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A Review on Carbon Dioxide Minimization in Biogas Upgradation Technology by Chemical Absorption Processes

Nuzhat Muntaha, Mahmudul I. Rain, Lipiar K. M. O. Goni, Md. Aftab Ali Shaikh, Mohammad S. Jamal, and Mosharof Hossain*



sustainable environment on Earth are two of the greatest challenges of the future. Biogas can be a very significant renewable source of energy that can be used worldwide. However, to make it usable, upgrading the gas by removing the unwanted components is a very crucial step. CO_2 being one of the major unwanted components and also being a major greenhouse gas must be removed efficiently. Different methods such as physical adsorption, cryogenic separation, membrane separation, and chemical absorption have been discussed in detail in this review because of their availability, economic value, and lower environmental footprint. Three chemical absorption methods, including alkanol-



amines, alkali solvents, and amino acid salt solutions, are discussed. Their primary works with simple chemicals along with the latest works with more complex chemicals and different mechanical processes, such as the DECAB process, are discussed and compared. These discussions provide valuable insights into how different processes vary and how one is more advantageous or disadvantageous than the others. However, the best method is yet to be found with further research. Overall, this review emphasizes the need for biogas upgrading, and it discusses different methods of carbon capture while doing that. Methods discussed here can be a basic foundation for future research in carbon capture and green chemistry. This review will enlighten the readers about scientific and technological challenges regarding carbon dioxide minimization in biogas technology.

1. INTRODUCTION

Progress and development of this fast-paced modern world rely heavily on energy. Sustainability, cost, environmental impact, and global warming are some issues that are directly linked to the consumption of energy. These issues have been driving us to look for energy sources such as solar, biomass, hydroelectric power, wind, and geothermal energy, which are not only costeffective but also renewable and sustainable.¹ To that end, researchers are still exploring new sources of energy which will be both renewable and environmentally benign. Biomass is produced in both rural and urban areas all over the world. It can be utilized for producing biogas, which can be a sustainable source of energy. Biogas, which is produced by anaerobic digestion, can be a conventional source of renewable energy.² Biogas primarily consists of a mixture of methane (CH_4) and carbon dioxide (CO_2) , with a trace amount of hydrogen sulfide (H_2S) , ammonia (NH_3) , nitrogen (N_2) , and hydrogen (H_2) .³ It is noteworthy that the trace amount of H₂S in biogas can cause corrosion to the carrying pipelines. In order to acquire clean biogas, H₂S removal is an important factor.⁴ Additionally, the presence of CO_2 results in a low heat value of the biogas.

However, biogas contains 50–60% methane, which increases the heat value when converted to energy.⁵ The methane content of biogas can be increased to 90% that will cause an increase in the caloric value.⁶ While the caloric value of biogas varies from 4800 to 6900 kcal/m³, methane has a caloric value of 9100 kcal/m^{3.2,4–7} Biogas can be a clean source of energy, as it can be upgraded to biomethane by removing the carbon dioxide in it.⁸

Biogas is already being used for a myriad of applications, including daily cooking in rural areas of Bangladesh, in the instruments being used for heating, electricity production in thermal power plants, producing liquid biogas (LBG) or compressed biogas (CBG) from purified biogas, etc. Using biogas as transport fuel, the emission of greenhouse gases can

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Scheme 1. CO₂ Capturing Process Using Chemical Absorption



Figure 1. Schematic representation of conventional CO₂ capture process.

be lowered significantly. On the other hand, in some countries, biogas is mainly used for the combined heat and power (CHP) generation for several industrial plants.⁹⁻¹² \hat{CO}_2 is a major component of biogas, and continuous release of this noncombusting gas results in significant increase of the greenhouse effect in the environment. Even though CO_2 can play a useful role as a chemical reactant, pressuring agent, refrigerant, or neutralizing agent, it must be removed to improve the quality of biogas and make it more methane-rich.¹³ Previously, various techniques were exploited to capture CO₂ from biogas. Water scrubbing, organic solvent scrubbing, pressure swing adsorption (PSA), membrane separation, cryogenic separation, etc. are some effective processes among them. The chemical absorption process is an attractive and advanced technique for CO_2 capture. In Scheme 1, the overall portrait of CO_2 absorption by adapting different absorption processes is illustrated in order to understand the whole procedure. Compared to the physical solvents and chemical solvents

with the aid of conceptual design, mass and energy analysis can quench CO_2 more efficiently with much less power consumption.¹⁴ This review will focus on the exploitation of a chemical absorption technique that will show how CO_2 can be removed efficiently using different chemical solvents.

2. CHEMICAL ABSORPTION OVERVIEW

2.1. Background. The chemical absorption process takes place under atmospheric pressure, and the temperature varies from 40 to 50 °C.¹⁵ The chemical absorption process is usually done after postcombustion of fuels to remove CO_2 . As the chemical absorption process involves covalent bonding between the molecules of absorbing liquid and CO_2 , the chemical reaction between absorbent and CO_2 molecules results in CO_2 removal from raw biogas.¹⁶

2.2. Solvent Selection. Acidic gases such as CO_2 get selectively absorbed by aqueous basic solvents under ambient temperature.¹⁷ The absorbents must be highly capable of

quenching CO₂ while being moisture-tolerant and showing high selectivity to CO₂ over other gases.¹⁸ It has been reported that approximately $0.5-250 \text{ mg h}^{-1}$ of circulating absorbent is necessary for continuous removal of CO₂ from biogas with a flow rate of $0.5-300000 \text{ m}^3 \text{ h}^{-1}$.¹⁹ If the gaseous impurities (CO₂) are more soluble in an absorber than in methane, the absorption procedure can be more successful.²⁰ Before a particular solvent is selected for the absorption process, a range of factors must be considered and are discussed below in brief.

2.2.1. Concentration of the Absorbent. In chemical absorption, the concentration of the absorbents plays an important role. The diffusion coefficient and absorption rate decreases with an increase in solution viscosity and gas loading rate.²¹ Additionally, the absorption rate is also influenced by the concentration of CO_2 in the gas stream and absorbing surface area.²²

2.2.2. pH of the Solvent. Absorption rate and absorption processes are affected significantly by the pH of the solvent. Adding acid or base lowers the absorption rate. While amine and ammonia have been reported to have worked best in the pH range of 11.5-12,²³ KOH and NaOH have been found to work best while the optimum pH is 13 and 12.9, respectively.²⁴

2.2.3. Regeneration of Sorbents. The energy required for regeneration, also known as the heat of absorption, should be substantially low. For physisorption, heat of absorption is generally -25 to -50 kJ mol⁻¹, whereas for chemisorption, it is up to -60 to -90 kJ mol⁻¹. The sorbent must have an advantage regarding regeneration energy consumption through a suitable pathway.²⁵

Selection of a suitable solvent is very important in the chemical absorption process. Apart from the properties mentioned above, some other factors, such as availability, cost efficacy, volatility, gas solubility, and nonhazardous nature, must be taken into consideration for an absorbent to be efficient and successful overall.²⁶

2.3. Absorption Process. The chemical absorption process is illustrated in Figure 1. The flue gas, which contains a mixture of CH_4 and CO_2 containing trace amounts of H_2S , enters the absorber column from below and starts going upward. At the same time, the solvent is injected into the absorber tower from the top under 1–2 bar of pressure. The flue gas and the solvent mix together in the counter current flow, and the CO_2 -rich solvent is gathered at the bottom of the column. The dissolution reaction is typically exothermic in nature, increasing the temperature of the solvent from 20–40 to $45-65 \, ^\circ C.^{27}$ This rich solvent is pumped to the heat exchanger, where an exchange of heat occurs between the rich stream and the lean stream. From there, the rich solvent is sent to the top of the stripper column.

At the stripper column, the reboiler at the bottom of the column boils the rich solvent by providing the heat of reaction, releasing CO_2 from it. CO_2 gas is extracted from the stripper column and processed (cooling and compression), yielding 80-90% pure CO_2 gas, which is a byproduct and can be stored and used for many other purposes.^{19,28,29} On the other hand, the boiled solvent which is now free from any CO_2 can be reused for the capturing process. This regenerated solvent is called the lean solvent. From the stripper column, the lean solvent at the bottom is pumped out and sent to the heat exchanger. Finally, from the heat exchanger, the lean solvent is sent to the absorber column to interact with the flue gas, and the whole process is repeated. The operation cost of this

process is not too high, with a large amount of heat required at the reboiler though.

3. CHEMICAL ABSORPTION PROCESS USING DIFFERENT SOLVENTS

Upgrading biogas to biomethane necessitates removal of minor impurities like H_2S , siloxanes, and sulfane and a major portion of CO_2 . In the chemical absorption process, different basic solvents, such as amine scrubbing, amino acid salt (AAS) scrubbing, caustic solvent scrubbing, etc., are used to absorb the acidic CO_2 gas. These techniques, along with their advantages and drawbacks, are discussed below in detail.

3.1. Amine Scrubbing. 3.1.1. Background. In the chemical absorption of CO₂, the biomass-derived biogas reacts in a liquid phase with the reactant.²⁹ A solution of amines works as an absorbent resulting in a reversible reaction for the absorption of CO₂.²⁸ As both amine and CO₂ gases are weak electrolytes, they dissociate partially in the aqueous phase. When biogas enters the absorption column and the water absorbs impurities, all of the gases (except for methane) form a complex mixture containing nonvolatile iconic species, very volatile species (like CO₂), and moderately volatile or nonvolatile species (water and amine). Solubility of the CO_2 in water is dramatically enhanced by the presence of amine.³⁰ Some amine solutions that are used for the removal of carbon dioxide from biogas are diethanolamine (DEA), monoethanolamine (MEA), diglycolamine (DGA), triethanolamine (TEA), diisopropanolamine (DIEA), methyldiethanolamine (MDEA), and a mixture of glycol and monoethylamine.

Amine can bind with both H_2S and CO_2 . Even though carbamates formed by the reaction of amine and carbon dioxide decompose on heating, amine binds with H_2S permanently.²⁸

$$\text{RNH}_2 + \text{CO}_2 \stackrel{\Delta}{\leftrightarrow} \text{RNHCO}_2^-$$

In aqueous solution, when an acidic gas like CO_2 is absorbed, the bulk concentration is low as it is partially absorbed in the aqueous solution. The reason behind this result is the vapor phase of the acid gas reaches a physical equilibrium with some unreacted molecules of acid gases in water. Hence, rather than the liquid, the equilibrium solubility of the acid gas containing unreactive solvent is governed by the partial pressure of the gas. However, the unreacted gas molecules presented in the bulk of the liquid phase and the difference between the gas concentration in the liquid at the gas—liquid interface is the driving force of the mass transfer that increases by adding amine in the aqueous solutions of acid gases.^{30,31} Thus amine solutions play an important role by increasing the absorption rate of the acid gases in the water.

Amine scrubbing using primary, secondary, and tertiary amine solutions has been used since the early years of the chemical absorption process.³² It has been reported that the removal of CO_2 in the gas stream occurs by an exothermic reaction of alkanolamines and carbon dioxide.³³ The reaction mechanism of primary and secondary amine for absorption is almost the same, which is the reaction of carbamate formation initiated by the zwitterion mechanism. Then the hydrolysis reaction occurs to produce bicarbonates, and after that, the carbonate species appear depending on the pH of the medium.³¹ Furthermore, there are some other conditions upon which the degree of the hydrolysis of carbamate depends, such as chemical stability and the concentration of an amine solution.

However, some works showed that adding some substituents at the carbon adjacent to the amine groups favors hydrolysis by creating instability of the carbamate.³¹ To support the statement, it was expected that steric hindrance might slow down the absorption of CO_2 , but an opposite result was observed when 1 mol of amine was introduced upon hydrolysis of the carbamate. Then it was concluded that the sterically hindered amines yield results better than those of the primary and secondary amines.³¹

MEA and DEA are alkanolamines that are commercially used as absorbents for removing CO2. Aqueous MEA is considered to be the most important absorbent because of its low solubility in hydrocarbons, low cost, rapid reaction rate, and thermal stability.³⁴ Krupiczka et al.³⁵ studied the absorption of CO2 with both 15% MEA and ionic liquids (ILs) under the same conditions, and they found that IL needed more time to absorb CO₂ from the gas mixture. Abdul Halim et al.³⁶ worked with MEA using a bench-scale absorption column packed with Sulzer metal gauze packing under high pressure (5.0 MPa). The authors observed different parameters including gas flow rates and liquid flow rates and studied the change in CO₂ removal percentage and volumetric mass transfer coefficient. Their work indicated that, at high pressure, volumetric mass transfer coefficient $(K_{\rm G}a_{\rm v})$ and the CO₂ removal (%) increases with MEA concentration much like the scenario that arises at atmospheric pressure. MEA has been reported as a first generation baseline solvent.³⁷ In order to reduce the energy consumption in the regeneration process and to increase the cyclic capacity, phase change solvents for CO₂ absorption became popular after it was suggested by some researchers.³⁸ So in the new proposal, there were two phases after CO₂ absorption where only the CO₂-rich phase goes to the stripper column for regeneration and the CO₂ lean phase gets driven to the absorber column. Zhang et al.³⁹ proposed a new approach with CO₂ phase changed absorbents (CPCA). Zhao et al.⁴⁰ worked with 1-propanol, 2-propanol, and tertiary butanol as the absorbents of CPCAs.³⁹ In this research, a group of novel CPCA absorbents were composed by mixing MEA/water miscible alcohol/H2O by keeping the concentration of MEA constant at 30% with various ratios of water (1-7%) and alcohols (from 1 to 7%). After absorption of CO₂, the cyclic capacity and the absorbent regenerability were investigated. Comparing the cyclic capacity between the CPCAs and the 30% of MEA/H2O, the cycle capacity of CPCAs was 62% higher than 30% MEA/H₂O with 2.59 mol CO_2/kg .

DEA is another very effective solvent for CO_2 removal. Pashaei et al.⁴¹ has worked with DEA for removing CO_2 using a stirred bubble reactor, under the condition of having the solvent both stirred and unstirred. It was found that when stirring speed was increased, CO_2 absorption in aqueous DEA solution increased, as well. This occurred because the contact area between CO_2 and DEA increased when the large bubbles were broken into small bubbles. As CO_2 loading has an inverse effect with mass transfer flux, mass transfer flux decreases, which results in an increase of CO_2 in the loading solvent at constant CO_2 partial pressure. They also proved that between the three different inlet concentrations (1.4, 2.0, and 0.7 M) when the conversion of DEA concentration was higher than 0.7 M, the influence of DEA was very fast on the absorption rate. Moreover, as the CO_2 partial pressure increases, the mass transfer coefficient decreases.⁴¹

Xu et al.⁴² introduced a new approach with amine infusing hydrogels (AIH). Their research team studied the performance of low concentrated DEA solution-infused hydrogels to absorb the CO₂ from flue gases because of its (DEA) low volatility and high reactivity. They used both synthetic and commercial hydrogels with very low concentrations of DEA (5.0, 10, and 20 wt %). The uptake of CO_2 was also monitored, and it was observed that the cross-linker level had minimal effect. However, with the increasing MBA (N,N'-methylenebisacrylamide) concentration, there was a significant increase in CO_2 uptake. With identical DEA concentration, the DEA-infused hydrogel showed more absorption capacity than the DEA solution. Reusability of this infused hydrogel was also investigated, and it maintained about 80% of the original absorption over 10 cycles of absorption-desorption. It was also found that when a certain amount of PEI (polyethylenimine) was introduced, it improved the regeneration of the DEA-infused hydrogel greatly.

Recently, aqueous piperazine (PZ) (30-40 wt %) with a fast reaction rate, good energy performance, low volatility and viscosity, and resistance to thermal degradation and oxidation has emerged as a benchmark second generation baseline solvent for amine scrubbing. $^{43,44}_{}$ Studies have shown that 8 molal (m) PZ (40 wt %, PZ) has double the absorption rate and superior performance in comparison to that of 7 m MEA (30 wt %, MEA).⁴⁵ Compared to MEA, PZ has lower volatility, is more stable at high temperature, and is less prone to oxidation. Due to limited solvent solubility, PZ is mainly used as a promoter for amines at slow reaction rates and low concentrations (<10 wt %).⁴⁶ Xu et al.⁴⁷ found out a new way to overcome the drawback of slow absorption of CO₂ gas using ammonia solvent. They used a NH₃/PZ blended solution in a spray tower for the absorption of CO₂. Different parameters, such as efficiency of CO₂ removal, mass ratio of ammonia loss, NH₃ concentration of outlet gas flow, and the volumetric overall mass transfer coefficient $(K_{GCO,}a_v)$, were inspected. It was found that as the amount of PZ and ammonia concentration increased, the CO2 removal efficiency and the volumetric overall mass transfer coefficient also increased. It was also observed that the CO₂ absorption using NH₃/PZ in a spray tower is as efficient as packed towers and can be a potential alternative for capture and storage of carbon dioxide.

Heydarifard et al.⁴⁸ worked with PZ solution (0-0.5 M) in a stirrer bubble column and studied both experimental and thermodynamic modeling. In the experimental section, they investigated the stirrer speed, PZ concentration, and CO₂ partial pressure. For the modeling data, they followed Pitzer's G^E model and the Gibbs–Duhem model for determining the mass transfer flux, solubility, CO₂ removal efficiency, and reaction rate. They reported that with increasing PZ concentration and liquid flow rate, the removal of CO₂ increases. However, if the CO₂ flow rate increased, the efficiency of CO₂ removal decreased. The thermodynamic model showed that the reaction rate increased when the concentration of PZ increased and the partial pressure of CO₂ decreased.

For CO_2 capture using amine solvents, capital cost can be high regarding the amount of the solvent used and also the regeneration energy. Capital cost and energy cost also depend on the CO_2 cyclic capacity and CO_2 absorption rate. Less solvent is required if CO₂ cyclic capacity increases.⁴⁹ Blending of different amine solvents can be an alternative for this high regeneration energy requirement. PZ is mainly used as a promoter with other amine solvents. However, solid precipitate formed from zwitterion carbamate causes a problem with using PZ, as it is insoluble in water. This problem can be addressed by blending low concentrated PZ with other useful amines.⁴⁹ Blending of a variety of alkanolamines is favored as it suppresses their unfavorable characteristics and combines favorable characteristics.⁵⁰ The presence of tertiary amine reduces the energy of regeneration due to its low reaction energy while the presence of a secondary amine increases the overall amine-CO₂ reaction rate.¹⁶ A blended solution of 20% DETA (diethelenetriamine) and 10% PZ showed an increase of 42% compared to 30% MEA. This blended solution also decreased the regeneration energy, making the solution costfriendly.⁵¹

AMP (amino methyl propanol) and MDEA (methyldiethanolamine) have low energy consumption for solvent regeneration, but they have a low absorption rate.^{52,53} Compared to 30% of MEA with (23 wt % AMP + 7 wt % PZ), it was reported that overall mass transfer coefficient $K_{v}a_{v}$ increases from 10 to 28 kmol/m³ h when the operation pressure is 0.1-4.0 MPa for the blended AMP + PZ, whereas for 30% MEA, at same operating pressure, the $K_v a_v$ increases from 8 to 23 kmol/m³ h.⁵⁴ This proves that, due to the higher mass transfer, the blended AMP + PZ is more effective at improving the CO_2 absorption reaction rate than is MEA. To increase the absorption rate, PZ can also be used with MDEA. For example, Khan et al.⁵⁵ took MDEA + PZ solution in four different mass fractions and compared the absorption rate of CO₂ and regeneration energy under different parameters, including temperature variation, gas flow rate, CO₂ partial pressure, and solvent concentration. The mass fraction of MDEA + PZ was 28/2, 25/5, 22/8, and 20/10, and with a higher PZ concentration (10 wt %), a higher CO_2 absorption rate was obtained. However, on the contrary, with the increasing mass of PZ, the regeneration energy is also increased. This is because carbamate and dicarbamate produced by PZ were insoluble in water.

3.1.2. Regeneration Process. Aqueous absorption of CO_2 capture on a large scale has a high capital cost, which is a major problem for the implementation of CO_2 capture technology.⁵⁶ Moreover, there are some problems with the amine scrubbing procedure, such as low regeneration rate, equipment corrosion, solvent degradation, and large energy consumption.⁵⁷

Solvent degradation and energy consumption occur in the regeneration step. While enriching an energy source, decreasing process energy consumption is one of the foremost challenges. Many researchers claimed that tertiary amines (MDEA) and the sterically hindered amines (AMP) can be easily regenerated compared to primary (MEA) and secondary amines (DEA).^{58,59}

In the overall cost of chemical absorption process, the energy of regeneration has a strong effect.⁶⁰ Flue gas heat recovery and an electrical reboiler provided the supplementary energy to complete the regeneration of MEA.⁶¹ In the chemical absorption process, most energy consumption accounts for the solvent regeneration in the reboiler. To reduce energy regeneration, three kinds of measurements can be taken: (1) process modifications, (2) optimizing operational parameters, and (3) developing better solvents.⁶²

Process modification is a way of minimizing energy consumption. A thorough review of 20 modifications from the literature and patents was done by Le Moullec et al.⁶³ Three categories were listed on the basis of their effect on processes, such as heat pumps, absorption enhancement, and heat integration. However, increasing the heat quality by applying an alternative mechanical modification on the heat pump can enhance the heat quality. Furthermore, the main concept of absorption enhancement is adapting necessary adjustments to increase CO_2 loading in the rich loading solution at the bottom of the absorber. The reboiler duty can be reduced if heat transfers between streams and loss of heat in the process which can be partially recovered is the general concept for heat integration.

Researchers have done several inspections regarding optimal specifications for process modifications where, under each category, different subclasses have detailed information.^{64,65} Solvent regeneration energy is influenced by several factors; for example, CO_2 loading in lean loading solution, pressure in the reboiler, and MEA concentration are some of the important factors. Another factor is the operation pressure in the reboiler or in the stripper. Reboiler duty is relevant to temperature of the solvent and height of the absorber and stripper. A decrease in energy regeneration can be achieved by increasing energy but maintaining high pressure, which requires more auxiliary power.⁶⁵ The energetic performance of a chemical absorption process depends on various kinds of solvent modifications. For example, some researchers reported that when 40 wt % of MEA is used instead of 30 wt % of MEA, the reboiler duty decreases by 23%.⁶⁶ In other research, it was found that ICA (intercool absorber) has little effect on MEA. For a mixture of AMP and PZ, it can reduce 7% reboiler duty. These modifications can increase overall complexity and capital cost and complicate the operability. The authors suggested that these modifications should be adopted on specific conditions.62

3.1.3. Biogas Upgrading by Amine Solvents. Chemical absorption of carbon dioxide by different alkanolamines is used after postcombustion. Amine scrubbing is a useful and promising procedure for CO₂ removal from biogas. Although there are some disadvantages for using amino solvents, it is still preferable for its efficiency. Generally, MEA is considered to be the most commonly used solvent.⁴⁵ Recently, other alkanolamines and blending of different alkanolamines have been used. A higher reaction rate, the ability of acid gas solubility in alkanolamines, and mass transfer properties are some excellent parameters of alkanolamines to remove acidic gases.⁶⁷ Several researchers have worked with alkanolamines with a variety of concentration ranges. Rajiman et al.⁶⁸ used a simulated biogas containing natural gas (97% CH₄, 2% CO₂, and 1% heavier hydrocarbon) mixed with 30-40% CO₂ in a fabricated packed column with 30% MEA. They investigated the efficiency of 30% MEA for the absorption of highly concentrated CO_2 (40– 50%) from simulated biogas, and the effect of CO_2 absorption under gas liquid flow rate variables was observed, as well. It was proven that MEA can remove CO₂ gas up to 94% when the concentration of CO_2 was 30%, and when the concentration of CO_2 increased to 40%, the efficiency of removing CO_2 decreased to only 84%. Also, when the liquid gas flow ratio was 0.6, CO_2 removal was 15% lower than when the liquid gas flow ratio was 0.7, which caused the CO₂ removal to reach 73%.

Table 1. Published Cases of Biogas Upgrading Using Amine Scrubbing Process

amine solutions and concentrations	reactor	operating parameters	feed gas composition	gas flow rate	product purity	regeneration conditions	ref
30% AMP	packed column	temp: 35–40 °C pressure: 0.987 atm	CH ₄ : 60% CO ₂ : 40%	$10 \times 10^{-3} \text{ N m}^{-3}/\text{day}$	97%	temp: 120 °C pressure: 2.4 atm	72
27% MEA 35% PEI ^a	fixed bed contactor	temp: 40 °C pressure: 1.01325 atm	CH ₄ : 55.7% CO ₂ : 41.5%	44.6 km/h	86.2%	temp: 127 °C pressure: 1.01325 atm	73
20% MEA	packed tower	temp: 30 °C pressure: 1 atm	CH ₄ : 60% CO ₂ : 39.8%	9.32 h ⁻¹	99.9%	temp: 80 °C	74
20% MEA 20% MDEA	packed column	temp: 25 °C pressure: 6 atm	CH ₄ : 55.6% CO ₂ : 44%	$1075 N m^3 h^{-1}$	91%	NA ^b	69
40% MDEA 3% DEA 7% PZ	packed column	temp: 60 °C pressure: 200 kPa	CH ₄ : 62% CO ₂ : 37%	$250 \text{ N m}^3 \text{ h}^{-1}$	99%	recycle with regeneration	70
4.5% MDEA 0.5% PZ	packed column	temp: 35 °C pressure: 1 atm	CH ₄ : 35% CO ₂ : 15%	100 mL/min	95%	temp: 80 °C	71
Polvethvleneimine ⁻ N	lot available						

Table 2. Published Cases of CO₂ Removal from Various Industries by Amine Scrubbing

$\begin{array}{ c c c c c } \hline amine solutions and concentrations & reactor & operating parameters & composition & gas flow rate & CO_2 \\ capture & regeneration conditions & ref \\ \hline 22\% AMP & packed column & temp: 45 °C & CO_2: 13\% & 1000 kmol/h & 77\% & recycle with regeneration & Pressure: 1 atm & H_2O: 4\% & Pressure: 1 atm & H_2O: 4\% & Pressure: 1 atm & N_2: 83\% & PZ & Packed column & temp: 40 °C & CO_2: 40-60\% & 4000 m^3/h & 98\% & temp: 120 °C & 76 & Pressure: 1 atm & N_2: 40\% & Pressure: 1 atm & Pressure: 1 atm & N_2: 40\% & Pressure: 1 atm & Pressure: 1 atm & N_2: 40\% & Pressure: 1 atm & P$								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	amine solutions and concentrations	reactor	operating parameters	feed gas composition	gas flow rate	CO ₂ capture	regeneration conditions	ref
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22% AMP 8% PZ	packed column	temp: 45 °C pressure: 1 atm	CO ₂ : 13% H ₂ O: 4% N ₂ : 83%	1000 kmol/h	77%	recycle with regeneration	75
30% DEA packed column temp: 50 °C CO2: 15% 71280 km/h 90% recycle with regeneration 77 MDEA packed column temp: 40 °C CO2: 12% 3100 t/h 90% recycle with regeneration 77 45% MDEA packed column temp: 40 °C CO2: 12% 3100 t/h 90% recycle with regeneration 40 5% PZ pressure: 1.086 atm H2O: 10% regeneration N2: 78% 78	30% DEA 15% PZ	packed column	temp: 40 °C pressure: 1 atm	CO ₂ : 40–60% N ₂ : 40%	4000 m ³ /h	98%	temp: 120 °C pressure: 1 atm	76
45% MDEA packed column temp: 40 °C CO2: 12% 3100 t/h 90% recycle with 40 5% PZ pressure: 1.086 atm H2O: 10% regeneration 10% <td< td=""><td>30% DEA</td><td>packed column</td><td>temp: 50 °C pressure: 1.086 atm</td><td>CO₂: 15% N₂: 77% H₂O: 5% O₂: 3%</td><td>71280 km/h</td><td>90%</td><td>recycle with regeneration</td><td>77</td></td<>	30% DEA	packed column	temp: 50 °C pressure: 1.086 atm	CO ₂ : 15% N ₂ : 77% H ₂ O: 5% O ₂ : 3%	71280 km/h	90%	recycle with regeneration	77
	45% MDEA 5% PZ	packed column	temp: 40 °C pressure: 1.086 atm	CO ₂ : 12% H ₂ O: 10% N ₂ : 78%	3100 t/h	90%	recycle with regeneration	40

Capra et al.,⁶⁹ Gong et al.,⁷⁰ and Lee et al.⁷¹ worked with a mixture of amines and showed that the removal of CO_2 was 91–95%. In Table 1, cases of biogas upgrading by removal of CO_2 using alkanolamines have been organized with different procedures. The temperature, pressure, and other conditions are separated from one case to another. The efficiency or the percentage of carbon dioxide is also changed for different conditions.

In Table 2, different cases of using alkanolamines to remove CO_2 in industries are listed. In this table, all of the amine solvents used are mixtures of various alkanolamine concentrations, and every procedure used a packed column for CO_2 absorption. Efficiency of CO_2 removal was up to 90%.

3.1.4. Problems using of the Amine Solvents. 3.1.4.1. Degradation. A major problem in chemical absorption of CO_2 capture is amine degradation. Degradation refers to the irreversible side reaction of amine solutions not only with CO_2 and O_2 but also with NO_x and SO_x .⁷⁸ Degradation causes problems like increasing viscosity, solvent loss, foaming, fouling, and corrosion. Ten percent of the total cost of the CO_2 absorption process is needed to address the problem of solvent degradation. There are two types of solvent degradation: (i) oxidative degradation that occurs due to the presence of a huge amount of O_2 in the flue gas and (ii) thermal degradation, which is caused by high CO_2 partial pressure in the stripper and high temperature.⁷⁹ Thermal degradation mostly occurs at a stripper pump and reboiler at

120–150 °C.⁸⁰ In oxidative degradation, the main degradation products are organic acids and volatile amine.⁷⁹

Lepaumier et al.⁸¹ and Eide-Haugmo et al.⁸² have done experimental work with different tertiary amines (DMP, MMEA, TMPDA, TMEDA, PMDETA) under same conditions with MEA and found out that thermal degradation is not affected by metals or glasses except for MMEA. MMEA showed less resistance to degradation, which was kept in metal stainless steel cylinders. The authors also observed that alkanolamines containing longer chains, cyclic amines without side chains, and the sterically hindered amines (AMP) were the most resistant to degradation.⁸² Oxidation degradation occurs in amines by formation of carbamate. In aqueous amine systems, dissolved metals can also catalyze the formation of oxidation products.^{83,84} The degradation rates are affected by CO₂ and SO₂ pressure, temperature, presence of metal ions, amine concentration, etc. Increasing O₂ pressure and the mass transfer rate also increase oxidative degradation.⁸⁵ However, temperature has more influence on oxidative degradation than O2-induced pressure, as it was observed that as activation energy decreases with increasing temperature, it involves formation of more degradation products.⁸

Degradation causes many types of problems in the total process of chemical absorption. When degradation products start forming, they induce foam and corrosion. Absorption capacity of amine decreases with a degradation process. A new approach of introducing effective chemicals, known as inhibitors, can play an important role in alleviating degradation. Chelating agents, O_2 scavengers, reaction inhibitors, and heavy metal salts are some chemicals used for the inhibition of the degradation process.^{83,87}

Voice et al.⁸⁸ tested nearly 100 additives to find a suitable inhibitor of MEA. Reactions were done in low gas flow (LGF) and high gas flow (HGF) apparatuses, and results were consistent in both cases. The study investigated that ammonia production could be used for screening MEA oxidation inhibitors. Depending on the production rate of ammonia, they anticipated and compared the performances of the new additives such as inhibitor A (Inh A), 2,5- dimercapto-1,3,4thiadiazole (DMcT), and diethylenetriamine pentaacetic acid (DTPA). However, novel chelating agents, such as DMcT and Inh A (both at 1.5 wt %), worked best at inhibiting lowtemperature MEA oxidation, whereas DMcT and Inh A were found to inhibit MDEA oxidation at 20 wt %. With hightemperature cycling, none of the additives was effective at preventing MEA oxidation. However, some other strategies, such as removal of dissolved metals from the solution, limiting the amount of the O_2 in flue gas, reducing the absorber and stripper temperature, or removing dissolved O2 prior to entering the cross exchanger, can help to minimize the degradation of solvents.88

3.1.4.2. Corrosion. Other than degradation, another major setback in the CO₂ capturing process is corrosion. Corrosion of the equipment can be caused by the side products that are formed from the solvent degradation process.⁸⁹ Along with the amine solvent, the CO₂ gas to be absorbed and higher temperature are equally responsible for causing corrosion. There are different types of corrosion, such as galvanic, general, pitting, crevice, intergranular, selective leaching, erosion, and stress corrosion cracking. The bottom of the absorbers, regenerators, pumps, and reboiler bundles are some of the plant areas which are susceptible to corrosion. Moreover, the valves and pumps where the acid gas is loaded and the temperature is high are also affected by corrosion.⁹⁰ Other than degradation byproducts, there are several other reasons, such as poor design of the plants, for example, insufficient steam for regeneration, high operating temperature in the reboiler, high flow velocity in the pipelines, and the presence of different process contaminations, are responsible for corrosion, as well.⁹¹

Heat-stable salts (HSS) such as acetate, formate, and oxalate are made by dissolving the anions of their respective acid forms in the MEA/PZ blended solution. The effect of HSS on the corrosion in gas treatment plants and which salt was the most corrosive among these salts was investigated by Nainar et al.⁹² The researchers did a detailed study on the corrosion causing potential MEA/PZ solution and compared it to using MEA alone. The blended solution of MEA/PZ solution was found to be more corrosive than MEA. The corrosion rate of carbon steel in the blended MEA/PZ was 0.55 mmpy, whereas in MEA, it was 0.49 mmpy. Further experiments showed that introduction of more MEA/PZ increased corrosion at a significant rate. In other reactions, it had been confirmed that high CO_2 loading, high amine concentration, partial O_2 pressure, and a rough surface increased the corrosion. Srinivasan et al.⁹³ showed that sodium thiosulfate, when exposed for a short time, was an effective corrosion inhibitor. For the concentration range of 250-10000 ppm, the inhibition efficiency was found to be 91-94%, but when the chemical was exposed to the process for a long period of time, it became

ineffective due to the instability of its passive film. Degradation products and corrosion are very inter-related, as the degradation byproducts cause the phenomenon of corrosion. So, if the rate of oxidation degradation decreases, the rate of corrosion also decreases. Sodium thiosulfate and formaldehyde were proven to be effective at inhibiting oxidative degradation catalyzed by Cu and Fe.⁸³

3.2. Alkali Solvent Scrubbing. 3.2.1. Background. Besides using alkanolamines, caustic solutions, such as sodium hydroxide, potassium hydroxide, and calcium hydroxide are also used for CO_2 capture. These solvents can be used both as liquid solvent and dry sorbents. Though alkanolamines are mostly used industrially all over the world, caustic solvents have the advantages of being in abundance, having low cost, and also efficacy in capturing CO_2 . Thus, the use of caustic solvents is getting more popular day by day and suppressing the use of traditional solvents like alkanolamines. A very common caustic solvent to absorb CO_2 is NaOH.⁹⁴ This solution has an absorption capacity higher than that of MEA. Usually, NaOH is used in a rotating packed bed system, and the reaction that occurs here is

 $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

Yoo et al.⁹⁵ have done much research and reported that the theoretical amounts of NaOH and MEA are 0.9 and 1.39 tons, respectively, to capture a ton of CO2. Thus, NaOH is more cost-effective than MEA. Researchers have been trying to reduce the cost of the whole process of CO₂ capturing for many years. Different scientists have already approached alternative ways so that the regeneration energy decreases. Considering this perspective, Ruiz et al.⁹⁶ developed a method where NaOH was used as a dry absorbent. In this approach, all of the reactions occurred at room temperature, and no regeneration energy was required, as well, rendering the process both energy-efficient and economical. After absorbing CO₂, the aqueous NaOH converted to solid Na₂CO₃ and was removed from the reaction column. Life cycle assessment of carbon capture not only would result in the storage and utilization of the captured carbon but also will help to reduce the carbon footprint from nature around the world. Furthermore, it can be a substitute of the commercially produced Na₂CO₃. The recovered CO₂ is required to be stored so that it can be used further, as CO₂ has other uses in various industrial processes. Therefore, researchers are trying to capture and utilize carbon dioxide as a solid precipitate of different carbonates. Han et al.⁹⁷ investigated a process, using both NaOH and methanol, by which both CO₂ capture and storage were possible. Mineral carbonation occurred by forming sodium methyl carbonate (SMC) precipitation, resulting in CO_2 storage. The reaction occurred when CO_2 was directly injected into a constant amount of NaOH in the following way:

$$CH_{3}OH(l) + CO_{2}(aq) + NaOH(aq)$$

$$\rightarrow CH_{3}COONa(s) + H_{2}O(l)$$

During the formation of the SMC, the temperature change was negligible. So, the solution contained dissolved SMC, a very small amount of water, physically absorbed CO_2 , and methanol. After carbonation of CO_2 as SMC, it was then separated from the solution, and the remaining solution was regenerated as methanol by evaporation. The study shows that

with the increase of NaOH concentration, the absorption of CO_2 also increased.

 Na_2CO_3 can be used as a solvent for CO_2 capture as it is an inexpensive and common solvent. However, the absorption rate of CO2 is very low when using Na2CO3 for the process of CO₂ absorption. This is because of the limitation of physical mass transfer. When the efficiency of Na₂CO₃ was compared to that of NaOH and MEA, it was found that the capital cost and regeneration energy was lower for Na₂CO₃. However, a much taller absorption column, in the case of using Na_2CO_3 , is required for Na₂CO₃ to interact more with CO₂. To solve this problem, Valluri et al.98 proposed introducing an additive called frothers, which is a surfactant with Na₂CO₃, to increase the absorption rate. This frothing agent does not need any extra energy, and it also does not have any effect on the solvent. Using these frothers, the surface tension of the liquidair interfaces of the bubbles decreases and the bubble size is decreased. This results in smaller and uniform bubbles, which increases the interaction time between the interfacial area of gas and liquid. This causes faster CO₂ gas absorption because the mass transfer increases, as well. The results showed 99.9% efficiency after using the frothing agents.

KOH is another potential solvent which can be used to remove CO_2 gas from natural gas. Alkali solvent KOH produces K_2CO_3 as a chemical commodity. Potassium carbonate solvent for capturing CO_2 was first proposed by Benson and Field, which was later named as Benfield process.⁹⁹ Smith et al.¹⁰⁰ reported that, in Benfield process, absorption of CO_2 occurs at a higher temperature (120 °C) and higher pressure, and with a faster reaction rate and high pressure as the driving force, the absorption process improves. The Benfield process is operated with highly concentrated solutions and higher temperature, as the solubility of the bicarbonate species increases at high temperature. Reaction between CO_2 and KOH is as follows:

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O_3$$

If the byproduct K₂CO₃ is produced in an adequate amount, it can be used in chemical industries as it has several industrial applications.¹⁰¹ In hot carbonate processes for bulk CO₂ absorption, aqueous potassium carbonate solutions are used because of the relative ease of regeneration, large capacity, high chemical solubility for CO_2 , and ease of handling.¹⁰² CO_2 absorption from confined places, such as aircraft, submarines, or spacecraft, is very difficult. To meet this challenge, K2CO3 was used by Guo et al.¹⁰³ They used activated carbon which was impregnated by K₂CO₃, and the experiment was done on a small laboratory scale. They investigated the effect of temperature, CO₂ loading, molar ratio of water, CO₂ concentration, and flow rate on the overall CO₂ absorption. It was found that to increase the carbonation reaction of CO₂ absorption, water vapor at high concentration was beneficial. The temperature during the experiment was maintained at 60 $^{\circ}\text{C}\textsc{,}$ and CO_2 concentration was 1%. The simulated confined space contained CO₂, H₂O, and balanced N₂. They concluded that when the temperature increased from 20 to 60 °C, the absorption of CO₂ decreased by decreasing the efficiency of the K_2CO_3/AC . This phenomenon resulted in lowering the carbonation conversion. The CO₂ absorption efficiency was also weakened by increasing the flow rate, but it could be enhanced by increasing the molar ratio of water and CO₂ concentration and with a sufficient amount of water treatment. An aqueous solution of $Ca(OH)_2$ is also used for CO_2

absorption. Ca is readily available, and it is nonhazardous and inexpensive, which make it a viable solution for CO_2 capture.¹⁰⁴ With the reaction of aqueous $Ca(OH)_2$ and CO_2 in a bubble reactor, $CaCO_3$ is produced. The precipitated $CaCO_3$ has a surface area and pore volume higher than those of limestone.¹⁰⁵ Ca binds with CO_2 as follows:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

 $Ca(OH)_2$ solution can be easily formed from limestone. Han et al.¹⁰⁴ stated that regeneration and reclamation of the byproduct CaCO₃ is available to dispose.

MgO can be another potential absorbent for CO₂ capture, but MgO is not typically used in chemical absorption processes due to its poor cyclic stability and low kinetics. To overcome this problem, incorporation of CaCO₃ followed by deposition of a mixture of alkali metal salts (AMS) in MgO is being considered as an alternative.¹⁰⁶ Studies have shown that alkali metal nitrates, also known as AMSs such as KNO₃, NaNO₃, and LiNO₃, play a significant role in decreasing the energy for activation of ionic bonds present in MgO. As a result, the CO₂ uptake ability of MgO increases. However, the practical application of AMS–MgO is limited because of the slow kinetics of the absorbents. Further investigations may solve this problem in the near future.

In different chemical absorptions in CO_2 removal procedures, alkali solvents sometimes are not preferred due to some disadvantages. First, NaOH cannot be regenerated as easily as MEA.⁹⁵ Second, as K₂CO₃ is less likely to degrade in the process, the heat of absorption is high and reaction rate is slow.¹⁸ Third, limestone is the only source of CaO, rendering the availability of CO_2 quite scarce. Also regeneration of CaO may result in loss of reactivity when multiple cycles of the reaction occur.¹⁰⁷ Han et al.¹⁰⁴ observed that concentration of Ca(OH)₂ has a strong influence in capturing CO₂. However, a higher concentration of Ca(OH)₂ eventually decreases the capacity of absorbing CO₂ by producing substantially agglomerated CaCO₃ with low crystallinity. Disposal of this huge amount of CaCO₃, which is produced during absorption, is also a major drawback.¹⁰⁴

3.2.2. Storage of Carbon Dioxide by Mineralization of Carbon. A variety of techniques are employed for the chemical absorption of CO2, which can again be used for various purposes. As global warming is becoming a serious issue day by day, researchers are finding alternative ways to utilize the CO_2 instead of releasing it to the atmosphere. Due to constant use of fossil fuels in transportation and industries and to generate energy, the release of this gas into the atmosphere environment has become nearly impossible. To reduce CO₂ from the environment and to utilize this gas for humankind, several steps are being taken. For example, a conventional geological method is carbon mineralization. Mineralization of CO₂ with different alkaline earth metals, such as Ca, Mg, and Fe, produces metal carbonates which can be stored and used as raw materials for different industrial sectors such as polymers and liquid fuels.¹⁰⁸ In this process, CO₂ converts to a solid, nonsoluble compound with low reactivity. When metal oxides, such as CaO or MgO, come in contact with CO_2 , they form $CaCO_3$ or $MgCO_3$.¹⁰⁹ Some natural metal oxides are serpentine, silicate, and olivine.¹⁰⁹ Different industrial residues such as bottom ash and air pollution control residues contain a huge amount of CaO. APC (air pollution control) residues can be found in steel slag, cement kiln dust, and waste materials.¹¹⁰

Table	e 3.	Publis	hed	Cases o	f Biogas	Upgrad	ing Using	Alkaline	e Sol	vent S	Scrubbing	g Process
						- P 5						

alkali solvent concentration	reactor	operating parameters	feed gas composition	gas flow rate	product purity	regeneration conditions	ref
HPC ^a (15 wt %)	absorption rector	temp: 60-90 °C	CH ₄ : 85-40%	$150-200 \text{ N m}^3/\text{h}$	98.1% CH ₄	temp: 100-105 °C	117
		pressure: 500–1200 kPa	CO ₂ : 15-60%		<5% CO ₂	pressure: 10 kPa	
3 M NaOH	laboratory	temp: 25 °C (constant)	CH ₄ : 80%	NA ^e	66%	NA ^e	118
	scale setup		CO ₂ : 16%				
2 N KOH	purification system	temp: 25 °C	CH ₄ : 70-74%	120 mL/min	38%	NA ^e	119
		pressure: 1 atm	CO ₂ : 25–29%		increased		
0.1 M NaOH	packed column	temp: 25 °C	CH ₄ : 58%	90 L/h	99%	NA ^e	120
		pressure: 1 atm	CO ₂ : 37%				
KOH (19 wt %)	packed column	temp: 30 °C	CH ₄ : 56.2%	19.8 Nm ³ /h	97%	regeneration with CaCO ₃ ; source of Ca was APC	112
		pressure: 1 atm	CO ₂ : 42%			temp: 45-55 °C	
500–1000 kg of MSWI ^d BA ^c	fixed bed reactor	temp: 10-30 °C	CH ₄ : 50%	$3.7 \text{ N m}^3/(\text{h t}_{BA})$	90%	NA ^e	113
		pressure: 1 atm	CO ₂ : 40%				

^aHot potassium carbonate. ^bAir pollution control residue. ^cBottom ash. ^dMunicipal solid waste incinerator. ^eNot available.

These residues show higher reactivity with carbon dioxide at their mild operating conditions.

Carbonation of minerals is an emerging technology in which researchers are showing immense interest. Generally, mineralization of carbon can be divided into two processes: in situ and ex situ. In these processes, even though there are some potential risk factors, carbon is sequestrated economically. The method in which sequestration occurs above the ground on an industrial scale and within a reactor is known as ex situ sequestration. In situ mineralization, also known as mineral trapping, involves a target form of alkaline mineral, and the solid carbonates are produced by a portion of CO_2 according to the target.¹¹¹

The procedure involves chemical absorption to capture CO₂ with NaOH or KOH followed by a regeneration step. The regeneration step is designed in such a way that the produced Na₂CO₃ or K₂CO₃ come in contact with industrial residues containing a significant amount of calcium hydroxide so that CO₂ can be stored. This process is called alkali absorption with regeneration (AwR).¹¹² The procedure contains two cycles: absorption and regeneration. In the absorption cycle, NaOH or KOH reacts with CO₂ present in biogas and produces CH₄-enriched gas. After CO₂ is absorbed in the regeneration cycle, the NaCO₃/K₂CO₃ solution reacts with the APC residue. As a result, NaOH/KOH is reproduced and solid CaCO₃ forms. The obtained alkali solutions are then fed back to the absorber to repeat the overall process.^{110,112}

In addition to the use of the APC residue in the AwR process, municipal solid waste incineration (MSWI) or bottom ash (BA) residues can be used in another novel technology which utilizes CO_2 to form $CaCO_3$. The process is called bottom ash biogas upgrading (BABIU).^{113,114} In this procedure, the first pretreatment of BA is done with the help of pure N₂ gas so that air can be removed from the pores of BA. Then, in order to enhance the CH_4 component in biogas, the reaction of CO_2 and H_2S is promoted with the alkaline products of the BA. The BA is then weathered, and coarse parts are removed. Then it is placed in the reactor, and biogas is pumped through the reactor.¹¹⁴ CO_2 and BA react as follows:

 $CO_2 + H_2O \leftrightarrow H_2CHO_3$

$$Ca(OH)_2 + H_2CO_3 \leftrightarrow CaCO_3 + 2H_2O_3$$

When the reactivity of BA becomes minimal, it is discharged from the reactor and dumped into the landfill.¹¹⁴

3.2.3. Biogas Upgrading by Caustic Solvent. Many solvents have been used in the CO₂ capture process, but most studies support the fact that alkaline solvents, such as hot potassium carbonate or alkanolamines, are the most effective ones.¹⁰² Again, alkanolamines are less convenient because they require high regeneration energy and are more susceptible to solvent degradation and corrosion. However, with alkaline solvents, the regeneration process can be maintained in several ways. Also, carbonation of minerals is one of the efficient ways to resist solvent loss. Baciocchi et al.¹¹⁵ referred to the use of three types of alkaline industrial residues, including APC from a waste incineration plant, stainless steel slag, which was sampled from the outlet of argon oxygen decarburization (AOD) and BA from the waste landfill to analyze the parameters on which maximum CO₂ intake depends. In the carbonation reaction, $Ca(OH)_2$ was kept as a reference material in order to calculate the regeneration of KOH percentage and calcite precipitation. Aroonwilas et al.¹¹⁶ reported that the removal rate of CO2 can vary depending on structural packing. Also, the temperature of the liquid can affect the mass transfer efficiency.

In Table 3, some reference cases of biogas upgrading using alkaline solvents are listed. In these cases, the CO_2 removal percentage is 60–90%.

3.2.4. Regeneration Process. As discussed before, alkali solvents cannot be easily regenerated. They can be regenerated at increased temperatures that, unfortunately, result in elevated energy consumption. For example, NaOH absorbs CO_2 and produces NaHCO₃, which is very soluble in aqueous solution. The reaction is

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$

NaHCO₃ easily decomposes to Na₂CO₃, CO₂, and H₂O at 160 $^{\circ}$ C.¹²¹ Na₂CO₃ is a thermally stable compound, and it decomposes to produce Na₂O at over 800 $^{\circ}$ C, which after adding water produces NaOH.¹²²

Baena-Moreno et al.¹²³ suggested a better approach for the NaOH/KOH solution that is more effective in the regeneration process. They proposed using solid $Ca(OH)_2$ when alkali solutions are being used as absorbents. The regeneration then occurs in the following way:

$$Na_{2}CO_{3}/K_{2}CO_{3}(aq) + Ca(OH)_{2}(s)$$

$$\rightarrow 2NaOH/KOH(aq) + CaCO_{3}(s)$$

This precipitated calcium carbonate can be used in different industrial sectors.¹²⁴ The addition of $Ca(OH)_2$ is economically convenient and also less energy intensive than the typical physical regeneration.¹²⁵

In the work published by Liang et al.,¹²⁶ CO₂ was captured using a solid dry sorbent Na_2CO_3 that was regenerated at 120–200 °C. The reaction was done in a fixed bed reactor, and Wegscheider's salt was formed in the process. The reaction occurs as shown below:

$$Na_2CO_3(s) + 0.6CO_2(g) + 0.6H_2O(g)$$

$$\leftrightarrow 0.4[Na_2CO_3 \cdot 3NaHCO_3](s)$$

Weescheider's salt

Perez-Salado Kamps et al.¹²⁷ reported CO₂ capture with K₂CO₃ and KCl solutions with particular emphasis given on the former. Using K₂CO₃ allows for the precipitation of KHCO₃, which plays a vital role in the "hot potassium carbonate (Benfield) process" and its modification by activating additives, such as secondary and primary amines (e.g., DEA or piperazine).^{89,128} The gas absorption takes place at approximately 343 K and at elevated pressures (up to about 2 MPa or more), whereas the solvent regeneration in the stripper occurs at higher temperatures (about 403 K) and lower pressures (around low partial pressures of the sour gases, such as CO_2 and H_2S). The absorption of CO_2 in aqueous solutions of K₂CO₃ might be hampered by slow chemical reaction kinetics for the formation of bicarbonate.¹²⁹ However, a relatively high temperature in the absorber significantly enhances the absorption rate of CO₂ and also the solubility of KHCO₃, thereby allowing operation with highly concentrated solutions.

Lee et al.¹³⁰ approached a novel way of capturing CO_2 by impregnating potassium carbonate with multiple solid sorbents such as activated carbon (AC), SiO₂, Al₂O₃, TiO₂, MgO, SiO₂, and various zeolites. They measured both the CO₂ capture capacity and the regeneration properties of the impregnated sorbents in the presence of H₂O in a fixed bed reactor during multiple cycles at various temperature conditions. According to their measurements, K₂CO₃/AC, K₂CO₃/TiO₂, K₂CO₃/MgO, and K₂CO₃/Al₂O₃ showed excellent CO₂ capture capacity values of 86, 83, 119, and 85 mg CO_2/g of sorbent, respectively. Moreover, the sorbents K₂CO₃/AC, K₂CO₃/ TiO₂, K_2CO_3/MgO_1 , and K_2CO_3/Al_2O_3 could be easily regenerated at 150, 150, 350, and 400 °C, respectively. However, for K₂CO₃/Al₂O₃ and K₂CO₃/MgO, the CO₂ capture capacity decreased gradually after regeneration. This is because of the formation of KAl(CO₃)₂(OH)₂, K₂Mg- $(CO_3)_2$, and $K_2Mg(CO_3)_2 \cdot 4H_2O$, which did not completely convert to the original K₂CO₃ phase. This problem was not present in K2CO3/AC and K2CO3/TiO2, where a KHCO3 crystal structure was formed during CO₂ absorption that could be readily converted to the original K₂CO₃ phase at a low temperature range of 130–150 °C. Their results also show that the rate of regeneration for the K₂CO₃/TiO₂ sorbent was faster than that of K_2CO_3/AC . Therefore, the authors concluded that the K_2CO_3/TiO_2 sorbent system is much better than others in terms of both absorption and regeneration.

Another work by Lee et al.¹³¹ with novel potassium-based dry sorbent KZrI₃O showed excellent CO_2 capture and

regeneration capabilities. It was prepared by impregnating K₂CO₃ with ZrO₂, and this newly developed sorbent was reported to show absorption at a rate of 91.6 mg CO_2/g at 50 °C, which was about 96% of the theoretical value of the sorbent. This new sorbent had an ability to absorb CO₂ in a low-temperature range of 50-100 °C even after 10 cycles of absorption and regeneration, without producing any new substances. The regeneration temperature was predicted to be 130-200 °C for this sorbent. Nevertheless, from the X-ray diffraction, Fourier transform infrared (FTIR), and temperature-programmed desorption analysis, it was found that during CO₂ absorption, no other new structures were formed as a byproduct except for the KHCO₃ crystal structure at 130 $^{\circ}$ C in the regeneration process. Thus, ZrO₂ can be used in the formation of KZrI₃O, which can be completely regenerated at temperatures less than 150 °C.

CaO itself or CaO-based sorbents can be excellent sorbents for CO₂ absorption. CaO absorbs CO₂ and forms CaCO₃ (carbonation step), which further can be regenerated via calcination to CaO. This process is called the calcium looping process.¹³² However, after several carbonation–calcination cycles, the reactivity of CaO decreases.¹³³ In a work described by Li et al., steam was introduced to enhance CaCO₃ calcination, and it had been observed that the reactivity of the CaO sorbent increased.¹³³ Steam also had enhanced effects on CaO carbonation and hydration, which were also thoroughly investigated in this study. The decomposition rate of CaCO₃ is hampered by high CO₂ partial pressure, which can be understood from eq 1:

$$R_{\rm r} = A \left[\exp\left(-\frac{E}{RT}\right) \right] (P^* - P_{\rm CO_2}) \tag{1}$$

where R_r is the rate of decomposition, P^* is the balanced pressure of CO₂, P_{CO_2} is the partial pressure of CO₂, A is the frequency factor (0.012 mol m⁻² s⁻¹ kPa⁻¹), and E is the activation energy (33.47 kJ mol⁻¹).

When steam sinters at a higher temperature in the calcination reaction atmosphere, P_{CO_2} decreases, which increases R_r according to eq 1; that is, the decomposition rate of CaCO₃ increases. Furthermore, when CaCO₃ is decomposed, the released CO₂ is initially absorbed by the active site of CaO*. Due to stronger binding ability between $\rm H_2O$ and O*, 134 a CaO*–OH_2 bond is formed instead of CaO^{*}-CO₂ and CO₂ is released when steam (H_2O) is present in the system. Thus, the partial pressure of H_2O (P_{H_2O}) increased while the partial pressure of CO_2 (P_{CO_2}) decreased after steam was introduced into calcination atmosphere, thus accelerating the regeneration process. It was also revealed from the study that hydrated CaO or $Ca(OH)_2$ performed much better in terms of reactivity of Ca(OH)₂ and cyclic reactivity of CaO due to formation of a particle pore structure from the hydration treatment. Another work of the calcium looping procedure was done by Blamey et al.,¹³⁵ in which the reaction was done in a fluidized bed reactor. In this experiment, regeneration took place after 13 calcination cycles. The study revealed that the fluidized bed reactor was unsuitable for the reactivation, and a fixed or moving bed reactor was a more preferable choice.

3.3. CO_2 Absorption by Amino Acid Salts. 3.3.1. Background. CO_2 absorption by alkanolamines is described in section 3.1 of this review. Alkanolamines are an efficient class of compounds for CO_2 absorption. However, some problems, such as higher cost, solvent degradation, higher regeneration temperature, corrosion, and other causes, made researchers look for alternatives, such as AAS.^{136,137}

Amino acid and alkaline substances react to produce AAS. A typical amino acid is an organic molecule consisting of an acidic carboxyl group, a basic amino group, and an organic alkyl or aryl side chain specific to each amino acid.¹³⁸ Usually, there are 20 standard amino acids consisting of four types, such as α -amino acid, β -amino acid, γ -amino acid, and δ -amino acid. These amino acids (α -amino acid, β -amino acid, γ -amino acid, and δ -amino acid) can be prepared primarily in four ways: using ionic liquids, organic amines, inorganic strong alkali, and adding activators.¹³⁹ Though AASs and alkanolamines have the same functional group, AASs do not deteriorate like alkanolamines in the presence of oxygen.¹⁴⁰ Furthermore, AASs provide an interesting advantage during CO₂ absorption which allows formation of solid precipitates as the CO₂ loading exceeds a certain value. The precipitate might be a neutral amino acid molecule, or a (bi)carbonate salt. Due to this, when the loading further increases, the chemical reaction equilibria are shifted in such a way that the equilibrium CO₂ pressure remains constant. This greatly improves the absorber performance as the driving force for absorption can be maintained at a high level even at high loadings. At the same time, it leads to reduced energy consumption during regeneration.¹³⁷ Versteeg et al.¹⁴¹ patented a process called DECAB for CO₂ absorption that was inspired from the aforementioned characteristics of precipitating amino acids, which is illustrated in Figure 2. Owing to having low volatility provided by the ionic structure, high achievable cycle loadings, higher surface tension, fast reaction kinetics, and greater stability toward oxygen, AASs are a great class of alternatives to conventional amine-based solutions. Moreover, the low toxicity and biodegradability associated with them make them fall into the category of green chemicals.^{137,142}

3.3.2. CO_2 Capture Using Amino Acid Salt Solution. Due to various advantages over common amine-based solvents, AAS solutions have become very strong and in-demand alternatives for removal of acid gas components from biogas, flue gas, etc. For example, the Alkazid process marketed by BASF is a significant example of commercial use of AAS.¹⁴³ However, both alkanolamines and AASs have identical functional groups which allows for similar absorption kinetics with CO_2 . Also, the reaction mechanism is also expected to be the same for both.¹⁴⁴

When a pure amino acid with the chemical formula of HOOC-R-NH₂ dissolves in water, the following reaction occurs:

HOOC-R-NH₃⁺
$$\leftrightarrow$$
 H⁺ + ⁻OOC-R-NH₃⁺
low pH neutral/mildly acidic pH
 \leftrightarrow 2H⁺ + ⁻OOC - R - NH₂
high pH

In the above equation, it is observed that a neutral molecule, also known as a zwitterion, exists in a bipolar form. It is formed due to the proton transfer from carboxylic acid to an amine group. The proton can be further removed from the amine group by adding a base to the solution, which leaves the molecule with a net negative charge. Deprotonation of zwitterions results by adding alkali hydroxides, which form deprotonated amino acid salt solutions.¹⁴⁵ In the DECAB

process, the salt solutions of amino acids are prepared by neutralizing it with KOH.^{137,141} The reaction gives a K-salt of amino acid in the following way:

$$-OOC-R-NH_3^+ + KOH \rightarrow K^+ + -OOC-R-NH_2 + H_2O$$

Here, the K-salt is the active group that can react with CO_2 like typical alkanolamines with the help of the $-NH_2$ group. The neutralization also helps to increase the solubility greatly.^{146,137}

Carbamate formation:

$$CO_{2} + 2^{-}OOC-R-NH_{2}$$
amine
$$\leftrightarrow ^{-}OOC-R-NH-COO^{-} + ^{-}OOC-R-NH_{3}^{+}$$
protonated amine

Hydrolysis of carbamate:

$$OOC-R-NH - COO^- + H_2O$$

 $\leftrightarrow OOC-R-NH_2 + HCO_3$
 $\Rightarrow mine bicychonate$

Formation of bicarbonate:

$$CO_2 + OOC-R-NH_2 + H_2O$$

$$\leftrightarrow OOC-R-NH_3 + HCO_3$$

protonated amine bicarbonate

According to the above reaction, formation of bicarbonate or carbamate depends on the pH of the solution after the carbon dioxide is absorbed. After carbon dioxide absorption, the reaction environment becomes more acidic and amino acid precipitations may have formed.¹⁴⁶ As the pH of the solution decreases, it favors the formation of a zwitterion species and limits solubility. This results in high CO₂ loading.¹⁴⁷

AAS solutions can also work as a promoter for CO_2 absorption. However, there are not many reports on the use of AAS solutions as promoters. Usually, potassium carbonate solvent is used for AAS solutions to work as a promoter. Major benefits associated with potassium carbonate solvents are better resistance to degradation in the presence of oxygen, the ability to run the absorption process at higher temperature, an economical regeneration process, and lower toxicity.¹⁴⁸

Shen et al.¹⁴⁹ have worked with arginine and found that it was an effective promoter for absorbing CO_2 with 35 wt % potassium carbonate solution.¹⁴⁹ Arginine is a basic amino acid with a guanidinium group as the side chain. The kinetic study of CO_2 absorption with potassium carbonate was performed, and it was found that the absorption rate increased with increasing concentration of arginine. Another work by Shen et al. showed that uptake of CO_2 was promoted by a factor of 2–3 with the addition of 5 wt % arginine.¹⁵⁰

Lim et al.¹⁵¹ worked with aqueous potassium salts of Lalanine and L-proline using a semibatch absorption system for measuring CO_2 absorption capacity and differential reaction calorimetry for analyzing the heat of absorption. The obtained results were compared with the absorption capacity of MEA and DEA, and it was found that L-alanine and L-proline can replace the existing amines as CO_2 loading was higher for Lalanine, and the heat of absorption for L-alanine and L-proline was much lower than that of MEA or DEA.

Guo et al.¹⁴³ used glycine under mild reaction conditions to react with CO_2 . They combined two techniques for the reaction between CO_2 and glycine. One method involved using

stopped-flow UV/visible spectrophotometry in aqueous media, and the other involved gas/liquid absorption using a wettedwall column. They investigated the kinetics of the mechanism of CO_2 absorption using glycine and observed that the rate of the reaction and activation energy needed for the absorption were almost the same with amino acid alanine salts at lower pH. This study also gives perceptions about how the CO_2 is affected while reacting with different functional groups in amine.

Thee et al.¹⁴⁸ have done a thorough research on the kinetic study of glycine, sarcosine, and proline amino acid promoted with potassium carbonate solvent in a wetted-wall column in their deprotonated form. Activation energy of the AAS was measured under industrial CO_2 capturing conditions, and it was found that the pseudo-first-order reaction rate was enhanced. The absorption rate of CO_2 , which ultimately results in the formation of potassium carbonate, was enhanced using AAS. The catalytic activity of glycine was compatible with MEA, whereas sarcosine and proline had catalytic activity greater than that of DEA.

Zarei et al.¹⁴⁶ studied about reaction kinetics, mechanism, equilibrium solubility, and absorption capability of carbon dioxide under various reaction conditions, such as concentration, absorption temperature, and pressure with aqueous potassium glutaminate solvent. The results obtained from the experiments showed that potassium glutaminate solvent has an absorption rate higher than that of the traditional alkanolamines and high capacity, as well. In addition to this, this solvent showed low oxidative degradation and corrosion rate.

Aronu et al.¹⁵² have worked with AASs formed from amino acid with organic bases (amines) in neutralization reactions. For an illustration, salts from neutralization of glycine with 3-(methylamino)propylamine (MAPA) (GLYMAPA), sarcosine with MAPA (SARMAPA), and β -alanine with MAPA (B-ALAMAPA) were formed. The screening test of these solvents was compared with MEA and potassium salt of sarcosine (KSAR). This research showed that CO₂ absorption potential for the amino acid salts that were neutralized with an organic base (amine) was better than that of amino acid salts neutralized with an inorganic base such as potassium hydroxide.

Hamzehie et al.¹⁵³ worked with a novel combination of potassium prolinate (KPr) blended with 2-amino-2-methyl-1propanol for CO_2 absorption. They reported that CO_2 loading decreases with increasing mass concentration of AAS. However, high CO_2 loadings were possible at low mass concentration of KPr when AMP was added as an additive to aqueous KPr solution.

In the work published by Li et al.,¹⁵⁴ they evaluated 24 common aqueous AAS solutions for their potential to capture CO_2 from a flue gas stream using a membrane contractor. According to their research, the performance of potassium sarcosinate is significantly better than MEA and many other AASs in terms of absorption kinetics and storage capacity under identical testing conditions.¹⁵⁵

The most recent work on the next generation of AAS for CO_2 capture was published by Xu et al.,¹⁵⁶ where liquid AAS hydrogel particles (LAHPs) were used as a novel absorbent for CO_2 capture from various sources. Hydrogels are a class of cross-linked hydrophilic polymers which can hold large amounts of water and other polar solvents.¹⁵⁷ Hydrogels have been reported to significantly improve the CO_2 absorption kinetics and capacity of amine-based absorbents

at ambient conditions in many previous works.^{158,159} LAHPs can be prepared readily by adding environmentally friendly superabsorbent hydrogel particles with AAS solutions and stirring the mixture for about 20 min under ambient conditions. This encloses the AAS solutions within the hydrogel particles, resulting in a large contact area for CO₂-AAS interactions which enhances the absorption rates and at the same time reduces solvent loss. Furthermore, the solid precipitation resulting from the CO₂ absorption by AAS also remains confined within the hydrogels, overcoming any deleterious effect that may have resulted. Breakthrough experiments under real industrial conditions (high flow rate and large quantity of absorbents) showed that the LAHPs could be used practically across a wide range of fields, such as CO₂ removal from enclosed systems (e.g., submarines at 0.5-1.0 vol % CO₂), postcombustion capture (e.g., 15.0 vol % CO₂ in N_2), and direct air capture (420 ppm CO_2).¹⁵⁶

3.3.3. Biogas Upgrading by Amino Acid Salts. Conventional alkanolamines such as MEA and DEA are the leading absorbents known for the biogas upgrading process due to their fast CO₂ absorption rates and high basicity. However, there are a number of drawbacks, such as loss of absorbent due to high volatility, degradation and corrosion of the equipment, and environmental and health hazards.^{160,161} AASs and alkanolamines both react with CO₂ in the same way because of the presence of identical amino functional groups in their molecules.¹⁶² However, unlike alkanolamines, the ionic nature of AASs offers negligible vapor pressure and better resistance to oxidative degradation, offering minimal absorbent loss. Furthermore, most AASs are naturally occurring and thus are biodegradable, making the disposal of these solvents easier with minimal environmental hazards.¹⁶¹ Another specific reason which makes AAS a more suitable absorbent for biogas upgrading is that it can capture CO₂ more efficiently, owing to the salting out effect, from the CO_2/CH_4 mixture, with lower CH₄ losses and higher CH₄ product yield.¹⁶³

Yan et al.¹⁶⁴ investigated the performances of five natural AASs for CO₂ capture from biogas. These AASs were potassium L-argininate (PA), potassium L-ornithinate (PO), potassium sarcosinate (PS), potassium glycinate (PG), and potassium L-prolinate (PP). CO₂ absorption potential and the reaction mechanism of a basic natural amino acid, L-arginine, were also studied in the research. The results showed that absorption rate generally increased with an increase in the basicity of AASs. The regeneration efficiency, however, decreased with the increasing basicity of AASs. Potassium Lornithinate and potassium glycinate were found to be the most suitable and efficient candidates for CO₂ absorption from biogas because of higher absorption kinetics, relatively lower absorption enthalpy, negligible absorbent loss, and higher regeneration efficiency compared to the others. It was also reported that L-arginine performed better than MEA due to saturated CO₂ absorption loading, absorption enthalpy, and regeneration efficiency even though it suffered from slow reaction kinetics. FTIR analysis showed that large amounts of bicarbonate and carbonate formation occurred during CO₂ absorption via L-arginine, suggesting that L-arginine is more

likely to act as a base in catalyzing the hydration of CO_2 . In another work by Song et al.,¹⁶⁵ CO_2 absorption with 10, 20, and 30 mass % sodium glycinate under different conditions was reported. It was found that with an increasing mass of sodium glycinate and increasing temperature, the solubility of CO_2 decreased. However, the most promising result was

Table 4. Published Cases of Biogas Upgrading Using Amino Acid Salt Solution Scrubbing Process

AAS solution concentration	reactor	operating parameters	feed gas composition	gas flow rate	product purity	regeneration conditions	ref
potassium glycinate, potassium lysine,	hollow fiber	temp: 25 °C	CH ₄ : 60%	500-1000 mL/min	92%	NAa	154
potassium arginine	membrane contractor	pressure: 1–10 bar	CO ₂ : 40%				
potassium glycinate, potassium L-argininate,	bubble column	temp: 35 °C	CH ₄ : 60%	2 L/min	$CH_4 = 99\%$	temp: 75 °C	166
potassium L-prolinate, potassium L- orthinate, and potassium sarcosinate		pressure: NA ^a	CO ₂ : 40%		CO ₂ < 1%		
potassium argininate (5 wt %)	membrane	temp: 30 °C	CH ₄ : 60%	12 L/h	95%	NA ^a	167
	contractor	pressure: 0.9 MPa	CO ₂ : 40%				
potassium L-argininate	gas liquid	temp: 25 °C	CH ₄ : 45-75%	51.03 kmol/(m ² h)	99.15%	NA ^a	168
	membrane contactor	pressure: 110 kPa	CO ₂ : 25–55%				
potassium glycinate	hollow fiber membrane contractor	temp: 40 °C	CH ₄ : 60%	1000 mL/min	96%	temp: 80 °C	169
		pressure: 0.005 MPa	CO ₂ : 40%				

^aNot available.



Figure 2. Schematic representation of the DECAB process.

reported with 10 mass % sodium glycinate. More recently, technologies like membrane gas absorption and artificial neutral network have also been reported to remove CO_2 using AASs.¹³⁹

In Table 4, some published cases of removing CO_2 from biogas are described with different reported procedures.

3.3.4. Regeneration Process. Regeneration of the precipitated amino acid for the purpose of redissolving it in the AAS solution is done by increasing the temperature and driving off the CO₂, much like the case of typical alkanolamines.¹³⁷ Brouwer et al.¹³⁷ showed that a CO₂ lean loading of 0.05 mol/ mol is achievable with a regeneration temperature of 120 °C. This provides a cyclic loading of 0.35 mol/mol, much higher than typical cyclic loadings of CO₂ for 6 M amino acid salt solution, which is 0.20–0.25 mol/mol CO₂ loading for MEA. Several modifications of the equipment design are needed in the case of AASs due to the use of these precipitating solvents in a (DECAB) mechanism, as shown in Figure 2.

The fast reaction kinetics and the enhanced driving force for absorption due to precipitation of the AASs compensate for the decrease in the specific surface area compared to packed columns. Therefore, expensive packing materials can be avoided, saving a huge amount of cost. Moreover, a spray column is preferable as the absorber column since it should have the capability to handle slurries. Furthermore, a heat exchanger is partly integrated within the stripper column for the modified temperature profile during the desorption process. When the loaded solvent with a rich loading of 0.4 mol/mol was heated to 80 °C, complete dissolution occurred. However, above 80 °C, the solvent started releasing CO_2 and complete regeneration required that the temperature at the bottom of the stripper be 120 °C. Thus, the temperature difference across the stripper is about 40 $^{\circ}$ C, which is much higher than MEA-based processes where it is about 15 $^{\circ}$ C. This is why heat integration within the stripper column is essential for AAS-based processes.¹³⁷

In order to reduce the regeneration temperature, Shen et al.¹⁷⁰ used ethanol instead of water to prepare potassium prolinate solution for CO₂ absorption. The isotherms obtained from their experiments revealed that the potassium prolinateethanol solution generally does not absorb much CO₂ as their aqueous counterparts at a low partial pressure of CO₂. However, the effect of temperature on CO₂ loading for the potassium prolinate-ethanol solution is much greater than that of aqueous one. Therefore, a larger cyclic absorption capacity can be achieved with narrow changes in temperature for the potassium prolinate-ethanol solution, which is a suitable characteristic necessary for regeneration at lower temperature. The solvent effect of ethanol in this case can be attributed to the fact that the stability of the resulting species is lower in nonaqueous systems, which in turn helps to reduce the regeneration temperature. Using potassium prolinateethanol solution, the CO₂-rich slurry was regenerated at 393 K or 119.85 °C. However, the process required a further heating of 343 K for 60 min to release maximum CO₂ as total loading did not decrease a lot and solids did not dissolve completely after the regenerated solids were transferred to the upper liquid phase initially.

Liu et al.¹⁷¹ used N-alkylglycinate salts in a PEG_{150} or polyethylene glycol (with 150 molecular weight) solvent for CO_2 absorption. They found that this solution has a significantly lower regeneration temperature of 40 °C with N_2 and 90 °C without N_2 . The effect can be attributed to the fact that the flexible polyethylene oxide chain can coordinate with alkali-metal cations, which leads to improved capacity for the counterions.

A very recent work by Xu et al.¹⁵⁶ used AAS encapsulated into solid polymer matrices to prepare LAHPs or liquid AAS hydrogel particles for CO_2 capture. Considering the remarkable water absorbing capacity of hydrogels, they can be readily regenerated using an industrial waste steam, which is significantly cost- and energy-effective.

Xu et al.¹⁵⁶ loaded about 2 g of CO₂-saturated LAHPs into the sample column connected to a water tank. The constituents of LAHPs in this case were 30 wt % potassium sarcosinate and 0.2 g of hydrogel per gram of AAS solution. The oven temperature was set at 120 °C under ambient pressure conditions where the sample was heated for 30 min, which resulted in maximum regeneration. In this way, a total of 10 absorption/desorption cycles were performed to evaluate the recyclability of the LAHPs. In the same work, they explored the recyclability of LAHPs further by replacing water with a higher boiling point solvent, ethylene glycol. They proposed that a 30 wt % solution of potassium sarcosinate in ethylene glycol could be infused into a cross-linked poly(Nhydroxyethylacrylamide) hydrogel. It was found that the sorbent was regenerated with minimal loss of solvent at 60 °C in a vacuum for 60 min.

4. CONCLUSION

Biogas is a mixture of methane, hydrogen sulfide, carbon dioxide, and some other components. By removing the carbon dioxide gas, the methane ratio in biogas can be increased. This process is known as biogas upgrading. Biogas is a significant source of renewable energy, and it can be upgraded to be

utilized in several sectors, such as power plants, vehicle fuel, or as a raw material in industries in efficient ways. CO₂ can be separated from biogas using several processes, such as water scrubbing, membrane separation, cryogenic separation, and chemical absorption. This review article discussed some recent and significant works on different methods of chemical absorption of CO_2 using different chemicals and the advantages, disadvantages, and relative efficiencies associated with them. This paper presented discussions on three types of solvents, such as amine solvents, alkali solvents, and AAS solvents. Overall, among the three types, alkanolamines are used to a greater extent than others owing to its greater efficiency to absorb CO₂. On the other hand, alkanolamines used for CO₂ absorption have several drawbacks, which have been discussed in detail. However, more researches in this area can solve these drawbacks in the days to come. The alkali solvents and aqueous solution of AAS with promoted potassium carbonate can be a good substitute of alkanolamines. Alkali solutions have some disadvantages including solvent degradation and less environmentally friendly properties, but these are cost-effective and also widely available. The use of AAS solutions to remove CO_2 is another very important method, as it has low toxicity, low volatility provided by the ionic structure, high achievable cycle loadings, higher surface tension, fast reaction kinetics, and greater stability toward oxygen. Even though some AAS solutions performed better than the other two solutions in many works reported in this review, it is needed to be used on a large scale to observe its performance in pilot plants. AAS solutions do have the potential of replacing other solutions for biogas upgrading by $\mbox{\rm CO}_2$ absorption. To that end, more research is needed to be done to help set a true standard and a reach a more definitive conclusion.

5. HIGHLIGHTS, MOTIVES, AND PROSPECTS

Biogas is a potential renewable source of energy which is costeffective, is eco-friendly, and can be upgraded up to $\geq 95\%$ biomethane by CO₂ minimization. A chemical absorption method using chemical solutions can remove CO₂ from biogas effectively, easily, and economically. CO₂ removal using alkanolamines, alkali solvents, and amino acid salts has been discussed to a great extent, highlighting their merits and disadvantages very elaborately. This review article will make readers and researchers aware of the potential of biogas to solve the world's energy crisis and encourage them to dig deep into the topic.

AUTHOR INFORMATION

Corresponding Author

Mosharof Hossain – Institute of Fuel Research and Development, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka 1205, Bangladesh; @ orcid.org/ 0000-0003-0834-4740; Phone: +8801741511376; Email: mosharof@bcsir.gov.bd

Authors

- Nuzhat Muntaha Institute of Fuel Research and Development, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka 1205, Bangladesh
- Mahmudul I. Rain Institute of Fuel Research and Development, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka 1205, Bangladesh; Department of

Chemistry, Jahangirnagar University, Dhaka 1342, Bangladesh

- Lipiar K. M. O. Goni Institute of Fuel Research and Development, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka 1205, Bangladesh
- Md. Aftab Ali Shaikh Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka 1205, Bangladesh; Department of Chemistry, University of Dhaka, Dhaka 1000, Bangladesh
- Mohammad S. Jamal Institute of Fuel Research and Development, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka 1205, Bangladesh

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c03514

Author Contributions

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Notes

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ABBREVIATIONS

- AAS = amino acid salt
- MEA = monoethanolamine
- DEA = diethanolamine
- DGA = diglycolamine
- TEA = triethanolamine
- DIEA = diisopropanolamine
- MDEA = methyldiethanolamine
- HPC = hot potassium carbonate
- HSS = heat-stable salts
- SMC = sodium methyl carbonate
- APC = air pollution control
- BA = bottom ash
- MSWI = municipal solid waste incinerator
- AwR = alkali absorption with regeneration
- BABIU = bottom ash biogas upgrading
- ANN = artificial neutral network
- DECAB = a separation process to remove CO_2 from flue gas based on precipitating solvents
- LAHP = liquid AAS hydrogel particles

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NOTE ADDED AFTER ASAP PUBLICATION

This article originally published with inaccurate data in the product purity column of Table 3. The corrected article published September 12, 2022.