# Amine-Based CO_2 Capture Technology Development from the Beginning of 2013—A Review

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ABSTRACT: It is generally accepted by the scientific community that anthropogenic CO_2 emissions are leading to global climate change, notably an increase in global temperatures commonly referred to as global warming. The primary source of anthropogenic CO_2 emissions is the combustion of fossil fuels for energy. As society's demand for energy increases and more CO_2 is produced, it becomes imperative to decrease the amount emitted to the atmosphere. One promising approach to do this is to capture CO_2 at the effluent of the combustion site, namely, power plants, in a process called postcombustion CO_2 capture. Technologies to achieve this are heavily researched due in large part to

● Carbon   ● Oxygen   ● Nitrogen   ● Hydrogen

the intuitive nature of removing CO_2 from the stack gas and the ease in retrofitting existing CO_2 sources with these technologies. As such, several reviews have been written on postcombustion CO_2 capture. However, it is a fast-developing field, and the most recent review papers already do not include the state-of-the-art research. Notable among CO_2 capture technologies are amine-based technologies. Amines are well-known for their reversible reactions with CO_2, which make them ideal for the separation of CO_2 from many CO_2-containing gases, including flue gas. For this reason, this review will cover amine-based technology developed and published in and after the year 2013.
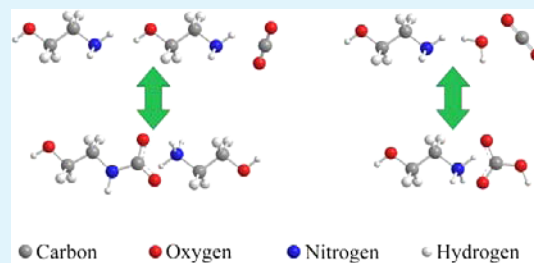
KEYWORDS: postcombustion CO_2 capture, amines, amine scrubbing, amine-functionalized sorbents, CO_2 absorption, CO_2 adsorption

■ INTRODUCTION

It has been observed that global CO_2 concentrations have been increasing since the beginning of the Industrial Revolution, roughly the year 1750. This increase has been attributed to anthropogenic CO_2 emissions, primarily from the combustion of fossil fuels for energy, and the rate of increase has grown as the consumption of fossil fuels has grown as well. Higher CO_2 concentrations have led to several environmental issues, notably an increase in global temperatures commonly referred to as global warming. This in turn leads to issues such as the melting of snow cover and ice caps, rising sea levels, and more severe weather patterns.[1−9] Preventing the increase in CO_2 concentrations is seen as essential to reducing the risks of global warming.

Technologies for remediating anthropogenic CO_2 are typically classified into three categories: postcombustion CO_2 capture, precombustion CO_2 capture, and oxy-fuel combustion. In postcombustion technology, the fossil fuels are combusted as in conventional energy generation, and then the CO_2 is captured from the effluent gas. This intuitive approach is heavily studied because it can be retrofitted to existing power plants. In precombustion CO_2 capture, the fossil fuel is gasified and reacted in a water gas shift reactor to produce H_2 and CO_2. The CO_2 is captured, while the H_2 is used for energy production. Oxy-fuel combustion utilizes pure or nearly pure O_2 for combustion, such that primarily CO_2 and H_2O are produced.[2,8,9] Of these three categories, postcombustion CO_2 capture is heavily studied because separating CO_2 at the exhaust

of combustion allows for easy and intuitive retrofitting of already existing CO_2 sources. Certain types of oxy-fuel combustion can also be retrofitted, but such an approach is less intuitive and decreases the efficiency of the furnace. Precombustion CO_2 capture requires a gasifier and therefore can only be applied to new facilities. For this reason, this review will focus on postcombustion CO_2 capture technologies; note, however, that postcombustion CO_2 is not necessarily the best of the three categories.

Several review papers have been written recently about postcombustion CO_2 capture, which typically includes absorption with both chemical and physical solvents, adsorption using solid sorbents, and membrane separations.[2,8−11] However, CO_2 capture is a fast-developing field with many new publications. Figure 1 presents the number of publications resulting from a search of the keywords CO_2 capture, flue gas, and amine on Web of Science. This rudimentary search likely underestimates the number of actual publications on this topic, but it does demonstrate the trend in publication rate. The most state-of-the-art research is already not covered by recent reviews.[2,11,12] For this reason, this review will consider publications only as early as the year 2013. Furthermore, CO_2 capture research tends to be dominated by amine-based technologies, which are well-known for the
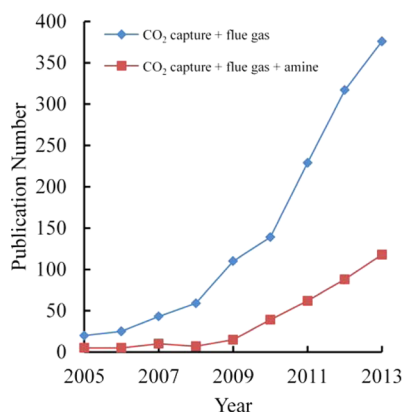
Figure 1. Number of publications each year from a search with the keywords CO_2 capture, flue gas, and amine on Web of Science.

reversible reactions with CO_2. Many types of nonamine-based technologies are researched for postcombustion CO_2 capture, which can include chemisorbents,[13,14] physisorbents,[15,16] and cryogenics.[17] However, while these technologies often have their own advantages such as higher stability or higher capacity for CO_2, they are still energy-intensive or undeveloped. Amine-based technologies are currently the most advanced and cost-effective means of postcombustion CO_2,[2,8−11] and as such this review is further limited to only amine-based CO_2 capture technologies.

■ AMINE SCRUBBING

Amine scrubbing captures CO_2 with an aqueous amine solution. In a typical amine scrubbing system designed for a power plant as shown in Figure 2, flue gas is passed through a
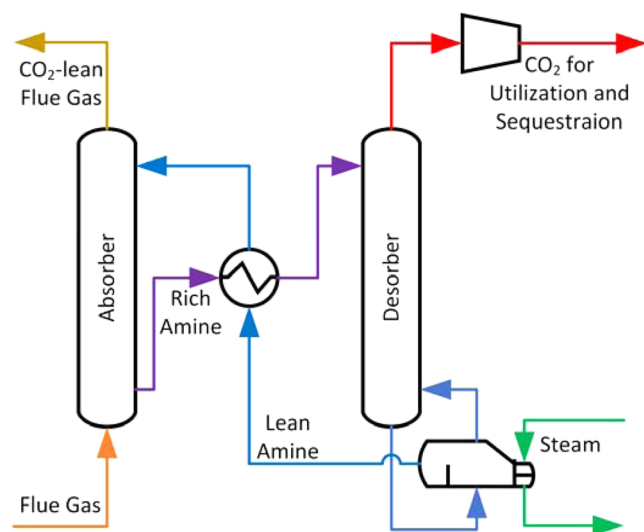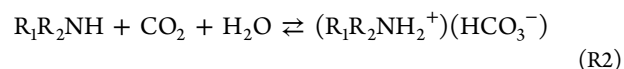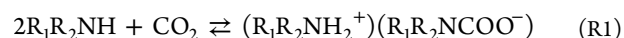

Figure 2. Typical amine scrubbing unit.

scrubber containing the aqueous amine, which absorbs the CO_2. The CO_2-rich amine is then sent to a stripper, where it is heated, typically with steam from the plant's steam cycle, and the CO_2 is released from solution and compressed for transport and sequestration. The most studied amine is monoethanol-amine (MEA), but many others can be used, such as piperazine (PZ). The process captures CO_2 primarily via carbamate formation R1 and bicarbonate formation R2.

$$2R_1R_2NH + CO_2 \rightleftarrows (R_1R_2NH_2^+)(R_1R_2NCOO^-) \quad (R1)$$

$$R_1R_2NH + CO_2 + H_2O \rightleftarrows (R_1R_2NH_2^+)(HCO_3^-) \quad (R2)$$

where R_2 is a hydrogen for primary amines. In a tertiary amine, or $R_1R_2R_3N$ where R_1, R_2, and R_3 are not hydrogens, only R2 can proceed. Regeneration of the solvent is done by heating the solution, which drives the equilibrium of R1 and R2 toward the reactants.

Amine scrubbing is currently regarded as the most economical technology for postcombustion CO_2 capture. The technology in general has been used for more than 60 years to remove CO_2 from natural gas. As such, the process is fairly well-developed. However, the conditions of flue gas and natural gas are substantially different, namely, the low partial pressure of CO_2 and high temperature of flue gas. The high temperatures can cause thermal degradation of the amines and losses through evaporation. Poisoning from SO_x and NO_x gases can occur. Amines are also corrosive and harmful to the environment. Furthermore, although it is considered the cheapest post-combustion CO_2 capture technology available, it is still an expensive technology. For these reasons, research continues into improving amine scrubbing.

Amine Loss. Amine can be lost through emissions due to their volatility, although traps are typically used that minimize this. However, amine emissions in the form of aerosols is still a concern.[18] Aerosols can more readily escape these traps, causing concern for the environment as well as increasing the required amine makeup. A more serious concern, however, is amine degradation. Amine degradation generally occurs through two methods. In oxidative degradation, amines are generally fragmented into other compounds such as organic acids, ammonia, and amides. In thermal degradation, high-temperature conditions, such as in the stripping column, tend to create larger molecules such as dimers, trimers, and amine chains. In both forms of degradation, the resulting compounds have poorer CO_2 capture properties than the original amine, including lower capacity and slower kinetics. The degradation products also can have an impact on the operating equipment (through corrosion, for example) or on the environment. While many degradation compounds have been identified and studied, work continues to identify new compounds and their potential impacts.[19]

A common approach to studying the degradation of amines is to simply leave them at a high temperature for long periods of time after exposing them to specified conditions. Although it does not reflect operating conditions for an amine scrubbing unit, this simplified approach allows for a reasonably quick study of degradation products. Zoannou et al.[20] used this approach to study the CO_2 capacity of MEA solutions that had been degraded. They used 30% w/v aqueous MEA solution that had initial loadings of 0.19 and 0.37 mol CO_2/mol MEA. They discovered that 1-(2-hydroxyethyl)-2-imidazolidone (HEIA) was the most prevalent thermal degradation product and that it increased in concentration with time, while MEA concentration decreased. Other products such as N-(2-hydroxyethyl)-2-ethylenediamine (HEEDA) and 2-oxazolidone existed in relatively small, steady concentrations, regardless of the time allowed for degradation. This suggests that HEEDA and 2-oxazolidone are intermediates in the formation of HEIA, supporting the finding of previous projects.[21,22] Most notably, however, Zoannou et al.[20] also studied the CO_2 capture of the

degraded solutions by taking samples of degraded amine, stripping them of CO_2, and measuring their new capacity of CO_2. The MEA solution initially loaded with 0.37 mol CO_2/mol MEA lost 95% of the MEA, but lost only 78% of its capacity of CO_2. The solution initially with 0.19 mol CO_2/mol MEA lost 83% of the MEA while losing only 74% of its CO_2 capacity. These results are shown in Figure 3. This is most
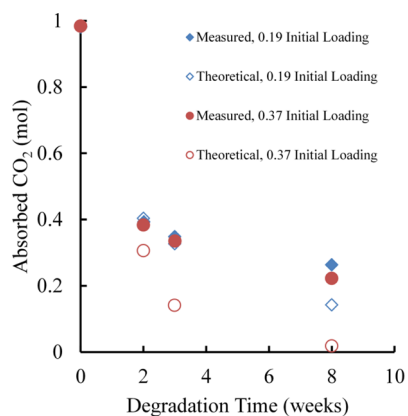

Figure 3. Measured amount of CO_2 absorbed by samples of degraded MEA compared to the theoretical amount based only on the amount of MEA remaining in solution. Degradation done with 30% w/v MEA solution at 160 °C and 20 MPa with 0.19 and 0.37 mol CO_2/mol MEA initial loading. Adapted from Zoannou et al.[20]

likely because the degradation products have a small affinity for CO_2, and it suggests that the amine makeup required in an industrial setting could be less significant than originally thought.

Rey et al.[23] discovered pyrazine and nine alkylpyrazines that are degradation products of MEA due to the presence of 2-aminoacetaldehyde, formaldehyde, and acetaldehyde, which are known to form from other reactions in MEA.[24,25] However, these compounds, which exhibit low to moderate toxicity, are formed in small amounts, which are not considered to pose a toxicological concern.[23]

Huang et al.[26] studied the effect of nitrite, sulfate, and thiosulfate, as well as fly ash, on the thermal degradation of MEA. These ions can be formed from the NO_x and SO_x gases that are present in flue gas. Although these compounds would be removed prior to postcombustion CO_2 capture, trace amounts would reach the amine absorber. In their study, Huang et al.[26] added each anion as a sodium salt to carbon-loaded MEA to make 5000 ppm of anion. The fly ash (as Kentucky fly ash, Powder River Basin fly ash, and Texas lignite fly ash) was added in a concentration of 2.0 wt %. The solutions were heated to regeneration temperatures of 125, 135, and 145 °C. It was observed that nitrite significantly increases the MEA degradation. The activation energy of degradation of pure MEA was measured to be 152 kJ/mol, but in the presence of nitrite it was 21.3 kJ/mol. Interestingly, the presence of all three types of fly ash inhibits the thermal degradation of MEA in the presence of nitrite. This is observed by the activation energy of MEA with nitrite and fly ash, which was measured to be 126 kJ/mol. The research team determined that this effect is not due to nitrite adsorption onto the fly ash but proposed that nitrite might form coordination complexes with the metals found in the fly ash. Alternatively, if the reaction occurs through a radical reaction, the radicals may react more readily with the fly ash. Fly ash alone, as well and sulfate and thiosulfate, had no

significant effect on thermal degradation of MEA. Huang et al.[26] assumed a closed solvent loop, and as such the concentrations of ions and fly ash are relatively high. This is unrealistic for an industrial setting, as a solvent loop that includes amine makeup and a purge would likely be required to maintain a steady CO_2 capture rate.

When nitrites react with amines, they can form a class of compounds called nitrosamines, which are carcinogenic and can easily escape into the atmosphere in the form of aerosols. Nitrosamines tend not to be stable when formed from primary amines and typically do not form with tertiary amines,[27−29] but they can become an issue when secondary amines are used. For example, Goldman et al.[27] considered the formation of N-nitrosopiperazine (MNPZ) when using PZ for CO_2 capture. PZ is considered over MEA because of its more favorable capacity and kinetics. In general, it is less prone to degradation, as well. Goldman et al.[27] found that the rate of MNPZ formation in the presence of sodium nitrite is first order in nitrite, hydrogen ion, and added CO_2 concentration. They estimated the activation energy of formation to be 84 kJ/mol. Furthermore, they proposed a mechanism similar to previous studies in which the carbonyl of the carbamate is subject to nucleophilic attach by the nitrite ion. The nitrosamine bond is then formed, while the carbonyl group leaves as a bicarbonate ion in a concerted step.[27,30] Fine et al.[28] developed a mathematical approach to modeling the formation of MNPZ. In their study, they determined that in an amine scrubber designed to capture 90% of CO_2, 90% of the NO_2 gas present will also be absorbed by the amine solution in the absorber either by directly forming MNPZ or by forming nitrite, which then reacts with PZ to form MNPZ in the stripper. The MNPZ will decompose in the stripper, allowing the concentration to reach steady state. Fine et al.[28] estimated that an amine scrubber for flue gas without NO_x removal would reach a steady-state MNPZ concentration of roughly 1 mM in ∼10 d. These results were comparable to measurements taken from a pilot plant, which had a steady-state MNPZ concentration of between 1 and 2 mM.

Nielsen et al.[31] studied the degradation of 8 m (mol/kg H_2O) PZ in a pilot plant using both synthetic flue gas composed of air with 12 kPa CO_2 and real flue gas from a coal-fired boiler. When actual flue gas was used, the concentration of MNPZ with time agreed well with the findings of Fine et al.,[28] above. The major thermal degradation products were ethyl-enediamine, hydroxyethyl-PZ, and aminoethyl-PZ. Both ethyl-enediamine and aminoethyl-PZ reached a peak concentration, and the concentration subsequently decreased, suggesting that these compounds further degraded. Hydroxyethyl-PZ continued to increase throughout the duration of the experiment, indicating its thermal stability. Corrosion of the stainless steel was observed through the accumulation of Fe^{2+}, Cr^{3+}, and Ni^{2+} ions, which all reached maximum concentrations of ∼1.2−2.2 mmol/kg solvent. The major oxidative degradation products observed were formate and acetate, which accumulated throughout the duration of the experiment, reaching 38.6 and 11.2 m, respectively. When similar tests were run using synthetic flue gas, thermal degradation products followed the same trend. The authors detected a small concentration of MNPZ of ∼2.8 mmol/kg under synthetic flue gas. This is interesting, because no NO_x was present to react with PZ to form MNPZ, suggesting that a small amount of nitrite formed from the degradation of PZ, which then reacted to form MNPZ. Also, relatively low concentrations of metal ions and oxidative degradation products are formed. The authors note

that the metal ions likely catalyze oxidative degradation, which explains why few oxidative degradation products form despite the high concentration of O_2.[31] However, there is no proposed explanation for the low concentration of metal ions and therefore the lower corrosion rate. This suggests, though, that other components of flue gas, such as NO_x and SO_x, are responsible for the corrosion. Alternatively, the metal ions could be coming from fly ash content; if this were true, other metals such as calcium would be present, but the authors do not mention if they monitored for these.

In a similar study, Chandan et al.[29] studied the formation of nitrosamines from morpholine. They considered the reaction of morpholine with NO_x gases in conditions representing the scrubber (20−40 °C, low carbon loading on amine), and found that as the morpholine concentration increased, the formation of nitrosamine actually decreased. This is the reverse of what is observed by Goldman et al.,[27] but this difference can be attributed to the differing experimental conditions. Additionally, Chandan et al.[29] note that the nitrosamine of morpholine actually decomposes at high temperatures typical of a stripper (125−145 °C). However, it likely does not decompose fast enough to prevent an accumulation of nitrosamine in the system, although further study is needed to verify this. Chandan et al.[29] also considered the reaction of morpholine with sodium nitrite in conditions mimicking a stripper (125−145 °C), similar to the conditions studied by Goldman et al.[27] The difference between the two, however, is that Chandan at al.[29] did not use carbon-loaded amine. They estimated an activation energy of 101 kJ/mol, which is likely high due to the formation of nitrosonium, NO^+, which comes from the splitting of HNO_2 into NO^+ and OH^-. Unlike carbon-loaded amine, which has a carbamate to react with, the NO^+ is believed to react with the nitrogen of the morpholine, producing a hydrogen ion as well.[29]

Alternative Amines and Mixtures. While MEA is widely researched and often considered the benchmark for amine scrubbing, many different amines or amines mixed with other compounds can be used. These alternatives have the potential to maximize the advantages of amine scrubbing while minimizing the disadvantages.

Li et al.[32] studied mixtures of piperazine/2-aminomethylpro-panol (PZ/AMP). They found that a mixture of 2 m PZ and 4 m AMP had a capacity comparable to that of 8 m PZ and higher than that of 7 m MEA. The mixture also demonstrated a viscosity much lower than that of 8 m PZ. The heat of adsorption was comparable to that of 7 m MEA. To improve the solubility of PZ compared to other amines, Sherman et al.[33] studied a mixture of 4 m PZ and 4 m 2-methylpiperazine. They found that the solubility window of the mixture was higher than that of 8 m PZ. Other properties remained similar to 8 m PZ or competitive with other amines and amine blends. Li et al.[34] studied the energy consumption of a mixture of MEA and methyl diethanolamine (MDEA). MDEA has a lower energy requirement for regeneration than MEA but has a slower reaction rate. They found that by using a mixture of MEA and MDEA, the overall energy consumption per ton of CO_2 decreases. More work of Li et al.[34] is discussed below, in Process Design and Optimization.

As demonstrated by the preceding paragraph, determining amine properties typically relies on systematic testing of each material to determine if it is practical for CO_2 capture. To simplify this and reduce the time required for amine selection, Porcheron et al.[35] developed a quantitative structure−activity

relationship graph machine (QSAR GM) to calculate the amine activity based on the molecular structure. In their approach, molecules are modeled as graphs, which can then be used to estimate the pK_a and pK_c (acidity and carbamate stability constants). These two parameters can be used to determine the CO_2 absorption isotherm of an amine solution. They used 46 amines to develop the statistical model for estimation, and then they subsequently used it to predict the pK_a of five other amines, chosen with a wide variety of structure. The majority of the amines used were monoamines. The model accurately predicted the pK_a of the five amines. Moreover, absorption isotherms for tertiary amines can be predicted solely with pK_a values (carbamates do not form with tertiary amines, so $K_c = 0$). The five predicted amines consisted of two tertiary amines, and their isotherms are presented in Figure 4. Research continues to predict pK_c and also to apply the technique to polyamines.
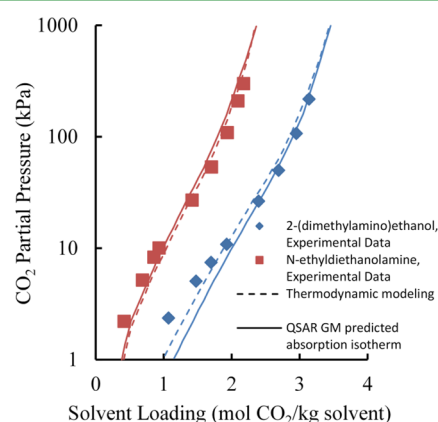

Figure 4. Isotherms of 2-(dimethylamino)ethanol (blue) and N-ethyldiethanolamine (red), including experimental data (points) and predations by thermodynamic modeling (dashed line) and QSAR GM (solid line). Adapted from Porcheron et al.[35]

It is generally accepted that R1 may proceed through a zwitterion mechanism. One amine functional group reacts with a CO_2 molecule to form $R_1R_2NH^+COO^-$. The unstable zwitterion is deprotonated by a base, typically another amine group. However, other bases can be used. With this in mind, Lu et al.[36] considered using a mixture of MEA and the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF$_4$). They used a doubly stirred absorber with pure CO_2 in the gas phase to perform their reaction. It was observed that the overall reaction rate constant was 2441.3 s^{-1} for the aqueous MEA/[Bmim]BF$_4$ mixture (303.15 K, 11.75 kPa, 0.7 kmol MEA/m^3, and 0.3 kmol [Bmim]BF$_4$/m^3) compared with 1860.3 s^{-1} for aqueous MEA under similar conditions (303.15 K, 12.10 kPa, and 0.7 kmol MEA/m^3). The rate constant increases under all conditions studied with the addition of [Bmim]BF$_4$. While this suggests that [Bmim]BF$_4$ helps catalyze the absorption of CO_2, it must be noted that many ionic liquids have a capacity for CO_2 of their own.[37−39] Further studies would be useful in determining if this observed increase is due to an enhanced effect of the mixture or is simply a cumulative observation of both individual components.

Process Design and Optimization. Li et al.[34] studied the regeneration of MEA by varying operating parameters including the solvent flow rate, solvent feed temperature, solvent loading, and reboiler temperature. To do this, they used a stripper 60

mm in diameter and 1 m in height random packed with 2.5 mm × 2.5 mm Dixon rings. They calculated the heat required for regeneration as the sum of the heat for desorption, the sensible heat, and the heat of vaporization of water, all of which are known values or can be easily measured. The energy consumption per ton of CO_2 captured tends to decrease as solvent flow rate increases to a minimum, and then it increases. The minimum value occurs between 60 and 80 g/min, depending on the concentration of MEA in solution. These results are shown in Figure 5. The energy consumption per ton
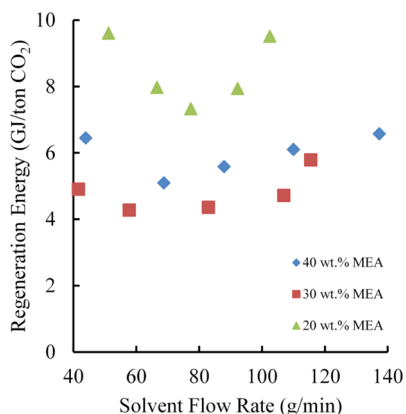

Figure 5. Effect of solvent flow rate on thermal regeneration energy of MEA solution. Adapted from Li et al.[34]

of CO_2 decreases as the solvent feed temperature increases. This is expected, because as the enthalpy of the feed increases, less energy must be added to regenerate the solvent. The energy consumption also decreases as the solvent loading increases. This is intuitive because much of the regeneration energy goes into heating the solvent, and this energy consumption tends to stay constant regardless of loading; as more CO_2 is produced as a result of the higher loading, the energy consumption per ton of CO_2 decreases. Finally, the energy consumption increases as reboiler temperature goes up, which makes sense because the reboiler is the primary energy input for solvent regeneration. This study demonstrates trends that can have a significant impact in process design. Note, however, that energy consumption in this study is only due to thermal energy in the stripper. It does not include pump work or compression work. Also, there is no discussion of how these results can scale to an industrial application. It remains unclear if either the quantitative results or the qualitative trends will be applicable at an industrial level.

The use of computers to model process designs helps to provide a quick, inexpensive way to test varying parameters on the overall system operation, and as such, the bulk of process design and optimization research was done with computers. Using a vapor−liquid equilibrium model for CO_2 in aqueous MEA developed by Wagner et al.,[40] von Harbou et al.[41] developed a rate-based model for a typical MEA absorption unit. The results were verified with four different column packings in both a laboratory set up that operates at ~10 kg
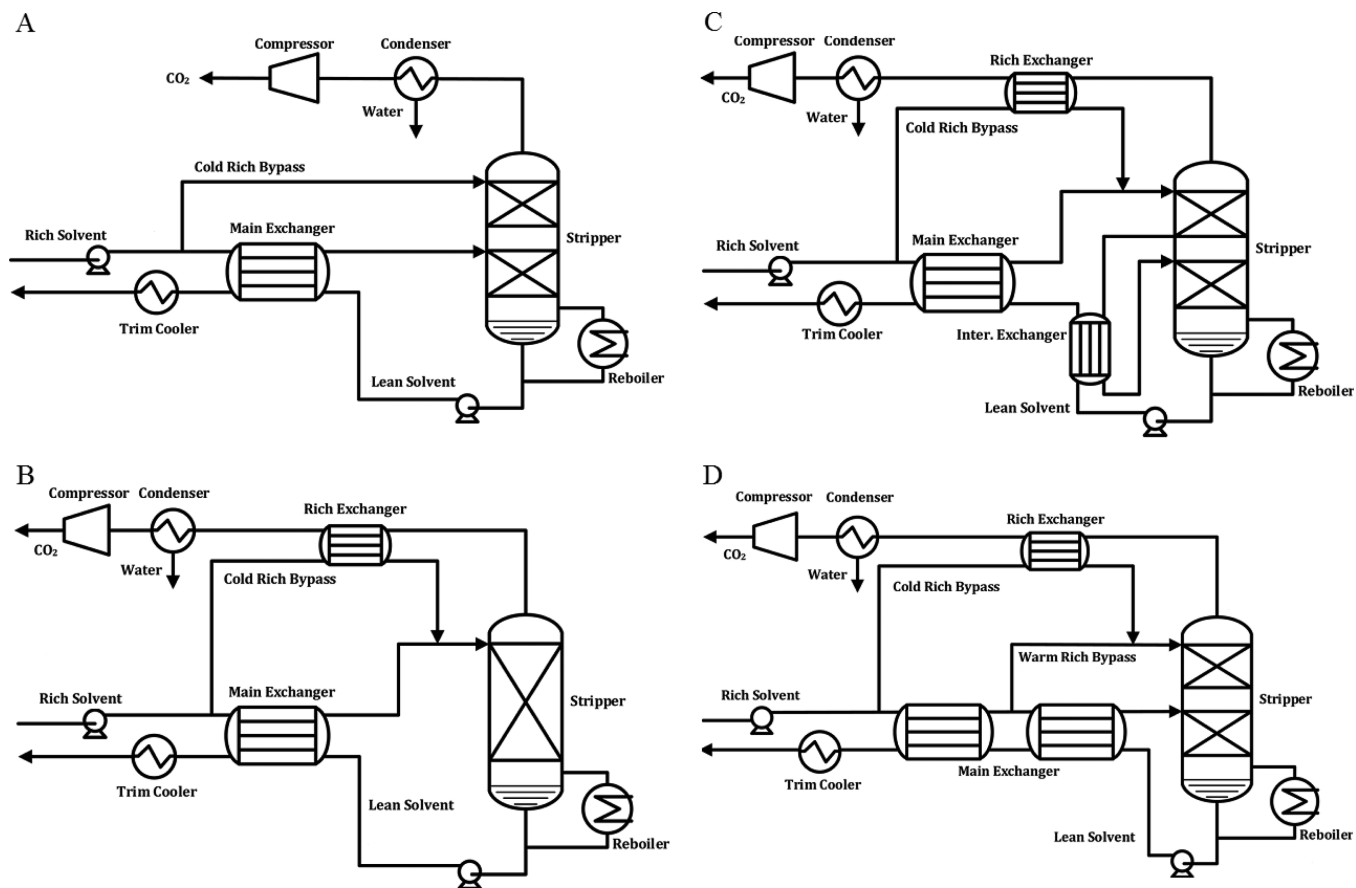

Figure 6. Flow diagrams of a simple stripper with cold rich bypass (A), simple stripper with rich exchanger bypass (B), interheated stripper with rich exchanger bypass (C), and interheated stripper with warm rich bypass and rich exchanger bypass (D). Adapted from Lin et al.[42]

Table 1. Equilibrium Capacity of Recently Developed Solid, Amine-Based CO_2 Sorbents under Dry Conditions

support	amine	equilibrium capacity (mmol/g)	CO_2 partial pressure (bar)	temp (°C)	ref
mesoporous carbon	PEI	4.7	1	30	54
mesoporous silica	TEPA	4.5	1	75	58
mesoporous silica	PEI	4.5	1	75	55
poly(methyl methacrylate)	PEI	4.4	1	50	52
Mil-101Cr	-NH_2 groups	4.3	1	20	66
silica microspheres	TEPA	4.3	1	75	53
silica microspheres	TEPA	2.6	1	35	53
mesoporous silica	PEI	2.6	1	30	55
silica aerogel	amino-alkyl-trialkoxysilane	2.4	0.81	40	65
nanoclay	APTMS	1.8	1	85	63
pore expanded silica	APTES	1.2	1	30	62
TiO_2/ZrO_2	APTMS	0.58	1	30	60
macroporous silica	linear poly-L-alanine	3.9	0.1	50	70
mesoporous silica	TEPA	3.5	0.1	75	58
fly ash extraction	PEI	3.3	0.1	90	56
silica gel	PEI+PZ	3.2	0.1	75	57
MCM-41 modified by carbon black	(3-trimethoxysilylpropyl) diethylenetriamine	1.7	0.05	25	61
mesoporous silica	(3-trimethoxysilylpropyl) diethylenetriamine	1.6	0.15	60	64
nanoclay	APTMS	1.6	0.1	85	63
Mil-101Cr (MOF)	-NH_2 groups	1.6	0.15	20	66
polymer/silica hollow fibers	APTMS	1.0	0.1	35	68
polymer/silica hollow fibers	PEI	1.0	0.14	35	69
TiO_2/ZrO_2	APTMS	0.41	0.1	30	60

CO_2/h and a larger pilot plant at Esbjerg, Denmark, which operates at 1000 kg CO_2/h. Using their model, they were able to predict the reboiler duty in almost all experiments with ±7% error. They note that choosing an appropriate model for the mass transfer is the most important source of error.

In a typical amine scrubbing unit, the loaded or rich amine, which comes off the bottom of the absorption column at a relatively cold temperature, is sent through a heat exchanger along with the regenerated or lean amine, which comes off the bottom of the stripper at a relatively high temperature. This heat exchange is done to integrate the heat usage in the unit and reduce overall operating costs. While this setup is typical of amine scrubbing, alternative layouts have been proposed. Lin et al.[42] used Aspen Plus modeling software to model some of these alternatives. The main alternatives they studied are a cold rich bypass, a rich exchanger bypass, an interheated stripper, and a warm rich bypass. For clarity, flow diagrams of the cases studied by Lin et al. are show in Figure 6. All alternative methods are aimed at reducing heat loss by preventing water vaporization or by recovering some of the latent heat of vaporized water. The cold rich bypass a helps reduce a flash at the top of the stripper, which would normally cause heat loss through water vaporization, by quenching the fluid with a cold inlet. The rich exchanger bypass allows the latent heat of vaporized water to be partially recovered, and offers the added advantage of being able to more easily tune the water balance by not reintroducing the water to the stripper as with the cold rich bypass. The interheated stripper allows the lean hot stream to be cooled further than with the main heat exchanger, allowing the cold rich feed to be cooled further than in a typical set up. This helps to quench the fluid at the top of the stripper just as the cold rich bypass but to a lesser degree. Lin et al. modified the basic interheated stripper with a rich exchanger bypass. The warm rich bypass helps recover steam heat from the hot lean stream. This approach is also modified in Lin et

al.'s study by the addition of a rich exchanger bypass. Lin et al. also studied these heat recovery methods using a flash separator instead of a stripper column; although a flash separator is generally considered less efficient, it has the potential of having lower capital cost. Obviously, the interheated stripper does not have an equivalent when using a flash separator. Their simulation considered both 8 PZ and 9 m MEA. The results of the simulation showed that all heat recovery methods reduced the total energy consumption (measured as equivalent work, or the sum of heat work, pump work, and compression work) for each amine solution. In all cases, the warm rich bypass with rich exchange bypass performed the best, reducing the energy required by 6.2% for MEA and 9.7% for PZ. The percentage decrease of energy was even larger for a flash separation, 12.4% for MEA and 16.2% for PZ. However, flash separations remained slightly more energy intensive than using a stripper.[42] These promising simulation results show that the energy requirement of amine scrubbing can be reduced with proper process design, but the results must still be verified in the laboratory or a pilot unit.

In a similar study, Walters et al.[43] developed a dynamic model for the regeneration of PZ using a two-stage flash separator. As mentioned above, flash separation has the potential to reduce the capital cost of CO_2, and although it is often considered less efficient that a stripping tower, it is important to investigate many possibilities to reduce the overall cost of CO_2 capture. Furthermore, developing dynamic models, which can account for plant shutdown and start up, unplanned disturbances, and other nonsteady-state situations, is not well-reported even though dynamic operation of CO_2 capture is important.[43,44] The model developed by Walters et al. was verified and optimized against the steady-state results of a pilot plant.[43] Verification against transient operation has yet to be done.

Well-designed process control is essential to the effective operation of any unit. Nittaya et al.[45] developed three different control schemes for a CO_2 capture from a power plant unit using MEA scrubbing. They found that a heuristic model that pairs the percent carbon capture with the lean amine feed to the scrubber and the temperature of the reboiler to the heat duty of the reboiler gave the fastest response to disturbances in the system. However, such a control scheme could fail if the reboiler temperature is not in a controlled loop or an error arises in the loop, such as valve stiction.

■ SOLID SORBENTS

It is often assumed that amine-based solid sorbents capture CO_2 via the same or similar reactions as aqueous amines, R1 and R2 above, where R2 or an analogous reaction can still proceed without the presence of bulk water because flue gas typically contains high concentrations of water vapor.[46] While evidence suggests that only R1 and similar reactions occur with or without the presence of water,[47−49] the chemistry of CO_2 capture with amine-functionalized solids will be left for other reviews. In theory, CO_2 capture with solid sorbents requires less energy than with aqueous amines primarily because there is no need to heat bulk water to regenerate the capture media. Other advantages of solid sorbents over liquid solvents can include higher CO_2 capacity, higher resistance to flue gas contaminants, and higher stability, among many others.[9,46,50] Despite these potential advantages, CO_2 capture with solid sorbents is much less developed than with liquid solvents, and research continues to minimize the cost of CO_2 capture.

Sorbent Development. Research into solid amine sorbents is at a much less-developed stage compared to aqueous amines, and as a result recent research has been dominated by the development and characterization of new materials. Table 1 provides a summary of some of the solid sorbents reported since 2013. Research at this stage focuses largely on measuring the capacity of the sorbents. While each study often performs a qualitative study of sorption and desorption kinetics, the results are difficult to compare from one paper to the next.

Amine-based solid sorbents can be separated into classes based on their preparation method.[46,51] Class 1 sorbents are prepared by physically impregnating an amine onto the surface of a support. Class 2 sorbents are prepared by chemically grafting the amine or amine functional group to the surface of the support. Class 1 sorbents tend to have a higher capacity than Class 2 sorbents due to their higher amine content but also tend to suffer from stability issues due to the loss of amine through evaporation. Class 3 sorbents are similar to Class 2 sorbents in that the amine is covalently bonded to the support, but the amine is prepared through in situ polymerization, generally resulting in hyperbranched amines. A few Class 3 sorbents were reported within the time frame of this review, and some of them will be discussed below.

Clearly, the highest capacity sorbents in Table 1 tend to be Class 1 sorbents composed of mesoporous supports impregnated with polyethylenimine (PEI) or tetraethylenepentamine (TEPA).[52−58] Mesoporous supports, which have pores with diameters of 2−50 nm,[59] are commonly used because they have high surface areas, and their typically large pore volumes help prevent the pores from becoming plugged by the amine.[54,55] PEI and TEPA are commonly used because they are relatively large molecules, and as a result they are less volatile and therefore less prone to losses. Furthermore, PEI and TEPA are

used because they are polyamines, so they have inherently high CO_2 capacities per molecule.

The Class 2 sorbents listed in Table 1 are prepared by reacting an aminosilane with a premade supporting material[60−64] or by precipitating the sorbent from an aminosilane and precursor.[65] The exception to this was the work by Khutia and Janiak,[66] who functionalized a metal organic framework (MOF) with nitro groups and then reduced the nitro groups to amine groups.

MCM-41, a silica-based structure, is often studied as a support for amine-based CO_2 sorbents. However, these high surface area materials (∼1000 m^2/g) tend to have relatively low pore diameters and pore volumes (∼4 nm and ∼1 cm^3/g, respectively). This leads to the pores becoming plugged and hindering CO_2 sorption. The pores can be expanded, but this typically requires toxic or expensive materials and processes.[61,62] Loganathan et al.[62] prepared MCM-41 and varied the amount of ammonia, one of the required preparation materials. As the amount of ammonia decreased, the pore size and volume of the resulting MCM-41 increased without decreasing the surface area. The resulting support had a surface area, pore volume, and pore diameter of 1045 m^2/g, 2.59 cm^3/g, and 30 nm, respectively. After functionalizing the support with (3-aminopropyl)triethoxysilane (APTES), the sorbent capacity was comparable to or higher than similar sorbents, which used alternative pore expansion methods.[62] Gholami et al.[61] added carbon black to the synthesis of MCM-41, and the resulting sorbent also had a large number of pores in the 20−30 nm range. The surface area, however, decreased to 726 m^2/g. They observed a CO_2 capacity comparable to similar sorbents, but it is difficult to compare due to the method used to measure CO_2 capacity.

Because TiO_2 is generally more stable than SiO_2, Aquino et al.[60] used various amines to functionalize TiO_2 and TiO_2/ZrO_2. While the TiO_2-based sorbents did generally exhibit better stability, demonstrated through hydrothermal treatment, the SiO_2 sorbents had much higher CO_2 capacity, due in large part to the more porous nature of SiO_2 compared to that of TiO_2, leading to a higher amine loading.

Hollow fiber sorbents have been considered by some researchers because they offer a structured packing material with high mass transfer. Additionally, the fibers can be modified to act as tubes that can be used for heat transfer, which can be used to reduce the potential negative effects of exothermic adsorption as well as for rapid temperature changes for sorbent regeneration.[67−69] Rezaei et al.[68] and Fan et al.[69] both developed Class 1 sorbents by impregnating PEI onto cellulose acetate/silica hollow fibers. Both reported equilibrium sorbent capacities of ∼1 mmol CO_2/g sorbent under dry, simulated flue gas conditions. Rezaei et al.[68] also prepared a class 2 sorbent using APTMS with the same supporting fibers. Again, the capacity was roughly 1 mmol/g under the same conditions. Although these capacities are relatively low compared to those of other sorbents, they can likely be improved, and combined with the other advantages of hollow fiber sorbents, this technology shows promise.

Liu et al.[70] considered using a macroporous silica support, which is less prone to plugging and has increased mass transfer relative to mesoporous supports. They functionalized a support with linear L-alanine; because the functionalization is done via in situ polymerization, this material would be categorized at Class 3, although the resulting amine is not hyperbranched. Regardless of classification, the resulting sorbents demonstrated

very high capacity for CO_2, reaching as high as 3.86 mmol CO_2/g sorbent under 10% CO_2 balanced with Ar.

MOFs are often considered a next-generation CO_2 sorbent, typically studied as a physical sorbent with high capacity and stability. However, like most physical sorbents, they can be functionalized with amine groups in an effort to further improve their capacity and selectivity.[71] Khutia et al.[66] functionalized Mil-100Cr, a chromium-based MOF noted for its water stability, with NH_2 groups. Although the surface area of the MOF reduced from 3237 to 2687 m^2/g with the addition of NH_2, the CO_2 capacity increased from 3.5 to 8.8 wt % (0.82 to 2.2 mmol/g) under a CO_2 partial pressure of 0.15 bar. The functionalized MOF is shown with thermogravimetric analysis (TGA) to be stable up to ~300 °C. A high selectivity for CO_2 over N_2 is estimated from the adsorption isotherms of each pure component, but no experiments were conducted using a mixed gas.[66] Interestingly, the capacity of this sorbent at 20 °C increases from 1.6 to 4.3 mmol CO_2/g sorbent at 0.15 and 1 bar, respectively, an increase of ~170%. Most amine-based sorbents function via chemisorption and have only small increases in capacity with increasing pressure, such as those prepared by Roth et al.[63] and Zhao et al.,[58] which increase by ~30% and ~15%, respectively, over the same pressure change. This suggests that the capacity of the MOF sorbent still has a significant contribution from physisorption, rather than being primarily chemisorption.

By using in situ Fourier-transform infrared spectroscopy (FTIR), Tumuluri et al.[72] determined that sorbents that have low amine density (measured in N atoms/nm^2) have favorable regeneration kinetics. High amine density allows adsorbed CO_2 to be stabilized by hydrogen bonding, increasing the energy required to desorb it. This study provides information useful to the development of new sorbents. However, the authors considered only dry adsorption gas; further work is necessary to determine if the same results are seen with a moist gas.

Jo et al.[73] modified TEPA using acrylonitrile via Michael addition reactions. This resulted in primary amines being converted to secondary amines and subsequently resulted in secondary amines being converted to tertiary amines. The modified TEPA was then impregnated onto poly(methyl methacrylate) to form CO_2 sorbents. The authors found that as more acrylonitrile is added, the capacity of the sorbent decreased. However, the thermal stability of the sorbent increases due to an increase in the attraction between amine molecules. Additionally, the kinetics of adsorption and desorption increase. Finding a balance between the capacity, stability, and kinetics could have significant impact on the economics of CO_2 capture.

Class 3 sorbents are similar to Class 2 sorbents in that the amine is covalently bonded to the surface of the support, but in Class 3 sorbents, the amine is usually hyperbranched, increasing the amine content. In theory, this can maintain the advantages of Class 2 sorbents, such as improved stability and mass transfer, while also increasing the capacity for CO_2. The conventional approach to preparing these materials involves the ring-opening polymerization of chemicals such as aziridine in a liquid medium.[74] To use these materials in an industrial setting, however, larger, structured materials must be used rather than small particles. Functionalizing such supports is difficult to do in the liquid phase due to diffusion limitations. To overcome this, Chaikittisilp et al.[75] studied the polymerization where the monomers are introduced in the vapor phase. This approach resulted in sorbents with capacity as high as 0.93 mmol CO_2/g

sorbent at 25 °C under 0.1 bar of dry CO_2. The reaction required higher temperatures (up to 80 °C) and longer reaction times (24 h at high temperatures, 168 h at room temperature) than the conventional synthesis method, which is typically done at room temperature overnight. Also attempting to overcome diffusion limitations, Lopez-Aranguren et al.[76] used compressed CO_2 as the reaction medium. They placed aziridine and a silica support, without physically contacting them, in an autoclave. The autoclave was charged to between 60 and 100 bar at 45 °C. The reaction only required 10 min. The resulting samples had a capacity as high as 0.95 mmol CO_2/g sorbent at 25 °C under 0.1 bar of dry CO_2. The Class 3 materials reported here have a relatively low capacity of CO_2 compared to sorbents listed in Table 1, even though Class 3 sorbents are expected to have a capacity higher than Class 2 sorbents. This is likely due to the dry conditions used for measuring capacity. Hyperbranched amines contain a high content of tertiary amines; tertiary amines can only capture CO_2 according to R2, which requires water.

Stability. While it is generally assumed that Class 2 and Class 3 sorbents are superior to Class 1 sorbents in terms of stability, few papers discussed the stability of sorbents over multiple cycles of use. Most studies that discuss long-term stability report CO_2 capacity of the sorbent over multiple adsorption/desorption cycles. However, the vast majority of papers only report less than a few dozen cycles, with 10 cycles being the most common.[52−54,58,63,64] These studies, typically done because they are easy experiments, are of limited use because sorbents would be exposed to hundreds or even thousands of cycles in an industrial setting. One exception to this, however, is Liu et al.,[70] who demonstrated a loss in CO_2 capacity of ~2% of macroporous silica functionalized with poly-L-alanine over 120 cycles. Furthermore, Begag et al.[65] studied the capacity of an amine-functionalized aerogel over 2000 adsorption/desorption cycles in a fixed bed. They found that the capacity dropped from 1.5 to 1.4 mmol CO_2/g sorbent, a relatively small change over such a large number of cycles.

Zhao et al.[77] determined that the presence of amine vapor in the reactor helped to prevent the loss of amine, thus preventing the CO_2 capacity from dropping, as seen in Figure 7. Jung et al.[52] observed a similar effect in their studies. This observation led Zhao et al.[77] to propose intentionally introducing amine vapor to prevent deterioration of the sorbent capacity. Since any amine-based capture technology would likely require an
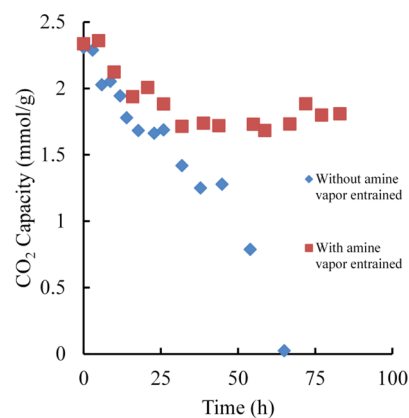

Figure 7. CO_2 capacity of TEPA/silica gel over time with and without entrained amine vapor. Adapted from Zhao et al.[77]

amine trap regardless, this may be an economically viable option. However, a detailed economic analysis is still required.

The vast majority of papers discuss the operation of sorbents under ideal conditions, typically a CO_2 concentration representative of flue gas (~10−15%) balanced with an inert gas, which is far from realistic. Rezaei and Jones[78] attempted to quantify the effects of NO, NO_2, and SO_2 gases, components that are commonly found in flue gas. They measured the capacity of each component in an inert on Class 2 sorbents, and then followed with sorption of CO_2 to determine the effect on CO_2 capacity. They found that the NO capacity on each sorbent was small (below 0.35 mmol/g) and had an almost negligible effect on the CO_2 capacity of the studied sorbents. NO_2 bonded to the sorbents irreversibly with high capacity; this resulted in a very dramatic drop in CO_2 capacity for each sorbent studied, reducing the CO_2 capacity by 60−95%. Tertiary amines had such a low capacity for SO_2 that the loss of CO_2 capacity was negligible. Secondary amines had the highest capacity for SO_2, but this bonding was relatively reversible because secondary amines had the smallest reduction in CO_2 capacity. The authors note that coadsorption of each impurity with CO_2 will be studied in the future.[78]

Process Design and Optimization. While the bulk of research into solid amine-based sorbents is sorbent development, a few papers have reported on process design. For example, Hoffman et al.[79] performed a parametric study using PEI impregnated onto silica. They considered several parameters for both sorption and regeneration, including CO_2 partial pressure, the presence of water vapor, and temperature. Notable among their findings is that the amount of water adsorbed to the sorbent remains constant regardless of the amount of CO_2 present. However, the amount of CO_2 adsorbed increases in the presence of water, as expected. Furthermore, the amount of water adsorbed can be as high as 10 times that of CO_2 (on a mole basis). With this in mind, the authors propose a CO_2 removal process that minimizes the heat duty of the regenerator by manipulating the amount of moisture on the sorbent. This process is largely theoretical at this point and needs further study, however.

Zhao et al.[80] constructed dual bubbling fluidized bed reactors and demonstrated ~85% CO_2 capture efficiency using PEI impregnated on silica under dry conditions. This efficiency increased to ~90−97% under moist conditions. While such work showing the feasibility of CO_2 capture using solid sorbents is promising, an economic analysis must still be performed.

A preliminary cost estimate was performed by Glier and Rubin[81] using a hypothetical, representative amine-based sorbent with a capacity of 1.8 mmol CO_2/g sorbent. The authors also conducted their analysis on an MOF physisorbent and a liquid amine solvent for comparison. The gross power output of the three cast studies is 566 MW for the solid amine, 612 for the MOF, and 539 for the liquid amine, compared to 650 for the plant with no capture, with a similar trend for the net power output. The advantage of solid sorbents, namely, their lower requirement for regeneration energy, is clearly evident in the higher power output compared to the liquid amine case. However, because of the capital costs involved, all three case studies become similar to one another. The estimated cost of electricity is 109, 99, and 110$/MWh for the solid amine, MOF, and liquid amine cases, respectively, compared to 60$/MWh without capture. The authors note that solid sorbents are not as well understood as liquid amines, and

this can add substantial error to estimating capital cost. The authors considered only one typical amine sorbent; studying more state-of-the-art sorbents could significantly improve the economic analysis.

FUTURE DEVELOPMENT

Research on amine-based technologies has dominated post-combustion CO_2 capture study in recent years due to the many aforementioned advantages. However, there are many technical challenges that must be overcome before these technologies can become industrialized. The largest challenge to amine scrubbing, already the most developed technology for CO_2 capture, remains the high energy demand of heating the solution for solvent regeneration. This can likely be addressed through improved heat integration. Other challenges, such as the formation of nitrosamines and amine loss, should be addressed not just because they increase the cost of CO_2 capture, but because they can pose serious health hazards.[8−10,44,50,82,83]

CO_2 capture with amine-functionalized sorbents is much less developed and faces far more technical challenges. Solid sorbents theoretically have a lower cost of CO_2 capture than aqueous solvents because there is no bulk water that requires heating; however, no solid sorbents have been able to realize this theoretical advantage to date. This is generally because solid sorbents are in the early phases of research; researchers focus primarily on developing new sorbents with high CO_2 capacity, and few economic analyses exist. Experimental studies of solid sorbents still show large energy requirements, the major component of which being for sorbent regeneration, due in large part to heat and mass transfer limitations. Heat and mass transfer may be addressed through reactor design or through the development of new sorbents that reduce these limitations; both will likely be needed. Sorbent stability, which is currently under-reported by most researchers, must also be addressed; industrial sorbents would likely be required to withstand multiple thousands of adsorption/desorption cycles.[8−10,46,50,84]

CONCLUSION

For capturing CO_2, amine scrubbing is a promising technology that is nearly ready to be applied industrially. As such, research in this field is largely toward process design and optimization, aiming to reduce the energy requirement, and thus the cost, of CO_2 capture. The majority of these works recently focus on using MEA because it has been proven to be effective, although some work continues in an effort to find new amines and mixtures that can potentially mitigate the disadvantages of amine scrubbing. Despite its advantages and its advanced stage of development, amine scrubbing remains a costly operation. Solid amine sorbents have the potential to retain some of the advantages of aqueous amines while eliminating the disadvantages, namely, the high energy requirement for regeneration. CO_2 capture using solid amines is much less developed, and as such research is dominated by sorbent development and characterization, with high molecular weight amines impregnated onto mesoporous supports demonstrating the highest capacity with reasonable stability. Substantial research must be done before this technology can be industrialized, such as continuing to increase sorbent stability and capacity. Process design and optimization with solid sorbents must also be addressed, as very little has been published in this field to date.

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Notes
The authors declare no competing financial interest.

■ **NOMENCLATURE**

AMP 2-aminopropanol
APTES (3-aminopropyl)triethoxysilane
APTMS (3-aminopropyl)trimethoxysilane
BET Brunauer−Emmett−Teller theory
CTAB cetyltrimethyl ammonium bromide
HEEDA *N*-(2-hydroxyethyl)-2-ethylenediamine
HEIA 1-(2-hydroxyethyl)-2-imidazolidone
LMTD log mean temperature difference
MDEA methyl diethanolamine
MEA monoethanolamine
MNPZ *N*-nitrosopiperazine
MOF metal organic framework
PEI polyethylenimine
PZ piperazine
QSAR GM quantitative structure−activity relationship graph machine
TEPA tetraethylenepentamine
XPS X-ray photoelectron spectroscopy
XRD X-ray diffraction

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