CO}_2(\text{aq})$. Apart from reactions (R2)-(R9) present in the reaction scheme for $\text{CO}_2\text{-NH}_3\text{-PZ-H}_2\text{O}$ system, the following reactions are involved for the $\text{CO}_2\text{-NH}_3\text{-PRO}^-\text{-H}_2\text{O}$ system.

Protonation equilibriums of proline



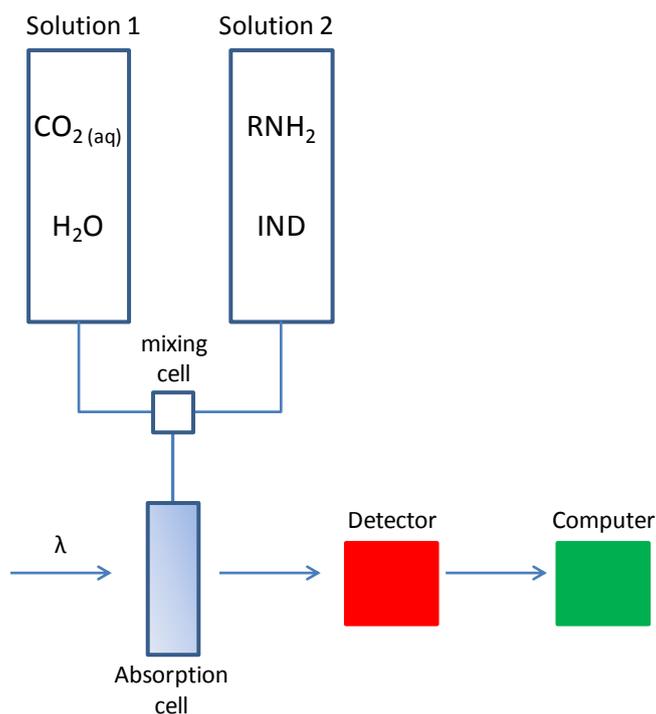
Carbamate formation



K_6 values used in this work were taken from our measurement (Yang, 2013). The values of K_{10} were taken from Sanaie (2005). $k_{7,\text{PRO}}$, $k_{-7,\text{PRO}}$ and $K_{8,\text{PRO}}$ are not available in the literature and will be determined in this work.

4.2 Stopped-flow reactor facility

Stopped-flow spectrophotometry is a common analytical technique used in the study of fast reaction kinetics on the millisecond timescale. A typical stopped-flow instrument incorporates a rapid mixing device which forces two or more solutions (contained in syringes) together through a high efficiency mixing chamber into an absorption cell after which the flow is abruptly stopped. A general schematic of the stopped-flow setup for the investigation of the CO_2 /amine kinetics is shown in Figure 3.



RNH_2 = amine, IND = coloured acid base indicator to observe pH changes during reactions.

Figure 3 General schematic of the stopped-flow setup

The progress of the reaction is monitored by observing changes in the absorbance of the solution with reaction time. This technique is well suited to the investigation of the fast kinetic reaction(s) between CO_2 and amines including ammonia, PZ and amino acids. However the lack of any useful absorption spectra in

the visible region between 350 – 700 nm requires a modification of the technique. The introduction of acid-base indicators to the system allows the indirect measurement of pH changes occurring in the solutions resulting from the formation of carbamic acid and carbonate species (carbonate, bicarbonate, carbonic acid) by observing changes in the absorbance spectrum of the indicator. Analysis of the resulting kinetic absorbance traces using the chemical model defined in the above section and additional reactions for indicators is used to determine corresponding reaction rate constants, and the equilibrium constant for the reaction of CO₂ with an amine. Alternatively, if the rate constants and equilibrium constants are given, the experimental absorbance results can be used to compare with the simulated results to determine if the developed chemical model is valid.

The kinetics of the reaction of amines with CO₂(aq) was performed on an Applied Photophysics DX-17 spectrophotometer equipped with a J&M Tidas MCS 500-3 diode-array detector; The reaction was followed by observing pH changes over the wavelength range 400-700 nm via coupling to acid-base indicators. Samples were thermostatted to the set temperature with an error of ±0.1 °C using a Julabo F20 water bath, and the exact temperature of the reaction recorded via a thermocouple within the stopped-flow reactor. Reactions were initiated by mixing aqueous solutions of amine (combined with the corresponding indicators) with a water solution saturated with a CO₂/N₂ gas mixture. All initial CO₂ concentrations, [CO₂]₀, were calculated from relative gas flow rates of N₂ and CO₂, assuming ideal behaviour, and the published saturation constant. Absorption changes were due to the protonation of thymol blue (log K = 9.05 at 25°C) as a result of the release of a proton from the carbamic acid, carbonic acid, and bicarbonate formed during the reactions.

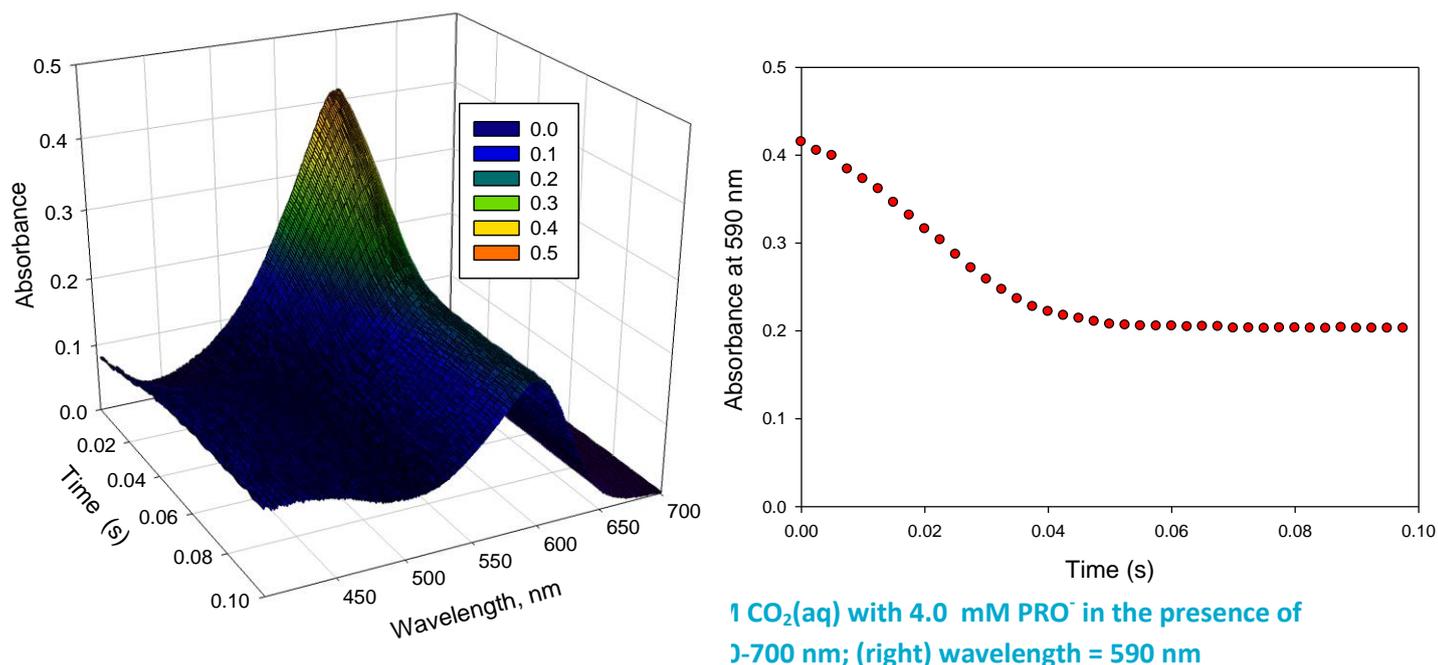
Table 1 lists the experimental conditions used in the stopped- flow kinetic study.

Table 1 Summary of the experimental conditions used in the stopped- flow kinetic study

Reactions	Temperature (°C)	Concentrations of CO ₂ (aq) (mM)	Concentrations of PZ, NH ₃ , PRO ⁻ (mM)	Concentration of indicator (µM)
CO ₂ (aq)+PZ/NH ₃	25	4.35	[PZ]=5; [NH ₃]=1,2,3,4,5	[Thymol blue]=12.5
	25	4.35	[PZ]=1,2,3,4,5; [NH ₃]=5	[Thymol blue]=12.5
CO ₂ (aq)+PRO ⁻	15	4.05	[PRO ⁻]=2,2.5, 4, 6	[Thymol blue]=12.5
	25	3.22	[PRO ⁻]=1.5, 2.5, 3, 4	[Thymol blue]=12.5
CO ₂ (aq)+PRO ⁻ /NH ₃	25	3.22	[PRO ⁻]=0.25 [NH ₃]=0.5, 1.5, 3.0	[Thymol blue]=12.5
	25	3.22	[NH ₃]=3 [PRO ⁻]=0.5, 1.5, 3.0	[Thymol blue]=12.5

Figure 4 (left) shows typical absorbance traces at wavelengths of 400-700 nm as a function of time in the reaction of 4.05 mM CO₂ (aq) with 4.0 mM PRO⁻ in the presence of 12.5 µM thymol blue at 15.0°C. For the

purpose of simplicity, the absorbance trace at wavelength of 590 nm is presented in the report, as shown in Figure 4 (right).



All of the stopped-flow measurement data were analysed collectively using ReactLab kinetics software (www.jplusconsulting.com) and in-house extensions of the software developed in Matlab.

4.3 Chemicals

High-purity CO₂ gas (BOC), N₂ (Coregas), potassium hydroxide (Sigma-Aldrich), piperazine (Sigma-Aldrich), L-proline (Sigma-Aldrich), thymol blue sodium salt (Sigma-Aldrich) were all used as obtained without further purification. Analytic grade ammonia with a weight concentration range of 25%-30% was purchased from Scharlau (Barcelona, Spain), and the exact ammonia concentration was determined by titration using standard hydrochloric acid (0.1 M solution, Fluka) with a titrator (Mettler Toledo T50). Potassium hydroxide solutions were prepared and standardized by potentiometric titration. Proline was neutralized with an equimolar amount of potassium hydroxide to generate deprotonated bases prior to the stopped-flow reactor experiments. Ultra-high-purity Milli-Q water boiled to remove CO₂ and used to prepare all stopped-flow solutions.

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<http://www.conference.net.au/chemeca2013/papers/26934.pdf>

5 Results and Discussion

5.1 Stopped flow kinetic study of the reaction of CO₂ with PZ/NH₃

A major goal of the kinetic research here involves the identification of the chemical mechanism and validation of the modelling approach and chemical constants for the individual amine components (NH₃/PZ) in blended systems of these amines from the analysis of fast stopped- flow kinetic measurements. The understanding gained from the initial validation study allows the assessment of the major chemical pathways for CO₂ in the blended solutions.

5.1.1 Validation of the kinetic model

The effect of the ratio of PZ and ammonia concentrations on the kinetic reactivity of a series of mixed aqueous solution of PZ/ammonia with CO₂ solutions were investigated with the stopped- flow reactor at 25 °C. Figures 5 (a) and (b) show absorbance traces at 590 nm over time in the reaction of a CO₂ solution (4.37 mM) with: (a) a series of PZ solutions containing 5.0 mM PZ and additional amounts of ammonia (initial ammonia concentration [NH₃]₀ = 1.0 mM– 5.0 mM); (b) a series of blended amines solutions containing 5.0 mM ammonia and additional amounts of PZ (initial PZ concentration [PZ]₀ = 1.0– 5.0 mM). 12.5 μM thymol blue was added as an indicator. This series of stopped-flow measurement data were analyzed globally (i.e single set of rate/equilibrium constants is common to all measurements) using a combined chemical model (R1)-(R18). It should be noted in this mechanism it is assumed there is no catalytic effect between PZ and ammonia and their reactions with CO₂.

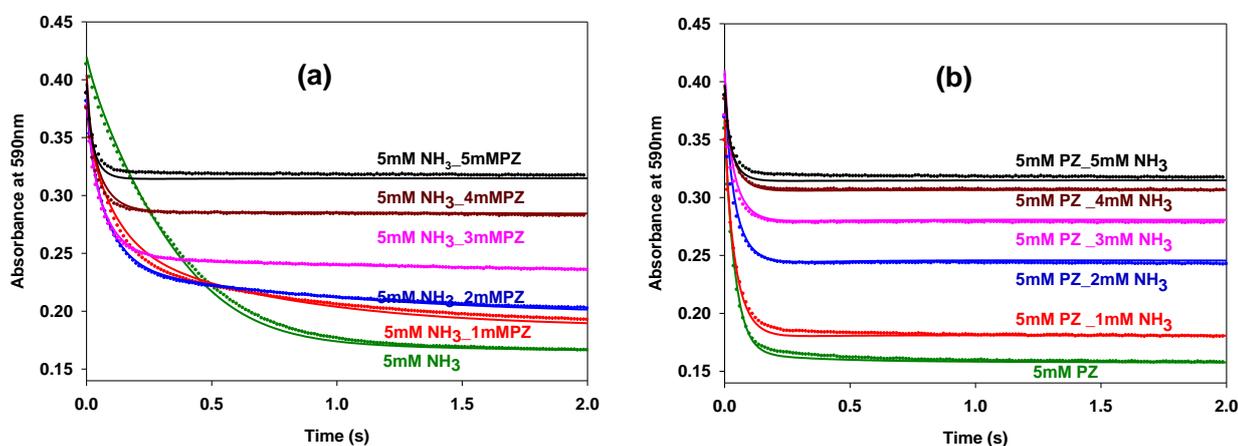


Figure 5 Measured and fitted absorbance versus time at 590 nm in the reaction of 4.37 mM CO₂ (aq) (a) with initial ammonia concentration of 5 mM blended with various PZ concentrations (0 to 5 mM); (b) with initial PZ concentration of 5 mM blended with various ammonia concentrations (0 to 5 mM) in the presence of 12.5 μM thymol blue indicator. Markers are the measured data and calculated traces are displayed as solid lines

As can be seen from Figure 5, the agreement between the measured and calculated data is good considering there was no regression of the constants with the experimented data set. Significant deviation

of the calculated data from the measured data was not observed, thus confirming the validity of the chemical mechanism and assumption the reactions in the blended ammonia/PZ system are in fact a combination of only the individual contributions of the two amine to the overall reaction.

5.1.2 Kinetic simulations

Kinetic simulation of reaction of CO₂ with PZ/ammonia

To better understand the reactions involved in CO₂ absorption into the blended amines system, PZ/ammonia, an example concentration profile displaying the species concentration (reactants + products) as well as pH variation over time in the reaction of 4.37 mM CO₂ with a solution containing 5 mM ammonia and 3 mM PZ is described in Figure 6(a) and Figure 6(b). The superior reactivity of PZ is clear with the majority of free PZ being consumed quickly (~0.05 seconds), as shown in Figure 6 (a), while ammonia is slower reacting. This is due to the fact that the differences in reactivity between CO₂ react with PZ and ammonia, with 24300 and 450 m³/kmol.s at 298 K, respectively (Conway, 2013; Wang, 2011). Hence the free ammonia in the blended amines solutions plays the major role in proton accepting, resulting in high NH₄⁺ concentration in solution (approximate 2.4 mM shown in Figure 6 (b)). This can be explained by the similar pKa values between PZ, PZCOO⁻ and ammonia (9.77, 9.66, and 9.237 respectively at 298K). It is likely that free ammonia, available at higher concentrations, is more favoured to accept proton and hence buffers the solution, resulting in the concentration of PZ species (PZ, PZH⁺ and PZCO₂⁻) being maintained at a high level and making the majority contribution to CO₂ absorption. This point will be demonstrated in the following section – CO₂ reaction pathways.

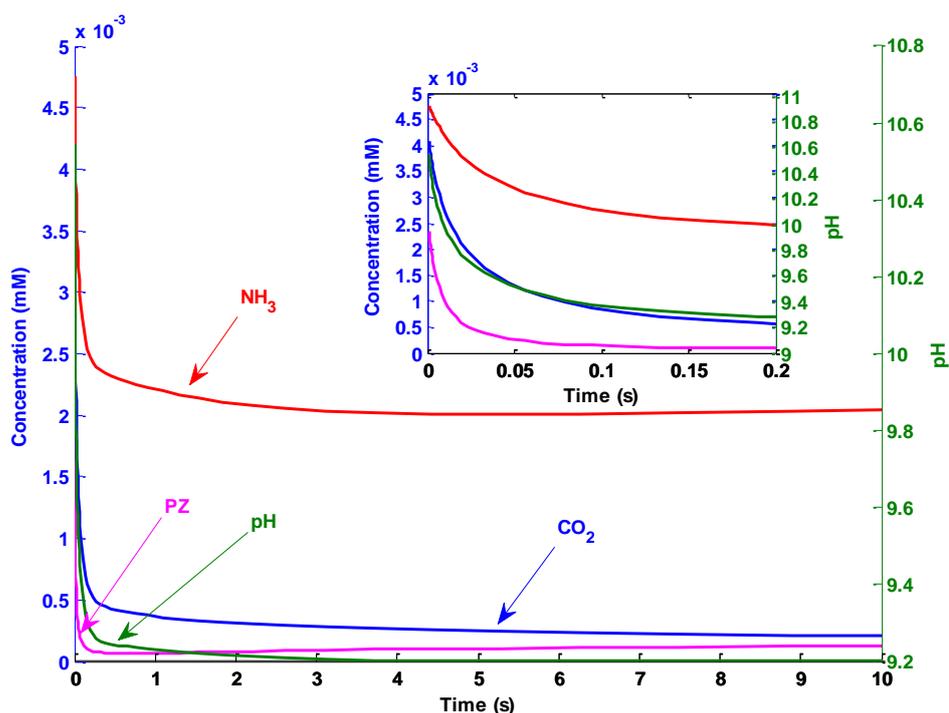


Figure 6(a) Calculated concentration profiles of reactants (PZ, ammonia and CO₂) as well as the pH change as a function of time (total 10s). The inset is an enlargement of the first 0.2 s of the reaction

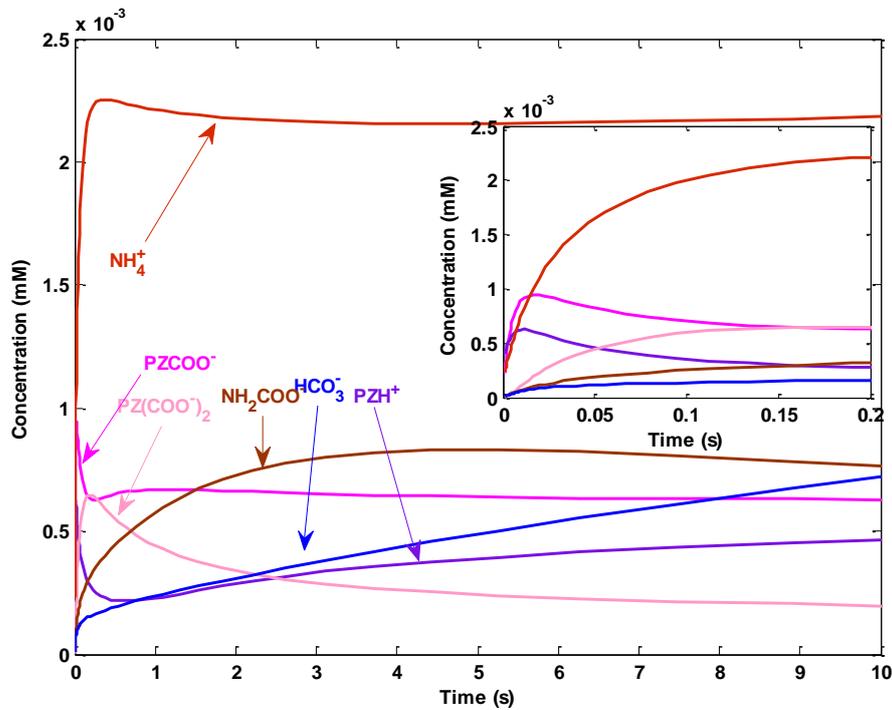


Figure 6(b) Calculated concentration profiles of some products (PZH^+ , PZCOO^- , $\text{PZ}(\text{COO}^-)_2$, NH_4^+ , NH_2COO^- , HCO_3^-) (total 10s). The inset is an enlargement of the first 0.2 s of the reaction

Figure 6(a) also shows that most CO_2 was absorbed within 0.1s due to the fast carbamate formation reaction. As shown in Figure 6(b), with an increase in reaction time, the concentrations of PZ, ammonia carbamates (PZCOO^- , $\text{PZ}(\text{COO}^-)_2$, and NH_2COO^-) increased rapidly initially to the maximum values and then dropped slowly due to the fact that the decomposition of PZ and ammonia carbamate species was becoming more important.

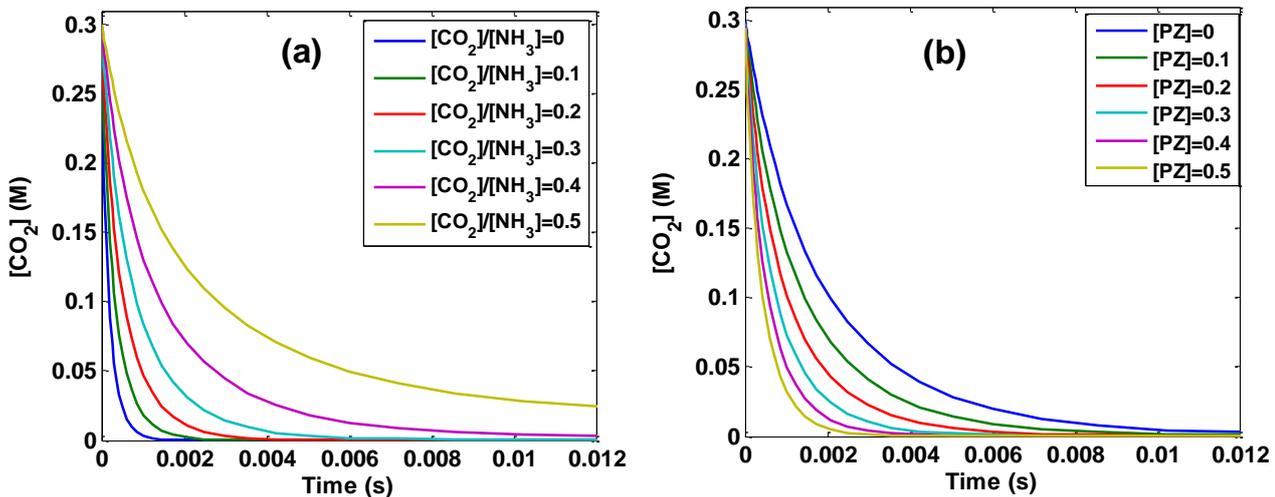


Figure 7 (a) CO_2 concentration profiles after reaction of 0.3 M CO_2 with 3 M ammonia/0.3 M PZ solutions with different $[\text{CO}_2]/[\text{NH}_3]$ ratios from 0 to 0.5; (b) CO_2 concentration profile after reaction of 0.3 M CO_2 with 3 M ammonia, $[\text{CO}_2]/[\text{NH}_3]$ ratio of 0.3 with different PZ concentrations from 0 to 0.5 M

Figure 7 (a) shows the CO₂ concentration profiles in the reaction of 0.3 M CO₂ with 3 M ammonia/0.3 M PZ solutions at different [CO₂]/[NH₃] ratios ranging from 0 to 0.5. Figure 7 (b) shows the CO₂ concentration profile after reaction of 0.3 M CO₂ with 3 M ammonia, [CO₂]/[NH₃] ratio of 0.3 with different PZ concentrations from 0 to 0.5 M. The concentrations of the equilibrated blended solutions of ammonia/PZ with different [CO₂]/[NH₃] ratios can be calculated based on the reaction scheme generated through the reactions among PZ-NH₃-CO₂-H₂O system, as shown in above section.

The CO₂ absorption rate (slope of the CO₂ concentration profile) decreases with the increasing of [CO₂]/[NH₃] ratio, and increases with the increasing of PZ concentration added into the blended ammonia/PZ solutions, which is consistent with the mass transfer results generated from the wetted-wall column (Yu, 2013).

CO₂ reaction pathways

A simple approach is described below and applied in this study to understand the promotion effect of PZ for the CO₂ absorption into blended ammonia/PZ solutions.

As described in the kinetic model, there are several species that can react with CO₂, making a contribution to total CO₂ absorption, including ammonia, PZ species (PZ, PZH⁺), PZ monocarbamate species (PZCOO⁻, PZCOOH), OH⁻ and H₂O. The reactivity, reaction rate, of PZ species with CO₂ follow the trend PZ > PZCO₂⁻ > PZH⁺ from our previous investigations (Conway, 2013). An extension of this trend to incorporate the reactivity of all species that could absorb CO₂ in the ammonia-PZ-CO₂-H₂O system show that the reactivity of these species follows the trend PZ > OH⁻ > PZCO₂⁻ > PZH⁺ > NH₃ > H₂O. CO₂ absorption contribution from PZ and PZH⁺ path ways are coupled to each other by the protonation reaction in reaction (R10). In this case, the CO₂ absorption contribution from PZ and PZH⁺ are calculated together as contribution from PZ species. Similarly, the CO₂ absorption contributions from PZCOO⁻ and PZCOOH are calculated together as contribution from PZ mono-carbamate species, as a result of the CO₂ absorption contribution from PZCOO⁻ and PZCOOH path coupled to each other by the protonation reaction in Equation (14).

The total reacted CO₂ concentration is the combination of CO₂ that reacts through each path way, as shown in equation (1).

$$-\frac{dCO_2}{dt} = r_{CO_2-total} = r_{CO_2-H_2O} + r_{CO_2-OH} + r_{CO_2-NH_3} + r_{CO_2-PZ} + r_{CO_2-PZCO_2^-} \quad (1)$$

where

$$r_{CO_2-H_2O} = k_1[CO_2] - k_{-1}[H_2CO_3] \quad (2)$$

$$r_{CO_2-OH} = k_2[CO_2][OH^-] - k_{-2}[HCO_3^-] \quad (3)$$

$$r_{CO_2-NH_3} = k_7[CO_2][NH_3] - k_{-7}[NH_2CO_2H] \quad (4)$$

$$r_{CO_2-PZ} = k_{11}[CO_2][PZ] - k_{-11}[PZCO_2H] + k_{12}[CO_2][PZH^+] - k_{-12}[PZ(H^+)CO_2H] \quad (5)$$

$$r_{CO_2-PZCO_2^-} = k_{13}[PZCO_2^-][CO_2] - k_{-13}[PZ(CO_2^-)CO_2H] + k_{14}[PZCO_2H][CO_2] - k_{-14}[PZ(CO_2H)_2] \quad (6)$$

The calculation of the CO₂ reaction rate through each pathway is shown in equations (2)–(6). The concentration of reacted CO₂, reacting by each of the different pathways, $[\text{CO}_2]_i^t$ as well as the sum of these pathways, $[\text{CO}_2]_{\text{total}}^t$, can be calculated based on equations (7) and (8), respectively.

$$[\text{CO}_2]_i^t = \int_0^t r_{\text{CO}_2-i} dt \quad (7)$$

$$[\text{CO}_2]_{\text{total}}^t = \int_0^t r_{\text{CO}_2-\text{total}} dt \quad (8)$$

Figure 8 shows the calculated concentration profile of total reacted CO₂ as well as the reacted CO₂ with different reactive species in the reaction of 0.3M CO₂ with the equilibrated PZ/ammonia solution at $[\text{CO}_2]/[\text{NH}_3]$ ratio varied from 0 to 0.5. As shown in Figure 8, the CO₂ absorption is almost completed within 0.01s with CO₂ reacted with ammonia, PZ species and PZCOO⁻, forming carbamate species in the solution. The CO₂ absorption contribution from H₂O and OH are negligible due to the small concentration of OH⁻, and the slow reaction between CO₂ and H₂O.

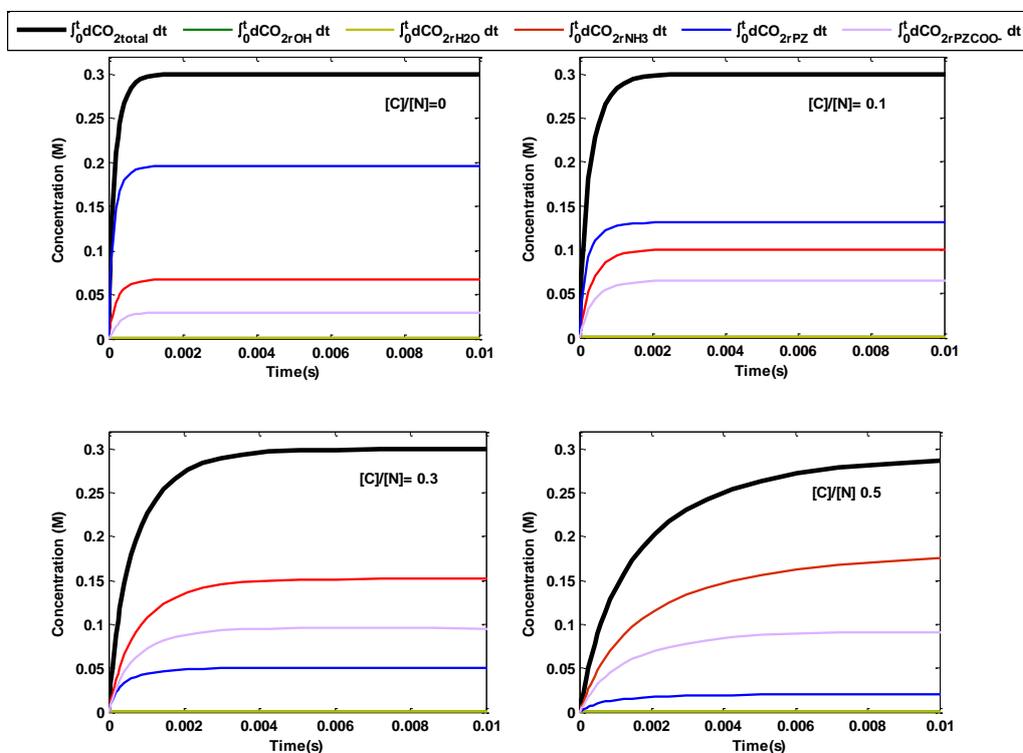


Figure 8 Concentration profiles of reacted CO₂ from each path way and the total reacted CO₂ concentration as a function of time at different $[\text{C}]/[\text{N}]$ ratios

Figure 9(left) shows the contribution distribution from each path way as a function of CO₂ loading at NH₃ concentration of 3M, PZ concentration of 0.3 M, and $[\text{C}]/[\text{N}]$ ratio ranging from 0 to 0.5.

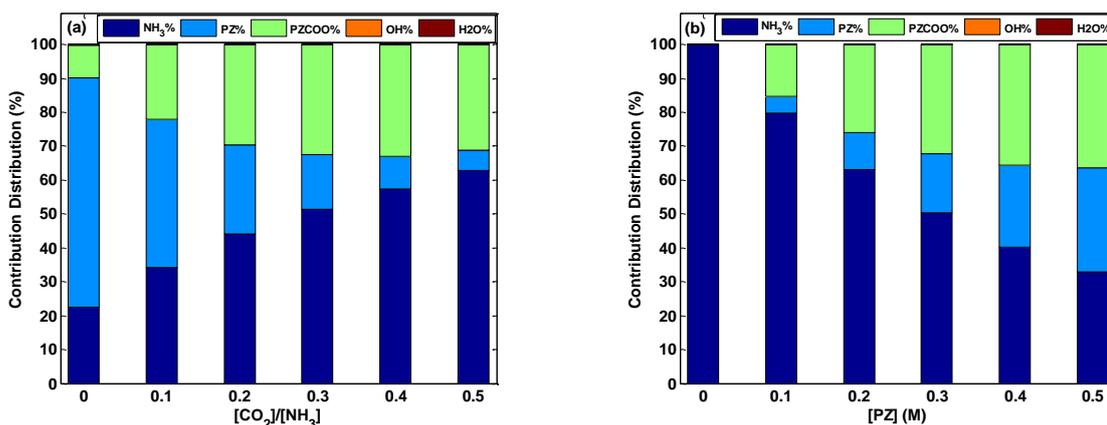


Figure 9 (left) Contribution distribution from each pathway as a function of CO₂ loading at NH₃ concentration of 3M and PZ concentration of 0.3 M; (right) Contribution distribution from each pathway as a function of PZ concentration at ammonia concentration of 3M and [C]/[N] of 0.3

As [C]/[N] ratio rose the absorption of CO₂ through reacting with ammonia increased, reaching approximately 60% at [C]/[N]=0.5. Similarly, the contribution of PZCO₂⁻ increased from 10% at 0 CO₂ loading to 30% at [C]/[N]=0.2. Upon a further increasing of [C]/[N] ratio, the contribution of PZCOO⁻ in total CO₂ absorption remained at the same level, which led to CO₂ absorption through reacting with PZCO₂⁻ becoming more significant than that of PZ. In other words, at high CO₂ loaded ammonia solutions PZCO₂⁻ is the most effective promotion species, to enhance the CO₂ absorption into aqueous ammonia solutions at high [C]/[N] ratios.

Figure 9 (right) shows the contribution distribution from each pathway as a function of PZ concentration at ammonia concentration of 3M, [C]/[N] of 0.3, and PZ concentration varied from 0 to 0.5M. With the increasing of PZ concentration added into the blended solutions, shown in Figure 7(b), the contribution of CO₂ absorption from ammonia dropped from almost 100% to 30%, becoming less important for the total CO₂ absorption. On the contrary, the contribution from PZ and PZCOO⁻ species, reacting with CO₂ absorption, increased with the increasing of PZ concentration. It is also confirmed by both Figure 9(left) and Figure 9(right) that the contribution of total CO₂ absorption from both OH⁻ and H₂O pathway was negligible.

5.2 Stopped flow kinetic study of the reaction of CO₂ with proline salt (PRO⁻)/ammonia

Using the stopped flow technique, we investigated the reaction of PRO⁻ and CO₂ and developed a detailed reaction scheme including all the reactions in the PRO⁻-NH₃-CO₂-water system. The unknown rate and equilibrium constants were obtained by global data fitting.

Figure 10 displays the absorbance (at 590 nm) change versus time of the reaction at various concentrations of PRO⁻ and temperatures of 15°C and 25°C in the presence of 12.5 μM thymol blue. The absorbance dropped rapidly in initial approximately 0.02 s, following by much slower absorbance change. Usually the absorbance change was recorded for about 10-15 s and the initial 0.1 s was the most critical time range.

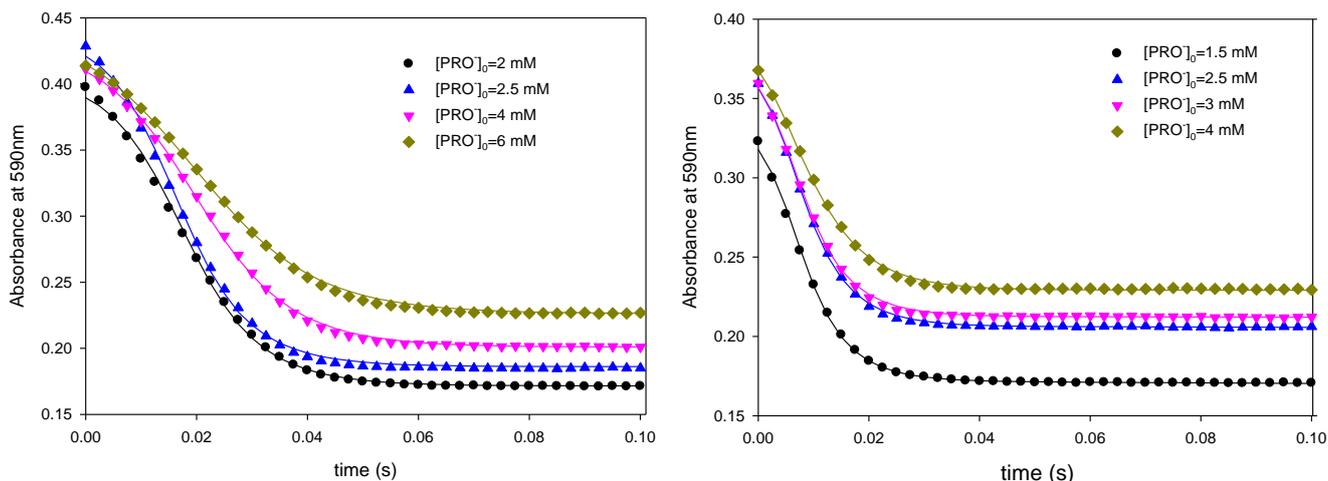


Figure 10 Absorbance at 590 nm versus time in the reaction of $\text{CO}_2(\text{aq})$ with different initial concentrations of PRO^- in the presence of $12.5 \mu\text{M}$ thymol blue. (a) ($[\text{PRO}^-]_0 = 2\text{-}6 \text{ mM}$); aqueous CO_2 ($[\text{CO}_2]_0 = 4.05 \text{ mM}$); $T = 15^\circ\text{C}$; (b) ($[\text{PRO}^-]_0 = 1.5\text{-}4 \text{ mM}$); aqueous CO_2 ($[\text{CO}_2]_0 = 3.22 \text{ mM}$); $T = 25^\circ\text{C}$. The solid markers are measured data and the lines are calculated profiles from data fitting

Global data fitting combines a number of carbamate formation measurements to fit 3 unknown parameters k_{7, PRO^-} , k_{-7, PRO^-} and K_{8, PRO^-} . Table 2 lists the corresponding rate and equilibrium constants at temperatures of 15 and 25°C .

Table 2 Corresponding rate and equilibrium constants at temperatures of 15 and 25°C

	15°C	25°C
$k_{7, \text{PRO}^-} (\text{M}^{-1} \text{s}^{-1})$	$33.1(\pm 0.1) \times 10^3$	$71.6(\pm 0.3) \times 10^3$
$k_{-7, \text{PRO}^-} (\text{s}^{-1})$	$48(\pm 1)$	$111(\pm 2)$
$K_{7, \text{PRO}^-} (\text{M}^{-1})$	$6.88(\pm 0.01) \times 10^2$	$6.4(\pm 0.2) \times 10^2$
$K_{8, \text{PRO}^-} (\text{M}^{-1})$	$1.45(\pm 0.03) \times 10^8$	$1.15(\pm 0.05) \times 10^8$

The study of the reaction of CO_2 with PZ/ammonia and sarcosine/ammonia suggests that the reaction of CO_2 with the mixture of ammonia and promoters (PZ or sarcosine) is simple combination of the individual reaction. Considering the similarity between sarcosine and proline, it is reasonable to assume that the reaction of CO_2 with PRO^-/NH_3 should be a simple combination of the reaction of CO_2 with PRO^- with the reaction of CO_2 with ammonia. Figure 11 shows the absorbance at 590 nm as a function of time in the reaction of 3.2 mM $\text{CO}_2(\text{aq})$ with various initial concentrations of NH_3/PRO^- blended solutions at 25°C in the presence of $12.5 \mu\text{M}$ thymol blue indicator. The dotted markers are experimental results from the stopped-flow study and the solid lines are calculated profile using the $\text{NH}_3\text{-PRO}^-\text{-CO}_2\text{-H}_2\text{O}$ reaction scheme which simply combines reactions in $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ and $\text{PRO}^-\text{-CO}_2\text{-H}_2\text{O}$ systems without additional reactions. Figure 11 illustrates that the calculated results agree reasonably well with the measured data. This

confirms the assumption that the reaction of CO_2 with PRO^-/NH_3 is a simple combination of the reaction of CO_2 with PRO^- with the reaction of CO_2 with ammonia is valid.

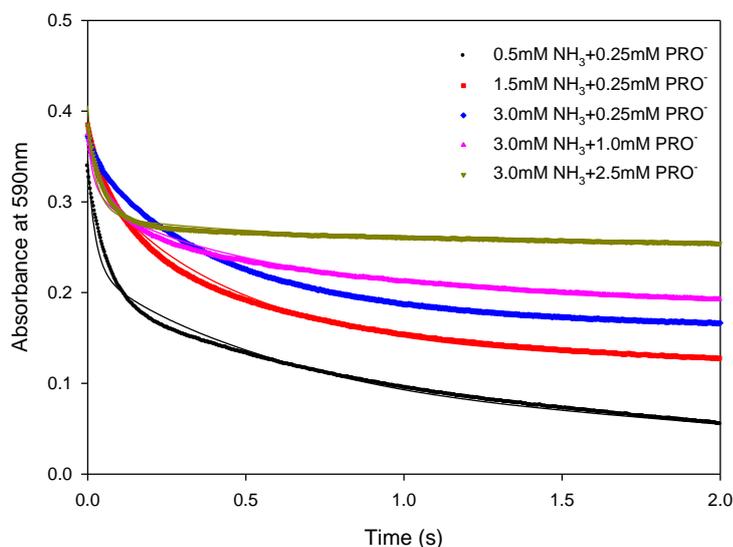


Figure 11 Absorbance at 590 nm as a function of time in the reactions of 3.22 mM CO_2 (aq) with various initial concentrations of NH_3/PRO^- blended solutions at 25°C. Dotted markers are measured data; lines are calculated profiles

Using the $\text{PRO}^-/\text{NH}_3/\text{CO}_2/\text{H}_2\text{O}$ reaction scheme, we can perform an analysis similar to that for PZ presented in the previous section and gain an understanding of role of PRO^- in the reaction of CO_2 with ammonia. One example of the analysis is the calculation of species profile as a function of reaction time in the reaction of CO_2 with the mixture of ammonia/ PRO^- .

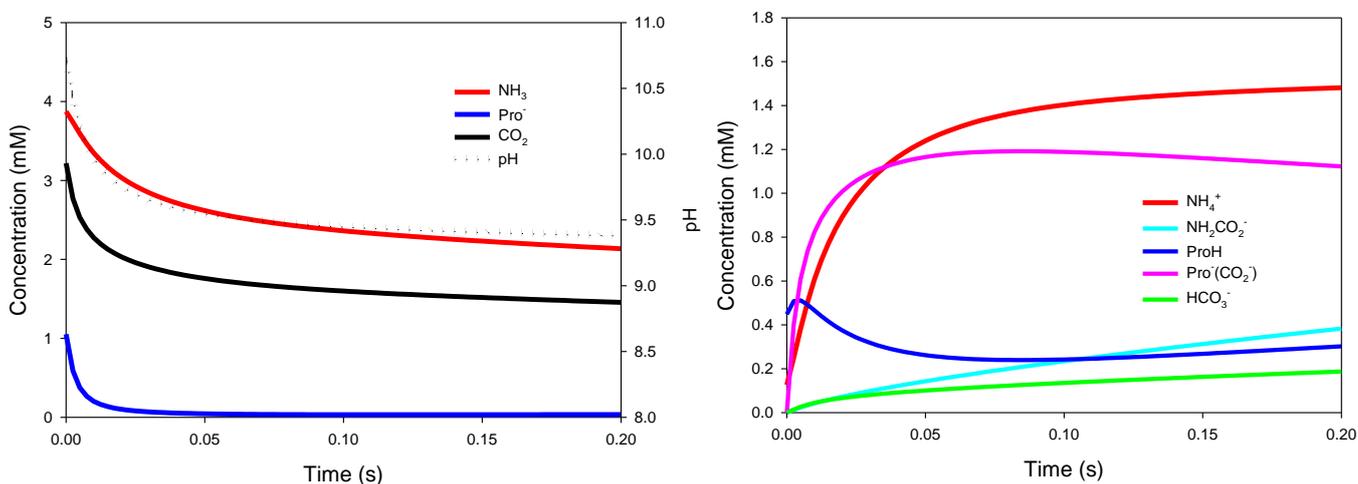


Figure 12 (left) Calculated reactant concentration profiles and pH (dotted line) and products (right) in the reaction of 3.3 mM CO_2 (aq) with 4 mM ammonia + 1.5 mM PRO^- blended solution at $T=25^\circ\text{C}$. Initial 0.2 s

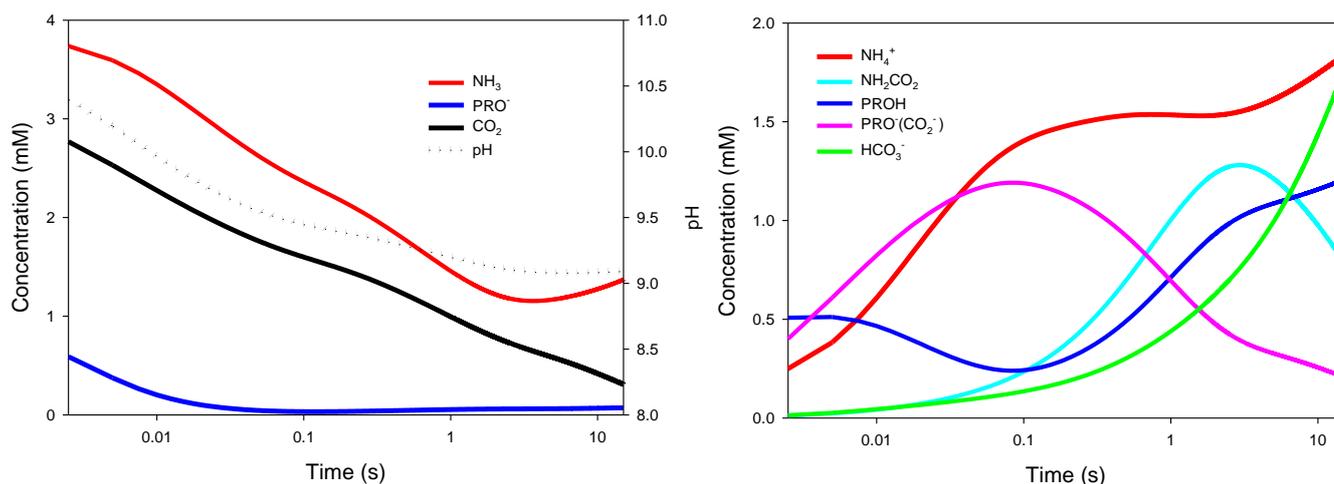


Figure 13 (left) Calculated reactant concentration profiles and pH (dotted line) and products (right) in the reaction of 3.3 mM CO₂(aq) with 4 mM ammonia + 1.5 mM PRO⁻ blended solution at T=25°C . Total 15 s

Figures 12 and 13 show the calculated species concentration profiles and pH as a function of time in the reaction of 3.3 mM CO₂(aq) with 4 mM ammonia + 1.5 mM PRO⁻ blended solution. As shown in the initial 0.2 s of the reaction, PRO⁻ concentration drops dramatically, accompanied by a fast increase of PROH and PRO⁻(CO₂⁻). The concentration of ammonia drops more slowly than the concentration of PRO⁻, accompanied by a slow increase of NH₂CO₂⁻ and a relatively faster increase of NH₄⁺. In this period, the major reaction for CO₂ consumption is proline/ammonium carbamate formation.

Figure 13 (right) shows the calculated reactants and products concentration profiles in 15 s, using a common logarithmic time axis. After the initial 0.1 s, most PRO⁻ was consumed and the contribution of PRO⁻ to the consumption of CO₂(aq) was small. During the reaction time of 0.1 to 1, ammonia made the major contribution to the consumption of CO₂(aq) and the amount of reaction product, NH₂CO₂⁻ increased accordingly. After 1 s, the change in PRO⁻ and ammonia concentration was small and the contribution of PRO⁻ and ammonia to the consumption of CO₂(aq) was less important than the slow reactions between CO₂(aq) and OH⁻/water to form bicarbonate. As a consequence, HCO₃⁻ concentration increased during the reaction. The continuous decrease in CO₂ concentration caused the decomposition of ammonium carbamate and proline carbamate. The pH of the solution ranged from 10.7 to about 9.0 during the reaction, followed by the changes in PROH and NH₄⁺ concentration, which were mainly determined by the pH.

The analysis of the species concentration profiles reveals that the role of PRO⁻ in the mixture is that it can react with CO₂ at a much faster rate than that of ammonia. However, it should be pointed out that with an increase in CO₂ content in the mixture, its role in CO₂ absorption dropped significantly.

It should be pointed out that the kinetics of the reaction of CO₂(aq) with PZ/ammonia mixture or PRO⁻/ammonia mixture was performed at 25°C only. It is well known that absorption temperature has a big impact on ammonia loss and an increase in absorption temperature will lead to an increase in ammonia loss. To reduce ammonia loss, it is ideal to operate CO₂ absorption at low temperatures. Considering

Australian ambient conditions, it is hoped that the CO₂ absorption process can be operated at 15-30°C. We chose 25°C as the typical temperature considering the ammonia loss and Australian ambient condition. In addition, the rate and equilibrium constants related to the reactions of CO₂(aq) with PZ species (PZ, PZH⁺, PZCOO⁻) were taken from Conway et al. (2013). They accurately determined the rate and equilibrium constants at 25°C only. However, we believe that the temperature variation in the range of 15-30°C will not affect the general conclusions made in the report. The effect of temperature on ammonia loss will be covered in the following reports.

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6 Conclusions

The project has made a good progress and has completed the milestones listed in the reporting period.

The focus of the project in the reporting period was to perform stopped-flow kinetic studies of the reaction of $\text{CO}_2(\text{aq})$ with ammonia blended with selected promoters and develop detailed kinetic models for the NH_3 -promoter- CO_2 - H_2O systems. The availability of the detailed kinetic models for NH_3 -promoter- CO_2 - H_2O systems can help elucidate the role of the promoters and improve the solvent formulation. Piperazine (PZ) and proline salt (potassium proline, PRO^-) were selected since they were confirmed to be effective promoters in our previous studies.

The fast kinetic reactions of $\text{CO}_2(\text{aq})$ with blended solutions containing ammonia/PZ were investigated at 25°C using stopped-flow spectrophotometry by following the pH changes over the wavelength range 400-700 nm via coupling to pH indicators. Global analysis of the kinetic measurements using a chemical model which incorporated the complete reaction sets of the individual amines with CO_2 , NH_3 - CO_2 - H_2O and PZ- CO_2 - H_2O , resulted in good agreement with experimental data. This confirmed the simple combination of those reactions involved in PZ- CO_2 - H_2O and NH_3 - CO_2 - H_2O can explain the reaction mechanism between CO_2 and blended NH_3 /PZ solutions. The analysis of CO_2 reaction pathways based on the developed kinetic model for PZ- NH_3 - CO_2 - H_2O showed that PZ plays a major role in promoting CO_2 reaction in the solution with low CO_2 content, while with an increase in CO_2 loading in the solution, the contribution to CO_2 reaction from reactive amine species (PZCO_2^-) and ammonia become more important.

The stopped-flow spectrophotometry was also used to study the fast kinetic reactions of $\text{CO}_2(\text{aq})$ with PRO^- at 15 and 25°C . A detailed reaction scheme including all the reactions in the PRO^- - CO_2 water system has been developed and all unknown rate and equilibrium constants were reported at 15 and 25°C . The kinetic study of the reaction of $\text{CO}_2(\text{aq.})$ with NH_3/PRO^- blended solutions at 25°C confirms that the simple combination of those reactions involved in PRO^- - CO_2 - H_2O and NH_3 - CO_2 - H_2O can explain the reaction mechanism between CO_2 and blended NH_3/PRO^- solutions.

7 Future work

In the next 6 months, we will follow the plan specified in the proposal and carry out the following work

- Validation of the rate based model using the previous pilot plant results. The focus is on the CO₂ regeneration in the stripper.
- Conducting the SO₂ and NH₃ absorption experiments
- Process modelling of the combined removal of SO₂ and CO₂ using aqueous ammonia
- Further optimisation of the solvent formulation to develop aqueous ammonia based solvents which can match MEA in terms of CO₂ absorption kinetics.

8 Appendix - Status of Milestones

Date Due	Description	ANLEC Funding (\$)	Status
15/06/2012	Contract signing	\$ 212,630	Complete
30/03/2013	Completion of recruitment of PhD students and research project officer Delivery of a progress report approved by ANLEC R&D which shows the following: (1) Results have been generated from wetted wall column screening experiments and promoters for stopped flow reactor experiments have been identified. (2) The framework for the rate based model has been established and the comparison between the modelling work and pilot plant results has been made. (3) Analytic methods for gas and liquid analysis have been established.	\$ 68,042	Complete
30/09/2013	Completion of experiments for screening promoters and optimisation of solvent formulation on wetted wall column Delivery of a progress and technical report approved by ANLEC R&D which includes: (1) Status of the research activities and milestone (2) Approaches and methodologies used in the screening experiments (3) Results obtained (4) Evidence that the following has been achieved: a. The new aqueous ammonia based solvent can absorb CO ₂ as least 2 times as fast as the solvent based on aqueous ammonia alone Delivery of an industry report approved by ANLEC R&D which includes a description of: (1) Recent advancement of solvent development for post combustion capture including aqueous ammonia around the world (2) Results from this research project (3) The impact of research achievements from this project on the advancement of aqueous ammonia based PCC processes for application in Australia	\$ 68,042	Complete
31/03/2014	Completion of experiments on stopped flow reactor Delivery of a progress and technical report approved by ANLEC R&D which includes: (1) Status of the research activities and milestones (2) Approaches and methodologies used in the stopped flow reactor experiments (3) Results from stopped flow reactor experiments and discussion	\$ 59,537	Complete This report
30/09/2014	Completion of process modelling for elucidation of promotion mechanism and completion of SO ₂ and NH ₃ absorption experiments Delivery of a progress and technical report approved	\$ 59,537	50%

- by ANLEC R&D which includes:
- (1) Status of the research activities and milestone
 - (2) Approaches and methodologies used in the process modelling and SO₂ and NH₃ absorption experiments
 - (3) Results obtained
 - (4) Evidence that the following has been achieved:
 - a. Develop a novel aqueous ammonia based solvent which can achieve a CO₂ absorption rate that can match the standard MEA based solvent
 - b. Develop a rigorous rate based model for the aqueous ammonia based CO₂ capture process and validate the model with results from previous pilot plant trials
 - c. Achieve the combined removal of SO₂ and recovery of ammonia and eliminate additional flue gas desulfurization. This includes:
 - Identification and validation of experimental conditions under which SO₂ in the flue gas is selectively removed in preference to CO₂ by ammonia (flue gas pre-treatment). More than 90% of SO₂ will be removed in the pre-treatment stage in which CO₂ removal is negligible.
 - Ammonia in the flue gas can be reduced to an acceptable level by SO₂ solution (flue gas post-treatment).

Delivery of an industry report approved by ANLEC R&D which includes a description of:

- (1) Recent advancement of solvent development for post combustion capture including aqueous ammonia
- (2) Summary of results obtained from this research project
- (3) Impact of the research achievements from this project on the advancement of aqueous ammonia based PCC processes for application in Australia

31/03/2015	Completion of high pressure experiments. Delivery of a progress and technical report approved by ANLEC R&D which includes: (1) Status of the research activities and milestone (2) Approaches and methodologies used in the high pressure experiments (3) Results obtained	\$ 59,537	Ongoing 20% complete
31/08/2015	Submit Draft of Final Report to ANLEC R&D for review	\$ 68,042	Not yet started
30/09/2015	Completion of process modification, evaluation and demonstration of advanced ammonia technology; Completion of development of rigorous process development and delivery of scale up design. Final Report submitted as acceptable to ANLEC R&D Delivery of an industry report which includes a	\$ 255,157	Not yet started

description of:

- (1) Recent advancement of solvent development for post combustion capture including aqueous ammonia
 - (2) Summary of results obtained from this research project
 - (3) Impact of the research achievements from this project on the advancement of aqueous ammonia based PCC processes for application in Australia
 - (4) Evaluation of technical and economic feasibility for application of the improved process developed from this project
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