Towards Computational CO$_2$ Capture and Storage Models: A Review

Natt Makul[*]

Department of Civil Engineering Technology, Faculty of Industrial Technology, Phranakhon Rajabhat University, Bangkhen, Bangkok 10220, Thailand

ARTICLE INFO

ABSTRACT

This review is aimed to increase knowledge on computational CO$_2$ capture and storage models that are gradually evolving in the design and development to act as more effective carbon capture agents with acceptable toxicity and costs and complementary adjuncts to experiments for comprehending amino-CO$_2$ reaction mechanisms. Also, the review discussed experimental research of degradation reactions of aqueous organic amines, measurements, kinetics and forecasts of amine pK$_a$ values and amine-CO$_2$ equilibria. Also, the researcher comprehensively discussed the computational simulation of mechanisms of carbon capture reactions. In the contexts of experimental and computational studies, the comparative advantages of bicarbonate, carbamic acid, termolecular and zwitterion are described. Computational approaches shall gradually evolve in the design and development to act as more effective carbon capture agents with acceptable toxicity and costs and complementary adjuncts to experiments for comprehending amino-CO$_2$ reaction mechanisms. Some of the main research findings indicate that advancements in quantum computing might help in simulating larger complex molecules such as CO$_2$. Moreover, the simulations might discover new catalysts for CO$_2$ capture that are more efficient and cheaper than present models. CO$_2$ capture and storage (CCS) could minimize the CO$_2$ emission volume by 14%. The first stride in CCS is capturing CO$_2$. It accounts for 70% -80% of this technology total costs. Virtually, 50% of the costs to operate the post-combustion capture (PCC) plants are related to steam costs. It is thus important to acquire the best possible data to avoid unnecessary costs and overdesigns.

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*Corresponding Author
Email: natt@pnru.ac.th
Tel: (+669) 000-79997

1. Introduction

The developments and scaling up of cost-efficient carbon capture processes are of great significance to allow the extension of these technologies to minimize emissions of greenhouse gases [1]. With the objective of designing a computational toolset that would allow the industry to more efficiently determine, develop, scale up, run and optimize promising ideas, this initiated the carbon capture simulation initiative (CCSI). Advanced multiscale modeling and simulations have the potentials to drastically reduce the costs and time of developing new carbon capture technology. The CCSI is a partnership among universities, national laboratories and industry [2]. The CCSI is designing, developing, scaling-up, operating and optimizing a range of such tools, including risk-analysis frameworks, validated high-fidelity device-scale computational-fluid-dynamics (CFD) models with quantified uncertainties, high-resolution filtered CFD sub-models, advanced dynamic process control frameworks, uncertainty quantification and process quantification tools, dynamic process and steady-state models, and basic data sub-models. These models and tools allow fundamental data sub-models to be deployed within comprehensive process models to optimize and synthesize processes, including kinetics and thermodynamics. The resulting processes inform the developments of more detailed simulations and process control systems of possible equipment to enhance the designs and minimize the scale-up risks [3]. An important part of these models and tools is quantifications and propagations of the uncertainties across scales.

Since the beginning of industrialization, there is little scientific doubt that concentrations of international atmospheric CO_2 have been growing, majorly because of energy generation by fossil fuels' combustion [4]. Fossil fuels are still currently the major energy production sources regardless of rapidly increasing and extensive investigations into renewable energy technologies. At least for the next couple of decades, fossil fuels are anticipated to remain the main source of energy production. High concentrations of CO_2 create grave ecological issues, remarkably increases in global temperatures, resulting in climate challenges such as more severe climate and weather patterns, increasing sea levels, and melting of polar regions [5]. The general agreement is that immediate reductions of CO_2 emissions from fossil-fuel-powered production are needed until more renewable energy sources or more efficient technologies can substitute fossil fuels. In the short-to-medium term, CO_2 capture and storage (CCS) among greenhouse gas ameliorations will be an integral green "bridging" technology. CCS could minimize the CO_2 emission volume by 14% as forecasted by Economic Cooperation and Development (OECD) and the International Energy Agency (IEA). The first stride in CCS is capturing carbon dioxide. It accounts for 70%-80% of this technology total cost. In the literature, various post-combustion CO_2 capture (PCC) technologies have been studied [6]. Such technologies include adsorption and other processes such as cryogenic process and micro algal bio-fixation process, absorption process and membrane separation as indicated in Fig. **1**.
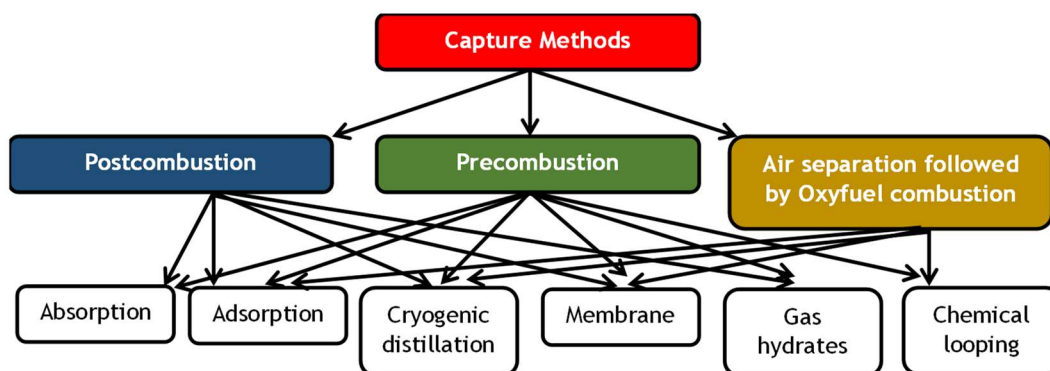

Figure 1: Methods and technologies utilized for CO_2 capture [19].

Nevertheless, the main challenge with amine-based gas scrubbing is the higher energy demands of the capturing agent regeneration phase even though PCC technologies have great advantages [7]. The designs of energy-efficient capture agents, improved process designs and technical improvements in the capture processes can greatly minimize the high regeneration energy requirements. Other problems, like amine loss and formations of nitrosamines, must be dealt with because they can pose grave health hazards and increase the costs of CO_2 capture.

Chemists and engineers have developed more effective adsorbents and absorbents by substantially optimizing existing processes and equipment [8]. Chemists produce experimental data on kinetic and thermodynamic energies (enthalpies, activation parameters and entropies), adsorbent and absorbent reactions with CO_2, and the corresponding equilibria and constant rates for the reactions that are important for a detailed comprehension of desorption and adsorption/absorption processes.

Ab initio simulation methods and computational quantum chemistry (QC) in concert can offer efficient and accurate predictions of structural and electronic features such as reaction species structures, transition state energies, free reaction energies, and reaction energetics [8]. Also, spectroscopic strategies like UV-vis, EPR, Raman and FTIR help in the practical experimental designs of contemporary adsorbent and adsorbent materials. Monte Carlo (MC) simulation approaches and classical molecular dynamics (MD) also play integral roles in relating macroscopic scale phenomena experimental observations to the molecular levels using atomistic molecular mechanics force fields. They can for instance produce central comprehension of the influences of solvent-solution interaction and the information of physicochemical ideas, transport behaviors (mass transfers, diffusivity and viscosity), and reaction dynamics to solution CO_2 captures and release performances [9]. At the pilot-plant scale, the interplays between quantum chemical and other molecular-level modeling and simulation approaches and chemical engineering experiments can offer cost-effective and efficient ways to interpret data, directing study into optimizing a plant for scale-up and deployments and process alternatives.

Advancements in quantum computing might help scientists simulate large and complex CO_2 molecules [10]. These simulations might reveal new catalysts for CO_2 capture that are more efficient and cheaper than present models. Currently, small molecules can be simulated up to a few dozen qubits. However, this should be scaled to the order of one million. Being able to easily and cheaply eliminate CO_2 directly out of the atmosphere would be greatly powerful in the battle against climate change [11]. Quantum computing can be the instrument the scientists require to design such an easy-to-deploy, clean and safe innovation. Now, the question is whether we can design error-corrected and large-scale quantum computers that are needed to profoundly realize important applications such as computational quantum-scale CO_2 capture and storage models. If scientists can design cost-efficient and practical technologies to capture CO_2, those technologies would immediately change the future of the biggest sector in the universe and offer technical solutions to one of the most puzzling challenges facing humanity [12]. This research explored the computational-scale and storage models to capture CO_2.

The developments and scale-up of the cost-efficient carbon capture process are of great significance to allow the widespread deployments of these technologies to greatly minimize the emissions of greenhouse gases [13]. One of the greatest problems for modern energy investigators is the challenge of thermodynamically scalable and effective carbon capture. The combustion of fossil fuels leads to carbon dioxide emissions into the atmosphere. The anthropogenic CO_2 emission is now changing the climate. For decades to come, combustion will remain a major global energy system component even though various alternatives to combustion are being considered [14]. Today's CO_2 capture technologies are energy-intensive, expensive and cumbersome.

Some of the notable remaining obstacles are the lack of economic incentives for investments and the costs involved as carbon capture and storage (CCS) is making its way forward to development globally [15]. CCS is an important tool or technology for minimizing emissions of greenhouse gases and slowing down climate change for two main reasons. CCS is presently the only available tool for decarbonizing the heavy industry sectors. CCS is essential in complementing sources of renewable energy with the least carbon-intensity fossil fuel power-driven sources of energy.

The overall goal of this work is to acquire an integrated and full chain model of carbon capture, transportation and storage processes that integrate the impacts on transportation and storage that can originate from having an intermittent and dynamic generation of CO_2 [16]. Regarding the storage processes, the concentration of this project will be on storage in depleted gas and oil reservoirs and saline aquifers and capture usage of products for carbon dioxide. Carbon dioxide-enhanced oil recovery (CO_2-EOR) offers a very vital economic incentive for carbon capture and storage and can assist in accelerating its usage. Also, at different points, the full chain model shall enable for identification of cost reduction potentials in the process [17]. The full chain model will establish how specific differences would impact the rest of the chain.

The concentration of this review is to highlight the current state-of-the-art in comprehending multifaceted and still not fully comprehended, mechanisms of reactions in amine systems involved in CO_2 capture as shown in Fig. **2** [18]. Also, the review aims to summarize the main contributions that the approach of computational chemistry have contributed to this crucially important area. Besides, the review aims to offer perspectives on the capabilities of these strategies for futures in silico-designs of more successful CO_2 capture amine-oriented materials.

The current research is majorly concentrated on the literature investigations that have utilized quantum chemical approaches in modeling the CO_2 capture reaction mechanisms and physicochemical properties and chemical thermodynamics of aqueous amine absorbents by these solutions [19]. This knowledge will be combined with major experimental investigations to create contemporary theoretical frameworks for comprehending the complexities of reactions of CO_2-amines.
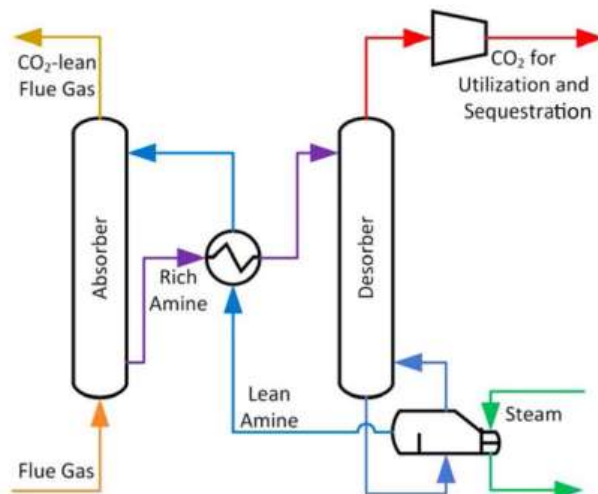

Figure 2: Scrubbing industrial process of a typical amine [18].

2. Theoretical Methods

In this section, we detailed the computational and theoretical approaches best-appropriate to model the phenomena of CO_2/aqueous-amine solutions. We majorly concentrated on the estimates made at specific theory levels and how these affect the reliability and accuracy of these models for corroborating and interpreting experiments and predicting properties of materials, reaction mechanisms and energetics [20]. In this chapter, we provided sufficient critiques and summaries of fundamental theoretical methods to enable the audience to comprehend and acknowledge consequent computational investigations of amine-oriented carbon captures.

Computational modeling of kinetic and thermodynamic characteristics is an active research field although it is mature [21]. The modeling principles and standards are straightforward: suitable molecular modeling methods are utilized to model reaction systems by defining suitable interactions and establishing relationships between the macroscopic quantities and molecular interactions which are experimentally accessible. The prediction accuracies directly depend on the levels of necessary estimations and precisions of the computational methods and techniques made at each stage.

2.1. Molecular Simulation Methods

Brief overviews of the major molecular simulation methods and specific advanced techniques that are utilized in CO_2 absorption simulations in amine solutions are provided here [22]. Molecular simulations consider models having solute molecules immersed in a huge volume of solvent molecules and determine their behaviors based on cautious calculations of the interaction between each component [23]. Transport characteristics such as viscosity and equilibrium properties such as vapor pressure can be computed in statistical thermodynamics' frameworks provided the system forces and potential energy can be determined from atomic coordinates.

To represent bulk systems with a small number of molecules, these techniques generally use conditions of periodic boundaries [24]. This is carried out by replicating the simulation cells (often cubic) in all dimensions. Simulation is trying conducted in distinctive statistical and mechanical ensembles that have fixed sets of state variables that are regulated in the experimental setups depending on the desired applications. The NVT ensembles or canonical ensembles where the temperature (T), the number of molecules (N) and the volume (V) are conserved, are utilized for single-phased fluids when densities are known [25]. The pressures are kept constant rather than volumes in the NPT or isothermal-isobaric ensembles. The average system volume is utilized in predicting fluid density. The Gibbs ensembles where two microscopic phases within the bulk stages are introduced without any explicit interfaces are the most commonly utilized ensembles for acquiring phase behaviors of mixtures and fluids like partition coefficients and solubility. The total number of molecules and temperature are also held constant [26]. The models compute equilibrium characteristics like the coexisting density of the liquid and vapors and saturated vapor pressures.

2.1.1. Molecular Mechanics/Quantum Mechanics/ (MM/QM) Simulation Methods

Since Quantum Monte Carlo methods or Ab initio molecular dynamics use full quantum chemical descriptions of all interacting species that include many molecules of explicit waters, they are very expensive. In water, chemical reactions usually involve fewer water molecules [27]. While treating the remainder of the water molecules applying classical simulation methods, it is appealing to utilize quantum chemical descriptions of water molecules involved in the capture reactions of carbon dioxide. Such techniques MM/QM divide the system into two sections: the non-reacting remainders of the systems (treated molecular mechanically) and locally chemically active sections (treated by QM methods), as indicated in Fig. **3**.
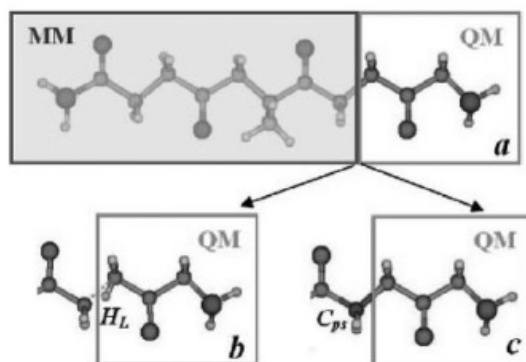

Figure 3: (a) A molecular system division into parts treated by MM and QM techniques. The boundary modeling between parts utilizing the (b) connection atoms, HL, or (c) pseudo-atoms [20].

The QM region should include all atoms participating in electronic processes and the simulation results need not rely on how the system division is done while this division is somehow arbitrary [28]. Only a few water molecules participate in solvent effects such as hydrogen bonding in typical absorption processes. The system total energy is computed as indicated in the Eq. (1).

$$U = U_{QM} + U_{MM} + U_{QM/MM} \tag{1}$$

For instance, Xie *et al*. [1] have utilized these techniques to investigate the differences between the mechanisms of CO_2 absorptions in mono-ethanolamine and aqueous 2-amino-2-methyl-1-proponal. Lee and co-researchers [21] also used the methods to research mechanisms of CO_2 absorptions in six amine solutions and the improvements of CO_2 captures in mixed amine solution.

2.2. Hybrid Solvent Models

To study CO_2 absorptions in amine solution, some investigators have applied hybrid solvent models [29]. Usually, this model is slightly related to other previous models. Having a few major explicit water molecules and QM core treatments of the solutes, hybrid CSM/QM/MM models for example are related to explicit schemes. The

MM methods and techniques treat the next water layers that bond to continuum representations in subsequent layers as indicated in Fig. **4**.
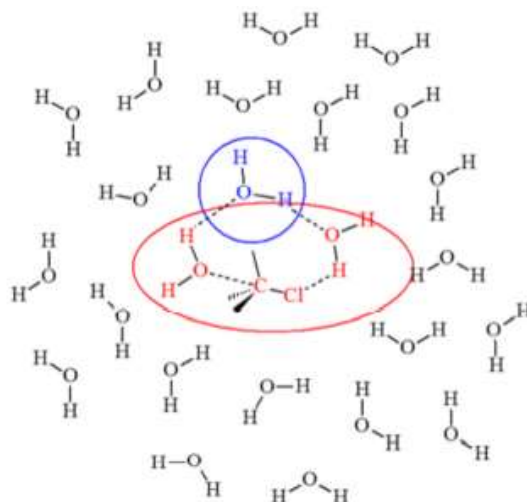

Figure 4: MM/QM division representation. The core is the QM section (blue is intermediate theory level and red is high theory level. The CSM or MM parts constitute the second layers (black) [22].

There are various challenges that have to be cautiously considered even though the hybrid solvent model has had some successes [30]. Firstly, there are no basic rules for selecting the solvent molecules' number and their conformations. In the first solvation partition, the number of water molecules strongly depends on the confirmation of solutes that can fluctuate during the reaction course. The absence of suitable constraints of explicit solvent molecules and outer solvation shells close to the implicit/explicit boundaries to prevent diffusions into the implicit phases dramatically influence interaction energies and solute behaviors [31]. Experience and care are thus needed to correctly utilize the hybrid solvent models (mixed implicit/explicit models).

The setting of their conformational states and initial placements of solvent molecules can be accomplished utilizing molecular simulation techniques as with explicit solvent approaches. In addition, various researchers have developed a combination of computational methods using water clusters of different sizes since it has been notably hard to model water due to non-negligible synergistic effects and hydrogen-bonding. For instance, Temelso *et al.* [3] decided to apply thirty-eight clusters varying from two to ten water molecules each, Leverentz and co-investigators [2] used fifteen water clusters having six to seventeen molecules each and Bryantsev and co-researchers [4] developed twenty-seven water clusters consisting of twenty water molecules each. One need to make sure that there are no hydrogen-bonding rearrangements in the explicit parts when researching the reaction mechanisms of CO_2 absorptions into solutions of aqueous amines since the net losses or gains of one hydrogen bond in the water clusters would negatively affect the reaction energy [32]. It is worth noting that important advancements have been made by using multilayer approaches that combine MM and QM or QM description with implicit solvent strategies in the fields of hybrid strategies.

2.3. Approaches for Computing pK$_a$ Values

In capture design and selection, one of the most important parameters is the pK_b basicity of amine functional groups in CO_2 capture solutions [33]. It provides direct measures of proton transfer thermodynamics. The basicity (pK_b) of amine functional groups in CO_2 captures solutions is an integral component of understanding the corresponding absorption capacity and reactions of CO_2. In aqueous solutions, the protonated amines' pK_a values can be readily measured by experiments such as acid-base titrations [34]. Large databases are readily available for measuring the protonated amines' pK_a values in aqueous solutions. Nevertheless, for promising amines not yet synthesized, chemists should also estimate their pK_a values. Employing computational methods, reliable techniques for forecasting pK_a values are thus of great significance in screening new amines for CO_2 captures. This part highlights and compares the most effective approaches for correctly predicting and computing pK_a values,

even though not all the methods have been used to amines. See Seybold *et al*. [23] for recent and comprehensive overviews of computational estimations of pK_a values.

The methods for calculating pK_a values of small molecules vary from majorly empirical to first-principle methods [24]. To establish the complex relationship between the molecular structures and properties and pK_a values, empirical strategies usually utilize machine learning. Early research by Hall for example developed linear relationships between pK_a values of tertiary, primary and secondary amines and Taft σ^* values. However, the correlations between different molecular characteristics and pK_a values are often restricted to particular groups of compounds. Generally, it is unwise to use these relationships to other clusters and molecules of the data sets [25]. Thus, the following summary concentrates on first-principle methods to pK_a predictions, consistent with the concentration of this review being greatly quantum chemical methods CO_2 captures in absorbents of aqueous amines. The formula for the dissociation reactions of the conjugate acids of the amines is shown in Eq. (2):

$$R_1R_2R_3NH^+_{(aq)} \rightleftharpoons R_1R_2R_3N_{(aq)} + H^+_{(aq)} \tag{2}$$

In which hydrogen or alkyl groups (tertiary, primary or secondary amines) are represented by the R_n. pK_a is described as shown in Eq. (3):

$$pK_a = -\log K_a$$

$$K_a = \frac{[R_1R_2R_3N][H^+]}{[R_1R_2R_3NH^+]} \tag{3}$$

For the computation of the pK_a values, two major methods have been utilized. One of the approaches is the direct computation method, where the reactions free energies are directly computed in the solutions, thus preventing separate calculations of solvation free energies and gas phases [31]. The second method utilizes thermodynamic cycles to approximate pKa for computations of reaction free energies in the solvation free energies for products and reactants and the gas phases.

3. Experimental Phenomena

In this chapter, we provided information about appropriate experimental methodologies [32]. To determine the free energies, activation parameters, equilibrium constants and kinetics for aqueous amine-CO_2 chemistry among an apparently countless range of physical and chemical properties, a variety of experimental methods are utilized. Often, chemical equilibrium investigations in solutions of carbonated amines use ^{1}H and ^{13}C NMR spectroscopy in determining the concentration and nature of chemical species present the liquid phases as functions of CO_2 compositions and amines [33]. This simple strategy to chemistry observations permits the computations of activation parameters and equilibrium constants that can be utilized to interpret absorbent behaviors among a variety of amines or used in the speciation modeling within the measurement data limits.

Systems of heterogeneous reactions involving the interaction of more than a single phase can be experimentally hard due to the need of isolating chemical reactivity from the gas-liquid mass transfer effects in dynamic systems. The most appropriate experimental approaches to research the kinetics of reactions depend on the time scales of the reactions being investigated [34]. Generally, aqueous CO_2 reacts quite quickly with secondary and primary amines that are best researched with approaches having appropriately quick temporal resolutions, like stopped-flow conductivity and stopped-flow spectrophotometry. Typically, these approaches need homogenous reaction media.
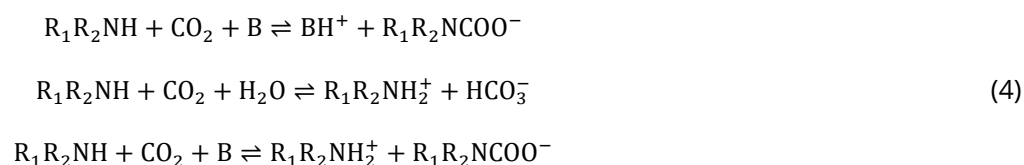
A common method is to rapidly react one solution of aqueous amines with a solution pre-saturated with CO_2 [35]. With respect to the low CO_2 solubility (milli-molar range at atmospheric pressure, this method is somehow restricted, needing concentration of amines to be equal, instead of the molar solutions or concentrations applied in the industry. Using specialized equipment, greater dissolved CO_2 solutions can be accomplished at increased pressures [36]. The methods that alternatively depend on measuring CO_2 mass transfer rates to the liquid phase from the gas phase (such as stirred batch reactors, wetted-wall reactors, and disc reactors) can be deployed to

establish the kinetics of CO_2-amine reactions at industrially appropriate concentrations of amines. Nevertheless, the methods are also complex because the techniques need the chemical reactions to correctly interpret the results of experiments and decouple CO_2 diffusion effects via the liquid and gas [37]. Direct spectroscopic methods such as IR or NMR spectroscopy can be employed for the determinations of kinetic constants for slower reactions (such as the reactions of CO_2 with tertiary or hindered amines with bicarbonates and amines).

4. General Mechanism of CO_2 Absorption in Aqueous Amines

We critically examined CO_2 absorption simulations in different amino-based aqueous solutions in this section [38]. I summarized the diverse mechanisms of reactions that have been recommended in the studies in this chapter.

CO_2 captures are majorly through the formation of bicarbonates and carbamates in the overall chemical processes as shown in Eq. (4).

$$R_1R_2NH + CO_2 + B \rightleftharpoons BH^+ + R_1R_2NCOO^-$$

$$R_1R_2NH + CO_2 + H_2O \rightleftharpoons R_1R_2NH_2^+ + HCO_3^- \tag{4}$$

$$R_1R_2NH + CO_2 + B \rightleftharpoons R_1R_2NH_2^+ + R_1R_2NCOO^-$$

In which B is any base (alkaline) such as HCO_3^-, H_2O, and R_1R_2NH and R_2 is hydrogen for primary amine [39]. The protons will eventually transfer to a second amine R_1R_2NH if B is not an amine and the general reactions for the formation of carbamates become the last equation above. Only bicarbonate mechanisms are possible in tertiary amine or a tertiary alkanolamine. For alkanolamine solutions, the direct reactions of CO_2 with hydroxyl ions are of little significance. The alkaline-catalyzed bicarbonate mechanisms recommended by Donaldson and Nguyen [24] is thought to be the best appropriate for tertiary amine. For the unhindered secondary and primary amines, previous experimental results and findings have indicated that the bicarbonate reactions are negligible. The carbamate formations take place much more quickly than the bicarbonate formations. [40] By heating the solutions, the regenerations of the capture agents are completed that drive the equilibriums first and second equations toward the reactants.

Carbamate ions are mainly produced through reactions of equation one before bicarbonate generation, in solutions of secondary or primary amines and under optimal conditions [41]. The nitrogen atoms lose hydrogen atoms to the hydrogen-bond networks when the nucleophilic alkanolamine nitrogen atoms bond to CO_2. For this process, various competing reactions have been suggested in the literature.

4.1. Zwitterion Mechanisms

Initially, the hydrogen atoms remain on the amine nitrogen atoms, leading to zwitterion intermediates of $R_1R_2NH^+COO^-$. These steps are followed by transfers of protons to second molecules of amines. Danckwerts [6] recommended the zwitterion mechanisms. Versteeg et [7] reintroduced zwitterion mechanism. Initially recommended by Caplow [8], zwitterion mechanisms are two-step simplifications of three-step mechanisms in which water is the base B. Starting with the formation of carbonates, the two reaction steps are shown in Eq. (5):

$$CO_2 + R_1R_2NH \; \overset{k_1 k_{-1}}{\rightleftharpoons} \; R_1R_2N_H^+ - COO^-$$

$$R_1R_2NH^+COO^- + B \xrightarrow{k_B} R_1R_2NCOO^- + HB^+ \tag{5}$$
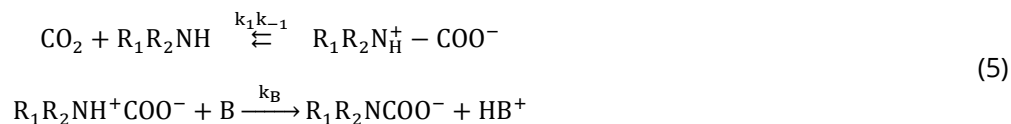
The carbamate concentrations are smalls at very low CO_2 loadings (that is often the scenario in the industry) and thus can be considered irreversible. The CO_2 reaction rates (rCO_2) in aqueous solutions with the application of steady-intermediate conditions can be expressed in Eqs. (6) – (7):

$$r_{CO_2} = \frac{k_1[R_1R_2NH]}{1 + \frac{k_{-1}}{k_B[B]}}[CO_2] \qquad (6)$$

$$r_{CO_2} = k_1[CO_2][R_1R_2NH] \qquad (7)$$

In which $k_B[B]$ represents the zwitterion deprotonation rate constant by combinations of bases and by protons-accepting species in the systems, like R_1R_2NH, OH^-, HCO_3^-, H_2O, or CO_3^{2-} [41]. The formula above portrays fractional orders between one and two regarding the amine concentrations.

4.2. Termolecular Mechanisms

Bond formations between CO_2 and nitrogen atoms and proton transfer from the alkanolamine to the base B, takes place simultaneously. This provides termolecular reactions, a single-step that produces the $R_1R_2NCOO^-$ carbonate products. Crooks and Donnellan [9] suggested these mechanisms and except for intermediate species, are somehow similar to the zwitterion mechanisms explained above. The reactions proceed through complex and loosely bound encounters. The reaction can be exhibited as shown in Eq. (8):

$$R_1R_2NH + CO_2 + B \leftrightarrow CO_2 + R_1R_2NH \cdots B \rightarrow BH^+ + R_1R_2NCOO^- \qquad (8)$$
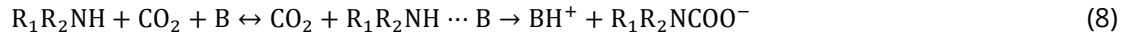
In which amine R_1R_2NH, H_2O and OH^- are the predominant bases [42]. The rate of reactions can be represented as shown in Eq. (9):

$$r_{CO_2} = \left(k_{amine}[R_1R_2NH] + k_{H_2O}[H_2O] + k_{OH^-}[OH^-]\right) \times [CO_2][R_1R_2NH] \qquad (9)$$

When the amine concentration is higher than the CO_2 concentration (often the scenario industrial uses), its amine concentration can be regarded as constant [43]. The equation (9) can thus be reduced to Eq. (10):

$$r_{CO_2} = k_{obs}[CO_2] \qquad (10)$$

In which k_{obs} represents the recorded reaction rate constant that can be experimentally measured and denoted as shown Eq. (11):

$$k_{obs} = \left(k_{amine}[R_1R_2NH] + k_{H_2O}[H_2O] + k_{OH^-}[OH^-]\right) \times [R_1R_2NH] \qquad (11)$$

These equations suggest that if available, OH^-, H_2O, R_1R_2NH and other alkaline solutions can affect the reactions in parallel directions [44]. These behaviors are equivalent to the zwitterion mechanisms exhibited by $k_{-1} \gg k_B[B]$. Some computational chemists have therefore presumed that in the termolecular mechanisms, a zwitterion need not be totally absent [45]. The only requirements are that the zwitterion deprotonations are rates determining $k_{-1} \gg k_B[B]$. The zwitterion deprotonates much less favorably than it loses CO_2. These ideas have been used in some computational investigations. Deprotonations occur majorly through water and amines in aqueous amine solutions. The reaction orders are regarding bother amines and CO_2 when the contribution of OH^- and amines to carbamate formation is neglected and water (the solvent) is the dominant base [46]. The rate equation can be denoted as shown in Eq. (12):

$$r_{CO_2} = k_{H_2O}[H_2O][CO_2][R_1R_2NH]^2 = k'[CO_2][R_1R_2NH] \qquad (12)$$

In which k' is k_{H_2O}. The reactions are the second-order with regard to MEA when the amines are the dominant bases [47]. Then the rate is shown in Eq. (13):
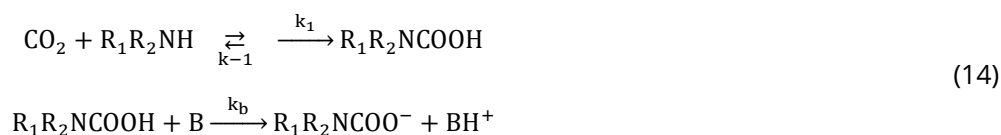
$$r_{CO_2} = k_{amine}[CO_2][R_1R_2NH]^2 \qquad (13)$$

The numbers of fitted parameters in zwitterion mechanisms are greater than in the termolecular mechanisms.

4.3. Carbamic Acid Mechanisms

In protonation and alkanolamine of the carboxyl groups on the same molecules (producing intermediate R_1R_2NCOOH carbamic acids), instantaneous proton transfer can take place either through concerted proton relays

or directly. The base B consequently reacts with intermediate carbamic acid to form the carbamate products. These are the best possible case behind the current intermediate carbamic acid mechanisms of McCann and co-researchers [11] because they never specified how the carbamic acids might be formed in the original stage. In this mechanism, the two sequential steps are shown in Eq. (14):

$$CO_2 + R_1R_2NH \underset{k-1}{\overset{k_1}{\rightleftarrows}} \xrightarrow{} R_1R_2NCOOH$$

$$R_1R_2NCOOH + B \xrightarrow{k_b} R_1R_2NCOO^- + BH^+$$

(14)

Carbamic acid mechanism varies from zwitterions' method in the intermediate identity. The intermediate identity (carbamic acids, not zwitterions) varies even though all of the rate laws are similar to the zwitterion mechanisms [43]. Thus, differentiating between carbamic acid mechanism and zwitterion mechanism through computational modeling should properly and correctly treat the comparative carbamic and zwitterion stability forms.

4.4. Bicarbonate Mechanisms

Donald and Nguyen [10] recommended that tertiary alkanols-amine may react with CO_2 directly. Also referred to as the base-catalyzed hydration mechanisms, they suggested bicarbonate mechanisms as shown in Eq. (15).

$$R_1R_2NH + CO_2 \Leftarrow R_1R_2NH_2 + HCO_3^-$$ (15)

Nevertheless, direct interactions between tertiary amines and CO_2 can be possible at exceedingly high pH in contrast to Donaldson and Nguyen [24] recommendations, thus leading to formations of monoalkyl-carbonates. Nonetheless, at pH values lesser than 12.408, the reactions are negligible. For the bicarbonate mechanism, the rate expression can be denoted as shown in Eq. (16):

$$r_{CO_2} = k''[CO_2][R_1R_2NH]$$ (16)

When computing the above different mechanisms, many investigators on the amine/CO_2 reaction mechanisms have considered proton relays or transfers [45]. Fig. **5** exhibits proton relays upon chemisorption of CO_2 to amines. The differences among the mechanisms are ultimately hard to differentiate for two major reasons. The first reason is that as the reaction condition fluctuates, the mechanisms can change [46]. For instance, the amines are likely to be the proton accepting bases in any of the commended mechanisms at high unreacted amine concentration and low absorbed CO_2 concentration. Other bases such as water can begin to make contributions as the unreacted concentrations of amines are depleted and more CO_2 concentrations are absorbed [47]. This can change the rate-restricting steps. The more stimulating reason is that to correctly differentiate among the mechanisms needs certain observations of the intermediate species formed during the reactions between the CO_2 and amines. Currently, the experimental methods and approaches deployed to research these reactions do not enable quite adequate time resolutions for this to be possible [48]. Exploring the intermediate structures require either the applications of fast time-resolved approaches such as pump-probe spectroscopies or the applications of reduced temperatures to extend the intermediate species lifetimes.

5. Simulations of Thermodynamic Characteristics During Absorption of CO_2 into Absorbents of Aqueous Amine

In this section, we discussed the physicochemical properties' molecular modeling of amine materials, like the equilibrium distributions in systems of aqueous carbon dioxide amines.

The absorbent choice with optimal thermodynamic characteristics is the original step in the designs of amine-oriented absorber for CO_2 captures [49]. When selecting CO_2 capture agents, there are different chemical and physical molecular properties that should be considered. The amine basicity or alkalinity for instance is a pointer of its capability to react with carbon dioxide. The solvent flow rate needed is affected by chemical equilibria.

During chemisorption, comprehending the thermodynamic process taking place can help in the investigation of the capture agent solution effects on absorption of CO_2 and their constituent reactions [50]. This can ultimately help in designing new amines with low regeneration energy requirements and high absorption capacity.
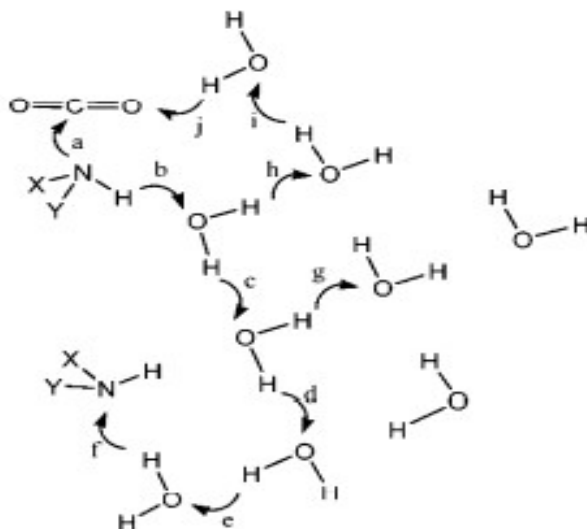

Figure 5: Putative proton relay or transfer for CO_2 to amine chemisorption [8].

It is consequently vital to design instruments to define and forecast characteristics appropriate to the absorption of CO_2, like CO_2 diffusivities, equilibrium constants and solubility in diverse amine solutions [51]. Computational modeling and models that predict absorptions of CO_2 by new amine shall increase new discoveries of important amine substances. Experimentally, modeling approaches can simulate accessible characteristics which can, in turn, be utilized in guiding studies for better capture agents and offering further fields of concentration for experiments [52]. For instance, Monte Carlo simulation can study equilibria conversions of different species with good accuracy in reaction mixtures and quantum techniques can compute constants of absorption equilibria. To compute CO_2 diffusion coefficients in reaction mixtures, molecular dynamics simulations can be utilized [53]. In the literature, there are various illustrations in which computational modeling and models have been utilized to forecast characteristics such as reaction enthalpies, chemical equilibria, free solvation energies, activity coefficients and basicity of amines.

5.1. Thermodynamic Equilibrium

The reactions between aqueous amine and CO_2 during absorptions generate bicarbonates and carbamates [54]. Based on the equilibria constants, investigators can forecast the overall performances of capture agents for these species formations. In systems, the species distribution knowledge enables estimations of the CO_2 captured amounts and the energies required for regenerations of absorbents. These aspects strongly depend on carbamate stability and aqueous amine basicity [55]. The accurate characterizations of the structures and the thermodynamic equilibria before and after CO_2 captures are important for optimizations and designs of amine-treating process.

In the literature, there are various investigations on systems of CO_2-amines [1]. Notable advances have been recently made on the experimental side. To study structural properties of amine solutions after absorptions of CO_2, X-ray scattering has been used. Infrared absorption spectra have been utilized in monitoring these processes in situ. The kinetics and chemical equilibrium are hard to experimentally research at the molecular levels due to the rapid reaction rates and usual mechanisms of complex reactions [2]. To enhance the comprehension of the microscopic characteristics of the scrubbing solutions, theoretical methods have been used. Enthalpies of reactions between amines and CO_2 are some of the vital characteristics for the designs of CO_2 removal factories and plants. Virtually, 50% of the costs to operate the PCC plants are related to steam costs [3]. It is thus important to acquire the best possible data to avoid unnecessary costs and overdesigns. In this area, many computational and experimental investigations have been reported.

and outlined future study directions. Amines' physicochemical characteristics play vital roles in their CO_2 capture suitability. Chemical characteristics, including solubility, enthalpies, protonation constants, equilibriums, and kinetics are directly associated with the original and ongoing capture process costs. Fundamental understandings
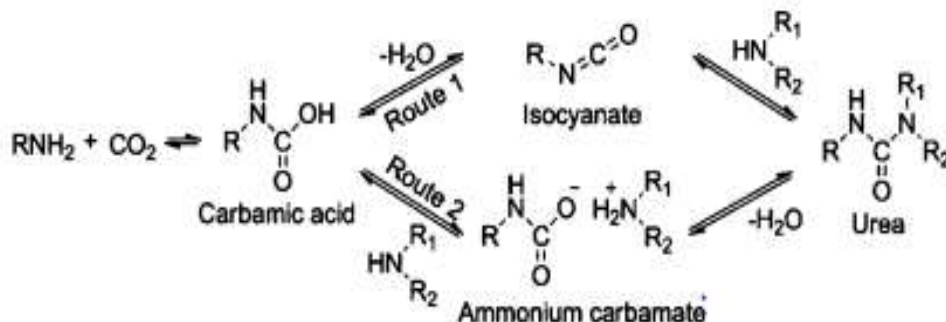

Figure 6: Amine deactivations by formation of open-chain urea recommended by Sayari *et al*. [17].

of these characteristics will promote the discoveries and designs of new carbon capture substances that capture and discharge carbon dioxide more effectively and have improved safety, the lower whole of life costs and less degradation. Using well-established techniques such as spectroscopic techniques (UV-vis, FTIR, and Raman), ionic and gas chromatography, potentiometric titrations, wetted-wall columns (WWC) and vapour-liquid equilibria (VLE), many amine characteristics can be presently investigated and experimentally measured. Nevertheless, the costs and time of synthesis of non-commercial amines and amine characterization experiments are hindrances to promoting advancements in this area. The shortcoming of availabilities of large amounts of amine substances can clearly limit large scale tests. Across a variety of amine chemo-types, sophisticated computer predictions and modeling of structure-activity correlations, physical and chemical characteristics, and mechanisms of amine reactions, can thus play vital roles in supplementing or complementing restricted experimental data. Synergistic combinations of computer and experimental techniques help in identifying the optimal characteristics for amine capture agents more rapidly than just experiment alone. Ultimately, such approaches will fast track future generations of amine-oriented CO_2 capture substances.

References

[1]   Xie HB, He N, Song Z, Chen J, Li X. Theoretical investigation on the different reaction mechanisms of aqueous 2- amino-2-methyl-1-propanol and monoethanolamine with CO_2. Ind Eng Chem Res. 2014; 53: 3363-3372. https://doi.org/10.1021/ie403280h

[2]   Leverentz HR, Qi HW, Truhlar DG. Assessing the accuracy of density functional and semiempirical wave function methods for water nanoparticles: comparing binding and relative energies of (H2O)16 and (H2O)17 to CCSD (T) results. J Chem Theory Comput. 2013; 9: 995-1006. https://doi.org/10.1021/ct300848z

[3]   Temelso B, Archer KA, Shields GC. Benchmark structures and binding energies of small water clusters with anharmonicity corrections. J Phys Chem A 2011; 115: 12034-12046. https://doi.org/10.1021/jp2069489

[4]   Bryantsev VS, Diallo MS, van Duin AC, Goddard WA. III Evaluation of B3LYP, X3LYP, and M06-class density functionals for predicting the binding energies of neutral, protonated, and deprotonated water clusters. J Chem Theory Comput. 2009; 5: 1016- 1026. https://doi.org/10.1021/ct800549f

[5]   Seybold PG, Shields GC. Computational estimation of pKa values. WIRES Comput Mol Sci. 2015; 5: 290-297. https://doi.org/10.1002/wcms.1218

[6]   Danckwerts P. The reaction of CO_2 with ethanolamines. Chem Eng Sci. 1979; 34: 443-446. https://doi.org/10.1016/0009-2509(79)85087-3

[7]   Versteeg G, Van Dijck L, Van Swaaij W. On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions. An overview. Chem Eng Commun. 1996; 144: 113-158. https://doi.org/10.1080/00986449608936450

[8]   Caplow M. Kinetics of carbamate formation and breakdown. J Am Chem Soc. 1968; 90: 6795-6803. https://doi.org/10.1021/ja01026a041

[9]   Crooks JE, Donnellan JP. Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution. J Chem Soc Perkin Trans 2 1989; 331-333. https://doi.org/10.1039/p29890000331

[10]   Donaldson TL, Nguyen YN. Carbon dioxide reaction kinetics and transport in aqueous amine membranes. Ind Eng Chem Fundam. 1980; 19: 260-266. https://doi.org/10.1021/i160075a005

[11]   McCann N, Phan D, Wang X, Conway W, Burns R, Attalla M, Puxty G, Maeder M. Kinetics and mechanism of carbamate formation from CO_2 (aq), carbonate species, and monoethanolamine in aqueous solution. J Phys Chem A 2009; 113: 5022-5029. https://doi.org/10.1021/jp810564z

[12]   Puxty G, Rowland R, Attalla M. Comparison of the rate of CO_2 absorption into aqueous ammonia and monoethanolamine. Chem Eng Sci. 2010; 65: 915-922 https://doi.org/10.1016/j.ces.2009.09.042

[13]   Ali SH. Kinetics of the reaction of carbon dioxide with blends of amines in aqueous media using the stopped-flow technique. Int J Chem Kinet. 2005; 37: 391-405. https://doi.org/10.1002/kin.20059

[14]   Alper E. Kinetics of reactions of carbon dioxide with diglycolamine and morpholine. Chem Eng J. 1990; 44: 107-111. https://doi.org/10.1016/0300-9467(90)80063-I

[15]   Henni A, Li J, Tontiwachwuthikul P. Reaction kinetics of CO_2 in aqueous 1-amino-2-propanol, 3-amino-1-propanol, and dimethylmonoethanolamine solutions in the temperature range of 298-313 K using the stopped-flow technique. Ind Eng Chem Res. 2008; 47: 2213-2220. https://doi.org/10.1021/ie070587r

[16]   Vevelstad SJ, Eide-Haugmo I, da Silva EF, Svendsen HF. Degradation of MEA; a theoretical study. Energy Procedia 2011; 4: 1608-1615. https://doi.org/10.1016/j.egypro.2011.02.031

[17]   Sayari A, Heydari-Gorji A, Yang Y. CO_2-induced degradation of amine-containing adsorbents: reaction products and pathways. J Am Chem Soc. 2012; 134: 13834-13842. https://doi.org/10.1021/ja304888a

[18]   Dutcher B, Fan M, Russell AG. Amine-based CO_2 capture cechnology development from the beginning of 2013: A review. ACS Appl Mater Interfaces 2015; 7: 2137-2148. https://doi.org/10.1021/am507465f

[19]   Dillon D, Wheeldon J, Chu R, Choi G, Loy C. A Summary of EPRI's engineering and economic studies of post combustion capture retrofit applied at various north American host sites. Energy Procedia 2013; 37: 2349-2358. https://doi.org/10.1016/j.egypro.2013.06.116

[20]   Harding JH, Duffy DM, Sushko ML, Rodger PM, Quigley D, Elliott JA. Computational techniques at the organicinorganic interface in biomineralization. Chem Rev. 2008; 108: 4823- 4854. https://doi.org/10.1021/cr078278y

[21]   Kim S, Shi H, Lee JY. CO_2 absorption mechanism in amine solvents and enhancement of CO_2 capture capability in blended amine solvent. Int J Greenhouse Gas Control 2016; 45: 181-188. https://doi.org/10.1016/j.ijggc.2015.12.024

[22]   Improta R, Santoro F, Blancafort L. Quantum mechanical studies on the photophysics and the photochemistry of nucleic acids and nucleobases. Chem Rev. 2016; 116: 3540-3593. https://doi.org/10.1021/acs.chemrev.5b00444

[23]   Seybold PG, Shields GC. Computational estimation of pKa values. WIRES Comput Mol Sci. 2015; 5: 290-297. https://doi.org/10.1002/wcms.1218

[24]   Donaldson TL, Nguyen YN. Carbon dioxide reaction kinetics and transport in aqueous amine membranes. Ind Eng Chem Fundam. 1980; 19: 260-266. https://doi.org/10.1021/i160075a005

[25]   Conway W, Wang X, Fernandes D, Burns R, Lawrance G, Puxty G, Maeder M. Comprehensive kinetic and thermodynamic study of the reactions of CO_2 (aq) and HCO3-with monoethanolamine (MEA) in aqueous solution. J Phys Chem A 2011; 115: 14340-14349. https://doi.org/10.1021/jp2081462

[26]   Vevelstad SJ, Eide-Haugmo I, da Silva EF, Svendsen HF. Degradation of MEA; a theoretical study. Energy Procedia 2011; 4: 1608-1615. https://doi.org/10.1016/j.egypro.2011.02.031

[27]   Stocker T, Qin D, Plattner G, Tignor M, Allen S, Boschung J, Nauels A, Xia Y, Bex V, Midgley P. Cambridge University Press: New York, 2013.

[28]   Annual Energy Review; Energy Information Administration: Washington, D.C., 201110.2172/1029326.

[29]   Lee SY, Park SJ. A review on solid adsorbents for carbon dioxide capture. J Ind Eng Chem. 2015; 23: 1-11. https://doi.org/10.1016/j.jiec.2014.09.001

[30]   L'Orange Seigo S, Dohle S, Siegrist M. Public perception of carbon capture and storage (CCS): A review. Renewable Sustainable Energy Rev. 2014; 38: 848-863. https://doi.org/10.1016/j.rser.2014.07.017

[31]   McCulloch S. "20 Years of Carbon Capture and Storage: Accelerating Future Deployment"; International Energy Agency: Paris, 2016.

[32]   Kenarsari SD, Yang D, Jiang G, Zhang S, Wang J, Russell AG, Wei Q, Fan M. Review of recent advances in carbon dioxide separation and capture. RSC Adv. 2013; 3: 22739-22773. https://doi.org/10.1039/c3ra43965h

[33]   Lee ZH, Lee KT, Bhatia S, Mohamed AR. Post-combustion carbon dioxide capture: Evolution towards utilization of nanomaterials. Renewable Sustainable Energy Rev. 2012; 16: 2599- 2609. https://doi.org/10.1016/j.rser.2012.01.077

[34]   Liu J, Thallapally PK, McGrail BP, Brown DR, Liu J. Progress in adsorption-based CO_2 capture by metal-organic frameworks. Chem Soc Rev. 2012; 41: 2308-2322. https://doi.org/10.1039/C1CS15221A

[35]   Luis P, Van Gerven T, Van der Bruggen B. Recent developments in membrane-based technologies for CO_2 capture. Prog Energy Combust Sci. 2012; 38: 419-448. https://doi.org/10.1016/j.pecs.2012.01.004

[36]   MacDowell N, Florin N, Buchard A, Hallett J, Galindo A, Jackson G, Adjiman CS, Williams CK, Shah N, Fennell P. An overview of CO_2 capture technologies. Energy Environ Sci. 2010; 3: 1645-1669. https://doi.org/10.1039/c004106h

[37]   Rubin ES, Mantripragada H, Marks A, Versteeg P, Kitchin J. The outlook for improved carbon capture technology. Prog Energy Combust Sci. 2012; 38: 630-671. https://doi.org/10.1016/j.pecs.2012.03.003

[38]   Samanta A, Zhao A, Shimizu GKH, Sarkar P, Gupta R. Post-combustion CO_2 capture using solid sorbents: A review. Ind Eng Chem Res. 2012; 51: 1438-1463. https://doi.org/10.1021/ie200686q

[39]   Shakerian F, Kim KH, Szulejko JE, Park JW. A comparative review between amines and ammonia as sorptive media for post-combustion CO_2 capture. Appl Energy 2015; 148: 10-22. https://doi.org/10.1016/j.apenergy.2015.03.026

[40]   Yang H, Xu Z, Fan M, Gupta R, Slimane RB, Bland AE, Wright I. Progress in carbon dioxide separation and capture: A review. J Environ Sci. 2008; 20: 14-27. https://doi.org/10.1016/S1001-0742(08)60002-9

[41]   Yu CH, Huang CH, Tan CS. A review of CO_2 capture by absorption and adsorption. Aerosol Air Qual Res. 2012; 12: 745-769. https://doi.org/10.4209/aaqr.2012.05.0132

[42]   Zhao B, Su Y, Tao W, Li L, Peng Y. Post-combustion CO_2 capture by aqueous ammonia: a state-of-the-art review. Int J Greenhouse Gas Control 2012; 9: 355-371. https://doi.org/10.1016/j.ijggc.2012.05.006

[43]   D'Alessandro DM, Smit B, Long JR. Carbon dioxide capture: Prospects for new materials. Angew. Chem Int Ed. 2010; 49: 6058-6082 https://doi.org/10.1002/anie.201000431

[44]   Dutcher B, Fan M, Russell AG. Amine-based CO_2 capture technology development from the beginning of 2013: A review. ACS Appl Mater Interfaces 2015; 7: 2137-2148. https://doi.org/10.1021/am507465f

[45]   Dillon D, Wheeldon J, Chu R, Choi G, Loy C. A Summary of EPRI's engineering and economic studies of post combustion capture retrofit applied at various north American host sites. Energy Procedia 2013; 37: 2349-2358. https://doi.org/10.1016/j.egypro.2013.06.116

[46]   Zhao M, Minett AI, Harris AT. A review of technoeconomic models for the retrofitting of conventional pulverised-coal power plants for post-combustion capture (PCC) of CO_2. Energy Environ Sci. 2013; 6: 25-40. https://doi.org/10.1039/C2EE22890D

[47]   Arshad MW, Svendsen HF, Fosbøl PL, von Solms N, Thomsen K. Equilibrium total pressure and CO_2 solubility in binary and ternary aqueous solutions of 2-(diethylamino) ethanol (DEEA) and 3-(methylamino) propylamine (MAPA). J Chem Eng Data 2014; 59: 764-774. https://doi.org/10.1021/je400886w

[48]   Bougie F, Iliuta MC. Sterically hindered amine-based absorbents for the removal of CO_2 from gas streams. J Chem Eng Data 2012; 57: 635-669. https://doi.org/10.1021/je200731v

[49]   Rochelle G, Chen E, Freeman S, Van Wagener D, Xu Q, Voice A. Aqueous piperazine as the new standard for CO_2 capture technology. Chem Eng J. 2011; 171: 725-733. https://doi.org/10.1016/j.cej.2011.02.011

[50]   Bougie F, Iliuta MC. CO_2 absorption in aqueous piperazine solutions: experimental study and modeling. J Chem Eng Data 2011; 56: 1547-1554. https://doi.org/10.1021/je1012247

[51]   Le Tourneux D, Iliuta I, Iliuta MC, Fradette S, Larachi F. Solubility of carbon dioxide in aqueous solutions of 2-amino-2- hydroxymethyl-1, 3-propanediol. Fluid Phase Equilib. 2008; 268: 121- 129. https://doi.org/10.1016/j.fluid.2008.04.003

[52]   Mehdizadeh H, Gupta M, Kim I, Da Silva EF, HaugWarberg T, Svendsen HF. AMP- CO_2-water thermodynamics, a combination of UNIQUAC model, computational chemistry and experimental data. Int J Greenhouse Gas Control 2013; 18: 173-182. https://doi.org/10.1016/j.ijggc.2013.06.002

[53]   Zhu D, Fang M, Lv Z, Wang Z, Luo ZSelection of blended solvents for CO_2 absorption from coal-fired flue gas. Part 1: Monoethanolamine (MEA)-based solvents. Energy Fuels 2012; 26: 147-153. https://doi.org/10.1021/ef2011113

[54]   Bougie F, Iliuta MC. CO_2 absorption into mixed aqueous solutions of 2-amino-2-hydroxymethyl-1, 3-propanediol and piperazine. Ind Eng Chem Res. 2010; 49: 1150-1159. https://doi.org/10.1021/ie900705y

[55]   Murshid G, Shariff AM, Lau KK, Bustam MA, Ahmad F. Physical properties of piperazine (PZ) activated aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD + PZ). J Chem Eng Data 2012; 57: 133-136. https://doi.org/10.1021/je2008523