Research Status of Amine-Based CO$_2$ Capture Technology

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Abstract

Global warming is a severe challenge we currently face, with the excessive emission of greenhouse gases such as CO$_2$ being a primary cause of global climate change. Carbon Capture, Utilization, and Storage (CCUS) technologies are essential means to address global warming. The amine absorption method, characterized by its high absorption efficiency, fast absorption rate, and low operational costs, has become the most researched and mature carbon capture technology. This article reviews the recent domestic and international research status of amine-based CO$_2$ absorption, focusing on the mechanism of CO$_2$ absorption by amine solutions and the progress in absorbent research. Furthermore, it provides an outlook on the development direction of this technology.

Keywords: *Organic amines, CO$_2$ absorption, Carbon capture, Chemical absorption in tackling the challenges of climate change.*

I. 1INTRODUCTION

With the rapid advancement of industrial levels, the demand for energy has significantly increased. The massive combustion and emission of CO$_2$ from fossil fuels (such as coal, oil, and natural gas) have accelerated the process of global warming [1], leading to numerous ecological and environmental issues. These include the melting of glaciers, rising sea levels, reduction of wildlife habitats, and forest fires, which severely threaten the sustainable development of the ecological environment and human health and safety [2, 4]. Moreover, IPCC research reports indicate that without the implementation of deep emission reduction measures across various sectors, achieving the goal of limiting global warming to 1.5°C will be difficult [5].

Currently, the main methods to achieve carbon emission reduction include improving energy efficiency, developing clean and renewable energy resources, and Carbon Capture, Utilization, and Storage (CCUS) technologies. CCUS technology involves separating CO$_2$ from industrial processes, energy use, or the atmosphere, directly using it or injecting it into underground layers to permanently reduce CO$_2$ emissions. The International Energy Agency (IEA) considers CCUS technology a key technology capable of directly reducing emissions and lowering atmospheric CO$_2$ concentrations [6]. CO$_2$ capture is the primary link in the operation of CCUS, accounting for more than 60% of the total energy consumption of CCUS and determining the operating costs [7]. Chemical absorption, due to its high efficiency and low cost, is widely used in CO$_2$ capture, especially suitable for processing large-volume, low CO$_2$ partial pressure gases, showing great industrial potential [8]. In the process of further reducing the cost of chemical absorbents, newly discovered organic amine absorbents, characterized by their low price, low regeneration energy consumption, and fast absorption rate, have attracted widespread attention [9,10].

In summary, the amine-based CO$_2$ capture technology has demonstrated high capture efficiency and economic value, leading to extensive research by scientists to uncover the underlying reaction mechanisms and develop new and efficient absorbents. This article focuses on the mechanism of CO$_2$ absorption by organic amines and the progress in absorbent research, aiming to provide references for the optimization and development of CO$_2$ capture technology.

II. THE MECHANISM OF CO$_2$ ABSORPTION BY ORGANIC AMINES

2.1 Primary and Secondary Amines Absorption Mechanism

In the reaction of primary and secondary amines with CO$_2$, the presence of active hydrogen atoms on the nitrogen allows these amines to directly react with CO$_2$, forming zwitterions. These zwitterions then continue to react with molecules in the solution, resulting in the formation of carbamates. as shown in the reactions (1) and (2). The overall reaction is represented as reaction (3).

$$CO_2 + RR'NH \rightleftharpoons RR'NH^+COO^- \qquad (1)$$

$$RR'NH^+COO^-+RR'NH \leftrightharpoons RR'NH_2^++RR'NCOO^- \qquad (2)$$

$$CO_2+2RR'NH \leftrightharpoons RR'NH_2^++RR'NCOO^- \qquad (3)$$

The reaction of primary and secondary amines with CO_2 is exothermic, and the reaction products can be regenerated by heating to recover the organic amines. From the overall reaction, it is clear that for primary and secondary amines, which only have one nitrogen atom, their maximum absorption capacity is thermodynamically limited to 0.5 mol/mol. Thus, while primary and secondary amines have a fast absorption rate, their absorption capacity is relatively low.
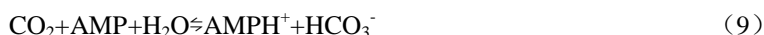
2.2 Tertiary Amines Absorption Mechanism

Tertiary amines, lacking active hydrogen atoms on the nitrogen, cannot directly react with CO_2 to form carbamates. Instead, their role in the absorption process is akin to that of a catalyst for the reaction between CO_2 and H_2O. They attract H^+ ions produced by the dissociation of H_2O, facilitating the combination of CO_2 with O-H bonds to form bicarbonates, as illustrated in reactions (4) and (5). The overall reaction is given as reaction (6).

$$CO_2+H_2O \leftrightharpoons H^++HCO_3^- \qquad (4)$$

$$H^++RR'R''N \leftrightharpoons RR'R''NH^+ \qquad (5)$$

$$RR'R''N+H_2O+CO_2 \leftrightharpoons RR'R''NH^++HCO_3^- \qquad (6)$$

From the overall reaction equation, it can be seen that, theoretically, 1 mol of tertiary amine can absorb 1 mol of CO_2. However, due to the much lower absorption reaction rate of tertiary amines compared to primary and secondary amines, the actual absorption capacity is less than 1 mol/mol, significantly limiting the effectiveness of tertiary amines in capturing CO_2.

2.3 Hindered Amines Absorption Mechanism

For sterically hindered amines, the large functional groups attached to the nitrogen atom obstruct their reaction with CO_2 and affect the stability of the formed carbamates, making them more prone to decompose into bicarbonate ions. AMP (Aminomethyl propanol) is an example where the absorption mechanism is demonstrated through reactions (7) and (8), with the overall reaction presented as reaction (9).

$$CO_2+2AMP \leftrightharpoons AMPCOO^-+AMPH^+ \qquad (7)$$

$$AMPCOO^-+H_2O \leftrightharpoons AMP+HCO_3^- \qquad (8)$$

$$CO_2+AMP+H_2O \leftrightharpoons AMPH^++HCO_3^- \qquad (9)$$

III. PROGRESS IN THE RESEARCH OF ABSORBENTS

The organic amine absorption method, celebrated for its affordability, recyclability, and superior separation capabilities, stands as the most extensively employed CO_2 capture technology presently [11]. Nonetheless, it grapples with challenges like considerable solvent loss, elevated energy demands, and equipment corrosion [12]. To surmount these obstacles, researchers globally are on a quest for novel absorbents that boast excellent performance, reduced energy requirements for regeneration, diminished corrosion, and enhanced cost-effectiveness, including mixed amines, phase change absorbents, ionic liquid absorbents, and nanofluid absorbents. The quintessential CO_2 absorbent would merge attributes such as rapid absorption pace, low energy consumption for regeneration, eco-friendliness, high stability, degradation resistance, and minimal corrosiveness to apparatus. Numerous research initiatives, both within and outside the nation, have been mobilized around the creation of novel absorbents, marking significant advancements.

3.1 Mixed Amine Absorbents

Traditional organic amine absorbents have two main disadvantages in the CO_2 absorption process: 1) A single amine absorbent cannot simultaneously meet the requirements for high absorption rate, large absorption capacity, low regeneration energy consumption, and small loss; 2) The desorption process requires the consumption of a large amount of latent heat, leading to high energy losses [12]. To achieve better absorption performance and improved desorption effects, researchers have adopted the method of mixing and matching organic amines with complementary characteristics [13], effectively overcoming the shortcomings of single amine absorbent performance. Ahmad's study found that a mixture of monoethanolamine (MEA) and N-

methyldiethanolamine (MDEA) exhibited the best results, offering high selectivity for acidic gas absorption with lower corrosiveness [14]. Zhang's research on a mixed absorbent composed of MEA, MDEA, and piperazine (PZ) demonstrated an increase in CO$_2$ cyclic capacity and desorption rates compared to a system using only MEA, with regeneration energy consumption reduced by 15.22% to 49.92% [15]. Lu Shijian found that adding activators such as MEA, DEA, PZ, and AMP to a base liquid of MDEA enhanced the saturated absorption capacity of the absorbent [16]. Dash's study on a 20% (mass fraction) AMP + 20% (mass fraction) 1-methylpiperazine (1MPZ) mixed amine absorbent system showed that its CO$_2$ cyclic capacity could reach up to 1.7mol/L, significantly surpassing the traditional 30% MEA aqueous solution [17]. These findings indicate that mixed absorbents improve absorption performance and regeneration energy efficiency compared to traditional single-component amine absorbents, compensating for their limitations, with many commercially applied absorbents now being mixed amine types.

3.2 Phase Change Absorbents

Phase change absorbents are named for their characteristic phase separation during the CO$_2$ absorption process, which can be divided into liquid-solid and liquid-liquid phase change absorbents. They offer a novel approach to CO$_2$ capture with significant potential in reducing operational energy consumption. PERRY developed a 1,3-bis(3-aminopropyl) tetramethyl disiloxane that acts as a liquid-solid phase change absorbent, notable for its thermal stability, low energy consumption, and high CO$_2$ cyclic processing capability [18]. LU studied an "amino-imidazole bifunctional ionic liquid-ethanol-water" phase change system for capturing CO$_2$, demonstrating good stability, recyclability, and a high absorption capacity of up to 1.548mol/mol [19]. ZHENG introduced a triethylenetetramine (TETA) + ethanol liquid-solid phase change absorbent, enhancing CO$_2$ solubility and achieving a CO$_2$ removal rate of up to 81.8% [20]. WANG discovered a unique phase change amino acid salt absorbent with high CO$_2$ loading capacity, forming liquid-solid phases after CO$_2$ absorption, where the solid phase of bicarbonates constitutes 90% of the total CO$_2$ load. However, phase change absorbents face issues like absorbent degradation and volatility during CO$_2$ capture, prompting extensive theoretical and experimental research [21]. ZHANG proposed an N,N-dimethylcyclohexylamine (DMCA) + N-methylcyclohexylamine (MCA) + AMP system, showing good resistance to oxidative and thermal degradation and lower regeneration energy consumption [22]. WANG's MEA+ tetrahydrothiophene system, enhanced by the physical additive tetrahydrothiophene, significantly improved thermal degradation capability, as shown in Aspen Plus process simulations [23]. KIERZKOWSKA-PAWLAK introduced a methylaminopropylamine (MAPA) + diethylethanolamine (DEEA) system, characterized by low volatility and energy consumption [24]. ZHANG's MEA+1-propanol+water system showed a cyclic load capacity of up to 1.7mol/kg, effectively reducing energy consumption [25]. Overall, phase change absorbents have significant energy-saving potential, but further research is needed on formulations, phase change mechanisms, and system processes based on these absorbents.

3.3 Ionic Liquid Absorbents

Ionic liquids (ILs), composed of cations and anions, are organic salts that remain liquid at room temperature [26]. They are known for their thermal stability, low vapor pressure, and status as environmentally friendly "green solutions." In 1999, BLANCHARD first introduced the concept of ionic liquids, showcasing their excellent absorption performance and laying the foundation for their use in CO$_2$ absorption [27]. In recent years, many scholars have conducted research on the absorption capacity of ionic liquids for CO$_2$ under various temperatures and pressures [28]. Traditional CO$_2$ absorption by ionic liquids mainly relies on physical interactions between the ionic liquids and CO$_2$, trapping CO$_2$ within the ionic liquid's mesh pores through unique hydrogen bond networks and the special interactions between anions and CO$_2$ [29]. Traditional ionic liquids, including imidazolium, pyridinium, pyrrolidinium, and amino acid-based types, offer good stability and low vapor pressure. However, their high viscosity, slow adsorption and desorption rates, and high costs prevent traditional ionic liquids from fully meeting the requirements for CO$_2$ absorbents. Consequently, scientists have conducted extensive experimental research to overcome these limitations [30, 31]. However, most studies are still at the laboratory stage, and broader application requires further practice and research to ensure the sustainability of the absorption reaction.

3.4 Nanofluid absorbents

Nanofluids formed by uniformly dispersing nanomaterials such as nanoparticles, nanotubes, and nanofibers into a base liquid, represent a new type of absorbent. They can significantly enhance gas-liquid mass transfer efficiency and reduce the energy consumption of thermal regeneration, thereby improving CO2 absorption performance [32, 33]. These nanofluids have been proven to significantly enhance gas-liquid mass transfer efficiency and reduce the energy consumption of thermal regeneration, thereby improving CO$_2$ absorption performance. Saidi's research on the reinforcement effect of carbon nanotubes and silica (SiO$_2$)

nanofluids on CO$_2$ absorption demonstrated that both carbon nanotubes and SiO$_2$ nanoparticles significantly improved the mass transfer performance of the base fluid, increasing the $_{CO2}$ absorption rate, with carbon nanotubes showing better performance than SiO$_2$ nanofluids [34]. Zhao compared the enhancement effects of different nanofluids (SiO$_2$, titanium dioxide (TiO$_2$), and alumina (Al$_2$O$_3$)) on CO$_2$ absorption, finding that 60nm TiO$_2$ had the most significant promoting effect on TETA absorption of CO$_2$, with an enhancement factor of 1.42 [35]. Jiang's study on the impact of nanofluids on MEA and MDEA absorption of CO$_2$ found that, aside from SiO$_2$, other nanoparticles enhanced the absorption of CO$_2$ in MEA and MDEA. The enhancing effect of nanoparticles first increased and then decreased with the growth of particle size and concentration, reaching an optimal point, with nanoparticles showing a better enhancing effect on MDEA than MEA [36]. Wang's research on the impact of nanoparticles on the absorption of CO$_2$ by amine absorbents showed that nanoparticles had varying enhancing effects on different amine absorbents, with the order of effectiveness being PZ > MEA > MDEA [37].

IV. CONCLUSION

Over the past decade, research on organic amine absorbents has made significant progress, with the primary research direction still focused on increasing absorption rates, capacities, and reducing regeneration energy consumption. Current developments in CO$_2$ absorption organic amine absorbents are mainly concentrated on known substances, with fewer studies on newly synthesized organic amines, which urgently requires further exploration. Overall, the development of organic amine absorbents tends towards more economical and efficient solutions. Future research should focus on developing new absorbents with improved performance, starting from mechanism and process system optimization to reduce energy consumption and enhance performance. Additionally, exploring the compatibility of new organic amine absorbents with carbon capture processes is crucial to further optimize and apply the technology.

REFERENCES

[1] Luo Z B, Long R, Wang X B. Technology of photocatalytic CO$_2$ reduction enhanced by heat [J]. Progress in Chemical Engineering, 2021, 40(09): 5156-5165.

[2] Liu C, Han X, Cao Y, Zhang S, Zhang Y, Sun J. Topological construction of phosphorus and carbon composite and its application in energy storage [J]. Energy Storage Materials, 2019, 20: 128-139.

[3] Zhu X, Fu Q, Zhu X. Progress on renewable synthetic fuels [J]. Chinese Journal of Inorganic Chemistry, 2020, 65: 1814-1823.

[4] Tian X X, Wu W R, Liang J H, Li Y Z. Research progress in CO$_2$ emission reduction and transformation through resource utilization [J]. Shandong Chemical Industry, 2022, 51(08): 95-97.

[5] Wang Z N, Yuan J S, Pang B. The interpretation and highlights on mitigation of climate change in IPCC AR6 WGIII report [J]. Climate Change Research, 2022, 18(5): 531-537.

[6] IEA. Special report on carbon capture utilization and storage [R/OL]. Energy Technology Perspectives 2020.

[7] Lu S J,Zhao D Y, Liu H. The researeh of netearbon reduction model for CCS-EOR projects and cases study [J]. International Journal of Simulation and Process Modelling, 2017, 12(5): 401.

[8] Leung D Y C, Caramanna G, Maroto-Valer M M. An overview of current status of carbon dioxide capture and storage technologies [J]. Renewable & sustainable energy reviews, 2014(39): 426-443.

[9] Liu M, Gadikota G. Single-step, low temperature andintegrated CO$_2$ capture and conversion using sodium glyci-nate to produce calcium carbonate [J]. Fuel, 2020(275): 1-10.

[10] Rosen J,Geary T,Hilmi A. Molten carbonatefuel cell performance for CO$_2$ capture from natural gascombined cycle flue gas [J]. Journal of the Electrochemi-cal Society, 2020, 167(6): 494-505.

[11] Sun L C, Wang Z G, Wu C, Wang K L, Zhang S M, Han W Q. Research on the design and operation optimization of a ten-thousand-ton-scale carbon capture project in coal-fired power plants [J]. Hua Electric Technology, 2021, 43(6): 69-78.

[12] Ren E Z, Zhang H Y, Yang Y. Study of CO$_2$ capture performance in nonaqueous absorbents comprised by ethanolamine and alcohols [J]. Natural Gas Chemical Industry, 2021, 46(S1): 68-73.

[13] Khan A A, Halder G, Saha A K. Experimental investigation onefficient carbon dioxide capture using piperazine (PZ) activated aqueousmethyldiethanolamine (MDEA) solution in a packed column [J]. International Journal of Greenhouse Gas Control, 2017(64): 163-173.

[14] Ahmad Z, Kadir N B A, Bahadori A, Zhang J. Optimization study on the CO$_2$ and H$_2$S removal in natural gas using primary, secondary, tertiary and mixed amine [J]. AIP Conference Proceedings, 2019.

[15] Zhang R, Zhang X W, Yang Q, Liang Z, Wu X. Analysis of thereduction of energy cost by using MEA-MDEA-PZ solvent for post-combustion carbon dioxide capture (PCC) [J]. Applied Energy, 2017(205): 1002-1011.

[16] Lu S J, Liu J W, Yu J L, Li Q, Zhao D Y, Zhu Q M. Capturing CO$_2$ from EOR produced gas using MDEA-based composite absorbents [J]. Natural Gas Chemical Industry (Cl Chemistry and Chemical Engineering), 2019, 44(6): 79-92.

[17] Dash S K, Parikh R, Kaul D. Development of efficient absorbent for CO$_2$ capture process based on (AMP+1MPZ) [J]. Materials Today: Proceedings, 2022(62): 7072-7076.

[18] Perry R J, Wood B R, Genovese S. CO$_2$ capture using phase-changing sorbents [J]. Energy & Fuels, 2012, 26(4): 2528-2538.

[19] Lu B H, Zhan X h, Li X. Mechanism of CO$_2$ capture into amino-azolyl dual-functionalized ionic liquid biphasic solvent [J]. Scientia Sinica Chimica [J]. 2021, 51(12): 1660-1670.

[20] Zheng S D, Tao M N, Qing L, Li Q N, Yi H, Yao S. Capturing CO$_2$ into the precipitate of a phase-changing solvent after absorption [J]. Environmental Science & Technology, 2014, 48(15): 8905-8910.

[21] Wang X, Akhmedov N Q, Hopkinson D. Phase change amino acid salt separates into CO$_2$-rich and CO$_2$-lean phases upon interacting with CO2 [J]. Applied Energy, 2016, 161: 41-47.

[22] Zhang J, Qiao Y, Wang W. Development of an energy efficient CO$_2$ capture process using thermos morphic biphasic solvents [J]. Energy Procedia, 2013, 37: 1254-1261.

[23] Wang L D, Zhang Y F, Wang R J, Li Q, Zhang S, Li M. Advanced Monoethanolamine Absorption Using Sulfolane as a Phase Splitter for CO2 Capture [J]. Environmental Science and Technology, 2018, 52(24): 14556-14563.

[24] Kierzkowska-Pawlak H S K. Heat of absorption of CO_2 in aqueous solutions of DEEA and DEEA plus MAPA blends-A new approach to measurement methodology [J]. International Journal of Greenhouse Gas Control, 2020, 100(1): 93-102.

[25] Zhang W D, Jin X, Tu W, Ma Q, Mao M, Cui C. A novel CO_2 phase change absorbent: MEA/ 1-propanol/H_2O [J]. Energy & Fuels, 2017, 31(4): 4273-4279.

[26] Jiang W M. Simulation and experimental research of CO_2 chemical absorption system [D]. Hangzhou: Zhejiang University, 2015.

[27] Blanchard L A, Dan H, Beckman E J. Green processing using ionic liquids and CO_2 [J]. Nature, 1999, 399(6731): 28-29.

[28] Cui G K, Lu S Z, Wang J J. Functional ionic liquids for carbon dioxide capture and separation [J]. CIESC Journal, 2020, 71(1): 16-25.

[29] Li M Y, Lu C J, XU L H. Research progress in CO_2 capture by ionic liquids-alkanolamineaqueous solutions [J]. Odern Chemical Industry, 2021, 41(2): 70-74.

[30] Jin Y, Wei H K, Duan D H. Investigation of CO_2 absorption property of hydroxypyridine ionie: liquid and their complex system [J]. New Chemical Materials, 2018, 46(7): 209-211.

[31] Guo Y T, Bao H Y, Yuan J M. Experimental study on CO_2 absorption by ionic liquid [TETAH]$^+$[BF]$^-$-ethylene glycol mixed solvent [J]. Acta Scientiae Circumstantiae, 2020, 40(2): 492-496.

[32] Tavakoli A, Rahimi K, Saghandali F, Scott J, Lovell E. Nanofluidpreparation, stability and performance for CO_2 absorption and desorptionenhancement:a review [J]. Journal of Environmental Management, 2022(313): 114-125.

[33] Ye H, Liu Q, Peng B. Review on CO_2 absorptionenhancement by nanoparticles in amine solutions [J]. Thermal PowerGeneration, 2021(50): 74-81.

[34] Saidi M. CO_2 absorption intensification using novel DEAB amine based nanofluids of CNT and SiO_2 in membrane contactor [J]. Chemical Engineering and Processing-Process Intensification, 2020(149): 107-118.

[35] Zhao Z Q, Zhang Z X, Jiang YC. Effect of nanoparticles and dispersant on CO_2 absorption by TETA solution [J]. Clean Coal Technology, 2021(27): 231-236.

[36] Jiang J Z, Zhao B, Zhuo Y Q, Wang S J. International Journal of Greenhouse Gas Control [J]. 2014(29): 135.

[37] Wang T, Yu W, Fang M, He H, Xiang Q, Ma Q. Wetted-wall column study on CO_2 absorption kinetics enhancement by additive of nanoparticles [J]. Greenhouse Gases: Science and Technology, 2015(5): 628-637.