Recent progress and new developments in post-combustion carbon-capture technology with amine based solvents

Zhiwu (Henry) Liang^{1,6(*)}, Wichitpan Rongwong^{1,4,6}, Helei Liu¹, Kaiyun Fu¹, Hongxia Gao¹,
Cao Fan¹, Rui Zhang¹, Teerawat Sema^{1,6}, Amr Henni⁶, Kazi Sumon⁶, Devjyoti Nath⁶,
Don Gelowitz⁶, Wayuta Srisang⁶, Chintana Saiwan^{3,6}, Abdelbaki Benamor⁴, Mohammed Al-Marri⁴
Huancong Shi⁶, Teeradet Supap^{3,6}, Christine Chan^{2,6}, Qing Zhou^{2,6}, Mohammad Abu-Zahra⁵
Malcolm Wilson^{1,6}, Wilfred Olson¹, Raphael Idem^{1,3,6(*)}, Paitoon (PT) Tontiwachwuthikul^{1,2,3,4,6(*)}

¹Joint International Center for CO₂ Capture and Storage (iCCS), Department of Chemical Engineering,
Hunan University, Changsha, 410081, CHINA.

²Energy Informatics Laboratory, Faculty of Engineering and Applied Science, University of Regina,
3737 Wascana Parkway, Regina, Saskatchewan S4S0A2, CANADA.

³Petroleum and Petrochemical College, Chulalongkorn University, Phya Thai Road, Patumwan,
Bangkok 10330, THAILAND.

⁴Gas Processing Center, Qatar University, Doha, QATAR.

⁵Institute Centre of Energy (iEnergy), Masdar Institute of Science and Technology, P. O. Box 54224,
Abu Dhabi, United Arab Emirates (UAE).

⁶International Test Centre for CO₂ Capture (ITC), Faculty of Engineering and Applied Science,
University of Regina, 3737 Wascana Parkway, Regina, Saskatchewan S4S0A2, CANADA.

* Authors for correspondence of the series: Dr. Paitoon (PT) Tontiwachwuthikul – Email:
Paitoon@uregina.ca Tel. +1-306-585-4688; Dr. Zhiwu Liang – Email: zwliang@hnu.edu.cn Tel: +86-136-
1848-1627; Dr. Raphael Idem – Email: Raphael.Idem@uregina.ca. Tel: +1-306-585-4470;

Abstract

Currently, post-combustion carbon capture (PCC) is the only industrial CO₂ capture technology that is already demonstrated at full commercial scale in the TMC Mongstad in Norway (300,000 tonnes per year CO₂ captured) and BD3 SaskPower in Canada (1 million tonnes per year CO₂ captured). This paper presents a comprehensive review of the most recent information available on all aspects of the PCC processes. It provides designers and operators of amine solvent-based CO₂ capture plants with an in-depth understanding of the most up-to-date fundamental chemistry and physics of the CO₂ absorption technologies using amine-based reactive solvents. Topics covered include chemical analysis, reaction kinetics, CO₂ solubility, and innovative configurations of absorption and stripping columns as well as information technology applications. The paper also covers in detail the post-built operational issues of corrosion prevention and control, solvent management, solvent stability, solvent recycling and reclaiming, intelligent monitoring, plant control as well as process automation. In addition, the review discusses the most up-to-date insights related to the theoretical basis of plant operation in terms of thermodynamics, transport phenomena, chemical reaction kinetics/engineering, interfacial phenomena, and materials. The insights will assist engineers, scientists, and decision makers working in academia, industry and government, to gain a better appreciation of the post combustion carbon capture technology.

50	Contents
51	1. Introduction and Background Information
52	2. Solvent Chemistry
53	2.1 Solubility
54	2.2 Reaction Kinetics
55	2.3 NMR analysis for ion speciation studies
56	2.4 alternative solvents for post combustion CO ₂ capture
57	3. Design, Modeling and Simulation of Post Combustion CO ₂ Capture Systems Using
58	Reactive Solvents.
59	3.1 Determination of column height for CO ₂ absorber
60	3.2 Developed process configurations for post combustion CO ₂ capture
61	4. Solvent Management
62	4.1 Corrosion
63	4.2 Solvent stability issues
64	4.3 Solvent recycling and reclaiming
65	5. Post-Built Operations
66	5.1 Expert Systems for Monitoring, Control and Diagnosis of the CO ₂ capture process
67	system
68	5.2 Intelligent Data Analysis for the CO ₂ capture process system
69	6. Conclusion and Summary
70	References
71	
72	
73	
74	
75	
76	

1. Introduction and Background Information:

Globally, the capture of CO₂ from industrial flue gases has become a critical environmental issue. The threat of climate change from increased levels of GHGs in the atmosphere is significant. According to the International Energy Agency, 2012, under current policies and mitigation strategies, worldwide energy-related CO₂ emissions will reach nearly 45 gigatonnes by 2035 (which is correlated with only a 50% probability of limiting average global temperature increase to 5.6°C) unless strong efforts are made to achieve the target of stabilizing greenhouse gas concentrations at 450 ppm CO₂-e. Mean global temperatures are on the rise, and various regions of the world have been experiencing adverse climate issues. Therefore, the need for research and development of cost-effective CO₂ capture technologies is urgent.

There are three major process options for CO₂ capture: pre-combustion, post-combustion, and oxyfuel combustion. Depending on the process, various technologies for CO₂ capture can be used, including absorption, adsorption, membranes, and hybrid applications of these three. At the moment, post-combustion carbon capture (PCC) is the only industrial CO₂ capture technology being demonstrated at full commercial scale. The major examples are the TMC Mongstad in Norway (300,000 tonnes per year CO₂ Captured) and BD3 SaskPower in Canada (1 million tonnes per year CO₂ captured).

A typical flow sheet of PCC process is similar to the industrial acid gas removal system utilizing a chemical absorbent is shown in Figure 1.1. The raw gas, which enters the unit through an inlet separator where entrained liquid and solid particulates are removed, flows from the bottom of the absorber upwards against a counter-current stream of the lean solution. The CO₂ in the flue gas is absorbed and the treated flue gas leaves the top of the absorber. The loaded ("rich") solution flows from the bottom of the absorber and passes through the lean-rich heat exchanger where it is heated by the hot, recycled lean solution. It

then enters the top of the stripper column. In some cases, a flash tank is installed upstream of the heat exchanger to desorb and some portions of the absorbed CO₂ by reducing the pressure on the rich stream.

Insert Figure 1.1 here

Upon entry into the stripper, some of the absorbed CO₂ is flashed. The solution then flows downward against a counter-current flow of water vapor generated in the reboiler. The stripping vapor removes most of the remaining CO₂ from the rich stream. The overhead mixture leaves the stripper through a condenser where most of the water vapor is condensed and returned to the stripper as reflux. The lean solution, which leaves the bottom of the stripper, exchanges heat with the rich solution in the lean-rich heat exchanger and then passes through a cooler before being pumped to the absorber.

Over the past ten years, there have been significant new developments in post-combustion capture processes. The IEA sponsored the 2nd Post Combustion Capture Conference (PCCC2, Bergen, Norway in 2013) as well as the 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12, Austin, USA in 2014), the most recent show-cases of these new developments in this R&D area. Significant portions of recent information on the subject can be found on the IEAGHG website (www.ieaghg.org).

The purpose of this review paper is to provide a comprehensive scientific review of the state of the art of amine-based CO₂ separation processes from combustion flue gas streams. Topics covered include solvent chemistry, CO₂ solubility, reaction kinetics, chemical analysis, unit design, and innovative configurations of absorption and stripping columns. In addition, this paper also covers the post-built operational issues of corrosion prevention and control; solvent management; solvent stability; solvent recycling and reclaiming; intelligent monitoring; plant control; process automation; and comprehensive, hands-on experience in pilot plant operation for PCC.

Section 2 mainly focuses on the solvent chemistry of CO₂ absorption using reactive solvents. First, recent studies of equilibrium solubility of CO₂ in various amine solutions are reviewed in Section 2.1. The relationship of equilibrium solubility of CO₂ and VLE through the thermodynamics framework and modeling is also analyzed. Subsequently, the reaction kinetics are comprehensively discussed, especially with respect to the experimental determination of kinetics data in Section 2.2. After that, Section 2.3 discusses how to analyse the chemical species in CO₂-amine systems using nuclear magnetic resonance (NMR) spectroscopy, as well as the experimental determination of liquid speciation at vapor-liquid equilibrium (VLE). These three sections related to solvent chemistry are useful and important knowledge for the effective design of post-combustion CO₂ capture systems using reactive solvents.

The design, modeling and simulation of post-combustion carbon capture processes using reactive solvents are discussed in detail in Section 3. Several design techniques (i.e., empirical, theoretical, laboratory, and pilot plant methods) are reviewed. In addition, some novel process configurations of CO₂ absorption systems and their influence on performance are also discussed.

The remaining sections 4 and 5 address post-built operational issues. Section 4.1 focuses on one of the major challenges of PCC, which is the material corrosion within the CO₂ absorption system, especially in coal-fired power generation plants. It provides analysis of the electrochemical reactions that cause corrosion, and the operating parameters and impurities in the system that can induce corrosion are discussed. Corrosion prevention strategies, namely chemical corrosion inhibitors, and their inhibiting mechanisms, are also given. Section 4.2 discusses the solvent management issues related to solvent degradation. The issues related to solvent recycling and reclaiming are discussed section 4.3. Once the solvents have been used, they can become degraded, and degradation products can then be released. Both oxidative

and thermal degradation, degradation mechanisms, and inhibition techniques are given in this section. Since those degradation products negatively impact the performance of CO₂ capture, Section 4.3 presents the most effective techniques (ion-exchange, ED reclamation, thermal reclamation, and hybrid-techniques) that can be used to separate the degradation products from their parent solvents.

The post-built issues related to process monitoring and operational data analysis are detailed in Section 5. Also discussed are the application of information and artificial intelligence technologies through (i) knowledge-based expert systems for effectively monitoring and controlling CO₂ capture processes and (ii) data mining techniques for identifying and determining the significant process parameters in CO₂ capture performance.

2. Solvent Chemistry

The past decade has seen remarkable progress in post-combustion CO₂ capture processes using reactive solvents because of their high capacities to provide near complete absorption and desorption of CO₂ and their exceptional ability to selectively absorb CO₂ from flue gas. Among various reactive solvents being studied for the PCC (amines, hot potassium carbonate, chilled ammonia and ionic liquids, etc.), amines are considered to be by far the most developed. Monoethanolamine (MEA), the first-generation and undoubtedly the most well-known amine-based absorbent, is marked by its high chemical reactivity with CO₂ and low cost to produce. These merits of MEA can reduce the absorber height and ensure a large-scale and stable operation. Although MEA-based scrubbing technology is suitable for the PCC from fossil-fired plants flue gas, it suffers from several issues, including high enthalpy of reaction, low absorption capacity, oxidative and thermal degradation, and corrosion (Rochelle, 2001). Hence, there has been a strong drive to develop other attractive absorbents to achieve high absorption/desorption performance, energy-efficient and thermally stable alternatives.

To develop a reliable and systematic design of PCC systems using reactive solvents and obtain an outstanding absorbent, understanding of the fundamental principles of solvent chemistry is of great importance. However, this is not an easy task due to the complex and complicated chemistry of the amine-CO₂-water systems in practical applications. As a result, a selection of optimum solvents requires combined considerations of thermodynamic, kinetic and stability properties of the amine-CO₂ system (Rochelle, et al., 2001), which all directly impact the performance and economics of a commercial scale operation.

In this section, we address three significant aspects related to solvents chemistry that are important when evaluating reactive solvents and selecting optimum operating conditions for PCC applications; solubility, reaction kinetics and chemical species analysis. The high CO₂ solubility of solvents provides an opportunity for a large CO₂ absorption capacity to be achieved, resulting in a reduced solvent circulation flow rate required for capturing a certain amount of CO₂. As the kinetics data of CO₂- solvent systems could directly reflect on the sizes of absorber or desorber columns, these studies will enable designers to predict the separation performance of these columns. However, the kinetics data can vary with experimental technique, reaction mechanisms, physical properties of absorbents and the interpretation method used. Therefore, the accurate experimental determination of kinetics data is of critical importance. Finally, qualitative and quantitative determinations of speciation distribution in a CO₂-solvent system can provide valuable information for the better understanding of the chemical reactions between CO₂ and reactive solvents. The ion speciation study can be very useful for further examination of reaction mechanism, reaction kinetics and thermodynamic behavior of CO₂ absorption.

2.1 Solubility

The knowledge of equilibrium solubility of CO₂ in a solvent as a function of temperature and pressure is critical in developing an optimal capture process. The

equilibrium data facilitate the determination of delta loading (defined as the difference of solubility in the lean and rich solvent), the solvent cyclic absorption capacity and thus the determination of the required solvent circulation rate, and the size of the absorption unit to achieve a certain CO₂ removal rate. The estimation of heat of absorption as an indicator of heat requirement for regeneration can also be generated from solubility data as a function of temperature and pressure.

Solubility of CO₂ in many new systems has been reported in recent years to facilitate developing a solvent with high cyclic capacity with optimal heat of absorption that might ultimately reduce regeneration costs. Amine screening studies were performed by Chowdhury et al. (2009); Chowdhury et al. (2011); Chowdhury et al. (2013); Porcheron et al. (2011a); Porcheron et al. (2011b); Puxty et al. (2009); Singh et al. (2007), (2009), and Park et al. (2014). Reviews on the solubility of CO₂ in amine solutions were published by Anufrikov et al. (2007); Kumar et al. (2014) and Rayer et al 2012, and Henni et al. (2013). Rayer et al. (2013a) provided a comprehensive database of VLE data dealing with amine systems. The experimental techniques used for the measurement of solubility of CO₂ are generally classified as static analytic methods, static synthetic methods and flow methods and were recently reviewed in Anufrikov et al. (2007) and Rayer et al. (2012).

Henni et al. (2013) compared the high and low pressure CO₂ solubility of a number of aqueous amines (Figure 2.1) and reached the conclusions that the increase in hindrance to the amino groups increases the loading capacity, and the general trend of amines in order of loading capacity is *Primary amines* < *Hindered amines* < *Secondary amines* < *Tertiary amines* < *Diamines*. The effect of temperature and addition of co-solvent was also reviewed for many systems. We present below a brief review of recent works on amine systems not mentioned in Rayer et al., 2012. Tables 2.1 and 2.2 present the binary and mixed (ternary/quaternary) amine systems and Table 2.3 lists the amine-based systems studied very

recently. In addition, heats of absorption of CO₂ in primary and tertiary amines are measured by Arcis et al. (2014) and Rayer et al. (2012) respectively.

Insert Figure 2.1 here

Insert Table 2.1 here

Insert Table 2.2 here

Insert Table 2.3 here

Acyclic Primary amine (MEA, etc.) based solvents

Wagner et al. (2013) measured the solubility of CO₂ in aqueous MEA solution (15 and 30 wt%) using headspace chromatography and the synthetic gas solubility method, and the new data agree with data in the literature within the (wide) scattering of reported data. Voice et al. (2013) reported that the cyclic capacity of aqueous 8M 3-(methylamino) propylamine (MAPA) was lower than that of 7 M MEA (0.42 vs 0.79). At CO₂ partial pressure of 0.1 kPa and 40°C, the loadings for MEA, 3-amino-1-propanol (3A1P), 4-amino-1-butanol and 5A1P are 0.38, 0.41, 0.42 and 0.44, respectively, indicating slight increase in CO₂ solubility with the number of carbon atoms in the chain of the alkanolamines (Idris et al., 2015).

Acyclic Secondary amine (DEA, etc.) based solvents

Bajpai and Mondal (2013) showed that AEEA increased the solubility of CO₂ in DEA and the (DEA+AEEA) systems have a higher CO₂ solubility than (DEA + PZ) and (DEA + MDEA) mixtures. AEEA could be a good substitute for MEA if not for its high thermal degradation at 140 °C as reported by Davis and Rochelle (2009), or if a lower regeneration temperature was used as is the case of non-aqueous media.

Yamada et al. (2013) showed that aqueous solution of two secondary amines, 2-(isopropylamino) ethanol (IPAE) and 2-(propylamino) ethanol (PAE) have superior cyclic capacity than both MEA and DEA. The delta loading between (T=313K, P_{CO2}=20 kPa) and

($T=393\text{K}$, $P_{\text{CO}_2}=100\text{ kPa}$) of 30 wt% DEA, PAE and IPAE are 41.9, 51.2 and 67.8g CO_2/kg solvent. The moderate stability of IPAE carbamate and the alcohol chain length were influential in the resulting high cyclic loading.

Tertiary amines

Zoghi and Feyzi (2013) and Najafloo et al. (2015) reported on the CO_2 solubility in the ternary solvent ($\text{H}_2\text{O}+\text{MDEA}+\text{AEEA}$). The solubility of CO_2 was significantly enhanced by addition of AEEA, but the increase in CO_2 solubility was nonlinear with the proportion of AEEA in the mixed solvent. VLE data of CO_2 in aqueous 2-(diethylamino)-ethanol (DEEA) were published by Sutar et al. (2013), Monteiro et al. (2013), and Xu et al. (2014b).

From a series of amine screening experiments, Chowdhury et al. (2013) identified seven tertiary amines as more suitable than MDEA. Compared to MDEA, they had higher absorption rates, slightly higher cyclic capacities and lower or comparable heats of reaction. Liang et al. (2015) showed that the CO_2 equilibrium solubility of 1-dimethylamino-2-propanol (1DMA2P) is higher than that of MEA and MDEA. At 313K and 101 kPa CO_2 partial pressure, the loading of MEA, MDEA and 1DMA2P are 0.75, 0.87 and 0.91 g CO_2/kg solvent, respectively. The estimated heat of CO_2 absorption for 1DMA2P was lower than those for MEA, DEA and MDEA.

Solubilities of CO_2 in two tertiary amines, N,N-dimethylethanolamine (DMEA) and in triethylene diamine (TEDA) were reported by Tong et al. (2013a). The rich loading (40°C, 15 kPa) ratio for DMEA, TEDA and MDEA are reported to be 0.6 mol CO_2 /molDMEA, 0.3 mol CO_2 /mol TEDA and 0.5 mol CO_2 /mol MDEA, respectively, indicating that DMEA might be a better solvent than TEDA.

Cyclic amine (Piperazine, Morpholine etc.) based solvents

1,8-*p*-menthane-diamine (MDA): The sterically hindered alicyclic compound 1,8-*p*-menthane-diamine (MDA) has a cyclic ring with two primary NH_2 groups and is reported to

have higher absorption capacity and lower heat of regeneration than MEA (Kim et al., 2011), and that aqueous (AMP+MDA) solutions have higher absorption rates than MEA and AMP solutions (Lee et al., 2012). Li et al. (2014d) reported that, in the high-loading region, the solubility of CO₂ per amino group in MDA solution was higher than in MDEA, PZ and MEA, possibly due to the steric hindrance effect.

3-piperidinemethanol: Conway et al. (2014) reported that 3-piperidinemethanol (3-PM) was superior to MEA in both absorption capacity and cyclic capacity and the larger CO₂ capacities are attributed to the lower stability 3-PM carbamate due to steric hindrance and the formation of larger amounts of bicarbonate compared to MEA. The cyclic capacities (difference in loading between 40 and 80°C at 15 kPa partial pressure) of 3-PM and MEA are 0.21 and 0.11 mol CO₂/ mol amine, respectively.

Piperazine derivatives: Li et al. (2014b) presented CO₂ solubility in 30 wt% 1-methyl piperazine (1-MPZ), 1-ethyl piperazine (1-EPZ), 1-(2-hydroxyethyl) piperazine (HEP), and 1,4-dimethyl piperazine (DMPZ) and their mixtures (Figure 2.2) at 40 and 120°C. Three solvents 1-MPZ, triethylenediamine (TEDA)+PZ and DMPZ+PZ had the best cyclic capacities. Boot-Handford et al. (2014) compared solvent performances using different criteria, and found that the combination of 5 M MDEA + 5 M PZ gave the best cyclic capacity among all PZ based solvents presented (Figure 2.3). Lin and Wong (2014) reported the combination PZ/DETA/MeOH/H₂O to have good cyclic efficiency at 80 and 120°C.

Insert Figure 2.2 here

Insert Figure 2.3 here

2.1.1 Thermodynamic models and process simulation

The development of models capable of predicting the complex behavior of the absorption/desorption process under wider thermodynamic conditions and for different

binary/ternary solvents remain a challenge. Rayer et al. (2012) gave an overview of rigorous thermodynamic models with recent applications. Kumar et al. (2014) listed about 36 studies with their modeling approach. Recently, Boot-Handford et al. (2014) briefly discussed the thermodynamic models with recent applications. The models used to correlate or predict the VLE of CO₂/aqueous alkanolamine solutions fall into the following three categories (Téllez-Arredondo and Medeiros, 2013)

(i) Non-rigorous models: These empirical models are based on equilibrium constants of chemical reactions and do not consider solvent non-ideality through activity coefficient. The Kent-Eisenberg is one of the earliest models and it is still used today in modified forms (e.g., Chang et al., 2013; Hsu et al., 2014; Li et al., 2014; Oktavian et al., 2014).

(ii) Rigorous excess Gibbs energy model (gamma-phi models): eNRTL is a widely used thermodynamic model (Zhang and Chen, 2011; Matin et al., 2013; Haghtalab et al., 2014; Li et al., 2014, Xu et al., 2014b). Wagner et al. (2013) used a rigorous thermodynamic model based on the extended Pitzer equation for (CO₂+H₂O+MEA) system that correlated experimental speciation data well, but still could be improved by re-parameterization with more experimental data. Arcis et al. (2014) also developed a similar rigorous model (gamma-phi) to model CO₂+H₂O+MEA (and CO₂+H₂O+AMP) system and the binary parameters were optimized with 348 (and 379) experimental VLE data points. The model qualitatively predicted their measured heat of absorption data. Faramarzi et al. (2009) used eUNIQUAC model to correlate binary (MEA+H₂O and MDEA+H₂O) and ternary (MDEA+MEA+ H₂O) systems.

(iii) Equation of state model: A number of equation of state models (phi-phi approach), capable of representing molecular association, are increasing in use e.g. PC-SAFT (Pahlavanzadeh and Baygi, 2013), electrolyte EOS (Diab et al., 2013), SAFT-VR (Rodriguez et al. 2012), CPA (Zoghi et al. 2012; Zoghi and Feyzi, 2013), PR-TS (Haghtalab and

Shojaeian, 2015), electrolyte SAFT-HR EoS (Najafloo et al., 2015), eCTS EoS (Téllez-Arredondo and Medeiros, 2013) . Diab et al. (2013) incorporated experimental speciation data in the electrolyte EoS model and consequently, the model was able to represent liquid phase speciation and CO₂ partial pressure in a satisfactory manner.

Rigorous thermodynamic models such as eNRTL are available in commercial process simulators such as ASPEN-PLUS to simulate CO₂ absorption by amines. Kent-Eisenberg and Li-Mather equilibrium models are also available on Aspen HYSYS, and eNRTL in ASPEN PLUS (Oi 2012). The CO₂ capture process is a very energy intensive process and process simulation is most important in the economic analysis of a process to identify the major sources of energy cost. Raynal et al. (2011) attempted to show the roadmap of lowering the cost of post-combustion CO₂ capture. Using the ASPEN-PLUS simulation software, they showed that for 30% aqueous MEA process, most of the operating cost was associated with the stripper operation. Previously, Abu-Zahra et al. (2007) presented an economic baseline for post-combustion CO₂ capture, and showed that a higher MEA concentration would require less energy.

As reviewed above, we can conclude that (i) no single experimental technique exists to generate reliable data at wide temperature and pressure conditions necessary to develop a sound thermodynamic model, (ii) CO₂ solubility increased with the number of carbon atoms in the chain of linear alkanolamines, (iii) the performance of a thermodynamic model can be improved by incorporating liquid speciation data, (iv) addition of AEEA enhanced the solubility of CO₂ in aqueous DEA and MDEA solutions, (v) IPAE and PAE were found to have better cyclic capacity than both MEA and DEA, (vi) (DIPA+AMP+PZ) blend was found to be suitable for removal of CO₂ in the presence of H₂S, (vii) CO₂ solubility in MDA was higher than that in MDEA, PZ and MEA. 3-PM also had a higher cyclic capacity than MEA, (viii) piperazine received increased attention in recent years and the blend 5 M

MDEA + 5 M PZ was found to have better cyclic capacity among many other PZ blends, (ix) CO₂ solubility in 1 DMA2P was higher than in DEA and MDEA, (x) PZ was shown to increase CO₂ solubility in aqueous Ionic Liquid (IL) solvents, and (xi) the presence of IL instead of water had a negative effect on absorption capacity.

2.2 Reaction Kinetics

2.2.1. Experimental determination of the CO₂ absorption rate

For amine-based CO₂ capture technology, reaction kinetics, which indicates how fast CO₂ reacts with amine is one of the most important parameters for design and simulation of an absorption column. It greatly affects the mass transfer performance as well as plant design. The reaction kinetics of CO₂ absorption into amine solutions have been studied for several decades. Various gas-liquid contactors have been used for measuring the CO₂ absorption rate and obtaining reaction kinetic data. Examples of these equipment types, their advantages and disadvantages, are shown in Table 2.4. The absorption rate data obtained can then be interpreted for estimations of rate constants using a simplified kinetics model based on reaction mechanisms (i.e., zwitterion, termolecular, or base-catalyzed hydration mechanisms) or a comprehensive numerically solved reaction kinetics model that takes into account the coupling between chemical equilibrium, mass transfer, and chemical kinetics of all possible reactions.

Insert Table 2.4 here

Aboudheir et al. (2003) summarized the value of kinetics parameters in terms of reaction rate constants for MEA obtained from different gas-liquid contactors at various concentrations (0.05 M to 4.8 M) and temperatures (295 K to 353 K). They pointed out that the use of different measurement methods provides different values of the reaction rate constant, even when the experiments were operated under similar MEA concentration and

temperature. This would be because of the difference in physics and chemistry associated with the absorption process in the contactors. However, among the experimental gas-liquid contactors, wetted wall columns and laminar jet absorbers have been found to be the ones most used in the literature. This is because (i) their absorption surface area can be measured directly (for laminar jet absorber, the surface area can be varied) (Astaria et al., 1983; Bishnoi and Rochelle, 2002) and (ii) the physical diffusivity of CO₂ into the absorbent can be accurately determined (Astaria et al., 1983; Bishnoi and Rochelle, 2002; Saha et al., 1995). In addition, the laminar jet absorber is suggested for fast absorption processes because of its short contact time (Astaria et al., 1983; Bishnoi and Rochelle, 2002). For toxic solvents, a stirred cell reactor is recommended since it is a closed system (Astaria et al., 1983; Pani et al., 1997). Lastly, for novel solvent screening, a stopped-flow apparatus is suggested. This is because (i) a very small quantity of solvent is required and (ii) the experimental procedure is simple (Alper, 1990; Pani et al., 1997). However, the limitation is that only very low solvent concentrations can be applied. This is because only at low concentrations, the conductance of an ion compound formed from the reaction is a linear function with its concentration and a first order-kinetic equation. Accordingly, an exponential equation can be applied (Kierzhkowska-Pawlak et al., 2012).

2.2.2. Reaction rate/kinetics model

After measuring the CO₂ absorption rate using the experimental gas-liquid contactors, interpretation of the experimental kinetics data is required for determining the second order reaction rate constant. Recently, a simplified model based on reaction mechanism and a numerically solved comprehensive model has been generally applied and widely accepted to be used for investigating the reaction kinetics of CO₂ absorption.

2.2.2.1 Simplified model based on reaction mechanism

In this approach, the reaction rate/kinetics data obtained from the gas-liquid contactor are interpreted based on the proposed mechanism between CO₂ and amine (i.e., zwitterion, termolecular, and base catalyzed hydration mechanisms). In addition, the single and blended amines solutions are also treated differently.

Firstly, the overall rate of CO₂ absorption (r_{ov}) is defined as:

$$r_{ov} = k_{ov}[CO_2] \quad \text{Equation 2.1}$$

Where $[CO_2]$ is the CO₂ concentration in liquid phase and k_{ov} is the experimental overall reaction constant. For fast pseudo first order absorption reactions, the specific CO₂ absorption rate N_{CO_2} can be expressed as:

$$N_{CO_2} = C_{CO_2}^* \sqrt{k_{ov} D_{CO_2}} = \frac{P_{CO_2}}{He} \sqrt{k_{ov} D_{CO_2}} \quad \text{Equation 2.2}$$

Where $C_{CO_2}^*$ is the interfacial concentration of CO₂, D_{CO_2} , P_{CO_2} and He are diffusivity and partial pressure of CO₂ and the Henry constant, respectively. From equation 2.2, the k_{ov} can be obtained from the measurement of CO₂ absorption rate from the gas-liquid contactors mentioned in the above section using the following equation (Sema et al. 2012):

$$k_{ov} = \left(N_{CO_2} \frac{He}{P_{CO_2}} \right)^2 \frac{1}{D_{CO_2}} \quad \text{Equation 2.3}$$

In addition to the CO₂-amine reaction in aqueous amine solution, there are two other reactions related to hydration of CO₂ and bicarbonate from CO₂. The hydration reaction has been found to be very slow compared with other reactions and can be neglected (Blauwhoff et al., 1984). However, the formation of bicarbonate from CO₂ and OH⁻ is faster than that of the hydration reaction and should be included for determination of overall reaction rate.

(i) *Primary and secondary amines*

For the primary and secondary amines (e.g., MEA and DEA), the overall reaction rate for CO₂ absorption based on the zwitterion mechanism (Danckwerts, 1970 and 1979) can be written as:

$$r_{ov} = k_{ov}[CO_2] = r_{CO_2-R_1R_2NH}^Z + r_{OH^-}^* \quad \text{Equation 2.4}$$

$$= \frac{k_{2,R_1R_2NH}^Z [CO_2][R_1R_2NH]}{1 + \frac{k_{-1}^Z}{k_{R_1R_2NH}[R_1R_2NH] + k_{OH^-}[OH^-] + k_{H_2O}[H_2O]}} + k_{OH^-}^* [CO_2][OH^-]$$

The apparent rate constant (k_{app}) then can be defined as:

$$k_{app} = k_{ov} - k_{OH^-}^* [OH^-] \quad \text{Equation 2.5}$$

Therefore, k_{app} for aqueous primary or secondary amine solution can be written as:

$$k_{app} = \frac{k_{2,R_1R_2NH}^Z [R_1R_2NH]}{1 + \frac{k_{-1}^Z}{k_{R_1R_2NH}[R_1R_2NH] + k_{OH^-}[OH^-] + k_{H_2O}[H_2O]}} \quad \text{Equation 2.6}$$

Where $k_{2,R_1R_2NH}^Z$ is a second order reaction rate constant of primary or secondary amines based on the zwitterion mechanism. $k_{R_1R_2NH}$, k_{OH^-} , and k_{H_2O} are reaction rate constants for deprotonation of the zwitterion intermediate by R_1R_2NH , OH^- , and H_2O , respectively.

The experimental values of k_{app} at a specific temperature are now correlated with the zwitterion mechanism in order to obtain individual rate constants of $k_{2,R_1R_2NH}^Z$, k_{OH^-} , and k_{H_2O}

(ii) Tertiary amine

Tertiary amine (e.g., TEA and MDEA) does not react with CO₂ directly, but it acts as a base that catalyzes the hydration of CO₂ (base catalyzed hydration mechanism, Donaldson,

and Nguyen, 1980). The apparent rate constant for tertiary amine based on the base catalyzed hydration mechanism can be expressed as in Yu et al. (1985):

$$k_{app} = k_{R_3N} [R_3N] \quad \text{Equation 2.7}$$

The kinetics of CO₂ absorption into aqueous solution of tertiary amine (e.g., TEA and MDEA) have been studied by Benitez-Garcia et al. (1990); Haimour et al. (1987); Yu et al. (1985). They have found that the reaction order with respect to the tertiary amine concentration is 1, which is in good agreement with the base catalyzed hydration mechanism.

2.2.2.2. Numerically solved comprehensive model

One of the very first numerically solved comprehensive reaction rate/kinetics models, which takes into account the coupling between chemical equilibrium, mass transfer, and chemical kinetics of all possible chemical reactions, was developed by Hagewiesche et al. (1995). The developed model for blended MDEA-MEA is governed by a system of partial differential-nonlinear algebraic equations based on the mass transport equation, as shown in Equations 2.8 and 2.9 (Astaria et al., 1983). The mass balance of all chemical species in a mass transfer film, including CO₂, amine and their products were taken into consideration. The set of these partial differential-nonlinear equations will be solved simultaneously to account for the effects of chemical reactions and diffusivities on the concentration of each species. Their developed reaction rate/kinetics model is capable of predicting the CO₂ absorption rate, the enhancement factor, and the rate coefficient of reaction between CO₂ and MEA. Later, the numerically solved comprehensive reaction rate/kinetics models were applied for unloaded DEA, MDEA (Rinker et al., 2000; Rinker et al., 1996) and concentrated highly loaded MEA (Aboudheir et al., 2003).

$$D\nabla^2 C = u \cdot \nabla C + \frac{\partial C}{\partial t} + R \quad \text{Equation 2.8}$$

$$D \left[\frac{\partial C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{1}{r^2} \frac{\partial^2 C}{\partial \theta^2} + \frac{\partial C}{\partial z} \right] = \left[u_r \frac{\partial C}{\partial r} + \frac{u_\theta}{r} \frac{\partial C}{\partial \theta} + u_z \frac{\partial C}{\partial z} \right] + \frac{\partial C}{\partial t} + R \quad \text{Equation 2.9}$$

Recently, the comprehensive reaction rate/kinetics model has been extended to other promising amine systems such as blended MEA-MDEA and blended MDEA-PZ by Edali et al. (2009) and Idem et al. (2009a). In their studies, the partial differential-nonlinear algebraic equations have been solved using two numerical techniques: the finite difference method (FDM) based on the Barakat-Clark scheme and the finite element method (FEM) based on COMSOL software in both 1D modeling in which only mass transfer of all species in the film thickness direction is considered and 2D modeling in which the mass transfer in the film length direction are included. They have found that both FDM and FEM produce very accurate predictions of CO₂ absorption rate results. Also, no significant difference between the results obtained from FDM and FEM were observed. Therefore, they suggested that the FEM based on COMSOL software could be used for the numerical solution of the partial differential-algebraic equations because coding the program of the numerical scheme can be eliminated.

2.2.3. Kinetics behavior

The second order CO₂ absorption rate constants (k_2) for conventional amines and some novel amines obtained from the simplified kinetics modeling, and comprehensive numerical solved kinetics modeling are summarized in Table 2.5. It can be seen that reaction rate constants extracted from the simplified kinetics model are comparable with those extracted from the comprehensive numerically solved kinetics model. However, the comprehensive numerically solved kinetics model seems to be the most comprehensive and accurate model among the three because it takes into account the coupling between chemical equilibrium,

mass transfer, and chemical kinetics of all possible chemical reactions. Moreover, the recently developed comprehensive numerically solved kinetics models have been expanded to (i) 1D and 2D modeling and (ii) various operating temperatures, amine concentrations, gas-liquid contact times, and CO₂ loadings (Edali et al., 2009; Herron and Green, 2001; Schijven and Šimůnek, 2002).

Insert Table 2.5 here

2.3 NMR analysis for ion speciation studies

NMR spectroscopy is an indispensable methodology in analytical chemistry. The functional groups, the carbon backbones, and C-C double and triple bonds can be detected directly, mostly with liquid phase ¹H and ¹³C spectra. NMR can test the ion species in the complicated amine-CO₂-H₂O systems quantitatively to develop VLE models.

The equilibrium of CO₂ absorption into water soluble amines, exhibits both vapor-liquid equilibrium and chemical equilibrium (Liu et al., 1999). The ion speciation with the exact concentrations of cations, free molecules, and anions in the solvent under different CO₂ loadings are of research interest. Ion speciation plots can provide an important databases for CO₂ absorption (20 –40°C) (Fan et al., 2009; Holmes et al., 1998; Jakobsen et al., 2005) and regeneration (90°C) (Shi et al., 2014a). It can be detected experimentally with NMR spectroscopy combined with other equilibrium methods. Given a certain CO₂ loading and temperature, the major ion concentrations can be obtained from the speciation plots immediately, similar to on-line tests.

2.3.1. Reaction Schemes: CO₂-amine interactions

CO₂-amine reaction schemes are within the solvent chemistry. After the amine-CO₂-H₂O systems reach VLE and chemical equilibrium, the amine solutions contain multiple cations, (AmH⁺) free molecules (Am), and anions (carbamate, HCO₃⁻, CO₃²⁻), simultaneously. These “ternary” systems contain 8-9 ionic or neutral species. Their concentrations are

constrained by reaction equilibrium and mass balance.

MEA: Overall reaction:

2.3.2. NMR analysis of amine-CO₂-H₂O systems

The ion concentrations can be tested with NMR quantitative analysis. The foundation was to establish a direct relationship between the chemical shift δ (ppm) and concentration C (mol/L) of ions.

Most researchers have applied a pH meter with NMR technology to detect the ion speciation of amine-CO₂-H₂O systems (Holmes et al., 1998; Jakobsen et al., 2005). The pH measurement is used to determine the amount of two species appearing as a common peak, such as amine/amineH⁺ or bicarbonate and carbonate. The pH meter tests the concentration of [H⁺] in order to detect the free amine (Am) and protonated amines (AmH⁺) with deprotonation constant K while the NMR instrument tests the carbamate, bicarbonate, and

carbonate. NMR is effective in ion concentration testing due to several advantages: the specific ions possess their own chemical shifts both in ^1H and ^{13}C NMR spectra (Fan et al., 2009; Holmes et al., 1998; Jakobsen et al., 2005). Holmes et al. (1998) performed NMR analysis of $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ systems with both ^1H and ^{13}C spectra. They developed several useful equations (Equations 2.23-2.26) for calculation of carbamate and bicarbonate/carbonate. The ^{13}C NMR of $\text{HCO}_3^-/\text{CO}_3^{2-}$ is one peak because of the fast proton exchange.

$$[\text{NH}_2\text{CO}_2^-] / \{[\text{HCO}_3^-] + [\text{CO}_3^{2-}]\} = R \quad \text{Equation 2.23}$$

$$\text{carbamate} / (\text{bicarbonate} + \text{carbonate}) = R$$

$$[\text{NH}_2\text{CO}_2^-] = R / (1+R) \times [\text{CO}_2]_o \quad \text{Equation 2.24}$$

$$[\text{CO}_3^{2-}] = (\delta - 160.33) / [(168.09 - 160.33)(1 + R)] \times [\text{CO}_2]_o \quad \text{Equation 2.25}$$

$$[\text{HCO}_3^-] = (168.09 - \delta) / [(168.09 - 160.33)(1 + R)] \times [\text{CO}_2]_o \quad \text{Equation 2.26}$$

Equation 2.23 demonstrates that the area ratios of two ^{13}C peaks, $\text{NH}_2\text{-COO}^-$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$, which represent the exact amount of these two species, under a specific code (NMR manual) with AAD (Absolute Average Deviation) of 7.5% (Holmes et al., 1998). Equation 2.24 is the concentration of carbamate ($\text{NH}_2\text{-COO}^-$, MEA-COO^-) from CO_2 loading. Equations 2.25 and 2.26 are the concentrations of carbonate and bicarbonate, where 168.09 and 160.33 ppm (Holmes et al., 1998) are the chemical shifts of water soluble samples Na_2CO_3 and NaHCO_3 at 25°C . The $[\text{CO}_2]_o$ represents total absorbed CO_2 , based on mass balance where $[\text{CO}_2]_o = C_{\text{Amine}0} \times \text{loading } \alpha$. Under other operating temperatures, the chemical shifts of Na_2CO_3 and NaHCO_3 should be tested again to be replaced them in Equations 2.25 and 2.26.

2.3.3. Ion speciation plots development under VLE models

VLE models of $\text{MEA-CO}_2\text{-H}_2\text{O}$ have been studied since the 1980s. The equilibria are very sensitive to temperature because the reaction constants K shift with temperature

(Jakobsen et al., 2005). Under constant temperature, the concentration of anions did not change at certain CO₂ loading.

Austgen et al. (1989) simulated the VLE computationally and plotted the simulated speciation plot with electrolyte-Non-Random-Two-Liquid (e-NRTL) equations. Later on, Liu et al. (1999) applied the same method to a MEA-CO₂-H₂O system with extra chemical equilibrium constants, Henry's constant, experimental data, and data regressions to fit the simulation data with the experiments. Figure 2.4 is a simulated ion speciation plot of a MEA-CO₂-H₂O system under absorption and desorption conditions (Liu et al., 1999), but the regeneration plot was inaccurate because water vaporized at 120 °C.

Insert Figure 2.4 here

2.3.4. Major NMR analyses from peer researchers

A recent review (Shi et al., 2012a) indicated several groups performed NMR analyses of the VLE model with different amine-CO₂-H₂O systems (Fan et al., 2009; Holmes et al., 1998; Jakobsen et al., 2005). Based on the conventional pH + NMR methods, NMR analysis was successful in combination with other equilibrium measurements, such as pH meters and K constant (Böttinger et al., 2008a; Böttinger et al., 2008b; Fan et al., 2009; Holmes et al., 1998; Jakobsen et al., 2005). As the acidity increased upon CO₂ loading, there are increased amounts of MEAH⁺, and the MEA / MEAH⁺ peaks were shifted downfield (δ increase), whereas the carbamate peaks were shifted upfield in the ¹H NMR spectra. For the same reason, ¹³C NMR peaks of MEA / MEAH⁺ were shifted upfield (δ decrease), but the carbamate peaks remained unchanged. Most works focused on ternary systems of amine-CO₂-H₂O. The individual ionic concentrations had not been evaluated with NMR spectra independently before 2005 (Jakobsen et al., 2005).

2.3.5 NMR analyses at CETI (Clean Energy Technology Institute)

The main achievements within the University of Regina were in three aspects: (1)

standard work flow chart, (2) a novel NMR calibration method, and (3) ion speciation plots for blended amine systems at higher temperature.

(i) **Standard flow chart**

Usubharatana (2009) developed a “Standard Flowchart”(Figure 2.5) for NMR analysis MEA-CO₂-H₂O systems. This flowchart of experimental procedures can be applied to all ternary amine-CO₂-H₂O (primary, secondary, and tertiary amines) systems with pH + NMR analysis.

Insert Figure 2.5 here

(ii) **Novel amine synthesis and NMR identification**

Syntheses of novel amines have been a major focus. One of the most promising novel amines developed as a tertiary amine similar to MDEA is DEAB (4-Diethylamino-2-butanol). Meanwhile, ¹³C NMR was applied to identify the molecular structure of DEAB in Figure 2.6. The molecule contains 8 carbon atoms but exhibits 6 ¹³C peaks because of structural symmetry (Shi et al., 2012a; Shi et al., 2012b).

Insert Figure 2.6 here

(iii) **NMR analyses of DEAB-CO₂-H₂O with conventional and novel calibration methods**

NMR analysis of the DEAB-CO₂-H₂O system was performed by Shi et al. (2012a); Shi et al. (2012b). CO₂-DEAB-H₂O solutions were tested at different CO₂ loadings from 0.0 to 0.8 at 24.5°C and at different DEAB concentrations from 0.5 to 2.0 mol/L with the VLE plot in Figure 2.7.

Insert Figure 2.7 here

Two NMR analysis methods were applied. The conventional pH meter + ¹³C NMR spectra were applied first. DEAB has been recently synthesized with no data from literature available on the deprotonation constant K; therefore a simplified pH test was applied to detect the K value at 24.5°C (Shi et al., 2012b).

The second method, a NMR calibration methodology, was developed by Shi et al. (2014b); Shi et al. (2012b). Not only DEAB, the ^{13}C chemical shifts of MEA, DEA, MDEA all shifted with protonation, either upfield or downfield (Jakobsen et al., 2005). Seven samples were prepared of pure DEAB (0% protonation) and protonated DEAB at different ratios of $\text{AmH}^+ / \text{C}_{\text{Am}0}$ at 20%, 40%, 60%, 80%, 100%, and 120% (verified full protonation) respectively. ^{13}C NMR analyses of these samples are given in Table 2.6 (Shi et al., 2012b). The shielded region (C_1 , C_3 , C_6) was selected as a calibration set with curves drawn (Figure 2.6). Three correlations were established between the chemical shifts of AmH^+ / Am mixtures and their exact protonation ratios. Therefore, the concentrations of protonated amine (AmH^+) and free amine (Am) were generated independently, with no need of a pH meter or K constant. Direct accuracy deviation tests were completed to compare both methods. The AAD% of pH + NMR was 3.1%, providing adequate accuracy; but the result of our novel calibration method was 1.9%, showing it to be more accurate (Shi et al., 2014b).

Insert Table 2.6 here

(iv) NMR analysis of MEA-DEAB- CO_2 - H_2O (quaternary systems)

This is the most recent development of the application of NMR into quaternary systems. The initial NMR tests of quaternary systems were conducted (Bottlinger et al., 2008b) for MDEA-PZ- CO_2 - H_2O , with inaccurate results. Maneeintr et al. (2010) performed an ion speciation of MEA-MeOH- CO_2 - H_2O with basic experiments.

Recently, the ion speciation tests of quaternary systems were generated with high accuracy along with NMR calibration techniques (Shi et al., 2014b). Both methods (conventional and calibration) were performed on blended amine MEA-DEAB- CO_2 - H_2O systems at 24°C from 5M/0.5M to 5M/1.5M and loadings from 0 to 0.52 (Shi et al., 2014b). Later, the calibration method was performed on MEA-DEAB- CO_2 - H_2O (5M/1.25M) at higher temperatures, from 40 to 70°C (Figure 2.8). These exhibited advantages over pH +

NMR techniques, since NMR could be performed to 70°C, but a pH meter cannot reasonably test samples above 40-45°C. Moreover, the quaternary systems at higher temperatures (40-70°C) can develop VLE plot of 90°C with extrapolation (Shi et al., 2014b).

Insert Figure 2.8 here

2.4 Alternative solvents for post combustion CO₂ capture

2.4.1 Amino acid salts

Amino acid salts are a class of chemical absorbents for CO₂ capture normally referred to as aqueous alkaline salts of amino acids which contain two important functional groups, namely amine (-NH₂) and carboxylic acid (-COOH). However, Taurine that contains a sulfonic acid group instead of the carboxylic acid can also be considered as an amino acid (Lerche, 2012) and is one of the popular amino acids that have been tested for CO₂ capture.

Potassium (K) and sodium (Na) are normally used as a counter ion with amino acids to form salts. However, it was reported that using K provides a higher reactivity toward CO₂ than using Na (Majchrowicz et al., 2014). Amino acid salts have drawn a lot of attention from researchers in the field of CO₂ capture due to their many advantages. Their volatilities are very low because of their salt nature, resulting in low solvent losses during the regeneration process, and since they already exist in nature, the use of amino acid salts is expected to be more environmentally friendly than using alkanolamine solvents (Aronu et al., 2010). In addition, they have a very good resistance to oxidative degradation making them a suitable choice for treating flue gases that contain large amounts of oxygen (Kumar et al., 2003b). However, amino acid salts have their own drawback. They will precipitate at high concentrations or high CO₂ loading, resulting in a lower mass transfer rate and a possibility of damaging the process equipment (Kumar et al., 2003a).

The amino acid salts for CO₂ absorption have been extensively studied by research groups from the University of Twente. The crystallization of products between CO₂ and amino acid salts was investigated by Kumar et al. 2003a. They mentioned that the solid particles formed by the crystallization could cause problems such as fouling and plugging in process equipment and lowering the volumetric mass transfer coefficient, but it also offers an opportunity to enhance the equilibrium conversions between CO₂ and amino acid salts in the liquid phase by removing those solid products. Their study also showed that crystallized solid product found was in the form of protonated amine. In another work by Kumar et al 2003b, the CO₂ solubility was studied in a region where the crystallization occurred and they showed that the crystallization can increase CO₂ absorption capacity of the potassium taurate solvents. A new process concept for CO₂ capture based on the precipitation of the amino acid zwitterion species during the absorption of CO₂ was proposed by Sanchez Fernandez et al. 2013. Unlike the convectional CO₂ capture process, a separator was added after the absorption column to separate the crystallized products from the desorber and recycle a part of the used solvent back to the absorber. Simulation results showed that the specific reboiler energy of this process is 2.4 GJ/tCO₂, 35% lower when compared to the MEA baseline. In addition, the research from the University of Twente also included the study of diffusion coefficients in amino acid salt systems (Hamborg et al., 2008) and determinations of physiochemical properties (N₂O solubility, viscosity and density) (Holst et al., 2008) in potassium salt of amino acid salts.

Due to the high surface tensions of amino acid salts, they have been claimed as a suitable absorbent to be used in membrane gas absorption processes (MGA) that use the membrane as phase barrier for the mass transfer between gas and liquid phases. When using amino acid salts, MGA can operate in the non-wetted mode in which all membrane pores are filled with the gas and the overall mass transfer resistance is much lower than those of the partially

wetted and wetted modes that could be found when using amine absorbents due to their low surface tensions. The performance of potassium salt of taurine in MGA was investigated by Kumar et al. 2002. The breakthrough pressures calculated from the Laplace–Young equation indicated that the amino acid salts were difficult to wet the membranes. The long-term performance tests of mixed absorbents between MEA and sodium glycinate were performed by Rongwong et al. 2009. The applicability of 16 common amino acids to be used in MGA process was investigated by Song et al 2012. The results showed that among all the amino acid salts, salts of serine gave the highest surface tension values and the lowest pore wettability.

Kinetic and solubility studies of CO₂ in amino acid salts

Due to the advantages of using amino acid salts mentioned above, various amino acid salts have been tested for the CO₂ capture process. Amino acid salts react with CO₂ via the zwitterions mechanism since a strong base is added in the preparation of amino acid salts resulting in the amino acid having an amine group (-NH₂) similar to a primary amine (Lerche, 2012). The kinetic data available in the literature for the reaction between CO₂ and amino acid salts was well summarized in Sodiq et al. 2014 and table 2.7 shows some recent works on the CO₂ solubility of amino acid salts.

Insert Table 2.7 here

2.4.2 Phase-change solvents

Phase change solvents such as the Alstom chilled ammonia (CAP) process (Kozak et al., 2009), the DMX process (Raynal et al. 2011) and thermomorphic biphasic solvent (TBS) systems (Agar et al., 2008), constitute a new set of reactive solvents and have shown their prominent advantages for CO₂ capture. These solvents form two immiscible phases upon CO₂ loading, either precipitate/liquid phases or two liquid phases. The concept of using phase change solvents is to recycle the CO₂-lean phase (liquid phase) back to the absorber without

regeneration while only the CO₂-rich phase (either precipitate or liquid phase) is transported back to the stripper. In this way, the CO₂-lean liquid phase maintains a large driving force for CO₂ absorption to absorb more CO₂ while the CO₂-rich phase with its lower circulation rate and richer CO₂ loading can achieve lower consumption of sensible heat and vaporization heat for regeneration. The end result is higher efficiency for both CO₂ absorption and desorption.

A blend of 5M 2-(diethylamino)ethanol (DEEA) and 2M 3-(methyamino) propylamine (MAPA), an example of phase change solvents, has been tested in both bench and pilot plant scales. Studies have found that the 5M DEEA/2M MAPA possesses a reasonably fast absorption rate and easy stripping of CO₂ (Arshad et al., 2013; Pinto et al., 2014a). It enables CO₂ stripping at either elevated pressure or lower temperature compared with traditional 30 wt% MEA, resulting in reduced energy consumption for regeneration. Moreover, neither high viscosity nor foaming issues were observed in the pilot plant test (Pinto et al., 2014b). Clearly, phase change solvents represent significant potential for CO₂ capture, however, more experimental data are required to confirm their potential.

2.4.3 Ionic liquids

Ionic liquids are non-volatile liquid (salts), composed of a cation and an anion and are usually liquid at room temperature. Ionic liquids are called designer solvents as numerous combination of cation and anion are possible. It was shown that CO₂ is remarkably soluble in these solvents, which spurred interest in these solvents. Much research was done in the last fifteen years to develop competitive solvents based on ionic liquids. Conventional ionic liquids absorb CO₂ through physical absorption, and were found not competitive with conventional amines due to lower capacity and high viscosity. Later, task-specific ionic liquids were designed to enhance absorption capacity by chemical absorption incorporating a reactive functional group in the cation or the anion (Bates et al., 2002). However, the

conventional aqueous amine system remained preferred overall due to lower cost, higher capacity, and low viscosity (Yusoff et al., 2013).

The mixture of amines and ionic liquid has recently attracted the attention of many researchers to produce potential solvent (Haghtalab and Shojaeian, 2015). The addition of piperazine (PZ) was shown to greatly enhance the solubility, and to reduce the viscosity of IL, 1-ethyl-3-methyl-imidazolium acetate ([Emim][Ac]) (Li et al., 2014e). High absorption capacity was observed in aqueous blended system of (4 M MDEA and 1 M guanidinium trifluoromethanesulfonate [gua][OTf]. For example, at 800 kPa partial pressure and at 303.15 K, the solubility of CO₂ was found to be at 0.667 mol CO₂/mole absorbent (Sairi et al., 2011 and Sairi et al., 2015).

From the perspective of amine-based solvent, mixture of ionic liquids and amine as a solvent has the potential of less energy intensive regeneration process as the heat capacity of IL is typically one third that of water, but has the disadvantage of making the solvent more viscous than the aqueous amine. For example, two low viscosity ionic liquids (ILs), 1-(2-hydroxyethyl)-3-methyl-imidazolium dicyanamide ([C₂OHmim][DCA]) and 1-butyl-3-methylimidazolium ([Bmim][DCA]) were mixed at a concentration range from 10 to 50 wt%. with aqueous MEA and the solubility of CO₂ in the mixed solvent was measured over a range of CO₂ partial pressure of 10–800 kPa and at 313.15 K and 333.15 K (Xu et al., 2014a). They found a negative effect on solubility of the addition of IL, probably due to a salting out effect. However, if the IL is present at low concentration, the negative effect on solubility is less pronounced, and the addition of IL may be advantageous from the greater benefit of decreased regeneration cost. The solubility of CO₂ in mixture of [bmim][Ac] with MDEA, DEA, DIPA, AMP were also measured (Shojaeian and Haghtalab, 2013). Replacing the aqueous portion of the MDEA solution by [bmim][acetate] enhances CO₂ loading and reduces the enthalpy of solution of CO₂ significantly (Haghtalab and Shojaeian, 2015). The

solubility data were correlated using a new equation of state, the PR-TS EoS, based on the Peng–Robinson (PR) EoS and the Two-State Association Model (TSAM) for association energy contribution.

3. Design, Modeling, and Simulation of Post Combustion CO₂ Capture Systems Using Reactive Solvents.

3.1. Determination of column height for CO₂ absorber

One of the most important steps for designing of a post-combustion CO₂ capture process is to determine the height of the absorber column required for a given CO₂ capture operation. There are several methods to design absorber height as given in Figure 3.1 (Tontiwachwuthikul, 1991; Tontiwachwuthikul et al., 1989; Tontiwachwuthikul et al., 1994), including the empirical method in route A, theoretical method in route B, laboratory method in route C, and pilot plant method on route D. All these methods start by defining independent parameters (*e.g.*, flow rate of gas and liquid phases, flue gas composition, gas-liquid contacting system, etc.) and obtaining physical properties data to determine the superficial velocities of gas and liquid phases. These will then be used for estimation of an absorption rate or a mass transfer coefficient that directly relates to the column height.

Insert Figure 3.1 here

3.1.1 Empirical Design Method (route A)

In this method, the column height is calculated from the average overall volumetric mass transfer coefficient, $(K_G a_v)_{ave}$ as in the following equation

$$z = \frac{G_I}{K_G a_v P} \int_{y_{A,Gin}}^{y_{A,Gout}} \frac{dy_{A,G}}{(1 - y_{A,G})^2 (y_{A,G} - y_A^*)} \quad \text{Equation 3.1}$$

where a_v , G_L , K_G , P , $y_{A,G}$, and y_A^* denote interfacial area per unit volume of packing (m^2/m^3), inert gas molar flow rate ($\text{kmol}/\text{m}^2 \text{ s}$), overall gas mass transfer coefficient ($\text{kmol}/\text{m}^2 \text{ s kPa}$), total pressure (kPa), and mole fraction of component A in gas bulk, and in equilibrium with liquid bulk, respectively., $\frac{G_L}{K_G a_v P}$ represents the height of a transfer unit

(HTU), while $\int_{y_{A,in}}^{y_{A,out}} \frac{dy_A}{(1-y_{A,G})^2 (y_{A,G} - y_A^*)}$ represents the number of transfer units (NTU) .

The $(K_G a_v)_{ave}$ can be obtained from experimental measurement at the bottom and top of the absorber which can be given as

$$(K_G a_v)_{ave} = G_L \frac{\left(\frac{y_{A,G}}{1-y_{A,G}} \right)_{bottom} - \left(\frac{y_{A,G}}{1-y_{A,G}} \right)_{top}}{zP(y_{A,G} - y_A^*)_{lm}} \quad \text{Equation 3.2}$$

Where $(y_{A,G} - y_A^*)_{lm}$ is the log-mean driving force,

The volumetric mass transfer coefficient is assumed to be constant along the column height and is basically correlated as a function of the operating parameters such as flow rates, pressure and temperature. However, when it comes to mass transfer involved chemical reaction, this empirical method becomes unreliable since HTU changes significantly along the column height, unless well-understanding of the relationship of HTU with operating conditions are obtained and subsequently implementing equations calculation in simulation program (Mores et al., 2012).

3.1.2 Theoretical Design Method (Route B)

The theoretical design for absorption with chemical reaction was first proposed by Astarita (1967) and Danckwerts and Lannus (1970). Their efforts were primarily directed towards developing expressions for the local mass transfer coefficients. [ENREF 86A](#) rigorous design procedure for adiabatic gas absorption with chemical reaction was

subsequently described by Pandya (1983). Pandya's procedure accounted for the heats of absorption and reaction, solvent evaporation and condensation, chemical reactions in the liquid phase, and heat and mass transfer resistances in both phases.

A mathematical model based on Pandya's algorithm is used to illustrate the theoretical design approach presented as follows:

Overall differential material balance:

$$G_I \frac{d\left(\frac{y_A}{1-y_A}\right)}{dz} = -\left(\frac{L}{\nu_{AB}}\right) \frac{dC_B}{dz} \quad \text{Equation 3.3}$$

Mass transfer for component A:

$$G_I \frac{d\left(\frac{y_A}{1-y_A}\right)}{dz} = k_{G,A} a_v P (y_A - y_{A,i}) = I k_L^o a_v (C_{A,i} - C_A) \quad \text{Equation 3.4}$$

Heat balance for liquid phase:

$$L C_{P,L} \frac{dT_L}{dz} = G_I \left(\sum_j Y_j C_{P,j} \right) \frac{dT_G}{dz} + G_I H_R \frac{dY_A}{dz} \quad \text{Equation 3.5}$$

Heat balance for gas phase:

$$G_I \left(\sum_j Y_j C_{P,j} \right) \frac{dT_G}{dz} = h_G a_v (T_G - T_L) \quad \text{Equation 3.6}$$

where ν_{AB} , $C_{P,L}$, $C_{P,j}$, h_G , H , H_R , H_S , I , k_G , k_L^o , T and Y respectively denote stoichiometry, heat capacity of solution (kJ/m³ K), heat capacity of component j in the gas (kJ/kmol K), heat transfer coefficient (kJ/m² s K), Henry's constant (kPa m³/kmol), heat of absorption and reaction (kJ/kmol), heat of vaporization of solvent S (kJ/kmol), enhancement factor, gas mass transfer coefficient (kmol/m² s kPa), physical liquid mass transfer coefficient (m/s), temperature (K) and mole ratio; the five components presented in subscript comprise

an inert carrier gas (I), an acid gas (A) (*i.e.* CO₂), a reactant (B) in the liquid and a reaction product (C).

To determine the packing height for a given absorption duty, the above equations must be solved concurrently. A two-point boundary value problem in which the conditions of the lean absorbent and raw feed gas are known and those of the off gas and rich solution are partially specified is solved using numerical methods. Before the model equations can be evaluated, physico-chemical data such as solubility, diffusivity, and rate constants are required. They may be obtained from experimental measurements or correlations. However, considerable discrepancies between reported data from different sources must be taken into account as they can strongly affect the results.

Nowadays, a number of software programs can be successfully used to simulate the CO₂ capture processes with reactive solvents and to compliment laboratory and pilot plant tests. The examples of these software are Aspen Plus, Aspen HYSYS, ProMax, CHEMASIM, ProTreat and CO2SIM (Freguia and Rochelle, 2003; Mangalapally et al; Weiland et al., 2009; Amrollahi et al., 2011; Tobiesen et al, 2012; Gao et al., 2014; Øi et al., 2014).

[ENREF 14](#) [ENREF 126](#) **3.1.3 Laboratory Method (Route C)**

In this method, the rate of absorption per unit interfacial volume or mass transfer rate ($R_v, \text{kmol/m}^3 \text{ s}$) is assumed on the basis of the absorber hydrodynamics and the concentrations of reactants in gas and liquid phases. It can be obtained experimentally by varying the bulk gas and liquid compositions in a stirrer cell and there is no need to calculate physico-chemical data parameters, such as reaction rate, solubility and diffusivity. The absorber height then can be determined by

$$z = G_I \int_{y_{A,in}}^{y_{A,out}} \left(\frac{1}{R_v a_v (1 - y_{A,G})^2} \right) dy_{A,G} \quad \text{Equation 3.7}$$

It is noted that such a model can be used when the reaction rate is fast enough to take place only in the liquid film and there is no reaction occurring in the bulk of the liquid. Alper and Danckwerts (1976) developed a new model, the so called complete model. This model was developed from string-of-sphere column. The absorber height determined using this model can be calculated by:

$$\left(\frac{z}{z_m} \right) = \frac{\left(\frac{L}{a_v} \right)}{\left(\frac{L_m}{a_{v,m}} \right)} \quad \text{Equation 3.8}$$

where subscript m respectively represents the model column.

3.1.4 Pilot Plant Technique Method (route D)

This method was proposed by Tontiwachwuthikul (1991); Tontiwachwuthikul et al. (1989); Tontiwachwuthikul et al. (1994). The method is intended to scale up a pilot plant or bench-scale plant to an industrial scale plant. However, such a method needs to assume that hydrodynamic characteristics of the pilot plant or bench-scale plant are the same as those of the industrial scale plant. R_v can be determined by assuming it is a function of the fluid concentration as follows

$$R_v = \frac{G_I d \left(\frac{y_A}{1 - y_A} \right)}{dz} \quad \text{Equation 3.9}$$

R_v can also be obtained from the absorption rate from the liquid composition profile as follows:

$$R_v = L \frac{dC_A}{dz} + \left(\frac{L}{v_{AB}} \right) \cdot \frac{dC_B}{dz} \quad \text{Equation 3.10}$$

The absorber height can then be calculated by Equation 3.7. This method does not require the hydrodynamic and physico-chemical parameters. Another advantage of this

method is that it is applicable to all cases regardless of whether the rate of absorption is obtained by the reaction in the liquid film or in the bulk of the liquid or both, and no matter how fast or slow the reaction rate is.

3.2 Developed process configurations for post combustion CO₂ capture

Optimization of the process configuration by using process simulators, such as Aspen plus, Aspen HYSYS and ProMax for post-combustion CO₂ capture is undoubtedly one of the most promising ways to reduce energy consumption. Over the past decades, many emerging process configurations have been developed to reduce the energy consumption and capital cost for CO₂ capture. The absorber coupled with an intercooler (i.e. intercooling) can lower absorption temperature and enhance absorption capacity due to a new thermodynamic equilibrium being reached (Chang and Shih, 2005; Karimi et al., 2011; Kvamsdal et al., 2009; Oexmann et al., 2008; Plaza et al., 2010). However, it should be noted that the lower temperature will decrease the CO₂ absorption rate. Reddy et al. (2004) presented two different absorption flash stripping process configurations with a flash unit between the absorber/stripper and the lean-rich heat exchanger, working at a higher absorption pressure condition than the normal stripping pressure. Jassim and Rochelle(2006)proposed two novel process, i.e., absorption/stripping with vapor recompression and multi-pressure stripping with vapor recompression, which resulted in 3-11% reduction of total equivalent work compared to a simple stripper column. A modified split flow scheme with key feature of one division of rich-solution from the absorber and the other division of solution from stripper at the midpoint and bottom has been modeled by Aroonwilas and Veawab (2007). Oyenekan and Rochelle (2007) have developed a flashing feed stripper that is optimized to minimize equivalent work by adjusting the split ratio of the rich streams into the middle and upper sections. Also, a new configuration of the matrix stripper (295/160 kPa) has been simulated by Oyenekan and Rochelle(2007) using Aspen plus. Their studies found the total equivalent

work of the matrix stripper with reduction of by 8% in a comparison with the standard configuration. In addition, a modified matrix stripper configuration was evaluated technically and economically by Schach et al. (2010), which allowed the cost of CO₂-avoided and total required power to be reduced by 1.5% and 4.5%, respectively. Moreover, Liang, (2010) proposed two innovative configurations of stripping with two-split feeds and one head heat exchanger and stripping with three-split feeds by re-using the heat of overhead vapor to take full advantage of its latent heat. Gao et al., (2014) developed a heat pump distillation with a split feed process with the main advantage of recovering the latent heat of the overhead vapor to heat the rich solution. Other more complex configurations were proposed by researchers to reduce energy requirement for CO₂ capture.

In recent years, many excellent authoritative reviews have been provided for optimization of standard process configurations (Chakma, 1997; Plasynski and Chen, 2000; Eide et al., 2005; Cousins et al., 2011; Le Moullec and Kanniche, 2011). Eide et al. (2005) provided an overview of novel pre-combustion, post-combustion, and denitrogenation processes being investigated in Europe. Use of membrane contactors as an absorber was suggested for post combustion capture to reduce the size of the absorber column. Cousins et al. (2011) reviewed fifteen process configurations for chemical-based CO₂ capture processes in scientific journals and, mostly, in patented literature. The potential flow sheet modifications with large improvements, such as the inter-stage temperature control, multi-pressure stripping, matrix stripping, multi-component column and heat integration concepts were discussed for gas processing industries and the capture of CO₂ from flue gases. However, further process modeling and experimental validation are required to evaluate the technical-cost potential of these considerable process configurations. Le Moullec and Kanniche (2011) used Aspen Plus to simulate a number of MEA-CO₂ based process modifications and compared their performance in terms of efficiency penalty, leading to the conclusions as follows. In the CO₂

stripping operation, simple process modification with moderate vacuum pressure, lean solvent vapour compression, and staged feed of the stripper or the overhead stripper compression could allow a reduction of efficiency penalty by 4–8%. Also, the combination of individual modifications could result in a larger efficiency penalty reduction by 10% to 25%. However, results of these potential process modifications should be validated with pilot plant data before implementing in commercial applications.

[ENREF 85 ENREF 133 ENREF 102 ENREF 9 ENREF 133 ENREF 111 ENREF 62](#)**4. Solvent Management**

4.1 Corrosion

A lot of useful information on corrosion behavior of most conventional amines used in CO₂ capture process has already been provided in the corrosion studies extensively done in the past. These corrosion studies carried out mostly under a lab-scale environments often included effects of typical CO₂ absorption parameters specifically temperature, amine concentration, CO₂ loading and flue gas oxygen concentration. To completely characterize corrosion of amine systems, a recent study completed corrosion measurements to show the effects of various types of flue gas constituents other than oxygen (O₂) on a common construction material, carbon steel 1020 (Wattanaphan et al., 2013). Flue gas compositions tested in this study were fly ash containing different compounds of chloride (Cl; i.e. NaCl, HCl, and FeCl₂) and sulfate (SO₄; i.e. Na₂SO₄, FeSO₄·7H₂O, H₂SO₄) and compounds derived from sulfur dioxide (SO₂; i.e. H₂SO₃), sulfur trioxide (SO₃; i.e. H₂SO₄), and nitrogen dioxide (NO₂; i.e. HNO₃). In brief, corrosion rate has been found to be dependent on concentration of NaCl and HCl. The opposite effect has been observed for FeCl₂. Corrosion rate of systems containing all fly ash sulfate compounds has been found to increase with sulfate concentration. With the increase in concentration, all SO₂ and SO₃-derived compounds have increased corrosion rate to a maximum before falling off to a minimum and leveling off. NO₂

932 has shown an increase and level off trend in corrosion rate. Crucial information extracted
933 from results based on this work is that the same chemical species (e.g. Cl and SO₄) always
934 produce different corrosion effect if present in a different compound. This implies that the
935 source of these corrosive species must first be indentified so that corrosion in the amine plant
936 can be accurately evaluated. Lab-scale corrosion measurement based on an electrochemical
937 technique is still a popular method used to quickly assess corrosion tendency of new amine
938 based solvents being developed to replace high energy consuming conventional solvents such
939 as monoethanolamine. One recent work has used this technique to measure corrosion under
940 the absorber temperature and CO₂ rich loading conditions of CSIRO-1, a proprietary 2-
941 amino-2-methyl-1-propanol (AMP) and 3-piperidinemethanol (3-PM)-based solvent to
942 compare with MEA and other blend consisting of AMP and piperazine (PZ) (Pearson et al.,
943 2013). The corrosion rate of this newly blended solvent has been found to be 6-7 times lower
944 than conventional MEA and AMP/PZ blend possibly due to a limited concentration of proton
945 (H⁺) available in the reduction reaction at the cathodic side of the system. 30 wt% PZ,
946 proposed as an alternative solvent for CO₂ capture, has also been evaluated to show its
947 reduced corrosion rate compared to that of benchmark MEA (Zheng et al., 2014). Based on
948 scanning electron microscopic (SEM) and x-ray diffractometric (XRD) analysis, a stable iron
949 carbonate (FeCO₃) that formed quickly on the entire surface of corrosion specimen (carbon
950 steel A106) exposed to CO₂ loaded 30 wt% PZ and has been found to be a protective layer on
951 the metal, cutting down the corrosion rate. This finding has been suggested as a benefit in
952 using PZ as a CO₂ capture solvent as opposed to conventional MEA, which does not possess
953 this similar protective layer-forming property. Another laboratory test using weight loss
954 technique has been carried out to evaluate corrosion of 22 different amine structures exposed
955 onto metal specimens in liquid amine and gaseous space in the corrosion cell (Martin et al.,
956 2012). It is not a surprise to have seen MEA, as one of the 6 amines tested, show noticeably

high corrosion tendency towards the test steel specimens especially in the liquid phase system. Again, this emphasizes the importance of special care required for MEA users who must have a proper corrosion control in place during the CO₂ absorption process.

Therefore, corrosion problems generated by MEA can be properly managed. Another work also tested corrosion of CO₂ loaded MEA as affected by O₂, heat stable salts (HSS), temperature, and solvent flow rate using agitation. According to the work of Xiang et al. (2014), corrosion in MEA/CO₂ systems of carbon steel was time-dependant showing an initially higher rate before quickly dropping off to stabilize at a lower rate. This observed behavior was due to a FeCO₃ protective film formation detected by scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS). Also under a similar test time, O₂, HSSs, and flow rate all have shown to trigger noticeably higher corrosion rates compared to a system without these variables. Increase in temperature only has a slight effect on the corrosion rate as this limits availability of O₂ and CO₂, an important provider of oxidizing agents for corrosion processes. In an attempt to improve conventional solvents for a better CO₂ capture performance, MEA is often blended with other amine so that the mixture can have a higher CO₂ capture capacity yet consume less energy in the stripping process. Corrosion resistance is also another desired property that must be tested for prior to using them more commercially in a bigger CO₂ absorption scale of operation. A blend of MEA and an amino acid salt, particularly sodium glycinate (SG), is known to have high CO₂ absorbing characteristics. It has been studied to help increase the amine's CO₂ equilibrium solubility (Mazinani et al., 2011).

Electrochemical technique was performed in accordance with ASTM G5-94 corrosion testing procedure to also measure the corrosion tendency of the blend as a function of molar ratio of SG in the absence of CO₂. The measurement of corrosion rates was carried out at 308 K using a potentiostat with 3 electrode systems of Ag/AgCl reference electrode, Pt counter

electrode, and sample cell electrode attaching to a specimen. The results show an increasing trend of corrosion rate with an increase of SG molality in the mixture. The test could have possibly shown a higher corrosion tendency if CO₂ was also included during the measurement. In an amine solution, CO₂ once dissolved, will quickly form HCO₃⁻ and CO₃⁻ species known to induce more oxidation of iron (i.e. iron dissolution) which could be normally observed by an increase in cathodic current densities during electrochemical measurement (Nainar and Veawab, 2009). The increase in cathodic current densities due to CO₂ therefore results in an increase in corrosion rate. This shows precisely that other than the CO₂ pick-up capacity aspect, corrosion and other operational criteria must be taken into account when developing new amines for the CO₂ absorption process. No CO₂ plant will benefit fully from a solvent having only high CO₂ absorption capacity but being heavily corrosive.

It is clear that laboratory-based corrosion measurement can provide a well-controlled test environment essential for the systematic study of the corrosion effects of all CO₂ absorption parameters. However, equally important measurement directly from a commercial/pilot-scale plants must also be performed to show the true corrosive nature of the solvent while CO₂ is actually being capture in a real process. Corrosion of 30 wt% MEA-based pilot plants, namely Dong Energy's Ebsjerg and TNO's Maasvlakte have been recently been evaluated respectively using weight loss technique with corrosion coupons-plant inspection and on-line monitoring using electrochemical probes. Based on this test campaign (De Vroey et al., 2013), 6 corrosion coupons placed in different locations throughout Ebsjerg plant and one electrochemical probe installed at the stripper liquid outlet of the Maasvlakte have produced a consistent corrosion rate measurements that can be correlated well between the 2 plants. Based on the results, the corrosion rates on stainless and carbon steel measured from both plants would not be expected to affect the plants' structural integrity. However,

needs for extra attention to some critical areas including the stripper sump, high temperature lean solvent pipe exposed to turbulence flow, reboiler, and reclamer has been suggested. Results learned from corrosion control and measurement of a high pressure natural gas treating processes can also be usefully applied to flue gas-based amine process application. For example, methyldiethanolamine (MDEA) is being used to treat the Iranian coast offshore natural gas stream containing 0.6% H₂S and 2.5% CO₂ in which has been observed severe corrosion especially in the high temperature reboiler and rich amine stripper (Davoudi et al., 2014). This work has indicated that heat stable salts (HSSs) generated by reaction of MDEA and acids stronger than H₂S and CO₂ as well as by oxidation of the amine itself are the major contributing factors to severe corrosion in the reboiler. The analysis has shown that weakly bound acids including formate and acetate can dissociate from the amine and evaporate in a higher temperature section of the reboiler. Condensation of these free acids can possibly follow and deposit onto a colder part of the reboiler, thereby corroding the metal. Prevention techniques to protect the amine plant construction materials from being corroded are still an on-going area of research and development. Use of chemical additives can be simple, yet powerful, giving an instant effect in cutting down corrosion in the amine-based absorption unit. Sodium thiosulfate, claimed to have low toxicity, has been evaluated for its corrosion prevention effect in an MEA based system (Srinivasan et al., 2013). Electrochemical and weight loss techniques have been used to evaluate this compound in rich loaded 5 kmol/m³ MEA, 80°C, and the presence of contaminants. Short-term exposure of the inhibitor has shown that the compound has a corrosion protection power, with over 90% inhibition efficiency in all concentrations tested ranging from 250–10,000 ppm. However, the passive film known to protect the metal from being corroded has been found to become increasingly unstable in the long-term testing of the same thiosulfate inhibitor resulting in an ineffective performance of the compound. The inhibition effectiveness however, is not affected

significantly by chloride and formate heat stable salt. Other work has explored the use of room temperature ionic liquids (RTILs) as a potential corrosion inhibitor in an amine-based system (Hasib-ur-Rahman and Larachi, 2013). This work electrochemically measured corrosion of a carbon steel specimen in 30wt% MEA containing 10-30 wt% of 4 different imidazolium-based RTILs. Most RTILs have been found to reduce the specimen's corrosion rate of MEA alone system with acetate-based compounds being the most effective corrosion inhibitor in this study. Increased viscosity of MEA caused by the acetate compound has been suggested as a responsible factor of the reduced corrosion rate as this limits the diffusion of oxidizing agents in the corrosion process. Although, these chemical additives have shown potential in prevention of corrosion when used in the amine system, some corrosion additives often induce other operational problems. Based on our previous work (Bello and Idem, 2006), we have demonstrated earlier that a well-known sodium metavanadate corrosion inhibitor (NaVO_3) adversely affects MEA degradation by accelerating its reaction rate.

For future development, new inhibitors formulated will have to be tested to make sure their use does not induce other side effects in the amine plant such as degradation and foaming. Side effects of these inhibitors developed in future research must also be taken into account and included as part of the study.

4.2 Solvent stability issues

Degradation of amine is still one of the most active research areas within the CO_2 absorption process. Degradation research presented up to 2011 was heavily focused on chemical break-down of amine affected by various CO_2 capture parameters (e.g. amine type and concentration, flue gas composition, and metal contamination) and kinetics related to those effects as highlighted already in our previous review paper (Supap et al., 2011). However, the current research focus is being shifted towards mechanistic studies of amine degradation as often seen included in much recent degradation literature. One motivation

behind this change is probably to gain better knowledge and understanding of solvent stability chemistry, which is required to help develop a highly degradation resistant amine. Therefore, a systematic mechanistic study is required to achieve this goal. An equally important push also stems directly from an increased concern for environment and human health which can be potentially jeopardized by toxic emissions from amine degradation. A series of papers has been dedicated to the degradation work highlighting details of formation mechanism and toxicity of degradation products either previously or newly identified in monoethanolamine (MEA) solution. The first paper in the series critically reviewed amine degradation products and how they were formed in various solvents which included MEA, diethanolamine (DEA), methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), piperazine (PZ), and blended amines.

Proven mechanism work on degradation products plus SO_x and NO_x induced degradation have been identified as an area requiring further investigation. The second publication in the same series has highlighted the work on toxicity evaluation and formation mechanism based on a combination of condensation, dehydration, and oxidation of aldehydes of pyrazine and its derivatives claimed as newly found MEA degradation products (Rey et al., 2013). Mechanism studies of more MEA-based degradation products in the group of amides and nitrogen-based heterocyclic compounds have been added to the work in this research program (Gouedard et al., 2014). It is clear that even MEA still requires more work to fully understand its degradation chemistry needed for evaluation of the amine toxicity from emissions. Less studied amines also require similar research investigation as they are often used to also capture CO_2 . Thus, their degradation behavior especially in the aspect of how it occurs and related toxicity must be well understood before the amines are used more commercially in a larger-scale operation with zero or the least negative impact on humans and the environment. 2-methyl-2-amino-1-propanol (AMP) well known for its enhanced

equilibrium CO₂ loading property has been found to be the least degraded in the presence of oxygen (O₂) compared to other solvent systems, which were PZ, MEA, MDEA, and blended MDEA and PZ (Voice et al., 2013). A more systematic study has shown a significant effect of O₂ and CO₂ under thermal degradation conditions for AMP and other amines including MEA and PZ. Based on this study (Bougie and Iliuta, 2014), the degradation extent of AMP in the presence of O₂ only was much higher than that of MEA. AMP loss due to oxidation was tremendously cut down when CO₂ was added into the system, in which case, this could better represent a real condition during the CO₂ capture process. This specific result also implies that control of oxidative degradation of this amine can be partially achieved by properly adjusting its rich and lean CO₂ loading. This same strategy, having been discussed numerous times in our earlier publications, can be potentially adopted and used in a real capture plant. In terms of degradation mechanisms, the radical-based pathway of AMP oxidation modified from a previous work has been proposed based on the formation of products identified during the oxidation experiment (Wang and Jens, 2013). This mechanism has helped in further investigation of the same study to understand the role of MEA in protecting AMP from oxidative degradation when the amines are used together as a blended solvent. This mechanism work has been continued to account for formation of carboxylic acids identified in MEA, AMP, 2-amino-1-propanol (APN), and 2-amino-1-butanol (ABN) during the test (Wang and Jens, 2014). The mechanism of oxidation proposed for these amines were based on radical formation leading to generation of formate, acetate, glycolate, oxalate, and pyruvate. Other solvents investigated quite extensively in term of oxidative degradation are MDEA and PZ which are often mixed together or with MEA to improve the CO₂ absorption capacity and regeneration efficiency of the capture solvent. A study reviewed earlier (Voice et al., 2013) has also shown the degradation extent of MDEA and its blend with PZ are among the highest of all amines investigated in this work. However, PZ was less

susceptible to oxidation than the 2 previous amines, showing much lower amine loss measured by production of formate, a significant degradation product. The difference in second heteroatom (i.e. O, C, and N) ring sizes in both monoamine and diamine, and methyl substitution on the PZ ring have been evaluated to understand thermal degradation resistance of PZ and its derivatives (Freeman and Rochelle, 2011). In terms of degradation resistance measured particularly in this study by the fraction of initial amine versus time, PZ has was one of the 3 most stable amines tested in this study, probably due to its 6 membered-ring structure with no substitution group.

As mentioned earlier, emissions generated by degradation of amine can be potentially toxic and harmful to humans and the environment. The toxicity can possibly lead to serious injuries or even death. For example, a recent study has shown potential health risk if exposed to degraded MEA, MDEA, and PZ by inhalation with only MEA showing a significant increase of inflammation of cells in the lungs of laboratory mice when compared to a non-degraded sample (Rohr et al., 2013). This foreseen consequence has set a trend in future degradation research that should also add the emissions and toxicity aspect as another important objective to the study of degradation. More literature dealing with the emissions and their related toxicity generated by amine degradation have become available. Most of these studies are being focused on formation and harmful effects of nitrosamines and nitramines known as potential carcinogenic compounds. A study has tested initial the potential of MEA, AMP, MDEA, and PZ to generate nitrosamines in a laboratory with mixtures of nitric oxide (NO) and nitrogen dioxide (NO₂) and later on measured nitrosamines formation of these solvents from actual pilot plant samples(Dai et al., 2012). The laboratory results have shown the highest total nitrosamine formation in PZ, a secondary amine known to form the most stable nitrosamine, followed by AMP and MDEA with MEA containing the lowest total nitrosamine accumulation in the solvent. A similar trend has been observed in

pilot plant sample analysis in both solvent and wash water with a mixed AMP/PZ system having higher total nitrosamine concentration than that of MEA. Further investigation has been carried out to confirm the effect of different chemical structures of amines in forming N-nitrosamines (Dai and Mitch, 2013). Total N-nitrosamines have been identified as the dominant products in all amine groups with secondary amines generating the most total N-nitrosamines, followed by tertiary amines and primary amines respectively. This trend has been observed under both absorption and desorption conditions. Not only do different amine structures induce different levels of nitrosamine formation, but also, flue gas composition, especially NO_x and O_2 , can certainly trigger additional formation of nitrosamines. To study this effect of flue gas composition, a study has been conducted using morpholine, a secondary amine, to evaluate its potential in the formation of nitrosamines with a lab-made flue gas containing varying concentration of NO , NO_2 , O_2 , CO_2 , N_2 , and H_2O vapor (Dai and Mitch, 2014). In the presence of O_2 , both NO and NO_2 have linearly increased the formation of N-nitrosomorpholine in both solvent and wash water used to clean the treated gas before leaving the absorber column. The same study has also identified potential nitrosating agents which include nitrite, N_2O_4 , NO_2 , and N_2O_3 . NO has been seen as a non-significant nitrosating agent by itself, however, its reaction with its oxidizing product itself forming N_2O_3 can generate N-nitrosomorpholine as seen from the accumulation of this product in wash water sample. The health effect of nitrosamines and nitramines have been recently published. This study quantitatively evaluated 11 nitrosamines and nitramines associated with CO_2 capture processes on their effect on hamsters in terms of mutagenicity and chronic cytotoxicity and acute genotoxicity (Wagner et al., 2014). Mutagenic potency evaluation of these toxic compounds has shown N-nitrosamines 15 times more mutagenic than N-nitramine analogues. Studies related to kinetics and mechanism of amine degradation leading to nitrosamine formation and decomposition to help prevent a spread of compound toxicity is still limited.

Probably, this is due to nitrosamines often being formed in such a small concentrations that it prevents detection and accurate measurement of them in pilot plant. However, a study recently published has managed to investigate the decomposition of nitrosamines specifically of those formed from PZ and MEA. Based on this study of decomposition kinetics under basic and stripper temperature conditions of PZ, (Fine et al. (2014) derived N-nitrosopiperazine (MNPZ) and nitrosodiethanolamine (NDELA), and nitroso-(2-hydroxyethyl) glycine (NHeGly) from their pilot plant samples.. Kinetically, MNPZ has been found experimentally to decompose a lot faster in basic medium using NaOH than in PZ solution. NDELA and NHeGly on the other hand, have been too stable to degrade at a typical stripper temperature of 120°C. Incorporation of basic treatment (e.g. NaOH) in the reclaimer has been suggested as a remedy to help decompose these MEA derived nitrosamines more effectively and, thus control of the emissions can be managed.

It is clear that these recent studies of amine degradation and its related emissions are still being investigated extensively. As mentioned earlier, focus of degradation research can no longer be put only on how to develop the amine to be more resistant to chemical breakdown while capturing CO₂. The environmental aspect generated by such degradation in terms of emissions and their prevention strategies must also be included as one of the objectives of any study. This is setting a new research direction in degradation studies, which can be expected to include more work in the future.

4.3 Solvent recycling and reclaiming

In post-combustion amine-based CO₂ capture processes using reactive solvents, it is expected, in principle, that the solvent will be chemically stable in order to achieve a stable CO₂ capture operation. In reality, reactive solvents do degrade because of impurities in the flue gas of a fossil fuel-fired power plant (e.g., O₂, NO_x and SO_x) and/or severe operating conditions of the CO₂ capture plant. Thus, all amine solvents including singles and blends are

subject to degradation-producing products such as heat stable salts (HSSs) (Astarita et al., 1983; Wilson et al., 2004). For these reasons and to make the process both economically feasible and cost effective, as well as to minimize the overall plant energy consumption while maintaining solvent stability, appropriate reactive amines must be selected. Two of the criteria to select an appropriate solvent are: (i) minimum solvent degradation and (ii) ease to in which the solvent can be reclaimed or recycled.

Following our categorization (Tontiwachwuthikul and Idem, 2013, Supap et al., 2011, Tontiwachwuthikul, 2011), carboxylic acid degradation products once generated, can quickly tie up with additional molecule of amine forming a type of compound call heat stable salts (HSSs). Definitions of HSSs in the literature vary considerably; however, HSSs can be considered as the salts formed by the reaction of amine and its acidic degradation products and impurities (e.g. organic acids and HCl) which cannot be regenerated under normal stripper conditions (Tontiwachwuthikul and Idem, 2013; Supap et al., 2011). A sub-category of HSSs is the portion that can form from the reaction with an amine which is called heat stable amine salt (HSAS). Therefore, if there are no strong cations in the amine solution, HSASs are the same as HSSs. HSS anions formed could include acetate, formate, thiosulfate, sulfate, thiocyanate, oxalate, butyrate, and propionates. Other HSS anions introduced to the amine process from water make-up or flue gas are chlorides, phosphates, cyanides, and nitrates (Cummings and Mecum, 2000; Paitoon and Raphael, 2013; Supap et al., 2011). According to the literature (Bacon, 1987; Paitoon and Raphael, 2013; Supap et al., 2011) the recommended HSS level in amine should be less than 10% of the amine concentration (e.g., 30wt% MEA should contain a maximum of 3% HSSs) but 3% should be controlled to avoid operational problems. Further details of HSSs and their formation paths are reported extensively in the literature (Paitoon and Raphael, 2013; Supap et al., 2011). Operational problems triggered by the presence of HSSs and other amine degradation products include

reduction in solvent capacity and plant throughput, change of water balance and physical/chemical properties of solvent, high viscosity causing reduced mass transfer and increased pumping power, increase of foaming tendency and decrease of contact surface between gas and liquid, increase of solvent corrosiveness which affects process equipment, fouls and plugs heat exchangers and mass transfer equipment, increases energy/heating steam consumption, and increases the cooling duty (i.e., cooling water) (Supap et al., 2011; Tontiwachwuthikul and Idem, 2013).

In order to ensure a stable operation, these problems must be addressed and solvent degradation should be controlled. The solutions are generally categorized into solvent degradation prevention methods, and recycling and reclaiming methods, the latter of which are needed if degradation has already occurred. This section of the paper reviews the progress made in solvent degradation prevention, and solvent recycling and reclaiming methods since 2004.

4.3.1 Solvent Cleaning, Degradation Prevention, Recycling and Reclaiming Methods

Solvent cleaning and degradation prevention methods can be done in several ways which can be found in great details in our previous publications (ElMoudir, 2012a, ElMoudir et al., 2012b). In brief, purification of solvent to maintain its quality and absorption capacity should include clean-up the solvent which only solvent change-over, solvent purging/feeding, mechanical filtration, activated carbon filtration, and neutralization of organic/inorganic acids were used heavily decades ago. Use of chemical additive to cut down degradation can also help reduce work load of solvent purification process. Various degradation inhibitors have been constantly proposed over the past years (Idem et al., 2009b, Saxton and Rochelle, 2009, Lee et al., 2013, Leonard et al., 2014). Therefore, the capture process using different amines can pick and choose inhibitors appropriate for the solvents. Summary of more advanced approaches developed for amine reclaiming process can also be found as well in our previous

publications According to ElMoudir et al., 2012b, ion exchange based on separation of charged compounds can remove HSSs (e.g. formate, acetate, glycolate, and oxalate) quite effectively. Electrodialysis using ion-selective membrane under the influence of appropriate current and voltage can also be used as well to separate HSSs. Thermal reclaiming technique often requiring a large amount of energy input due to boiling-point based separation of compounds is also available for amine recovery. This technique in fact, is one of the oldest techniques used conventionally for the capture plant. However, the technique can be potentially be replaced by a less energy intensive technique such extraction which can be done under atmospheric pressure and lean-amine temperature. Such extraction method specifically developed for HSSs removal from MEA based solvent has been demonstrated by researchers from the University of Regina, Canada (Saiwan et al., 2012). Other techniques using hybrid reclaiming process and chemical conversion of degradation products to the amines are also available. However, it is rare to see improvement/new development of these techniques in the past 5-10 years in the open literatures (ElMoudir, 2012a).

4.3.2 Future perspective for the reclamation industry

The future trends for amine reclamation will likely take three paths: 1) improving the current technologies, 2) process integration between the current technologies, and 3) introducing new methods for reclamation. Regardless of method types and operations, the techniques used must be able to handle newly developed and complicated formulated solvents. Also, the techniques should be readily available to help improve solvent quality and recovery and process heat integration. In addition, they should be simple and should reduce the solvent loss in waste, the chemical consumption, and the capital and operational costs. Furthermore, overall wastewater quantity must be reduced, as these could also contain traces of amine. High levels of amine in wastewater could overload the wastewater treatment plant by killing the microbes in the system (Cummings and Mecum, 2000).

1257 In summary, there are a number new innovations regarding solvent management of the
1258 post-combustion capture process. These are some of the highlights:

- 1259 i. Solvent degradation inhibition seems to be one method of protecting solvent and will
1260 see more application in the future with development of new inhibitors.
- 1261 ii. Ion exchange and electro dialysis purification could be utilized to reduce heat stable
1262 salts and some degradation products. However, these technologies are not suitable for
1263 removal of the other degradation products, and this would make it challenging for
1264 these processes to be integrated into a CO₂ capture plant.
- 1265 iii. At present, thermal reclamation is the only technology that can remove all
1266 degradation products, heat stable salts, and non-volatile impurities (i.e., fine solid
1267 particles, corrosion products, and salts). Therefore, thermal reclamation is likely the
1268 most attractive purification option for CO₂ capture plants. However, not much has
1269 been reported about improvements to this method
- 1270 iv. Extraction can be applied to effectively separate HSSs and neutral degradation
1271 products from amine using proper extractant and diluent combinations with extracting
1272 conditions as demonstrated in the University of Regina's patented work (Saiwan et
1273 al., 2012).
- 1274 v. Effective degradation inhibitors such as those developed by ITC can protect up to
1275 98% of amine from being degraded, thereby reducing reclaimer load in CO₂ capture
1276 operations.
- 1277 vi. Combined reclamation processes have seen steady growth; however, they are only
1278 applicable in certain cases.
- 1279 vii. Many solvent reclamation technologies are under improvement/development with the
1280 aim of enhancing the process technology's key performance parameters such as

solvent recovery and utility consumption reduction, and efforts are also being made to develop simple and easy to operate processes.

5. Post-Built Operations

As mentioned previously, post-combustion carbon capture (PCC) is currently the only industrial carbon emission management technology that is ready for commercialization and wide-scale deployment. Two leading examples are the TMC Mongstad in Norway (300,000 tonnes per year CO₂ captured) and BD3 SaskPower in Canada (1 million tonnes per year CO₂ captured). As anticipated, these large-scale carbon capture units are starting to generate huge amounts of operational process data. These huge amounts of data sets can be very fruitfully utilized, using technologies of information and artificial intelligence, which have been widely acknowledged to be capable of generating knowledge useful for enhancing efficiencies of many industrial processes in the past. This can be true also in the field of carbon capture (Chan et al., 2011 and 2012)

This section presents two studies that focus specifically on applications of information and artificial intelligence technologies for supporting two tasks related to operation of the post-combustion CO₂ capture system. First, the knowledge-based system technology was applied for building two expert systems that perform monitoring, control, and diagnosis of the CO₂ capture process system (Zhou et al. 2009b, Zhou et al. 2011, Chan et al. 2012). Secondly, three data modeling techniques were applied for studying the nature of relationships among the key parameters of the post-combustion CO₂ capture process system (Zhou et al. 2008, Zhou et al. 2009a, Wu and Chan 2009, Zhou et al. 2010, Wu et al. 2010, Chan et al. 2011, Zhou et al. 2012, Zhou et al. 2013).

5.1 Expert Systems for Monitoring, Control, and Diagnosis of the CO₂capture process system

In the first application study, the research objective is to enhance efficiency and effectiveness in monitoring and control of the post-combustion CO₂capture process system using the knowledge-based system technology. CO₂capture is a process of complex physical and chemical phenomena that involves a large number of process variables such as pressure, flow, and temperature. When a fault is detected in the process system, the operator needs to identify and interpret the symptoms, analyze the current state, and determine the diagnosis in terms of which component(s) may have caused the fault and identify the cause for the failure of the component(s). If the abnormal condition cannot be remedied in a short time, instabilities in the process system will decrease efficiency of the CO₂ capture system and may even cause hazardous emergencies. Application of a knowledge-based expert system for monitoring, control and diagnosis of the CO₂ capture plant can be a promising approach to address these problems. By incorporating knowledge of an experienced operator, the expert system can perform fault diagnosis and provide suggestions for remedial actions in a timely manner. This would result in reduction in downtime, avoidance of system instability, and consequently, improved efficiency of the CO₂ capture process system.

Two prototype expert systems were developed for monitoring and control of the CO₂capture process system at ITC located at University of Regina in Saskatchewan, Canada. The first system is the Carbon Dioxide Capture Monitoring and Diagnostic (CDCMD) System implemented on the intelligent real-time system development tool of G2®(trademark of Gensym Corp, USA). The second system is called Knowledge-Based System for Carbon Dioxide Capture (KBSCDC), which was developed on DeltaV™ Simulate (trademark of Emerson Corp., USA). Acquisition and analysis of knowledge related to the post-combustion CO₂ capture process system is critical in development of the expert systems. The Inferential Modeling Technique (IMT) was adopted to guide the conceptual modeling process, and a

classification of the elicited knowledge about this complicated process system was completed by Zhou et al. (2009).

The objective of the CDCMD system was to monitor and control the key parameter of heat duty and operation of the heat-related reaction instruments while maintaining the desired CO₂ production rate at the plant. The knowledge of the reaction instruments and parameters were represented using the object-oriented entities of class hierarchy, rules, and procedures provided in the G₂ platform. The CDCMD system adopts a backward chaining mechanism for fault diagnosis, and continuously compares the measured real-time values with normal values of the parameters. When the system detects an overly low CO₂ production rate, it searches for the possible cause for this malfunction using the backward chaining inference method until a faulty component is identified. However, the CDCMD system has two limitations: (i) its knowledge base does not include the dynamic components, which include the substances circulating and reacting in the process system, and (ii) it only focuses on the parameters and reaction instruments associated with heat duty. Due to these limitations, the second expert system of KBSCDC, which has an extended knowledge base, was developed.

The knowledge base of the KBSCDC system includes more comprehensive and systematic information about the post-combustion CO₂ capture process system compared to the knowledge base of the CDCMD. Specifically, knowledge related to three additional aspects of the CO₂ capture process system are included in the KBSCDC system: (i) information about the dynamic objects of the process system, which include the fluids and gases, (ii) instead of focusing only on the parameter of heat duty, 25 important parameters belonging to 9 reaction instruments of the system are monitored, and (iii) the task knowledge related to how these 25 parameters can be controlled under normal and abnormal operational conditions is also incorporated.

The KBSCDC was implemented in the DeltaV Simulate platform. Based on the representational constructs of the platform, the knowledge was decomposed into logical modules, which included both plant areas and control modules that are integrated with control utilities and algorithms. The KBSCDC system monitors the operating conditions of the CO₂ capture pilot plant by continuously comparing the sensor-measured values of the 25 parameters with their normal values. When the system detects any deviation between the two sets of values, an alarm is activated to advise the operator that an abnormal condition has occurred. The KBSDC system performs the diagnosis, and the suggested remedial control action for the particular abnormal condition is displayed on the system interface. Upon receiving the message, the operator can apply the suggested control action by opening the faceplate of the faulty component. By correcting the abnormal condition, normal system operation is restored.

Both the CMCMD and KBSCDC systems support automatic monitoring and fault diagnosis of the post-combustion CO₂ capture process system, but the KBSCDC system consists of more comprehensive domain knowledge and problem-solving strategies. It also supports configuration of process control logic and simulation of the implemented control strategies. The primary differences between the CDCMD and KBSCDC systems are summarized in Table 5.1.

Insert Table 5.1 here

Development of the two prototype expert systems for monitoring, control and diagnosis of the CO₂ capture process system at ITC demonstrates the feasibility of applying expert system technology for automated decision support for the CO₂ capture process system. The expert systems can efficiently detect and provide remedial suggestions for abnormal conditions. In providing decision support to the operator in monitoring, control, and diagnosis of the CO₂ capture system, the expert systems help reduce downtime and enhance

system performance and efficiency. The expert systems can also be used as educational tools that support training of inexperienced operators of the plant.

5.2 Intelligent Data Analysis for the CO₂ capture process system

The second study on applications of data modeling techniques to the operational data of the post-combustion carbon dioxide capture process system has the objective of achieving a good understanding of the relationships among the key parameters of the process system. This understanding can help the operator to: (i) better analyze the current conditions of the process system, (ii) support his or her assessment of the underlying trends or events in plant operations, and (iii) take prompt and effective control actions that modify the relevant process parameters when the plant is not functioning efficiently. Hence, an additional objective of the study was to develop correlation models among the significant process parameters that influence performance of the CO₂ capture process system. In the process of generating the correlation models, better understanding of the relationships among the process parameters can be obtained.

The data for the study were collected over three years (2003-2006) from the amine-based post combustion CO₂ capture process system at the University of Regina located in Regina, Saskatchewan, Canada. Pre-processing of the dataset involves removing three types of data from the dataset so as to enhance accuracy and reliability of the developed models. Firstly, the data collected during short time frames of about half an hour were removed because they cannot reflect the changing trend of the plant operations. Secondly, if the plant operations were not stable in the morning and during the last hour before shutdown, the operational data during these time periods were considered unreliable and removed. Thirdly, the data which exhibited abrupt and erratic changes indicated abnormal performance of the system and were removed. A further step in preprocessing involved examining the data to ensure they covered the entire

operating ranges of the input and output process parameters; this step was necessary because the data critically determine quality of the developed models.

The input and output parameters in the correlation relationships were selected based on extensive literature review and opinions of the expert operator of the CO₂ capture plant at the University of Regina. The four output parameters used for evaluating efficiency and performance of the CO₂ capture pilot plant were defined as: (i) reboiler heat duty, (ii) CO₂ production rate, (iii) CO₂ absorption efficiency, and (iv) lean loading. Eight parameters identified to have significant influence on these four output variables were defined as input variables, and they include: (i) mass flow of CO₂ in the flue gas, (ii) CO₂ concentration in flue gas, (iii) off gas flow rate, (iv) amine circulation rate, (v) reboiler pressure, (vi) pressure of steam through reboiler, (vii) steam flow rate through reboiler, and (viii) amine concentration.

To develop the relationships that correlate the input and output variables, the three data modeling techniques of statistical regression analysis, artificial neural network (ANN) modeling combined with sensitivity analysis (SA), and adaptive network-based fuzzy inference system (ANFIS) modeling were sequentially applied to the set of operational data. The application process is illustrated in Figure 5.1. This sequential modeling process was adopted with the motivation that each subsequent method was applied in an attempt to address the weaknesses of the previous method. Applications of the three data modeling methods are presented as follows.

(Insert Figure 5.1 here)

The statistical regression analysis method was implemented on the Statistical Package of Social Sciences or SPSS® (trademark of SPSS Inc. USA). The modeling process involved the steps of: (i) correlation analysis, (ii) linear regression, (iii) curve estimation, and (iv) model assessment. These steps are shown in Figure 5.2. Three linear models

were developed for predicting the output variables of heat duty, CO₂ production rate, and lean loading, and a cubic power function was formulated for forecasting absorption efficiency. The developed models were evaluated based on the coefficient of determination (R^2), which measures the amount of variation in the output variable that is accounted for by the developed model. In other words, R^2 measures how well the regression model performs in predicting the target output parameter. It was observed that the values of R^2 for the four models ranged between 70% and 90%.

(Insert Figure 5.2 here)

It can be observed that the statistical regression analysis approach has several weaknesses. First, a R^2 value of between 70% to 90% is not good enough, and this can be due to the fact that the set of input variables was inadequate. Since the set was initially selected based on expert opinion, it is possible that some important input variables were excluded. Secondly, the SPSS package supports only a limited number of non-linear functions, which may not adequately describe the modeled relationships. Thirdly, the statistical regression approach requires that some multi-linear variables cannot be used simultaneously in one model even though they have significant correlation with the output variable. The partial inclusion of important input variables possibly decreased the accuracy of the developed model. To address these weaknesses, the ANN method combined with sensitivity analysis was adopted for modeling the data.

The ANN modeling process began with initial models for each output variable that included all eight input variables, and each model was implemented using a three-layered feed-forward back-propagation neural network constructed using WekaTM version 3.4.12 (Trademark of Weka). Then, sensitivity analysis was conducted to determine the relative significance of each input variable for a specific output variable, and the less significant input variables were eliminated. As a result, only the significant input variables remained to form

the refined input variable set for each output variable. The second round of ANN modeling involved using only the refined set of input variables for each output variable, and the process yielded predictive models for the four output variables.

These ANN models have predictive accuracies of between 85% and 99%, which represented superior results compared to the statistical regression analysis method. However, while the ANN approach generated good predictive models, they provided only black-box models that do not describe or shed light on the nature of the relationships among the process parameters. Since one of the research objectives was to generate a better understanding of the relationships among the process parameters, this weakness meant that the ANN approach is not satisfactory. Therefore, the ANFIS modeling approach was adopted.

The ANFIS technique was applied to the refined sets of input variables generated in the ANN modeling process, and the implementation tool adopted was the Neuro-Fuzzy Toolbox in MATLAB (Trademark of MATLAB, USA). A fuzzy inference system, which included tuned membership functions of the input variables and a fuzzy rule set, was developed for each output variable. The fuzzy inference systems generated from the ANFIS modeling process were tested, and the predictive accuracy of the ANFIS model was measured using the mean absolute percentage error. The results showed the predictive accuracies of the ANFIS-developed models ranged between 92% and 96%, that is on average are the highest compared to the models developed with the other two methods of statistical regression analysis and ANN.

This investigation on modeling the data from the post-combustion CO₂ capture process system produced two main contributions to the research field of CO₂ capture process systems. It completed a comprehensive exploration of the process parameters involved in the system and has generated a reliable set of input parameters for measuring performance of the CO₂ capture process system. Moreover, the fuzzy inference systems generated by the ANFIS

technique constitute a knowledge base, which is potentially useful for future studies of the post-combustion CO₂ capture process system.

For more detailed information about Section 5 (on applications of information and artificial intelligence technologies for supporting two tasks related to operation of the post-combustion CO₂ capture system), please consult the references mentioned above at the beginning of the section and/or the listed here (Chan et al. 2012, Zhou et al. 2012 and Chapters 9 and 10 in Tontiwachwuthikul, and Idem, 2013).

6. Conclusion and Outlook

There has been significant progress and new discoveries over the past 10 years on the development of amine-base solvents for the post-combustion carbon capture (PCC) technology, as detailed in the above sections. As is well known, the solvent selected for use in the process is the most important element in any capture process plant. In summary, parts of these new knowledge discoveries have been starting to move from the laboratory scale into pilot plant testing stages, followed by commercial demonstration. Some good examples are (i) the TMC Mongstad in Norway (300,000 tonnes per year CO₂ captured) and (ii) BD3 SaskPower in Canada (1 million tonnes per year CO₂ captured). A few more large-scale carbon capture facilities are being developed and/or planned as outlined in the recent proceedings of 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12, Austin, USA in 2014). In addition, significant portions of recent information on the subject can be found on the IEA GHG website (www.ieaghg.org).

The main challenge of this technology is still – how to reduce the energy consumption. Figure 6.1 shows the plot of the energy requirement when we have to capture one tonne of CO₂. As can be seen, we have come a long way from using single conventional amine (e.g. MEA) to capture CO₂ which uses a significant amount of energy, approximately 4.1 GJ per ton of CO₂ captured (or 1.8 ton steam per ton CO₂) in the 1980's. The current commercial

technologies indicate that the energy requirement has reduced by more than 30% to approximately 2.6 GJ (or 1.2 ton steam per ton CO₂ removed). With development of new chemicals and use of them for specially mixed solvents, the energy requirement of PCC could be reduced further to 2.0 GJ (or approximately 1.0 – 0.8 ton steam per ton CO₂ captured). Very recent studies show this level of energy requirement could also be reduced further to around 1.1 GJ (~ 0.6 ton steam per ton of CO₂) (Shi et al, 2014a and Shi et al, 2015). These new developments are still at the laboratory scale, yet to be tested in the pilot plants and semi-commercial operations. It is expected that more detailed information and test results of the process energy requirement will be available in the near future. In addition, the issues related to post-built operations such as corrosion, solvent degradation, solvent management, solvent emissions, process monitoring, and system-optimization are becoming important issues as more full-scale PCC plants are being operated. Specifically, how we can minimize the chemical emissions from the off-gas streams is of critical importance. In newer capture plants, a number of mixed solvents (up to 5-10 compounds) are also used. One of the main issues is how to keep the solvent compositions constant and the solvent highly effective over long time periods. Some of the developments in these areas were summarized in Sections 4 and 5. It is expected that more detailed information on the aforementioned issues and test results in large-scale as well as full-scale plants will be available in up-coming years (e.g. the 3rd IEA Post Combustion Capture Conference in Canada this year as well as the 13th International Conference on Greenhouse Gas Control Technologies, Switzerland in 2016).

(Insert Figure 6.1 here)

Acknowledgment

We acknowledge the research support over the past many years of the Industrial Research Consortium - Future Cap Phase II of the International Test Centre for CO₂ Capture (ITC) at the University of Regina. We also acknowledge the research support from the followings

organizations: Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Foundation for Innovation (CFI), Saskatchewan Ministry of Energy & Resources, Western Economic Diversification, Saskatchewan Power Corporation, Alberta Energy Research Institute (AERI) and Research Institute of Innovative and Technology for the Earth (RITE).

In addition, the financial supports from the National Natural Science Foundation of China (Nos. 21276068, U1362112 and 21376067), National Key Technology R&D Program (Nos. 2012BAC26B01 and 2014BAC18B04), Innovative Research Team Development Plan-Ministry of Education of China (No. IRT1238), Specialized Research Fund for the Doctoral Program of Higher Education (No. 20130161110025), Technology Development contract (No. Shanyan 12-34), Innovative Research Program for Graduate Student of Hunan Province, China (No. CX2013B158), Key project of international & regional scientific and technological cooperation of Hunan provincial science and technology plan (2014WK2037), and China's State "Project 985" in Hunan University--Novel Technology Research & Development for CO₂ Capture are gratefully acknowledged.

We would also like to acknowledge the financial support for parts of this work provided by an NPRP Grant # 7 - 1154 - 2 - 433 from the Qatar National Research Fund (a member of Qatar Foundation).

Abbreviations and Glossary

ADD	Absolute Average Deviation
Am	Free amine
AmH ⁺	Protonated amines
ANFIS	Adaptive network-based fuzzy inference system
a_v	Interfacial area per unit volume of packing (m ² /m ³)

1551	$C_{\text{Amine}0}$	Initial concentration of amine (kmol/m ³)
1552	CAP	Alstom chilled ammonia process
1553	$C_{\text{CO}_2}^*$	Interfacial concentration of CO ₂ (kmol/m ³)
1554	CDCMD	Carbon Dioxide Capture Monitoring and Diagnostic
1555	$C_{P,L}$	Heat capacity of solution (kJ/m ³ K)
1556	$C_{P,j}$	Heat capacity of component j in the gas (kJ/kmol K)
1557	D_{CO_2}	Diffusivity of CO ₂ (m ² /s)
1558	FDM	Finite difference method
1559	FEM	Finite element method
1560	GHG	Greenhouse Gas
1561	G_I	Inert gas molar flow rate (kmol/m ² s)
1562	h_G	Heat transfer coefficient (kJ/m ² s K)
1563	H	Henry's constant (kPa m ³ /kmol)
1564	He	Henry constant (kPa m ³ /kmol)
1565	H_R	Heat of absorption and reaction (kJ/kmol)
1566	H_S	Heat of vaporization of solvent S (kJ/kmol)
1567	HSAS	Heat stable amine salt
1568	HSSs	Heat stable salts
1569	HTU	Height of a transfer unit
1570	I	Enhancement factor
1571	ILs	Ionic liquids
1572	KBSCDC	Knowledge-Based System for Carbon Dioxide Capture
1573	κ_{-1}	Rate constant of the reverse reaction between CO ₂ and amine (m ³ /kmol s)
1574	K_{2,R_1R_2NH}	Second-order reaction rate constant (m ³ /kmol s)

1575	k_{app}	Apparent rate constant (s^{-1})
1576	k_{ov}	Overall reaction constant (s^{-1})
1577	k_G	Gas mass transfer coefficient ($kmol/m^2 s kPa$)
1578	k_{H_2O}	Deprotonation rate constants of intermediate by H_2O ($m^3/kmol s$)
1579	k_L^o	Physical liquid mass transfer coefficient (m/s)
1580	k_{OH^-}	Deprotonation rate constants of intermediate by OH^- ($m^3/kmol s$)
1581	$\kappa_{OH^-}^*$	Reaction rate constant between CO_2 and OH^- ($m^3/kmol s$)
1582	$k_{R_1R_2NH}$	Deprotonation rate constants of intermediate by R_1R_2NH ($m^3/kmol s$)
1583	κ_{RN}	Reaction rate between CO_2 and tertiary amine ($kmol/m^3 s$)
1584	K_G	Overall gas mass transfer coefficient ($kmol/m^2 s kPa$)
1585	$(K_G a_v)_{ave}$	Average overall volumetric mass transfer coefficient
1586	L	Liquid flow rate
1587	MGA	Membrane gas absorption
1588	NMR	Nuclear magnetic resonance
1589	NTU	Number of transfer units
1590	N_{CO_2}	Specific CO_2 absorption rate ($kmol/m^2 s$)
1591	P	Total pressure (kPa)
1592	PCC	Post-combustion carbon capture
1593	P_{CO_2}	CO_2 partial pressure (kPa)
1594	RTILs	Room temperature ionic liquids
1595	R_v	Mass transfer rate ($kmol/m^3 s$)
1596	$r_{co_2-R_1R_2NH}$	Reaction rate between CO_2 and primary/secondary amines ($kmol/m^3 s$)
1597	$r_{OH^-}^*$	Reaction rate between CO_2 and OH^- ($kmol/m^3 s$)

1598 r_{ov} Overall rate of CO₂ absorption (kmol/m³ s)

1599 T Temperature (K)

1600 TBS Thermomorphing biphasic solvent

1601 TSAM Two-State Association Model

1602 V_{AB} Stoichiometry

1603 VLE Vapor-liquid equilibrium

1604 Y Mole ratio

1605 $y_{A,G}$ Mole fraction of component A

1606 y_A^* Mole fraction of component A

1607 $(y_{A,G} - y_A^*)_{lm}$ Log-mean driving force

1608 Z Height of column (m)

1609 $[]$ Concentration (kmol/m³)

1610 **Greek letters**

1611 μ Liquid viscosity (g/cm s)

1612 α CO₂ loading (mol CO₂/mol amine)

1613 δ Chemical shift of species (ppm)

1614 **Superscript**

1615 Z Zwitterion mechanism

1616 **References**

1617

1618 Aboudheir, A., Tontiwachwuthikul, P., Chakma, A., Idem, R., 2003. Kinetics of the reactive
1619 absorption of carbon dioxide in high CO₂-loaded, concentrated aqueous monoethanolamine
1620 solutions. Chemical Engineering Science 58, 5195-5210.

1621

- Abu-Zahra, M.R.M., Niederer, J.P.M., Feron, P.H.M. and Versteeg, G.F., 2007. CO₂ Capture from Power Plants Part II. A Parametric Study of the Economical Performance Based on Mono-Ethanolamine. *International Journal of Greenhouse Gas Control* 1 (2),135–142.
- Agar, D.W., Tan, Y., Zhang, X., 2008. CO₂ removal processes by means of absorption using thermomorphic biphasic aqueous amine solutions. Patent WO/2008/015217.
- Alper, E., 1990. Reaction mechanism and kinetics of aqueous solutions of 2-amino-2-methyl-1-propanol and carbon dioxide. *Industrial & engineering chemistry research* 29, 1725-1728.
- Alper, E., Danckwerts, P., 1976. Laboratory scale-model of a complete packed column absorber. *Chemical Engineering Science* 31, 599-608.
- Amrollahi, Z., Ertesvåg, I.S., Bolland, O., 2011. Optimized process configurations of post-combustion CO₂ capture for natural-gas-fired power plant-Exergy analysis. *International Journal of Greenhouse Gas Control* 5 (6), 1393-1405.
- Anufrikov, Y.A., Kuranov, G., Smirnova, N., 2007. Solubility of CO₂ and H₂S in alkanolamine-containing aqueous solutions. *Russian Journal of Applied Chemistry* 80, 515-527.
- Arcis, H., Coulier, Y., Ballerat-Busserolles, K., Rodier, L., Coxam, J.Y., 2014. Enthalpy of Solution of CO₂ in Aqueous Solutions of Primary Alkanolamines: a comparative study of hindered and nonhindered amine-based solvents. *Industrial & Engineering Chemistry Research* 53, 10876-10885.
- Aronu, U.E., Hoff, K.A., Svendsen, H.F., 2011. Vapor–liquid equilibrium in aqueous amine amino acid salt solution: 3-(methylamino)propylamine/sarcosine. *Chemical Engineering Science* 66, 3859-3867.
- Aronu, U.E., Svendsen, H.F., Hoff, K.A., 2010. Investigation of amine amino acid salts for carbon dioxide absorption. *International Journal of Greenhouse Gas Control* 4, 771-775.

- Aroonwilas, A., Veawab, A., 2007. Integration of CO₂ capture unit using single-and blended- amines into supercritical coal-fired power plants: implications for emission and energy management. *International Journal of Greenhouse Gas Control* 1, 143-150.
- Arshad, M.W., Fosbøl, P.L., Solms, N., Svendsen, H.F., 2013. Heat of absorption of CO₂ in phase change solvents: 2-(Diethylamino)ethanol and 3-(Methylamino)propylamine. *Journal of Chemical & Engineering Data* 58, 1974-1988.
- Arshad, M.W., Svendsen, H.F., Fosbøl, P.L., von Solms, N., Thomsen, K., 2014. Equilibrium Total pressure and CO₂ solubility in binary and ternary aqueous solutions of 2-(Diethylamino) ethanol (DEEA) and 3-(Methylamino) propylamine (MAPA). *Journal of Chemical & Engineering Data* 59, 764-774.
- Astarita, G., 1967. *Mass transfer with chemical reaction*, Elsevier, NY, USA.
- Astarita, G., Savage, D.W., Bisio, A., 1983. *Gas treating with chemical solvents*. Jone Wiley & Sons: New York. USA.
- Austgen, D.M., Rochelle, G.T., Peng, X., Chen, C.C., 1989. Model of vapor-liquid equilibria for aqueous acid gas-alkanolamine systems using the electrolyte-NRTL equation. *Industrial & Engineering Chemistry Research* 28, 1060-1073.
- Bacon, T.R., 1987. *Amine Solution Quality Control through Design, Operation and Correction*. presented at the Gas Conditioning Conference. presented at the Gas Conditioning Conference, University of Oklahoma, Norman, OK,
- Bajpai, A., Mondal, M.K., 2013. Equilibrium Solubility of CO₂ in aqueous mixtures of DEA and AEEA. *Journal of Chemical & Engineering Data* 58, 1490-1495.
- Bates, E.D., Mayton, R.D. , Ntai, I. , Davis, J.H., 2002. CO₂ Capture by a Task-Specific Ionic Liquid. *Journal of the American Chemical Society*. 124, 926–927.
- Bello A., Idem R.O., 2006. Comprehensive study of the kinetics of the oxidative degradation of CO₂ loaded and concentrated aqueous monoethanolamine (MEA) with and without sodium

metavanadate during CO₂ absorption from flue gases. *Industrial & Engineering Chemistry Research* 45, 2569-2579.

Benitez-Garcia, J., Ruiz-Ibanez, G., Bidarian, A., Sandall, O.C., 1990. Kinetics of the reaction between carbon dioxide and triethylamine in aqueous solutions. *Chemical Engineering Science*, 45, 3407-3415.

Bishnoi, S., Rochelle, G.T., 2002. Absorption of carbon dioxide in aqueous piperazine/methyldiethanolamine. *AIChE Journal* 48, 2788-2799.

Blauwhoff, P., Versteeg, G., Van Swaaij, W., 1984. A study on the reaction between CO₂ and alkanolamines in aqueous solutions. *Chemical Engineering Science* 39, 207-225.

Boot-Handford, M.E., Abanades, J.C., Anthony, E.J., Blunt, M.J., Brandani, S., Mac Dowell, N., Fernández, J.R., Ferrari, M.C., Gross, R., Hallett, J.P., Haszeldine, R.S., Heptonstall, P., Lyngfelt, A., Makuch, Z., Mangano, E., Porter, R.T.J., Pourkashanian, M., Rochelle, G.T., Shah, N., Yao, J.G., Fennell, P.S. 2014. Carbon capture and storage update. *Energy & Environmental Science* 7, 130-189.

Böttinger, W., Maiwald, M., Hasse, H., 2008a. Online NMR spectroscopic study of species distribution in MEA-H₂O-CO₂ and DEA-H₂O-CO₂. *Fluid Phase Equilibria* 263, 131-143.

Böttinger, W., Maiwald, M., Hasse, H., 2008b. Online NMR Spectroscopic Study of Species Distribution in MDEA-H₂O-CO₂ and MDEA-PIP-H₂O-CO₂. *Industrial & Engineering Chemistry Research* 47, 7917-7926.

Bougie, F., Iliuta, M.C., 2014. Stability of aqueous amine solutions to thermal and oxidative degradation in the absence and the presence of CO₂. *International Journal of Greenhouse Gas Control* 29, 16-21.

Bougie, F., Iliuta, M.C., 2013. Solubility of CO₂ in and Density, Viscosity, and Surface Tension of Aqueous 2-Amino-1,3-propanediol (Serinol) Solutions. *Journal of Chemical and Engineering Data* 59, 355-361.

- Chakma, A., 1997. CO₂ capture processes—opportunities for improved energy efficiencies. *Energy conversion and management* 38, S51-S56.
- Chan, C.W., Zhou Q., Wu,Y., Tontiwachwuthikul.P., 2011. Modeling of the carbon dioxide capture process using machine intelligence approaches, *Engineering Applications of Artificial Intelligence*, 24 (4), 673-685.
- Chan, C.W., Zhou, Q., Tontiwachwuthikul, P., 2012. Applications of Knowledge-based system technologies for the carbon dioxide capture process system”, *Carbon Management* 3(1), 69-79.
- Chang, H., Shih, C.M., 2005. Simulation and Optimization for Power Plant Flue Gas CO₂ Absorption-Stripping Systems. *Separation science and technology* 40, 877-909.
- Chang, Y.C., Leron, R.B., Li, M.H., 2013. Equilibrium solubility of carbon dioxide in aqueous solutions of (diethylenetriamine+ piperazine). *The Journal of Chemical Thermodynamics* 64, 106-113.
- Chang, Y.T., Leron, R.B., Li, M.H., 2015. Carbon dioxide solubility in aqueous potassium salt solutions of l-proline and dl- α -aminobutyric acid at high pressures. *The Journal of Chemical Thermodynamics* 83, 110-116.
- Chen, X., Rochelle, G.T., 2013. Modeling of CO₂ absorption kinetics in aqueous 2-methylpiperazine. *Industrial & Engineering Chemistry Research* 52, 4239-4248.
- Choi, S.Y., Nam, S.C., Yoon, Y.I., Park, K.T., Park, S.J., 2014. Carbon dioxide absorption into aqueous blends of methyldiethanolamine (MDEA) and alkyl amines containing multiple amino groups. *Industrial & Engineering Chemistry Research* 53, 14451-14461.
- Chowdhury, F.A., Okabe, H., Shimizu, S., Onoda, M., Fujioka, Y., 2009. Development of novel tertiary amine absorbents for CO₂ capture. *Energy Procedia* 1, 1241-1248.

- Chowdhury, F.A., Okabe, H., Yamada, H., Onoda, M., Fujioka, Y., 2011. Synthesis and selection of hindered new amine absorbents for CO₂ capture. *Energy Procedia* 4, 201-208.
- Chowdhury, F.A., Yamada, H., Higashii, T., Goto, K., Onoda, M., 2013. CO₂ Capture by tertiary amine absorbents: a performance comparison study. *Industrial & Engineering Chemistry Research* 52, 8323-8331.
- Conway, W., Beyad, Y., Maeder, M., Burns, R., Feron, P., Puxty, G., 2014. CO₂ absorption into aqueous solutions containing 3-piperidinemethanol: CO₂ mass transfer, stopped-flow kinetics, ¹H/¹³C NMR, and vapor-liquid equilibrium Investigations. *Industrial & Engineering Chemistry Research* 53, 16715-16724.
- Cousins, A., Wardhaugh, L., Feron, P., 2011. A survey of process flow sheet modifications for energy efficient CO₂ capture from flue gases using chemical absorption. *International Journal of Greenhouse Gas Control* 5 (4), 605-619.
- Cummings, A.L, Mecum, S., 2000. Increasing Profitability and Improving Environmental Performance by Maintaining Amine Solvent Purity, *PROCEEDINGS OF THE LAURANCE REID GAS CONDITIONING CONFERENCE*, pp. 9-20.
- Dai, N., Shah, A.D., Hu, L., Plewa, M.J., McKague, Mitch, W.A., 2012. Measurement of Nitrosamine and Nitramine Formation from NO_x Reactions with Amines during Amine-Based Carbon Dioxide Capture for Postcombustion Carbon Sequestration. *Environmental Science & Technology*. 46, 9793-9801.
- Dai, N., Mitch, W.A., 2013. Influence of Amine Structural Characteristics on N-Nitrosamine Formation Potential Relevant to Postcombustion CO₂ Capture Systems. *Environmental Science & Technology*. 47, 13175-13183.
- Dai, N., Mitch, W.A., 2014. Effects of Flue Gas Compositions on Nitrosamine and Nitramine Formation in Postcombustion CO₂ Capture Systems. *Environmental Science & Technology*. 48, 7519-7526.

1788 Danckwerts, P.V., Lannus, A., 1970. Gas-liquid reactions. Journal of The Electrochemical
 1789 Society 117, 369C-370C.
 1790
 1791 Danckwerts, P.V., 1970. Gas-Liquid Reaction, McGraw-Hill, New York, USA.
 1792
 1793 Danckwerts, P.V., 1979. The reaction of CO₂ with ethanolamines. Chemical Engineering
 1794 Science 34, 443-446
 1795
 1796 Davis, J., Rochelle, G., 2009. Thermal degradation of monoethanolamine at stripper
 1797 conditions. Energy Procedia 1, 327-333.
 1798
 1799 Davoudi, M., Safadoust, A.R., Akbar Mansoori, S.A., Mottaghi, H.R., 2014. The impurities
 1800 effect on thermal degradation and corrosivity of amine solution in South Pars gas sweetening
 1801 plants. Journal of Natural Gas Science and Engineering 19, 116-124.
 1802
 1803 De Vroey, S., Huynh, H., Lepaumier, H., Absil, P., Thielens, M.L., 2013. Corrosion
 1804 Investigations In 2-ethanolamine Based Post- Combustion CO₂ Capture Pilot Plants. Energy
 1805 Procedia 37, 2047-2057.
 1806
 1807 Deng, D., Chen, Y., Cui, Y., Li, G., Ai, N., 2014. Low pressure solubilities of CO₂ in five
 1808 fatty amine polyoxyethylene ethers. The Journal of Chemical Thermodynamics 72, 89-93.
 1809
 1810 Derks, P. W. J., Kleingeld, T., Van Aken, C., Hogendoorn, J. A., & Versteeg, G. F. (2006).
 1811 Kinetics of absorption of carbon dioxide in aqueous piperazine solutions. Chemical
 1812 Engineering Science, 61(20), 6837-6854.
 1813
 1814 Diab, F., Provost, E., Laloué, N., Alix, P., Fürst, W., 2013. Effect of the incorporation of
 1815 speciation data in the modeling of CO₂-DEA-H₂O system. Fluid Phase Equilibria 353, 22-
 1816 30.
 1817
 1818 Dixit, O., Mollekopf, N., 2014. Designing absorption processes with aqueous diglycolamine.
 1819 Chemical Engineering & Technology 37, 1583-1592.
 1820

- Donaldson, T.L., Nguyen, Y.N., 1980. Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membrane. *Industrial and Engineering Chemistry Fundamental* 19, 260-266.
- Edali, M., Aboudheir, A., Idem, R., 2009. Kinetics of carbon dioxide absorption into mixed aqueous solutions of MDEA and MEA using a laminar jet apparatus and a numerically solved 2D absorption rate/kinetics model. *International Journal of Greenhouse Gas Control* 3, 550-560.
- Eide, L.I., Anheden, M., Lyngfelt, A., Abanades, C., Younes, M., Clodic, D., Bill, A., Feron, P., Rojey, A., Giroudiere, F., 2005. Novel capture processes. *Oil & gas science and technology* 60 (3), 497-508.
- ElMoudir, W., 2012a. Experimental studies for development of a purification process for single and mixed amine solvents. Ph.d Thesis, University of Regina, Canada.
- ElMoudir, W., Supap, T., Saiwan, C., Idem, R., Tontiwachwuthikul, P., 2012b. Part 6: Solvent recycling and reclaiming issues. *Carbon Management* 3, 485-509.
- Fan, G.j., Wee, A.G., Idem, R., Tontiwachwuthikul, P., 2009. NMR studies of amine species in MEA-CO₂-H₂O system: Modification of the model of vapor-liquid equilibrium (VLE). *Industrial & Engineering Chemistry Research* 48, 2717-2720.
- Faramarzi, L., Kontogeorgis, G.M., Thomsen, K., Stenby, E.H., 2009. Extended UNIQUAC model for thermodynamic modeling of CO₂ absorption in aqueous alkanolamine solutions. *Fluid Phase Equilibria* 282, 121-132.
- Fine, N.A., Nielsen, P.T., Rochelle, G.T., 2014. Decomposition of nitrosamines in CO₂ capture by aqueous piperazine or monoethanolamine. *Environ Sci Technol* 48, 5996-6002.
- Fuchs, E., Witzel, T., Stadler, K.P., 1996. "Decontamination of Tertiary Amines from Primary and Secondary Amines," U.S. Patent US 5.481,03702-Jan-1996.
- Freeman, S.A., Rochelle, G.T., 2011. Thermal Degradation of Piperazine and its Structural Analogs. *Energy Procedia*. 4, 43-50.

1855 Freguia, S., Rochelle, G.T., 2003. Modeling of CO₂ capture by aqueous monoethanolamine.
 1856 AIChE Journal 49 (7), 1676-1686.
 1857

1858 Gao, H., Zhou, L., Liang, Z., Idem, R.O., Fu, K., Sema, T., Tontiwachwuthikul, P., 2014.
 1859 Comparative studies of heat duty and total equivalent work of a new heat pump distillation
 1860 with split flow process, conventional split flow process, and conventional baseline process for
 1861 CO₂ capture using monoethanolamine. International Journal of Greenhouse Gas Control 24,
 1862 87-97.
 1863

1864 Gao, Y., Zhang, F., Huang, K., Ma, J., Wu, Y., Zhang, Z., 2013. Absorption of CO₂ in amino
 1865 acid ionic liquid (AAIL) activated MDEA solutions. International Journal of Greenhouse Gas
 1866 Control 19, 379–386.
 1867

1868 Gouedard, C., Rey, A., Cuzuel, V., Brunet, J., Delfort, B., Picq, D., Dugay, J., Vial, J.,
 1869 Pichon, V., Launay, F., Assam, L., Ponthus, J., Carrette, P.L., 2014. Amine degradation in
 1870 CO₂ capture. 3. New degradation products of MEA in liquid phase: Amides and nitrogenous
 1871 heterocycles. International Journal of Greenhouse Gas Control 29, 61-69.
 1872

1873 Guerra-Neto, D.d.B., Ferreira-Pinto, L., Giufrida, W.M., Zabaloy, M.S., Cardozo-Filho, L.,
 1874 Chiavone-Filho, O., 2014. Bubble point determination for CO₂+ ethanol + alkanolamines
 1875 (monoethanolamine, diethanolamine, or triethanolamine) at high pressures. Journal of
 1876 Chemical & Engineering Data 59, 3319-3323.
 1877

1878 Guo, C., Chen, S., Zhang, Y., 2013. Solubility of carbon dioxide in aqueous 2-(2-
 1879 aminoethylamine) ethanol (AEEA) solution and its mixtures with N-methyldiethanolamine/2-
 1880 amino-2-methyl-1-propanol. Journal of Chemical & Engineering Data 58, 460-466.
 1881

1882 Guo, C., Chen, S., Zhang, Y., Wang, G., 2014. Solubility of CO₂ in Nonaqueous absorption
 1883 system of 2-(2-aminoethylamine) ethanol+benzyl alcohol. Journal of Chemical &
 1884 Engineering Data 59 (6), 1796–1801.
 1885

1886 Hagewiesche, D.P., Ashour, S.S., Al-Ghawas, H.A., Sandall, O.C., 1995. Absorption of
 1887 carbon dioxide into aqueous blends of monoethanolamine and *N*-methyldiethanolamine.
 1888 Chemical Engineering Science 50, 1071-1079.

1889

1890 Haghtalab, A., Eghbali, H., Shojaeian, A., 2014. Experiment and modeling solubility of CO₂

1891 in aqueous solutions of Diisopropanolamine + 2-amino-2-methyl-1-propano + Piperazine at

1892 high pressures. The Journal of Chemical Thermodynamics 71, 71-83.

1893

1894 Haghtalab, A., Shojaeian, A., 2015. High pressure measurement and thermodynamic

1895 modeling of the solubility of carbon dioxide in N-methyldiethanolamine and 1-butyl-3-

1896 methylimidazolium acetate mixture. The Journal of Chemical Thermodynamics 81, 237-244.

1897

1898 Haimour, N., Bidarian, A., Sandall, O.C., 1987. Kinetics of the reaction between carbon

1899 dioxide and methyldiethanolamine. Chemical Engineering Science 42, 1393-1398.

1900

1901 Hamborg, E.S., van Swaaij, W.P.M., Versteeg, G.F., 2008. Diffusivities in Aqueous

1902 Solutions of the Potassium Salt of Amino Acids. Journal of Chemical & Engineering Data 53,

1903 1141-1145.

1904

1905 Harris, F., Kurnia, K.A., Mutalib, M.I.A., Thanapalan, M., 2009. Solubilities of Carbon

1906 Dioxide and Densities of Aqueous Sodium Glycinate Solutions before and after CO₂

1907 Absorption. Journal of Chemical & Engineering Data 54, 144-147.

1908

1909 Hartono, A., da Silva, E. F., & Svendsen, H. F. (2009). Kinetics of carbon dioxide absorption

1910 in aqueous solution of diethylenetriamine (DETA). Chemical Engineering Science, 64(14),

1911 3205-3213.

1912

1913 Hasib-ur-Rahman, M., Larachi, F., 2013. Prospects of using room-temperature ionic liquids

1914 as corrosion inhibitors in aqueous ethanolamine-based CO₂ capture solvents. Industrial &

1915 Engineering Chemistry Research 52, 17682-17685.

1916

1917 Henni, A., Li, J., Tontiwachwuthikul, P., 2008. Reaction kinetics of CO₂ in aqueous 1-amino-

1918 2-propanol, 3-amino-1-propanol, and dimethylmonoethanolamine solutions in the

1919 temperature range of 298-313 K using the stopped-flow technique. Industrial & Engineering

1920 Chemistry Research 47, 2213-2220.

1921

1922 Henni, A., Rayer, A.V., Sumon, K.Z., Sema, T., Idem, R., Tontiwachwuthikul, P., 2013.
 1923 Solubility of CO₂ in reactive solvents for post-combustion CO₂ capture. In: Recent Progress
 1924 and New Developments in Post-Combustion Carbon-Capture Technology with Reactive
 1925 Solvents. Edited by: P. Tontiwachwuthikul, R. Idem. Future Science Ltd.
 1926 DOI: 10.4155/9781909453340, 58-77.
 1927
 1928 Herron, J.T., Green, D.S., 2001. Chemical kinetics database and predictive schemes for
 1929 nonthermal humid air plasma chemistry. Part II. Neutral species reactions. Plasma Chemistry
 1930 and Plasma Processing 21, 459-481.
 1931
 1932 Hikita, H., Asai, S., Ishikawa, H., & Honda, M. (1977). The kinetics of reactions of carbon
 1933 dioxide with monoethanolamine, diethanolamine and triethanolamine by a rapid mixing
 1934 method. the chemical Engineering Journal, 13(1), 7-12.
 1935
 1936 Holmes, P.E., Naaz, M., Poling, B.E., 1998. Ion concentrations in the CO₂-NH₃-H₂O system
 1937 from ¹³C NMR spectroscopy. Industrial & engineering chemistry research 37, 3281-3287.
 1938
 1939 Holst, J.V., Kersten, S.R.A., Hogendoorn, K.J.A., 2008. Physiochemical Properties of
 1940 Several Aqueous Potassium Amino Acid Salts. Journal of Chemical & Engineering Data 53,
 1941 1286-129
 1942
 1943 Hsu, Y.H., Leron, R.B., Li, M.H., 2014. Solubility of carbon dioxide in aqueous mixtures of
 1944 (reline+ monoethanolamine) at T=(313.2 to 353.2) K. The Journal of Chemical
 1945 Thermodynamics 72, 94-99.
 1946
 1947 Idem, R., Edali, M., Aboudheir, A., 2009a. Kinetics, modeling, and simulation of the
 1948 experimental kinetics data of carbon dioxide absorption into mixed aqueous solutions of
 1949 MDEA and PZ using laminar jet apparatus with a numerically solved absorption-rate/kinetic
 1950 model. Energy Procedia 1, 1343-1350.
 1951
 1952 Idem, R., Tontiwachwuthikul, P., Saiwan, C., and Supap, T., 2009b. Method for Inhibition
 1953 Amine Degradation During CO₂ Capture from a Gas Stream, U.S. Patent WO 065218 A1.
 1954

1955 Idris, Z., Peresunko, N., Jens, K.J., Eimer, D.A., 2015. Equilibrium solubility of carbon
 1956 dioxide in aqueous solutions of 3-amino-1-propanol, 4-amino-1-butanol and 5-amino-1-
 1957 pentanol at low partial pressures. *Fluid Phase Equilibria* 387, 81-87.

1958

1959 International Energy Agency, 2012. *World Energy Outlook*. International Energy Agency,
 1960 Paris, France.

1961

1962 Jakobsen, J.P., Krane, J., Svendsen, H.F., 2005. Liquid-phase composition determination in
 1963 CO₂-H₂O-alkanolamine systems: An NMR study. *Industrial & engineering chemistry*
 1964 *research* 44, 9894-9903.

1965

1966 Jassim, M.S., Rochelle, G.T., 2006. Innovative absorber/stripper configurations for CO₂
 1967 capture by aqueous monoethanolamine. *Industrial and Engineering Chemistry Research* 45,
 1968 2465-2472.

1969

1970 Kadiwala, S., Rayer, A.V., Henni, A., 2012. Kinetics of carbon dioxide (CO₂) with
 1971 ethylenediamine, 3-amino-1-propanol in methanol and ethanol, and with 1-dimethylamino-2-
 1972 propanol and 3-dimethylamino-1-propanol in water using stopped-flow technique. *Chemical*
 1973 *Engineering Journal* 179, 262-271.

1974

1975 Kang, D., Park, S., Jo, H., Min, J., Park, J., 2013. Solubility of CO₂ in Amino-Acid-Based
 1976 Solutions of (Potassium Sarcosinate),(Potassium Alaninate+ Piperazine), and (Potassium
 1977 Serinate+ Piperazine). *Journal of Chemical & Engineering Data* 58, 1787-1791.

1978

1979 Karimi, M., Hillestad, M., Svendsen, H.F., 2011. Investigation of intercooling effect in CO₂
 1980 capture energy consumption. *Energy Procedia* 4, 1601-1607.

1981

1982 Kierzhkowska-Pawlak, H., Siemienieć, M., Chacuk, A., 2012. Reaction kinetics of CO₂ in
 1983 aqueous methyldiethanolamine solutions using the stopped-flow technique. *Chemical and*
 1984 *Process Engineering*, 33(1), 7-18.

1985

1986 Kim, S.T., Kang, J.W., Lee, J.S., Min, B.M., 2011. Analysis of the heat of reaction and
 1987 regeneration in alkanolamine-CO₂ system. *Korean Journal of Chemical Engineering* 28,
 1988 2275-2281.

1989

1990 Kozak, F., Petig, A., Morris, E., Rhudy, R., Thimsen, D., 2009. Chilled ammonia process for

1991 CO₂ capture. *Energy Procedia* 1, 1419-1426.

1992

1993 Kumar, P.S., Hogendoorn, J.A., Feron, P.H.M., Versteeg, G.F., 2002. New absorption liquids

1994 for the removal of CO₂ from dilute gas streams using membrane contactor. *Chemical*

1995 *Engineering Science* 57, 1639-1651.

1996

1997 Kumar, P.S., Hogendoorn, J.A., Feron, P.H.M., Versteeg, G.F., 2003a. Equilibrium Solubility

1998 of CO₂ in Aqueous Potassium Taurate Solutions:□ Part 1. Crystallization in Carbon Dioxide

1999 Loaded Aqueous Salt Solutions of Amino Acids. *Industrial & Engineering Chemistry*

2000 *Research* 42, 2832-2840.

2001

2002 Kumar, P.S., Hogendoorn, J.A., Timmer, S.J., Feron, P.H.M., Versteeg, G.F., 2003b.

2003 Equilibrium Solubility of CO₂ in Aqueous Potassium Taurate Solutions:□ Part 2.

2004 Experimental VLE Data and Model. *Industrial & Engineering Chemistry Research* 42, 2841-

2005 2852.

2006

2007 Kumar, G., Kundu, M., 2013. Vapor–liquid equilibrium of CO₂ in aqueous blends of (N-

2008 ethyl-ethanolamine +N-methyl-diethanolamine) and (N-ethyl-ethanolamine + 2-amino-2-

2009 methyl-1-propanol). *Journal of Chemical & Engineering Data* 58, 2959-2965.

2010

2011 Kumar, S., Cho, J.H., Moon, I., 2014. Ionic liquid-amine blends and CO₂BOLs: Prospective

2012 solvents for natural gas sweetening and CO₂ capture technology—A review. *International*

2013 *Journal of Greenhouse Gas Control* 20, 87-116.

2014

2015 Kvamsdal, H., Jakobsen, J., Hoff, K., 2009. Dynamic modeling and simulation of a CO₂

2016 absorber column for post-combustion CO₂ capture. *Chemical Engineering and Processing:*

2017 *Process Intensification* 48, 135-144.

2018

2019 Le Moullec, Y., Kanniche, M., 2011. Screening of flowsheet modifications for an efficient

2020 monoethanolamine (MEA) based post-combustion CO₂ capture. *International journal of*

2021 *greenhouse gas control* 5 (4), 727-740.

2022

2023 Lee, S.S., Mun, S.M., Choi, W.J., Min, B.M., Cho, S.W., Oh, K.J., 2012. Absorption
 2024 characteristics of new solvent based on a blend of AMP and 1, 8-diamino-p-menthane for
 2025 CO₂ absorption. *Journal of Environmental Sciences* 24, 897-902.

2026

2027 Lee, I.Y, Kwak, N.S, Lee, J.H, Jang, K.Y, Shim, J.G. 2013. Oxidative Degradation of
 2028 Alkanolamines with Inhibitors in CO₂ Capture Process. *Energy Procedia* 37, 1830 – 1835.

2029

2030 Lerche, B.M., 2012. CO₂ capture from flue gas using amino acid salt solutions, Ph.D. Thesis
 2031 Department of Chemical and Biochemical Engineering. Technical University of Denmark,
 2032 Denmark.

2033

2034 Leonard, G., Voice, A., Toye, D., Heyen, G. 2014. “Influence of Dissolved Metals and
 2035 Oxidative Degradation Inhibitors on the Oxidative and Thermal Degradation of
 2036 Monoethanolamine in Postcombustion CO₂ Capture. *Ind. Eng. Chem. Res.*, 53,
 2037 18121–18129.

2038

2039 Li, J., Henni, A., Tontiwachwuthikul, P., 2007. Reaction kinetics of CO₂ in aqueous
 2040 ethylenediamine, ethyl ethanolamine, and diethyl monoethanolamine solutions in the
 2041 temperature range of 298-313 K, using the stopped-flow technique. *Industrial & engineering
 2042 chemistry research* 46, 4426-4434.

2043

2044 Li, H., Frailie, P.T., Rochelle, G.T., Chen, J., 2014a. Thermodynamic modeling of
 2045 piperazine/2-aminomethylpropanol/CO₂/water. *Chemical Engineering Science* 117, 331-341.

2046

2047 Li, H., Moullec, Y.L., Lu, J., Chen, J., Marcos, J.C.V., Chen, G., 2014b. Solubility and
 2048 energy analysis for CO₂ absorption in piperazine derivatives and their mixtures. *International
 2049 Journal of Greenhouse Gas Control* 31, 25-32.

2050

2051 Li, J., Chen, L., Ye, Y., Qi, Z., 2014c. Solubility of CO₂ in the Mixed Solvent System of
 2052 Alkanolamines and Poly (ethylene glycol) 200. *Journal of Chemical & Engineering Data.*
 2053 59 (6), 1781–1787.

2054

2055 Li, J., Lin, X., Ning, P.G., Cao, H.B., Zhang, Y., 2014d. Measurement and modeling of the
 2056 solubility of carbon dioxide in aqueous 1, 8-p-menthane-diamine solution. The Journal of
 2057 Chemical Thermodynamics 71, 64-70.

2058

2059 Li, Y., Zheng, D., Dong, L., Nie, N., Xiong, B., 2014e. Solubilities of CO₂ in, and densities
 2060 and viscosities of, the piperazine+ 1-ethyl-3-methyl-imidazolium acetate+ H₂O System.
 2061 Journal of Chemical & Engineering Data 59, 618-625.

2062

2063 Liang, Y., Liu, H., Rongwong, W., Liang, Z., Idem, R., Tontiwachwuthikul, P., 2015.
 2064 Solubility, absorption heat and mass transfer studies of CO₂ absorption into aqueous solution
 2065 of 1-dimethylamino-2-propanol. Fuel 144, 121-129.

2066

2067 Liang, Z., 2010. Optimization of Post-Combustion Amine-Based Carbon Dioxide Capture
 2068 Process to Minimize Heat Requirments for Solvent Regeneration. Ph.D Thesis. University of
 2069 Regina, Regina, Canada.

2070

2071 Lin, P.H., Wong, D.S.H., 2014. Carbon dioxide capture and regeneration with
 2072 amine/alcohol/water blends. International Journal of Greenhouse Gas Control 26, 69-75.

2073

2074 Littel, R., Van Swaaij, W., Versteeg, G., 1990. Kinetics of carbon dioxide with tertiary
 2075 amines in aqueous solution. AIChE journal 36, 1633-1640.

2076

2077 Liu, H., Liang, Z., Sema, T., Rongwong, W., Li, C., Na, Y., Idem, R., Tontiwachwuthikul, P.,
 2078 2014. Kinetics of CO₂ absorption into a novel 1-diethylamino-2-propanol solvent using
 2079 stopped-flow technique. AIChE Journal 60, 3502-3510.

2080

2081 Liu, Y., Zhang, L., Watanasiri, S., 1999. Representing vapor-liquid equilibrium for an
 2082 aqueous MEA-CO₂ system using the electrolyte nonrandom-two-liquid model. Industrial &
 2083 engineering chemistry research 38, 2080-2090.

2084

2085 Ma'mun, S., Dindore, V. Y., & Svendsen, H. F. (2007). Kinetics of the reaction of carbon
 2086 dioxide with aqueous solutions of 2-((2-aminoethyl) amino) ethanol. Industrial & engineering
 2087 chemistry research, 46(2), 385-394.

2088

2089 Majchrowicz, M.E., Brilman, D.W.F., 2012. Solubility of CO₂ in aqueous potassium l-
 2090 proline solutions—absorber conditions. *Chemical Engineering Science* 72, 35-44.

2091

2092 Majchrowicz, M.E., Kersten, S., Brilman, W., 2014. Reactive Absorption of Carbon Dioxide
 2093 in l-Proline Salt Solutions. *Industrial & Engineering Chemistry Research* 53, 11460-11467.

2094

2095 Mandal, B. P., & Bandyopadhyay, S. S. (2005). Simultaneous absorption of carbon dioxide
 2096 and hydrogen sulfide into aqueous blends of 2-amino-2-methyl-1-propanol and
 2097 diethanolamine. *Chemical engineering science*, 60(22), 6438-6451.

2098

2099 Maneeintr, K., Idem, R.O., Tontiwachwuthikul, P., Wee, A.G., 2010. Comparative mass
 2100 transfer performance studies of CO₂ absorption into aqueous solutions of DEAB and MEA.
 2101 *Industrial & Engineering Chemistry Research* 49, 2857-2863.

2102

2103 Mangalapally, H.P., Notz, R., Hoch, S., Asprion, N., Sieder, G., Garcia, H., Hasse, H., 2009.
 2104 Pilot plant experimental studies of post combustion CO₂ capture by reactive absorption with
 2105 MEA and new solvents. *Energy Procedia* 1 (1), 963-970.

2106

2107 Martin, S., Lepaumier, H., Picq, D., Kittel, J., de Bruin, T., Faraj, A., Carrette, P.L., 2012.
 2108 New amines for CO₂ capture. IV. Degradation, corrosion, and quantitative structure property
 2109 relationship model. *Industrial & Engineering Chemistry Research* 51, 6283-6289.

2110

2111 Mathias, P.M., Jaspersen, L.V., VonNiederhausen, D., Bearden, M.D., Koech, P.K.,
 2112 Freeman, C.J., Heldebrant, D.J., 2013. Assessing anhydrous tertiary alkanolamines for high-
 2113 pressure gas purifications. *Industrial & Engineering Chemistry Research* 52, 17562-17572.

2114

2115 Matin, N.S., Remias, J.E., Neathery, J.K., Liu, K., 2013. The equilibrium solubility of carbon
 2116 dioxide in aqueous solutions of morpholine: experimental data and thermodynamic modeling.
 2117 *Industrial & Engineering Chemistry Research* 52, 5221-5229.

2118

2119 Mazinani, S., Samsami, A., Jahanmiri, A., Sardarian, A., 2011. Solubility (at low partial
 2120 pressures), density, viscosity, and corrosion rate of carbon dioxide in blend solutions of

2121 monoethanolamine (MEA) and sodium glycinate (SG). Journal of Chemical & Engineering
 2122 Data 56, 3163-3168.
 2123

2124 Mondal, M.K., Singh, J., Khatri, D., 2014. Equilibrium CO₂ capture in aqueous blend of
 2125 trisodium phosphate and Piperazine. Journal of Chemical & Engineering Data 59, 1175-1180.
 2126

2127 Monteiro, J.G.S., Pinto, D.D., Zaidy, S.A., Hartono, A., Svendsen, H.F., 2013. VLE data and
 2128 modeling of aqueous N, N-diethylethanolamine (DEEA) solutions. International Journal of
 2129 Greenhouse Gas Control 19, 432-440.
 2130

2131 Monteiro, J.G.S., Hussain, S., Majeed, H., Mba, E.O., Hartono, A., Knuutila, H., Svendsen,
 2132 H.F., 2014. Kinetics of CO₂ absorption by aqueous 3-(methylamino) propylamine solutions:
 2133 Experimental results and modeling. AIChE Journal 60, 3792-3803.
 2134

2135 Mores, P., Scenna, N., Mussati, S., 2012. A rate based model of a packed column for CO₂
 2136 absorption using aqueous monoethanolamine solution. International journal of greenhouse
 2137 gas control 6, 21-36.
 2138

2139 Nainar, M., Veawab, A., 2009. Corrosion in CO₂ Capture Process Using Blended
 2140 Monoethanolamine and Piperazine. Industrial & Engineering Chemistry Research. 48, 9299–
 2141 9306.
 2142

2143 Najafloo, A., Zoghi, A.T., Feyzi, F., 2015. Measuring solubility of carbon dioxide in aqueous
 2144 blends of N-methyldiethanolamine and 2-((2-aminoethyl) amino) ethanol at low CO₂
 2145 loadings and modeling by electrolyte SAFT-HR EoS. The Journal of Chemical
 2146 Thermodynamics 82, 143-155.
 2147

2148 Najibi, H., Maleki, N., 2013. Equilibrium solubility of carbon dioxide in N-
 2149 methyldiethanolamine+ piperazine aqueous solution: Experimental measurement and
 2150 prediction. Fluid Phase Equilibria 354, 298-303.
 2151

2152 Nouacer, A., Belaribi, F.B., Mokbel, I., Jose, J., 2014. Solubility of carbon dioxide gas in
 2153 some 2.5 M tertiary amine aqueous solutions. Journal of Molecular Liquids 190, 68-73.

2154

2155 Oexmann, J., Hensel, C., Kather, A., 2008. Post-combustion CO₂-capture from coal-fired
 2156 power plants: Preliminary evaluation of an integrated chemical absorption process with
 2157 piperazine-promoted potassium carbonate. *International journal of greenhouse gas control* 2,
 2158 539-552.

2159

2160 Øi, L.E., Bråthen, T., Berg, C., Brekne, S.K., Flatin, M., Johnsen, R., Moen, I.G., Thomassen,
 2161 E., 2014. Optimization of Configurations for Amine based CO₂Absorption Using Aspen
 2162 HYSYS. *Energy Procedia* 51, 224-233.

2163

2164 Oi, L.E., 2012. Comparison of Aspen HYSYS and Aspen Plus simulation of CO₂ absorption
 2165 into MEA from atmospheric gas. *Energy Procedia* 23, 360 – 369.

2166

2167 Oktavian, R., Taha, M., Lee, M.-J., 2014. Experimental and computational study of CO₂
 2168 storage and sequestration with aqueous 2-amino-2-hydroxymethyl-1, 3-propanediol (TRIS)
 2169 solutions. *The Journal of Physical Chemistry A* 118, 11572-11582.

2170

2171 Oyenekan, B.A., Rochelle, G.T., 2007. Alternative stripper configurations for CO₂ capture
 2172 by aqueous amines. *AIChE Journal* 53, 3144-3154.

2173

2174 Pahlavanzadeh, H., Fakouri Baygi, S., 2013. Modeling CO₂ solubility in aqueous
 2175 methyldiethanolamine solutions by perturbed chain-saft equation of state. *The Journal of*
 2176 *Chemical Thermodynamics* 59, 214-221.

2177

2178 Pandya, J., 1983. Adiabatic gas absorption and stripping with chemical reaction in packed
 2179 towers. *Chemical Engineering Communications* 19, 343-361.

2180

2181 Pani, F., Gaunand, A., Cadours, R., Bouallou, C., Richon, D., 1997. Kinetics of absorption of
 2182 CO₂ in concentrated aqueous methyldiethanolamine solutions in the range 296 K to 343 K.
 2183 *Journal of Chemical & Engineering Data* 42, 353-359.

2184

2185 Park, S., Song, H.J., Lee, M.G., Park, J., 2014. Screening test for aqueous solvents used in
 2186 CO₂ capture: K₂CO₃ used with twelve different rate promoters. *Korean Journal of Chemical*
 2187 *Engineering* 31, 125-131.

2188

2189 Paul, S., Ghoshal, A.K., Mandal, B., 2008. Absorption of carbon dioxide into aqueous
 2190 solutions of 2-piperidineethanol: Kinetics analysis. *Industrial & Engineering Chemistry*
 2191 *Research* 48, 1414-1419.

2192

2193 Pearson, P., Hollenkamp, A.F., Meuleman, E., 2013. Electrochemical investigation of
 2194 corrosion in CO₂ capture plants—Influence of amines. *Electrochimica Acta* 110, 511-516.

2195

2196 Pellegrini, L.A., Langè, S., Moioli, S., Picutti, B., Vergani, P., 2013. Influence of gas
 2197 impurities on thermodynamics of amine solutions. 1. aromatics. *Industrial & Engineering*
 2198 *Chemistry Research* 52, 2018-2024.

2199

2200 Pinto, D.D.D., Zaidy, S.A.H., Hartono, A., Svendsen, H.F., 2014a. Evaluation of a phase
 2201 change solvent for CO₂ capture: Absorption and desorption tests. *International Journal of*
 2202 *Greenhouse Gas Control*, 28, 318-327.

2203

2204 Pinto, D.D.D., Knuutila, H., Fytianos, G., Haugen, G., Mejdell, T., Svendsen, H.F., 2014b.
 2205 Evaluation of a phase change solvent for CO₂ capture: Absorption and desorption tests.
 2206 *International Journal of Greenhouse Gas Control* 28, 153-164.

2207

2208 Plaza, J.M., Chen, E., Rochelle, G.T., 2010. Absorber intercooling in CO₂ absorption by
 2209 piperazine-promoted potassium carbonate. *AIChE journal* 56, 905-914.

2210

2211 Plasynski, S., Chen, Z., 2000. Review of CO₂ capture technologies and some improvement
 2212 opportunities. Division of Fuel Chemistry, American Chemical Society-Preprints of
 2213 Symposia, 45, 644-649.

2214

2215 Porcheron, F., Gibert, A., Jacquin, M., Mougin, P., Faraj, A., Goulon, A., Bouillon, P.A.,
 2216 Delfort, B., Le Pennec, D., Raynal, L., 2011a. High throughput screening of amine
 2217 thermodynamic properties applied to post-combustion CO₂ capture process evaluation.
 2218 *Energy Procedia* 4, 15-22.

2219

2220 Porcheron, F., Gibert, A., Mougin, P., Wender, A., 2011b. High throughput screening of CO₂
 2221 solubility in aqueous monoamine solutions. *Environmental science & technology* 45, 2486-
 2222 2492.

2223

2224 Portugal, A.F., Sousa, J.M., Magalhães, F.D., Mendes, A., 2009. Solubility of carbon dioxide
 2225 in aqueous solutions of amino acid salts. *Chemical Engineering Science* 64, 1993-2002.

2226

2227 Puxty, G., Rowland, R., Allport, A., Yang, Q., Bown, M., Burns, R., Maeder, M., Attalla, M.,
 2228 2009. Carbon dioxide postcombustion capture: A novel screening study of the carbon dioxide
 2229 absorption performance of 76 amines. *Environmental science & technology* 43, 6427-6433.

2230

2231 Rangwala, H. A., Morrell, B. R., Mather, A. E., & Otto, F. D. (1992). Absorption of CO₂ into
 2232 aqueous tertiary amine/MEA solutions. *The Canadian Journal of Chemical*
 2233 *Engineering*, 70(3), 482-490.

2234

2235 Rayer, A. V., Sumon, K. Z., Sema, T., Henni, A., Idem, R. O., Tontiwachwuthikul, P., 2012.
 2236 Part 5c: Solvent chemistry: solubility of CO₂ in reactive solvents for post-combustion CO₂.
 2237 *Carbon Management* 3 (5), 467-484.

2238

2239 Rayer. A.V., Henni, A., 2014a. Heats of absorption of CO₂ in aqueous solutions of tertiary
 2240 amines: N-Methyldiethanolamine, 3-Dimethylamino-1-propanol, and 1-Dimethylamino-2-
 2241 propanol, *Industrial & Engineering Chemistry Research* 53 (12), 4953–4965

2242

2243 Rayer, A.V., Armugam, Y., Henni, A., Tontiwachwuthikul, P., 2014b. High-pressure
 2244 solubility of carbon dioxide (CO₂) in aqueous 1-methyl piperazine solution. *Journal of*
 2245 *Chemical & Engineering Data* 59, 3610-3623.

2246

2247 Raynal, L., Bouillon, P-A., Gomez, A, Broutin, P., 2011a. From MEA to demixing solvents
 2248 and future steps, a roadmap for lowering the cost of post-combustion carbon capture
 2249 *Chemical Engineering Journal* 171, 742– 752

2250

2251 Raynal, L., Pascal, A., Bouillon, P.A., Gomez, Z., le Febvre de Nailly, M., Jacquin, M., Kittel,
 2252 J., diLella, A., Mougin, P., Trapy, J., 2011b. The DMX process: An original solution for
 2253 lowering the cost of post-combustion carbon capture. *Energy Procedia* 4, 779-786.

2254

2255 Reddy, S., Scherffius, J., Gilmartin, J., Freguia, S., 2004. Improved split flow process and
 2256 apparatus. International Patent: WO 2004/005818 A2.

2257

2258 Rey, A., Gouedard, C., Ledirac, N., Cohen, M., Dugay, J., Viala, J., Pichon, V., Bertomeu,
 2259 L., Picq, D., Bontemps, D., Chopin, F., Carrette, P-L., 2013. Amine Degradation in CO₂
 2260 Capture. 2. New Degradation Products of MEA. Pyrazine and Alkylpyrazines: Analysis,
 2261 Mechanism of Formation and Toxicity. Int. J. Greenh. Gas. Con. 19, 576-583.

2262

2263 Rinker, E.B., Ashour, S.S., Sandall, O.C., 1996. Kinetics and modeling of carbon dioxide
 2264 absorption into aqueous solutions of diethanolamine. Industrial & Engineering Chemistry
 2265 Research 35, 1107-1114.

2266

2267 Rinker, E.B., Ashour, S.S., Sandall, O.C., 2000. Absorption of carbon dioxide into aqueous
 2268 blends of diethanolamine and methyldiethanolamine. Industrial & Engineering Chemistry
 2269 Research 39, 4346-4356.

2270

2271 Rinker, E.B., Sami, S.A., Sandall, O.C., 1995. Kinetics and modeling of carbon dioxide
 2272 absorption into aqueous solutions of N-methyldiethanolamine. Chemical Engineering Science
 2273 50, 755-768.

2274

2275 Rochelle, G.T., Bishnoi, S., Chi, S., Dang, H., Santos, J., 2001. Research needs for CO₂
 2276 capture from flue gas by aqueous absorption/stripping. US Department of Energy, Pittsburgh,
 2277 PA, USA.

2278

2279 Rochelle, G.T., Bishnoi, S., Chi, S., Dang, H., Santos, J., 2001. Research needs for CO₂
 2280 capture from flue gas by aqueous absorption/stripping. US Department of Energy, Pittsburgh,
 2281 PA, USA.

2282

2283 Rodriguez, J., Mac Dowell, N., Llovel, F., Adjiman, C., Jackson, G., Galindo, A., 2012.
 2284 Modeling the fluid phase behaviour of aqueous mixtures of multifunctional alkanolamines

2285 and carbon dioxide using transferable parameters with the SAFT-VR approach. *Molecular*
 2286 *Physics* 110, 1325-1348.

2287

2288 Rohr, A.C., McDonald, J.D., Kracko, D., Doyle-Eisele, M., Shaw, S.L., Knipping, E.M.,
 2289 2013. Potential Toxicological Effects of Amines Used for Carbon Capture and Storage and
 2290 Their Degradation Products. *Energy Procedia*. 37, 759-768.

2291

2292 Rongwong, W., Jiraratananon, R., Atchariyawut, S., 2009. Experimental study on membrane
 2293 wetting in gas-liquid membrane contacting process for CO₂ absorption by single and mixed
 2294 absorbents. *Separation and Purification Technology* 69, 118-125.

2295

2296 Saha, A.K., Bandyopadhyay, S.S., Biswas, A.K., 1995. Kinetics of absorption of CO₂ into
 2297 aqueous solutions of 2-amino-2-methyl-1-propanol. *Chemical Engineering Science* 50, 3587-
 2298 3598.

2299

2300 Saiwan, C., Idem, C., Tontiwachwuthikul, P., Akkarachalanont, P., Supap, T., 2012. U.S.
 2301 Patent International Application No. PCT/CA2012/0000632012.

2302

2303 Sairi, .A. , Yusoff, R. , Alias, Y. , Aroua, M.K., 2011. Solubilities of CO₂ in aqueous N-
 2304 methyl-diethanolamine and guanidinium trifluoromethanesulfonate ionic liquid systems at
 2305 elevated pressures, *Fluid Phase Equilib.* 300, 89–94.

2306

2307 Sairi, N. A., Ghani, G. A., Aroua, M. K., Yusoff, R., Alias, Y., 2015. Low pressure
 2308 solubilities of CO₂ in guanidinium trifluoromethanesulfonate–MDEA systems. *Fluid Phase*
 2309 *Equilibria* 385, 79–91

2310

2311 Sanchez Fernandez, E., Heffernan, K., van der Ham, L.V., Linders, M.J.G., Eggink, E.,
 2312 Schrama, F.N.H., Brilman, D.W.F., Goetheer, E.L.V., Vlugt, T.J.H., 2013. Conceptual
 2313 Design of a Novel CO₂ Capture Process Based on Precipitating Amino Acid Solvents.
 2314 *Industrial & Engineering Chemistry Research* 52, 12223-12235.

2315

2316 Schach, M.O., Schneider, R.d., Schramm, H., Repke, J.U., 2010. Techno-economic analysis
 2317 of postcombustion processes for the capture of carbon dioxide from power plant flue gas.
 2318 *Industrial & Engineering Chemistry Research* 49, 2363-2370.

2319

2320 Schijven, J.F., Šimůnek, J., 2002. Kinetic modeling of virus transport at the field scale.

2321 Journal of Contaminant Hydrology 55, 113-135.

2322

2323 Sema, T., Naami, A., Liang, Z., Shi, H., Rayer, A.V., Sumon, K. Z., Wattanaphan P, Henni

2324 A. Idem, R., Saiwan, C., Tontiwachwuthikul, P., 2012. Part 5b: Solvent chemistry: reaction

2325 kinetics of CO₂ absorption into reactive amine solutions, Carbon Management, 3, 201-220.

2326

2327 Saxton, A., J, Rochelle.,2009. Catalysts and inhibitors for MEA oxidation. Energy Procedia,

2328 1, 1179-1185.

2329

2330 Shi, H., Liang, Z., Sema, T., Naami, A., Usubharatana, P., Idem, R., Saiwan, C.,

2331 Tontiwachwuthikul, P., 2012a. Part 5a: Solvent chemistry: NMR analysis and studies for

2332 amine–CO₂–H₂O systems with vapor–liquid equilibrium modeling for CO₂ capture processes.

2333 Carbon Management 3, 185-200.

2334

2335 Shi, H., Naami, A., Idem, R., Tontiwachwuthikul, P., 2014a. Catalytic and non catalytic

2336 solvent regeneration during absorption-based CO₂ capture with single and blended reactive

2337 amine solvents. International Journal of Greenhouse Gas Control 26, 39-50.

2338

2339 Shi, H., Naami, A., Idem, R., Tontiwachwuthikul, P., 2014b. 1D NMR analysis of a

2340 quaternary MEA-DEAB-CO₂-H₂O amine system: liquid phase speciation and vapor-liquid

2341 equilibria at CO₂ absorption and solvent regeneration conditions. Industrial and Engineering

2342 Chemistry Research 53, 8577-8591.

2343

2344 Shi, H., Sema, T., Naami, A., Liang, Z., Idem, R., Tontiwachwuthikul, P., 2012b. ¹³C NMR

2345 spectroscopy of a novel amine species in the DEAB–CO₂–H₂O system: VLE model.

2346 Industrial & Engineering Chemistry Research 51, 8608-8615.

2347

2348 Shi, H., Idem, R., Tontiwachwuthikul, P., submitted February 2015. The theoretical reaction

2349 and minimum energies requirement for Amine-based post-combustion capture process and

2350 effective practical methods for heat duty reduction. International Journal of Greenhouse Gas

2351 Control (IJGGC).

2352

2353 Shojaeian, A. Haghtalab, A., 2013. Solubility and density of carbon dioxide in different
 2354 aqueous alkanolamine solutions blended with 1-butyl-3-methylimidazoliumacetate ionic
 2355 liquid at high pressure. *Journal of Molecular Liquids* 187, 218–225
 2356

2357 Shokouhi, M., Farahani, H., Hosseini-Jenab, M., 2014. Experimental solubility of hydrogen
 2358 sulfide and carbon dioxide in dimethylformamide and dimethylsulfoxide. *Fluid Phase*
 2359 *Equilibria* 367, 29-37.
 2360

2361 Singh, P., Niederer, J.P., Versteeg, G.F., 2007. Structure and activity relationships for amine
 2362 based CO₂ absorbents—I. *International Journal of Greenhouse Gas Control* 1, 5-10.
 2363

2364 Singh, P., Niederer, J.P., Versteeg, G.F., 2009. Structure and activity relationships for amine-
 2365 based CO₂ absorbents-II. *Chemical Engineering Research and Design* 87, 135-144.
 2366

2367 Sodiq, A., Rayer, A.V., Olanrewaju, A.A., Abu Zahra, M.R.M., 2014. Reaction Kinetics of
 2368 Carbon Dioxide (CO₂) Absorption in Sodium Salts of Taurine and Proline Using a Stopped-
 2369 Flow Technique. *International Journal of Chemical Kinetics* 46, 730-745.
 2370

2371 Song, H.-J., Park, S., Kim, H., Gaur, A., Park, J.-W., Lee, S.J., 2012. Carbon dioxide
 2372 absorption characteristics of aqueous amino acid salt solutions. *International Journal of*
 2373 *Greenhouse Gas Control* 11, 64-72.
 2374

2375 Srinivasan, S., Veawab, A., Aroonwilas, A., 2013. Low Toxic Corrosion Inhibitors for
 2376 Amine-based CO₂ Capture Process. *Energy Procedia* 37, 890-895.
 2377

2378 Supap, T., Saiwan, C., Idem, R., Tontiwachwuthikul, P.P., 2011. Part 2: Solvent
 2379 management: solvent stability and amine degradation in CO₂ capture processes. *Carbon*
 2380 *Management* 2, 551-566.
 2381

2382 Sutar, P.N., Vaidya, P.D., Kenig, E.Y., 2013. Activated DEEA solutions for CO₂ capture—A
 2383 study of equilibrium and kinetic characteristics. *Chemical Engineering Science* 100, 234-241.
 2384

2385 Svensson, H., Edfeldt, J., Velasco, V.Z., Hulteberg, C., Karlsson, H.T., 2014. Solubility of
 2386 carbon dioxide in mixtures of 2-amino-2-methyl-1-propanol and organic solvents.
 2387 International Journal of Greenhouse Gas Control 27, 247-254.
 2388

2389 Téllez-Arredondo, P., Medeiros, M., 2013. Modeling CO₂ and H₂S solubilities in aqueous
 2390 alkanolamine solutions via an extension of the Cubic-Two-State equation of state. Fluid
 2391 Phase Equilibria 344, 45-58.
 2392

2393 Tobiesen, F.A., Hillestad, M., Kvamsdal, H., Chikukwa, A., 2012. A General Column Model
 2394 in CO2SIM for Transient Modeling of CO₂ Absorption Processes. Energy Procedia 23, 129-
 2395 139.
 2396

2397 Tong, C., Perez, C.C., Chen, J., Marcos, J.-C.V., Neveux, T., Le Moullec, Y., 2013a.
 2398 Measurement and calculation for CO₂ solubility and kinetic rate in aqueous solutions of two
 2399 tertiary amines. Energy Procedia 37, 2084-2093.
 2400

2401 Tong, D., Maitland, G.C., Trusler, M.J., Fennell, P.S., 2013b. Solubility of carbon dioxide in
 2402 aqueous blends of 2-amino-2-methyl-1-propanol and piperazine. Chemical Engineering
 2403 Science 101, 851-864.
 2404

2405 Tontiwachwuthikul, P., 1991. New pilot plant technique for sizing gas absorbers with chemical
 2406 reactions, PhD. Thesis. University of British Columbia, Canada.
 2407

2408 Tontiwachwuthikul, P., Idem, R., Gelowitz, D., Liang, Z.H., Supap, T., Chan, C.W.,
 2409 Sanpasertparnich, T., Saiwan, C., Smithson, H., 2011. Recent progress and new development
 2410 of post-combustion carbon-capture technology using reactive solvents. Carbon Management
 2411 2, 261-263.
 2412

2413 Tontiwachwuthikul, P., Idem, R., 2013. Recent Progress and New Developments in Post-
 2414 Combustion Carbon-Capture Technology with Reactive Solvents. Future Science Book
 2415 Series, Future Science Ltd, London, UK.
 2416

2417 Tontiwachwuthikul, P., Meisen, A., Lim, C., 1989. Novel pilot plant technique for sizing gas
 2418 absorbers with chemical reactions. *The Canadian Journal of Chemical Engineering* 67, 602-
 2419 607.

2420

2421 Tontiwachwuthikul, P., Meisen, A., Lim, C., 1994. Methodologies for designing packed acid
 2422 gas absorbers with chemical reaction: a review, *Int. Conf. on Adv. Sci. & Technol. Exch.*

2423

2424 Usubharatana, P., 2009. A study of monoethanolamine-methanol hybrid solvents for carbon
 2425 dioxide capture by absorption. Ph.D Thesis University of Regina, Canada.

2426

2427 Vahidi, M., Zoghi, A.T., Moshtari, B., Nonahal, B., 2013. Equilibrium solubility of carbon
 2428 dioxide in an aqueous mixture of n-methyldiethanolamine and diisopropanolamine: an
 2429 experimental and modeling study. *Journal of Chemical & Engineering Data* 58, 1963-1968.

2430

2431 Versteeg, G., Van Dijck, L., Van Swaaij, W., 1996. On the kinetics between CO₂ and
 2432 alkanolamines both in aqueous and non-aqueous solutions. An overview. *Chemical*
 2433 *Engineering Communications* 144, 113-158.

2434

2435 Versteeg, G., van Swaaij, W.b., 1988. On the kinetics between CO₂ and alkanolamines both
 2436 in aqueous and non-aqueous solutions—II. Tertiary amines. *Chemical engineering science*
 2437 43, 587-591.

2438

2439 Voice, A.K., Vevelstad, S.J., Chen, X., Nguyen, T., Rochelle, G.T., 2013. Aqueous 3-
 2440 (methylamino) propylamine for CO₂ capture. *International Journal of Greenhouse Gas*
 2441 *Control* 15, 70-77.

2442

2443 Wang, T., Jens, KJ., 2013. Oxidative Degradation of AMP/MEA Blends for Post-Combustion
 2444 CO₂ Capture. *Energy Procedia*. 37, 306-313.

2445

2446 Wang, T., Jens, KJ., 2014. Possible Pathway for Oxidative Degradation of β -Hydroxyl
 2447 Alkanolamine for Post Combustion CO₂ Capture. *Energy Procedia*. 51, 259-266.

2448

2449 Wagner, E.D., Osiol, J., Mitch, W.A., Plewa, M.J., 2014. Comparative in Vitro Toxicity of
 2450 Nitrosamines and Nitramines Associated with Amine-based Carbon Capture and Storage
 2451 Environ. Sci. Technol. 48, 8203-8211.
 2452

2453 Wagner, M., von Harbou, I., Kim, J., Ermatchkova, I., Maurer, G., Hasse, H., 2013.
 2454 Solubility of carbon dioxide in aqueous solutions of monoethanolamine in the low and high
 2455 gas loading regions. Journal of Chemical & Engineering Data 58, 883-895.
 2456

2457 Wattanaphan, P., Sema, T., Idem, R., Liang, Z., Tontiwachwuthikul, P., 2013. Effects of flue
 2458 gas composition on carbon steel (1020) corrosion in MEA-based CO₂ capture process.
 2459 International Journal of Greenhouse Gas Control 19, 340-349.
 2460

2461 Wei, C.C., Puxty, G., Feron, P., 2014. Amino acid salts for CO₂ capture at flue gas
 2462 temperatures. Chemical Engineering Science 107, 218-226.
 2463

2464 Weiland, R.H., Hatcher, N., Nava, J., 2009. Tray hydraulic operating regimes and selectivity.
 2465 PTQ Gas 2010, 35-43.
 2466

2467 Wilson, M., Tontiwachwuthikul, P., Chakma, A., Idem, R., Veawab, A., Aroonwilas, A.,
 2468 Gelowitz, D., Barrie, J., Mariz, C., 2004. Test results from a CO₂ extraction pilot plant at
 2469 boundary dam coal-fired power station. Energy 29, 1259-1267.
 2470

2471 Wu, Y., Chan, C.W., 2009. A data analysis decision support system for the carbon dioxide
 2472 capture process. Expert Systems with Applications, 36, 9949-9960.
 2473

2474 Wu, Y., Zhou Q., Chan C.W., 2010. A comparison of two data analysis techniques and their
 2475 applications for modeling the carbon dioxide capture process. Engineering Applications of
 2476 Artificial Intelligence. 23, 1265-1276.
 2477

2478 Xiang, Y., Yan, M., Choi, Y.-S., Young, D., Nesic, S., 2014. Time-dependent
 2479 electrochemical behavior of carbon steel in MEA-based CO₂ capture process. International
 2480 Journal of Greenhouse Gas Control 30, 125-132.
 2481

2482 Xu, F., Gao, H., Dong, H., Wang, Z., Zhang, X., Ren, B., Zhang, S., 2014a. Solubility of CO₂
 2483 in aqueous mixtures of monoethanolamine and dicyanamide-based ionic liquids. *Fluid Phase*
 2484 *Equilibria* 365, 80-87.

2485

2486 Xu, Z., Wang, S., Qi, G., Trollebø, A.A., Svendsen, H.F., Chen, C., 2014b. Vapor liquid
 2487 equilibria and heat of absorption of CO₂ in aqueous 2-(diethylamino)-ethanol solutions.
 2488 *International Journal of Greenhouse Gas Control* 29, 92-103.

2489

2490 Xu, S., Wang, Y. W., Otto, F. D., & Mather, A. E. (1996). Kinetics of the reaction of carbon
 2491 dioxide with 2-amino-2-methyl-1-propanol solutions. *Chemical Engineering Science*, 51(6),
 2492 841-850.

2493

2494 Yamada, H., Chowdhury, F.A., Goto, K., Higashii, T., 2013. CO₂ solubility and species
 2495 distribution in aqueous solutions of 2-(isopropylamino) ethanol and its structural isomers.
 2496 *International Journal of Greenhouse Gas Control* 17, 99-105.

2497

2498 Yu, W.C., Astarita, G., Savage, D., 1985. Kinetics of carbon dioxide absorption in solutions
 2499 of methyldiethanolamine. *Chemical engineering science* 40, 1585-1590.

2500

2501 Yusoff, R., Aroua, M. K., Shamiri, A., Ahmady, A., Jusoh, N. S., Asmuni, N. F. , Bong, L.
 2502 C. and S. H. Thee., 2013. Density and Viscosity of Aqueous Mixtures of N-
 2503 Methyldiethanolamines (MDEA) and Ionic Liquids, *J. Chem. Eng. Data*, 58, 240–247

2504

2505 Zhang, Y., Chen, CC., 2011. Thermodynamic Modeling for CO₂ Absorption in Aqueous
 2506 MDEA Solution with Electrolyte NRTL Model. *Industrial & Engineering Chemistry*
 2507 *Research* 50, 163-175.

2508

2509 Zhang, X., Zhang, C. F., & Liu, Y. (2002). Kinetics of absorption of CO₂ into aqueous
 2510 solution of MDEA blended with DEA. *Industrial & engineering chemistry research*, 41(5),
 2511 1135-1141.

2512

2513 Zheng, C., Tan, J., Wang, Y., Luo, G., 2013. CO₂ solubility in a mixture absorption system of
 2514 2-amino-2-methyl-1-propanol with ethylene glycol. *Industrial & Engineering Chemistry*
 2515 *Research* 52, 12247-12252.

2516

2517 Zheng, L., Landon, J., Zou, W., Liu, K., 2014. Corrosion Benefits of Piperazine As an
 2518 Alternative CO₂ Capture Solvent. *Industrial & Engineering Chemistry Research* 53, 11740-
 2519 11746.

2520

2521 Zhou, Q., Chan, C., Tontiwachiwuthikul, P., 2009. A monitoring control and diagnostic
 2522 expert system for carbon dioxide capture process. *Expert systems with applications* 36, 1621-
 2523 1631.

2524

2525 Zhou, Q., Chan, C.W., Tontiwachwuthikul, P., 2008. A Regression Analysis Study on the
 2526 Carbon Dioxide Capture Process. *Industrial and Engineering Chemistry Research*.47,4937-
 2527 4943.

2528

2529 Zhou, Q., Chan C.W., Tontiwachwuthikul, P., Idem, R., Gelowitz, D., 2009a,. A statistical
 2530 analysisof the carbon dioxide capture process. *International Journal of Greenhouse Gas,*
 2531 *Control.* 3. 535-544.

2532

2533 Zhou, Q., Chan C.W., Tontiwachwuthikul, P., 2009b. An intelligent system for monitoring
 2534 and diagnosis of the carbon dioxide capture process. *Expert Systems with Applications*, 36,
 2535 1621-1631.

2536

2537 Zhou, Q., Chan C.W., Tontiwachwuthikul, P., 2010, Application of neuro-fuzzy technology
 2538 for analysis of the carbon dioxide capture process. *Fuzzy Sets and Systems*,161, 2597-2611.

2539

2540 Zhou, Q., Chan C.W., Tontiwachwuthikul, P., 2011. Monitoring and diagnosis of the carbon
 2541 dioxide capture process system using an intelligent system approach. *Journal of*
 2542 *Environmental Informatics*.18,75-83.

2543

2544 Zhou, Q., Wu, Y, Chan C.W., Tontiwachwuthikul, P., Idem, R., Gelowitz, D., 2012.
 2545 Application of data modeling and analysis techniques to the carbon dioxide capture process
 2546 system. *Carbon Management* , 3, 81-94.

2547

2548 Zhou, Q., Chan C.W., Tontiwachwuthikul, P., Idem, R., Gelowitz, D., 2013, Application of
2549 the neuro-fuzzy modeling technique for operational problem solving in a carbon dioxide
2550 capture process system. International Journal of Greenhouse Gas Control, 15, 32-41.
2551
2552 Zoghi, A.T., Feyzi, F., 2013. Equilibrium solubility of carbon dioxide in aqueous 2-((2-
2553 aminoethyl) amino) ethanol and N-methyldiethanolamine solution and modeling by
2554 electrolyte mPR-CPA EoS. The Journal of Chemical Thermodynamics 67, 153-162.
2555
2556
2557

2558
2559
2560
2561

Table 2.1 Solubility studies of CO₂ in aqueous amine mixtures

Amine+ H ₂ O+CO ₂	Temperature& Pressure	Modeling	Reference
Morpholine (MO, 34.8 - 43.5 wt%)	313.15 - 393.15 K & 157 - 0.439 kPa	eNRTL	Matin et al., (2013)
screening experiments of 24 tertiary amines (30 wt%)	313.15 - 393.15 K & 20 kPa	-	Chowdhury et al., (2013)
anhydrous ethyldiethanolamine (EDEA)	283.15 - 323.15 K & 33.74 - 6217.1 kPa	NRTL-RK	Mathias et al., (2013)
2-amino-2-methyl-1-propanol (AMP)	Didn't perform solubility experiment	γ - ϕ model	Arcis et al., (2014)
2-aminoethanol (MEA)	Didn't perform solubility experiment	γ - ϕ model	Arcis et al., (2014)
3-piperidinemethanol (3-PM, 0.1 - 3.0 M)	313 - 353 K	-	Conway et al., (2014)
monoethanolamine (MEA, 30 wt %)	313 - 353 K (System at atmospheric pressure)	-	Choi et al., (2014)
methyldiethanolamine(MDEA, 30 wt %)	313 - 353 K (System at atmospheric pressure)	-	Choi et al., (2014)
MEA (15 - 30 wt%)	313 - 393 K & 1 - 80 kPa	Extended Pitzer	Wagner et al., (2013)
1-methylpiperazine (1-MPZ, 15 - 30 wt%)	313.15 - 353.15 K & 182 - 7780 kPa	eNRTL	Rayer et al., (2014b)
2-(2-aminoethylamino)ethanol	303 - 323 K & 0.8 - 800	-	Guo et al., (2013)

(AEEA, 15 wt %)	kPa		
2-amino-1,3-propanediol (Serinol)	313.15 - 373.15 K & 0.5239 - 413.6 kPa	-	Bougie and Iliuta, (2014)
MEA (30 wt %)	313.15 - 393.15 K & 2.1 - 585.9 kPa	-	Arshad et al., (2014)
5M DEEA	313.15 - 393.15 K & 0.6 - 577.1 kPa	-	Arshad et al., (2014)
1-2M MAPA	313.15 - 393.15 K & 0.3 - 597.8 kPa	-	Arshad et al., (2014)
AEEA (30 wt %)	313 K & 1.42 - 718.90 kPa	-	Guo et al., (2014)
diethanolamine (DEA)	VLE Data used from literature	Electrolyte EoS based on Fürst and Renon model	Diab et al., (2013)
MEA/DEA/MDEA (Pure & binary)	VLE Data used from literature	Electrolyte Cubic Two State (eCTS) EoS	Téllez-Arredondo and Medeiros, (2013)
n,n-dimethylformamide	313.15 - 353.15 K & 0.201 - 2.434 MPa	(i) Extended Henry's law - Pitzer's model; (ii) new version of Redlich– Kwong (RK) for gas- ionic liquid systems	Shokouhi et al., (2014)
2-amino-1-ethanol (MEA, 30 wt%)	313.15 K & 0.0144 - 11.2351 kPa	-	Idris et al., (2015)
3-amino-1-propanol (5 molar and 30 wt%)	313.15 K & 0.0047 - 4.2314 kPa	-	Idris et al., (2015)

4-amino-1-butanol (5 molar and 30 wt%)	313.15 K & 0.0039 - 2.5681 kPa	-	Idris et al., (2015)
5-amino-1-pentanol (5 molar and 30 wt%)	313.15 K & 0.0032 - 2.0474 kPa	-	Idris et al., (2015)
methyldiethanolamine (MDEA)	VLE Data used from literature	Perturbed Chain-SAFT EOS (Smith–Missen algorithm)	Pahlavanzadeh and Fakouri Baygi, (2013)
1,8-p-menthane-diamine (MDA, 0.625 - 1.25 mol/L)	313.15 - 353.15 K & 0.55 - 776.0 kPa	Kent–Eisenberg	Li et al., (2014d)
MEA (15.3 wt%)	313.2 K & 14.2 - 915.3 kPa	-	Chang et al., (2013)
five fatty amine polyoxyethylene ethers (FAPE-1205, 1210, 1215, 1808, 1815)	303.15 - 323.15 K (equilibrium pressure = 89.9 - 517.2 kPa)	-	Deng et al., (2014)
DIPA (45 wt%)	313.15 - 343.15 K & 1.07 - 40.64 bar	eNRTL	Haghtalab et al., (2014)
MEA	313 - 393 K & 4.5 - 112.4 kPa	-	Yamada et al., (2013)
2-(isopropylamino)ethanol (IPAE)	313 - 393 K & 4.4 - 226.2 kPa	-	Yamada et al., (2013)
2-(propylamino)ethanol (PAE)	313 - 393 K & 4.4 - 214.3 kPa	-	Yamada et al., (2013)
1-methyl piperazine (1-MPZ)	313.15 - 393.15 K & 0.09 - 686 kPa		Li et al., (2014b)
1-ethyl piperazine (1-EPZ)	313.15 - 393.15 K &		Li et al., (2014b)

	0.43 - 700 kPa		
1,4-dimethyl piperazine (DMPZ)	313.15 - 393.15 K & 3.98 - 730 kPa		Li et al., (2014b)
1-(2-hydroxyethyl)piperazine (HEP)	313.15 - 393.15 K & 0.05 - 716 kPa		Li et al., (2014b)
thriethylenediamine (TEDA)	313.15 - 393.15 K		Li et al., (2014b)
2-(diethylamino)-ethanol (DEEA)	333.15 - 353.15 K & 3.747 - 191.907 kPa	eNRTL	Xu et al., (2014b)
2-amino-2-hydroxymethyl-1,3-propanediol (TRIS)	318.15 - 333.15 K & 2.31 - 11.76 MPa	Modified Kent–Eisenberg model	Oktavian et al., (2014)
1-dimethylamino-2-propanol (1DMA2P)	298 - 333 K & 8 - 101 kPa	-	Liang et al., (2015)
MEA (for validation)	313.15 K & 4.3 - 259.9 kPa	-	Nouacer et al., (2014)
AMP (for validation)	313.15 K & 2.8 - 227.5 kPa	-	Nouacer et al., (2014)
2-(2-(dimethylamino) ethoxy) ethanol [DMAEOE]	313.15 - 353.15 K & 14.901 - 218.013 kPa	-	Nouacer et al., (2014)
3-dimethyl amino-1-propanol [DiMAP]	313.15 - 353.15 K & 2.367 - 246.025 kPa	-	Nouacer et al., (2014)
1,2-bis (dimethyl amino) ethane [TEMED]	313.15 - 353.15 K & 6.374 - 205.10 kPa	-	Nouacer et al., (2014)
pyridine	313.15 - 353.15 K & 14.361 - 93.876 kPa	-	Nouacer et al., (2014)

methyl-4-morpholine	313.15 - 353.15 K & 15.476 - 213.44 kPa	-	Nouacer et al., (2014)
n,n-dimethylethanolamine(DMEA)	313.2 - 393.2 K & 1 - 300 kPa.	eNRTL	Tong et al., (2013a)
triethylene diamine (TEDA)	313.2 - 393.2 K & 1 - 300 kPa.	eNRTL	Tong et al., (2013a)
Diglycolamine (DGA)	(303-378) K and 43– 48)kPa		Dixit and Mollekopf, (2014)

Table 2.2 Recent solubility studies of CO₂ in mixed solvents

H ₂ O+Amine+CO ₂ +others	Temperature& Pressure	Modeling	Reference
--	--------------------------	----------	-----------

benzene + methyldiethanolamine(MDEA, 25- 50 wt%)	VLE Data used from literature	eNRTL	Pellegrini et al., (2013)
toluene + methyldiethanolamine (MDEA, 25-50 wt%)	Taken from the literature (298.14 - 393.27 K)	eNRTL	Pellegrini et al., (2013)
2-amino-2-methyl-1-propanol (AMP) (0.4 - 1.0 M) + ethylene glycol (EG)	303.2 - 353.2 K & 5 - 120 kPa	Non-Rigorous	Zheng et al., (2013)
30 wt% methyldiethanolamine (MDEA) + 3-methylamino propylamine (MAPA)	313 - 353 K & atmospheric pressure	-	Choi et al., (2014)
30 wt% methyldiethanolamine (MDEA) + diethylenetriamine (DETA)	313 - 353 K &atmospheric pressure	-	Choi et al., (2014)
30 wt% methyldiethanolamine (MDEA) + triethylenetetramine (TETA)	313 - 353 K &atmospheric pressure	-	Choi et al., (2014)
30 wt% methyldiethanolamine (MDEA) + tetraethylenepentamine (TEPA)	313 - 353 K & atmospheric pressure	-	Choi et al., (2014)
AEEA + N- methyldiethanolamine (MDEA, 5 and 10 wt %)	303 - 323 K & 0.8 - 800 kPa	-	Guo et al., (2013)
AEEA + 2-amino-2-methyl-1- propanol (AMP, 5 and 10 wt %)	303 - 323 K & 0.8 - 800 kPa	-	Guo et al., (2013)

MDEA + DIPA	313.2 - 358.2 K & 85 - 3984 kPa	Deshmukh–Mat her	Vahidi et al., (2013)
diethanolamine (DEA) + (2- aminoethyl)ethanolamine (AEEA) (Total concentration 0.92 to 3.22 mol/kg)	303.14 - 343.14 K & 10.13 - 20.26 kPa	-	Bajpai and Mondal, (2013)
potassium alaninate (K-ALA) + piperazine (Pz)	313.15 - 353.15 K & 0 - 1041.7 kPa	-	Kang et al., (2013)
potassium serinate (K-SER) + piperazine (Pz)	313.15 - 353.15 K & 0 - 783.4 kPa	-	Kang et al., (2013)
n-ethyl-ethanolamine (EAE) + n-methyl-diethanolamine (MDEA)	303.1 - 323.1 K & 0.3 - 550 kPa	-	Kumar and Kundu, (2013)
-ethyl-ethanolamine (EAE) + 2- amino-2-methyl-1-propanol (AMP)	303.1 - 323.1 K & 0.3 - 550 kPa	-	Kumar and Kundu, (2013)
2-amino-2-hydroxymethyl-1,3- propanediol (AHPD) + piperazine (Pz)	313.15 - 373.15 K & 0.8750 - 229.4 kPa	-	Bougie and Iliuta, (2014)
trisodium phosphate (TSP) + piperazine (PZ)	303 - 353 K & 9.96 - 20.28 kPa	-	Mondal et al., (2014)
5M DEEA + 1-2M MAPA	313.15 - 393.15 K & 0.4 - 521.9 kPa	-	Arshad et al., (2014)
30 wt % AEEA + 70 wt % BP	303 - 323 K & 0.90 - 780.18 kPa	-	Guo et al., (2014)
30 wt % AEEA + 70 wt % DEG	313 K & 51.17 - 744.42 kPa	-	Guo et al., (2014)

30 wt % AEEA + 70 wt % TEG	313 K & 46.61 - 833.29 kPa	-	Guo et al., (2014)
DGA (30 wt %) + poly(ethylene glycol) 200 (PEG200) (70 wt %)	313.15 - 393.15 K & 14.6 - 1464.5 kPa	Jou and Mather's model	Li et al., (2014c)
DEA (30 wt %) + poly(ethylene glycol) 200 (PEG200) (70 wt %)	313.15 - 393.15 K & 6.8 - 1468 kPa	Jou and Mather's model	Li et al., (2014c)
MDEA (30 wt %) + poly(ethylene glycol) 200 (PEG200) (70 wt %)	313.15 - 393.15 K & 81.1 - 1453.1 kPa	Jou and Mather's model	Li et al., (2014c)
0.25 monoethanolamine + 0.75 ethanol	313–343 K & bubble point pressure 0.85 - 11.40 MPa	-	Guerra-Neto et al., (2014)
0.25 diethanolamine + 0.75 ethanol	313–343 K & bubble point pressure 0.70 - 9.56 MPa	-	Guerra-Neto et al., (2014)
0.25 triethanolamine + 0.75 ethanol	313–343 K & bubble point pressure 2.02 - 19.52 MPa	-	Guerra-Neto et al., (2014)
n-methyldiethanolamine + piperazine	363 - 423 K & 26.3–204.3 kPa	modified Deshmukh–Mather model & PR	Najibi and Maleki, (2013)
diethylenetriamine (DETA) (15 - 25 wt%) + Piperazine (PZ) (5 - 15 wt%)	313.2 - 353.2 K & 0.8 - 923.0 kPa	Modified Kent–Eisenberg model	Chang et al., (2013)
2-((2-aminoethyl)amino)ethanol (AEEA) + n-methyldiethanolamine	308.2 - 368.2 K & 101 - 4445 kPa	Electrolyte modified PR EoS	Zoghi and Feyzi, (2013)

(MDEA)		(emPR-CPA EoS)	
DIPA (24 wt%) + PZ (21 wt%)	313.15 - 343.15 K & 0.99 - 39.62 bar	eNRTL	Haghtalab et al., (2014)
DIPA (24 wt%) + AMP (21 wt%)	313.15 - 343.15 K & 0.94 - 40.56 bar	eNRTL	Haghtalab et al., (2014)
DIPA + AMP + PZ	313.15 - 343.15 K & 0.97 - 41.53 bar	eNRTL	Haghtalab et al., (2014)
reline + monoethanolamine (MEA)	313.2 - 353.2 K & 50.2 - 858.8 kPa	Modified Kent– Eisenberg	Hsu et al., (2014)
n-methyldiethanolamine (MDEA) + 2-((2- aminoethyl)amino)ethanol (AEEA)	313.15 - 358.15 K & 5.5 - 240 kPa	electrolyte SAFT-HR (eSAFT- HR)	Najafloo et al., (2015)
20 wt% 1-MPZ + 10 wt% PZ	313.15 - 353.15 K & 0.03 - 643.0 kPa	-	Li et al., (2014b)
20 wt% DMPZ + 10 wt% PZ	313.15 - 353.15 K & 0.03 - 540 kPa	-	Li et al., (2014b)
20 wt% TEDA + 10 wt% PZ	313.15 - 353.15 K & 0.03 - 604.0 kPa	-	Li et al., (2014b)
2-amino-2-methyl-1-propanol (AMP)+N-methyl-2-pyrrolidone (NMP)	298.15 - 323.15 K & 2.2 - 301.7 kPa	-	Svensson et al., (2014)
2-amino-2-methyl-1-propanol (AMP)+triethylene glycol dimethyl ether (TEGDME)	298.15 - 323.15 K & 2.3 - 303.3 kPa	-	Svensson et al., (2014)
AMP+PZ	313.2 - 393.2 K	Kent–Eisenberg	Tong et al.,

	&5.7 - 463.5 kPa		(2013b)
PZ+AMP	VLE data used from literature	eNRTL	Li et al., (2014a)

Table 2.3 Recent solubility studies of CO₂ in mixed solvent containing ionic liquids

H ₂ O+Amine+IL+CO ₂	Temperature& Pressure	Modeling	Reference
piperrazine (PZ) + 1-ethyl-3-methyl-imidazolium acetate ([Emim][Ac])	313.15 - 343.15 K & 20.2 - 880.4 kPa	-	Li et al., (2014e)
MEA + [C2OHmim][DCA]	313.15 - 333.15 K & 10 - 800 kPa	-	Xu et al., (2014a)
MEA + [Bmim][DCA]	313.15 - 333.15 K & 10 - 800 kPa	-	Xu et al., (2014a)
MDEA + [bmim][acetate]	303.15 - 343.15 K & 0.1689 - 3.8711 MPa	PR-TS EoS	Haghtalab and Shojaeian, (2015)
MDEA + tetramethylammoniumglycinate ([N1111][Gly])	298.15 - 318.15 K & 0 - 300 kPa	-	Gao et al., (2013)

Table 2.4 Lab-scale gas-liquid contactors and their advantages and disadvantages for CO₂ absorption kinetic measurement (Sema et al., 2012)

Equipment	Advantages	Disadvantages
Stirred-cell	-Only gas phase measurement is	-Difficult to maintain the smooth and consistent

reactor		required	gas-liquid interface.
		-Suitable for toxic gases	
Wetted column	wall	-Operating in a counter current mode that is close to real systems	-Possibility of creating ripples in the liquid film. -Occurring of the inactive film at the bottom of column
Laminar absorber	jet	-Gas-liquid interface can be measured directly from a microscope -Suitable for very reactive liquid solvent	-Possibility of creating (i) turbulent liquid surface, (ii) a reduction in the liquid jet caused by gravity, and (iii) stagnant surface and ripples at the bottom of liquid jet
Wetted-sphere		- Laminar liquid surface can be generated and controlled easier than that of the laminar jet absorber.	-Surface area cannot be varied. -Possibility of creating ripples in the liquid film and inactive film at the column bottom
String-of-disc contactor		-Operating in a counter current mode that is close to real systems -Surface area can be varied by number of discs	- Absorption rate at specific concentrations of liquids and/or gas cannot be achieved due to changes of CO ₂ and reactive liquid along the length of the string.
Stop flow apparatus		-No effect of gas phase resistance -A small amount of solvent is required -Easy operation	-Can be used for only low amine concentrations

Table 2.5 The second order CO₂ absorption rate constants (k_2) and activation energy for amine absorbents obtained from the simplified kinetics modeling, and/or comprehensive numerically solved kinetics modeling.

Amine	Temp. (K)	k_2 (m ³ /kmol s)	Methodology	Ref.	Ea (kJ/mol)	Ref.
MEA	298	5,939	Simplified model	Versteeg et al., 1996	41.2	Hikita et al., 1977
	298	6,209	Numerical model	Edali et al., 2009		
DEA	298	576	Simplified model	Zhang et al., 2002	53.1	Roberts and Harris, (2000)
	298	412	Numerical model	Rinker et al., 1996		
MDEA	298	2.33	Simplified model	Haimour et al., 1987	47.9	Rangwala et al., 1992
	298	6.17	Numerical model	Rinker et al., 1995		
AMP	298	782	Simplified model	Xu et al., 1996	41.7	Alper, (1990)
	298	570	Numerical model	Mandal and Bandyopadhyay,		

				2005		
PZ	298	70,000	Simplified model	Derks et al., 2006	33.6	Bishnoi and Rochelle, (2002)
	298	65,460	Numerical model	Edali et al., 2009		
AEEA	298	12,100	Simplified model	Ma'mun et al., 2007	32.5	Ma'mun et al., 2007
DETA	298	17,510	Simplified model	Hartono et al., 2009	32.2	Rayer et al., (2013b)
1-AP	298	4,430	Simplified model	Henni et al., 2008	40.1	Henni et al., (2008)
3-AP	298	7,500	Simplified model	Henni et al., 2008	45.4	Henni et al., (2008)
TEA	298	3	Numerical model	Littel et al., 1990	35.8	Littel et al., (1990)
TREA	298	70	Numerical model	Versteeg et al., 1996	54.7	Versteeg et al., (1996)
DMMEA	298	27	Numerical model	Versteeg and van Swaaij, 1988	53.6	Versteeg and van Swaaij, (1988)
DEMEA	298	81	Simplified model	Li et al., 2007	50.5	Li et al., (2007)
1DMA2P	298	21	Simplified model	Kadiwala et al., 2012)	62.6	Kadiwala et al., (2012)
3DMA1P	298	32	Simplified model	(Kadiwala et al., 2012)	75.6	Kadiwala et al., (2012)
DEAB	298	420	Numerical model	(Sema et al., 2012)	62.6	Sema et al., (2012)
1DEA2P	298	91.5	Simplified model	(Liu et al., 2014)	94.2	Liu et al., (2014)
MAPA	298	15 times faster than MEA	Numerical model	(Monteiro et al., 2014)	39	Monteiro et al., (2014)
2-PE	303	1147	Simplified model	(Paul et al., 2008)	45.2	Monteiro et al., (2014)
2MPZ	298	44557	Numerical model	(Chen and Rochelle, 2013)		

Ea means Activation energy (kJ/mol)

Table 2.6 NMR calibration table of DEAB(4-diethylamino-2-butanol) (Shi et al., 2012a)

δ_{DEAB} (ppm)	Protonation Percentage (%)							$\Delta\delta$ (ppm)
	0	20	40	60	80	100	120	
C ₁	10.206	9.902	9.510	9.107	8.723	8.435	8.435	-1.771
C ₂	22.307	22.314	22.321	22.340	22.340	22.351	22.351	0.044
C ₃	33.935	35.591	33.148	32.258	32.258	31.935	31.935	-2.000
C ₄	46.315	46.549	48.846	47.450	47.450	47.677	47.677	1.362
C ₅	48.563	48.680	48.823	49.116	49.224	49.225	49.225	0.662
C ₆	67.218	66.961	66.632	65.969	65.731	65.731	65.731	-1.487

Table 2.7 CO₂ solubility studies of amino acid salts

Amino acid salts	Range of experiments	References
potassium taurate	333-373K, 4- 6 M concentration	Wei et al. 2014
sodium glycinate	298.15 and 313.15 K, 1, 5, 10, 15, 20, and 30 % wt	Harris et al., 2009
potassium glycinate, potassium threonate	293 and 323 K, 0.1 and 3.0 M for potassium glycinate and 1 mol M for potassium threonate	Portugal et al., 2009
3 (methylamino)propylamine/sarcosine	313, 333, 353 and 373, 1.0–5.0 M	Aronu et al., 2011
potassium prolinatate and potassium α -aminobutyrate	(313.2, 333.2, 353.2) K. 0.5, 1.0, and 2.0 M	Chang et al., 2015
potassium sarcosinate,	313.15 K, 333.15 K, and 353.15 K, 4 M	Kang et al., 2013
potassium salts solutions of L-proline	298 and 323 K 0.5, 1, 2 and 3 M	Majchrowicz and Brilman, 2012

Table 5.1 Comparison between CDCMD and KBSCDC systems

	CDCMD	KBSCDC
Development Environment	G2: an expert-system shell	DeltaV Simulate: a simulator of a process control system
Structure	Object-Oriented	Based on modules
Functions	Monitoring, Diagnosis	Monitoring, Diagnosis, Control
Targeted	5 parameters	25 parameters associated

Parameters	associated with reboiler	with 9 instruments
Reasoning Mechanism	Rule-based backward reasoning	Data-based fault detection

Figure 1.1 Simplified Diagram of a post-combustion capture process using reactive solvents.

Figure 2.1 Comparison of CO₂ solubility in aqueous alkanolamine systems (Rayer et al., 2013a)

<p>1-methyl piperazine (1-MPZ)</p>	<p>1-ethyl piperazine (1-EPZ)</p>	<p>1,4-dimethyl piperazine (DMPZ)</p>
<p>1-(2-hydroxyethyl)piperazine (HEP)</p>	<p>piperazine (PZ)</p>	<p>triethylenediamine (TEDA)</p>

Figure 2. 2 Some piperazine derivatives

Figure 2.3 Comparison of cyclic capacity (Data from Boot-Handford et al., 2014)

Figure 2.4 Liquid-phase speciation and concentration in a 2.5-M monoethanolamine solution with CO₂ loadings from 0 to 1. At temperatures of (A) 40°C and (B) 120°C. MEA: Monoethanolamine; MEAH: Protonated monoethanolamine. (Shi et al., 2012a)

Figure 2.5 Standard flowchart of experimental performance:

(A)

(B)

Figure 2.6 Structure and chemical shift of protonated 4-diethylamino-2-butanol and 4-diethylamino-2-butanol. (A) Protonated DEAB with its specific six carbon groups, these carbons are labelled in specific ^{13}C chemical shift order from shielded region to deshielded region (low to high). (B) Calibration curves plotted corresponds to Table 2.6 (Shi et al., 2012a)

Figure 2.7 Ion speciation (concentration plot) of DEAB-CO₂-H₂O using NMR combination method. (A) Ion speciation (concentration) plot of 1.50 mol/l DEAB-CO₂-H₂O system at 24.5°C. (B) Ion speciation (concentration) plot of 1.97 mol/l DEAB-CO₂-H₂O system at 24.5°C.(Shi et al., 2012a)

(a) 24°C

(b) 70°C

Figure 2.8 Ion speciation plot of MEA-DEAB-CO₂-H₂O plot under 25 and 70°C.(Shi et al., 2014b)

Figure 3.1 Design procedure of CO₂ absorber (modified from (Tontiwachwuthikul et al., 1989)).

Figure 5.1 Process of data modeling of CO₂ capture process parameters

Figure 5.2 Procedures in statistical regression analysis

Figure 6.1 The energy requirement of post-combustion capture technologies from the past, present and the future developments