CO$_2$ Capture from Dilute Gases as a Component of Modern Global Carbon Management

Christopher W. Jones

School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332; email: cjones@chbe.gatech.edu

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Abstract

The growing atmospheric CO$_2$ concentration and its impact on climate have motivated widespread research and development aimed at slowing or stemming anthropogenic carbon emissions. Technologies for carbon capture and sequestration (CCS) employing mass separating agents that extract and purify CO$_2$ from flue gas emanating from large point sources such as fossil fuel–fired electricity-generating power plants are under development. Recent advances in solvents, adsorbents, and membranes for postcombustion CO$_2$ capture are described here. Specifically, room-temperature ionic liquids, supported amine materials, mixed matrix and facilitated transport membranes, and metal-organic framework materials are highlighted. In addition, the concept of extracting CO$_2$ directly from ambient air (air capture) as a means of reducing the global atmospheric CO$_2$ concentration is reviewed. For both conventional CCS from large point sources and air capture, critical research needs are identified and discussed.

INTRODUCTION

Carbon capture and sequestration (CCS): capture of CO_2 from point sources followed by concentration, pressurization, and storage in a (semi)permanent state, typically in geological formations

Flue gas: exhaust gas from a combustion process comprising N_2, CO_2, H_2O, O_2, and contaminants such as SO_x, NO_x, Hg, and particulates

Carbon management is likely to be the issue that most defines the health and welfare of society over the next 50 to 100 years. The quest for societal well-being and economic growth continues to place huge demands on the earth's fossil fuel resources, and the consumption of those resources continues to contribute massive amounts of anthropogenic carbon dioxide to the atmosphere every day. With the insight gained over past decades regarding the impact of these emissions on the global climate, there is a pressing need for society first to limit and ultimately potentially to eliminate fossil fuel emissions to the atmosphere. A first step, limiting the growth of global CO_2 emissions and eventually decreasing global CO_2 emissions, while still using fossil fuels, will require development of carbon capture and sequestration (CCS) technologies.

CCS is most often discussed in the context of trapping CO_2 from large point sources, thus limiting emissions to the atmosphere. The most frequently targeted point sources are coal-fired power plants. Such large electricity-generating point sources account for approximately one-third of global emissions, with another third coming from the transportation sector. However, in a paradigm in which widespread fossil fuel use continues, extensive application of conventional CCS can at best slow the rate of increase of the global atmospheric CO_2 level, as it impacts only large, nonmobile point sources. Negative carbon technologies are also needed, that is, technologies that could actually reduce the atmospheric CO_2 concentration.

The conventional CCS process has three steps (**Figure 1**). The first is separation and concentration of CO_2 from flue gas or another large point source. The second is compression, pipelining, and transportation of the CO_2 to an appropriate storage site. The third is sequestration in a permanent or semipermanent location (e.g., terrestrial, subterranean, or oceanic locations). The first two steps (and especially the capture step) account for most of the cost of CCS, approximately
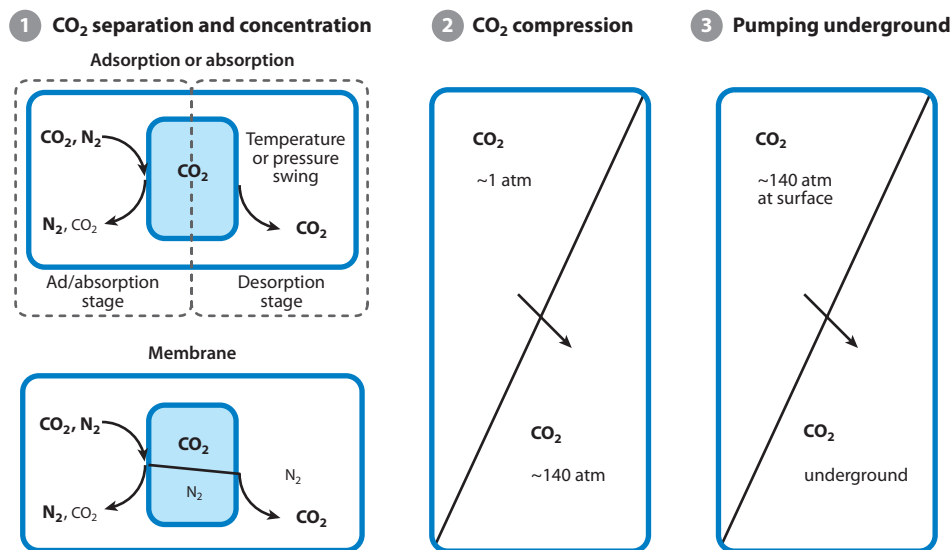

Figure 1

The three key steps in a conventional carbon capture and sequestration process. Step 1 is separation and purification of CO_2, which can be achieved in multiple ways. In the diagrams, species in bold have higher concentrations. Step 2 is compression of the CO_2 to pipeline pressures. In Step 3, the CO_2 is pumped underground for sequestration, displacing water.

75%. Thus, especially within the chemical engineering community, a major emphasis has been placed on developing more cost-effective capture methods.

For CCS at electricity-generating infrastructure, such as a coal-fired power plant, designs for postcombustion CO_2 capture processes are being evaluated. In these cases, CO_2 is separated from the power plant flue gas, which requires a technology that can separate CO_2 from a dilute (5–20% by volume), hydrated feed at relatively low temperature and pressure (near 1 atm, 35–75°C). Such postcombustion technologies can of course also be applied to new power plants, which offers potential for more effective overall process and heat integration. However, for new power plants, more often integrated gasification combined cycle (IGCC) processes (1, 2) are envisioned. Oxyfuel combustion (3) and chemical looping processes (4) are also under consideration.

In this review, selected recent advances in separation materials or methods for postcombustion CO_2 capture are explored. Readers interested in the state-of-the-art of precombustion capture (2), oxyfuel combustion (3) or chemical looping combustion (4), are directed to recent reviews. Those interested in CO_2 sequestration are directed to reviews on geologic (5, 6) and ocean sequestration (6), the approaches that may work on a scale that reasonably impacts global emissions. Of course, CO_2 can also be converted into fuels (7, 8), if a source of "free" energy is available (e.g., sunlight, algae farms) (9–11), and chemicals (12), although the latter disposition has effectively no impact on global carbon emissions due to scale.

In addition to postcombustion capture, approaches for the direct extraction of CO_2 from the ambient air are also considered. Air capture, unlike conventional CCS, can in principle account for all sources of anthropogenic carbon, including mobile sources such as cars, buses, and planes, if practiced on a sufficiently large scale (13–16). However, technologies for the extraction of CO_2 from ambient air are still in their infancy, and the ultradilute conditions ($\sim$390 ppm today) pose a significant challenge, one that only a few separation technologies might meet. Recent advances in direct air capture are discussed critically below.

IGCC: integrated gasification combined cycle

Air capture: removal of CO_2 from ambient air, typically followed by concentration, pressurization, and storage, as in conventional carbon capture and sequestration

THERMODYNAMICS OF CARBON CAPTURE AND SEQUESTRATION

To begin, it is important to understand the thermodynamics of a traditional postcombustion CCS process. Separating and concentrating CO_2 from a dilute gas obviously requires energy input. Because the power to operate the CCS process will most likely come from the electricity-generating plant, this energy cost is typically referred to as the energy penalty, or the fraction of fuel consumed by the plant that is sacrificed to provide electricity to run the CCS process. Thermodynamic calculations define the lowest possible energy penalty.

House and coworkers (17) analyzed a hypothetical pulverized coal–fired power plant, noting that coal plants are the most-targeted point sources; the United States has 1,493 in total. To calculate the minimum energy requirements associated with CCS, they defined six thermodynamic states, (a) reduced coal (fuel), (b) diluted CO_2 mixed with N_2 and H_2O in flue gas; (c) a concentrated N_2 stream at low pressure that is separated from the flue gas, (d) concentrated CO_2 at a low absolute pressure exiting the separation process, (e) concentrated CO_2 compressed for injection at the surface, and (f) concentrated CO_2 beneath pore water in a geological formation. This process requires work in moving from states (b) to (c) and (d) [W_a], (d) to (e) [W_b], and (e) to (f) [W_c]. House et al. calculated that the first energy cost, W_a, amounted to approximately 9 kJ/mol CO_2. Similarly, W_b, the energy required to compress the CO_2 to a pressure equivalent to that at the bottom of a typical well, was approximately 13 kJ/mol CO_2. Finally, the energy needed to inject concentrated CO_2 into a geological formation, displacing water in the pore space of the formation, was approximately 2 kJ/mol CO_2. These values sum to provide the lower bound of the total CCS

work, 24 kJ/mol CO_2 (or 6% of the primary energy content of the fuel), for 2 km injection and perfect second law efficiencies (17).

The authors went on to consider temperature swing and pressure swing separation processes, and they further calculated the minimum energy penalties for various conditions. In a temperature swing approach, gases are captured from the dilute gas mixture at low temperature and then released and concentrated by a swing to a higher temperature. Similarly, in a pressure swing approach, gases are captured at high pressure, and then CO_2 is concentrated and collected at lower pressures. The lower bound energy penalty was 19% for a pressure swing process and 11% for a temperature swing approach, which is lower because waste heat recovery contributes to the efficiency of the separation (17). The authors considered easily achieved energy penalties to be 33% and 40% for pressure and temperature swing approaches, respectively. They suggested a target value of 33% waste heat recovery for real processes under development, which would lead to energy penalties of 33% and 29% for pressure and temperature swing approaches, respectively. The large energy penalty of approximately one-third indicates that a substantial fraction of the fuel from the power plant will be directed at any conventional postcombustion CCS process. To this end, substantial research and development has been undertaken to reduce the energy associated with the gas separation, W_a, and hence the cost of carbon capture, assuming that the latter two energies, W_b and W_c, (representing steps 2 and 3 in **Figure 1**) will be fixed for any carbon capture process.

CO$_2$ CAPTURE BY ABSORPTION

The benchmark technology for CCS against which all emerging approaches are compared is CO_2 capture via aqueous amine absorption. The separation of CO_2 from gases using aqueous amine solutions has been known since the 1930s and is practiced commercially for CO_2 removal from natural gas, hydrogen, and other low-oxygen content gases (18). For the past several years, extensive evaluation of the scale-up of aqueous amine stripping, usually using 20–30% monoethanolamine (MEA) in water, has been completed. As a relatively mature technology, the fundamental aspects of amine absorption and stripping are generally well understood, and recent work has focused on process improvements and perturbations in amine structure for improved kinetics, stability, and other factors. MEA-based absorption processes quite likely will become a key part of the first generation of commercial postcombustion CO_2 capture technologies, assuming CCS is eventually widely applied (18). Today, as a benchmark, optimized MEA processes use approximately 0.37 MWh tCO_2^{-1} removed (18) with a thermodynamic minimum power demand of 0.11 MWh tCO_2^{-1} (11% energy penalty) from the analysis in the previous section. Because the field of CO_2 capture using amine solutions is mature relative to the others, it is not considered in detail here.

In parallel with the development of amine scrubbing processes, much research has examined alternative CO_2 separation approaches that might one day compete with amine scrubbing in second-generation CCS processes. Room temperature ionic liquids (RTILs), which typically have ultralow vapor pressures under ambient conditions and are often miscible with water, have received significant attention as possible alternative solvents. Early work on RTILs identified them as particularly good solvents for CO_2 relative to N_2, which makes them promising solvents for absorptive gas separations (19–24). These solubilities are on par with common organic solvents; RTILs also have the advantages of easy tunability and ultralow vapor pressures (19). Of the four main classes of cations used in RTILs, imidazolium, phosphonium, ammonium, and pyridinium, the imidazolium compounds have been most studied. A particular family of RTILs based on the 1-ethyl-3-methylimidazolium cation (C_2mim) has been the subject of numerous investigations. This family is a good example of a class of RTILs with useful and tunable solvent properties, including low melting points and viscosities, tunable densities, and small molar volumes (19). Early work

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Absorption: solvation of a gaseous molecule, such as CO_2, in a liquid

MEA: monoethanolamine

tCO$_2$: tonne of CO_2

RTIL: room temperature ionic liquids

C$_2$mim: 1-ethyl-3-methylimidazolium cation

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on this family of molecules showed that the nature of the anion had a significant impact on the CO_2 sorption properties (25–27), although some of these effects were muted by concomitant changes in molar volumes (19, 28). Ionic liquids have also been used for CO_2 absorption in supported form by the creation of supported ionic liquid films on porous supports such as silica gel (29).

A downside to the C_2mim family of RTILs for postcombustion CO_2 capture applications is their significant water solubility and the strong influence of hydration level on their solvent properties (19). However, by changing the functional groups on the imidazolium cations, tunable, hydrophobic RTILs have been prepared. One well-studied class of RTILs is the [Rmim][Tf$_2$N] family. Examples from this family with the side chain, R, being an alkyl, nitrile, or oligo(ethylene glycol) chain have been studied for CO_2 capture. Typically, polar chains such as nitriles and ethers gave improved performance compared with the alkyl examples (19, 28, 30–32). Although it may appear that an endless array of different RTILs could be constructed, the results thus far suggest that such screening efforts may be ill-advised, as no functional group appears to be able to impart a significant, step change in the physical CO_2 sorption properties of RTILs (19).

An alternative formulation of RTILs as CO_2 solvents combines the physical absorption properties of the ionic liquids with the chemical sorption properties of amines. This can be achieved in the form of a task-specific ionic liquid, such as an RTIL covalently functionalized with pendant amines (33–35), or with physical mixtures of amines and RTILs (36, 37). In RTIL functionalization, most often the cation is modified to contain the amine. In some cases, both the cation and anion are modified, for example, when using amino acid–based anions in the ionic liquid formulation (38, 39). Such RTILs could in some cases capture equimolar amounts of CO_2 (40). In general, combining amines with RTILs leads to significant CO_2 solubility enhancements, but at the cost of increased solution viscosity (41).

Ionic liquids have been utilized for CO_2 solubilization in other forms as well. For example, solvents have been designed that are simple organic liquids in the absence of CO_2 but become ionic liquids in the presence of CO_2 (42). Such species have been shown to be good solvents for CO_2 sorption and separation (43). Polymeric ionic liquids also have been prepared and used as solvents, with multiple similar initial reports showing that the polymeric materials had higher CO_2 capacities than their corresponding conventional RTILs (44–46). In this approach, styrenic or methacrylate monomers were functionalized with imidazolium (44–47) or ammonium (46, 48) cations, and their CO_2 solubilities were evaluated relative to their N_2 solubilities. Follow-up studies included phosphonium-based ionic liquids, and structure-property relationships for the materials were sought through variations of the cation and anion (49). Ammonium-based cations were found to be most effective, the BF$_4$ anion worked particularly well, and styrenic polymers gave better solubility than methacrylate polymers. The adsorption of CO_2 fit the dual-mode Langmuir model, which is typical of polymeric materials (49, 50). These polymerized ionic liquids also have been utilized in membrane form, and the application of these materials as well as traditional RTILs in membrane form is discussed below. The reader interested in more detail regarding the use of RTILs in CCS is directed to several recent reviews (19, 51–53).

As noted, the first large-scale applications of postcombustion CCS are likely to be dominated by amine absorption processes, as this technology is relatively mature. If this approach is considered first generation, then a variety of alternative solvents might be considered for second-generation applications; RTILs are well-studied in this regard.

CO_2 CAPTURE BY MEMBRANES

Permeation through CO_2-selective membranes is another potential means of separating CO_2 from flue gas for concentration and sequestration. Here, polymeric membranes are primarily

Adsorption: adhesion of a gaseous molecule, such as CO_2, on a solid substrate

considered, as these are the membranes most likely to be deployed on the scale needed for postcombustion CCS in an economical manner. Polymeric membranes permeate gas via a solution/diffusion mechanism, whereby the membrane permeability is a function of the gas solubility and gas permeability (54). The membranes considered here are primarily dense polymeric materials, although facilitated transport membranes [supported liquid membranes (SLMs) or hollow fiber contained liquid membranes (HFCLMs)] containing CO_2-solubilizing functional groups such as amines as well as mixed matrix membranes based on polymers with embedded molecular sieves such as zeolites or metal-organic frameworks (MOFs; see below) are also described.

When membranes were first considered for postcombustion CO_2 capture in the early 1990s, studies comparing them to the benchmark amine absorption technologies did not suggest that membranes would offer significantly better process options (55, 56). In subsequent years, most researchers focused on developing membranes that were increasingly selective for CO_2 over N_2. Furthermore, most process designs considered typically consisted of a single membrane stage or a simple multistage operation (55). However, more recent studies have suggested that modern membrane materials may allow membrane technologies to compete with amine solution CCS processes (55, 57–61). In making polymeric membranes more competitive, higher membrane permeabilities may be more critical than increased CO_2/N_2 selectivities (55, 59).

Merkel and coworkers (55) recently published an interesting study that described hypothetical multistage membrane processes that might be competitive for postcombustion CCS. They suggested cross-flow membrane modules, permeate-side vacuum, and permeate-side air sweeps as useful components of two optimal designs, assuming that membrane materials of 1,000 gas permeation unit (GPU) permeance and CO_2/N_2 selectivity of 50 were available (55). Furthermore, they presented arguments for membrane throughput as a key target for future research (55). Given the dilute nature of flue gas and the large gas volumes of a typical coal-fired power plant, the ability to effectively process huge volumes of gas is of primary importance. Furthermore, given the large cost of compressing these gas volumes, the authors argued that only minimal compression will be economically feasible and that a feed/permeate pressure ratio of five is the maximum expected to be viable. This premise fixed a compression cost associated with any membrane operation, and suitable process designs and membrane materials were suggested for development around this target. Merkel and coworkers suggested an optimum CO_2/N_2 selectivity of 20–40 for a membrane with a permeance of 1,000 GPU (55). Significantly larger selectivities would lead to larger membrane areas and costs, and significantly smaller selectivities would not produce a good separation.

Polymeric membranes with CO_2/N_2 selectivities ranging from 5 to 1,000 are described in the literature, but most selectivities fall in the range of 10–40 (54, 55). The main approach for increasing the selectivity of polymeric or polymer composite membranes is to increase the solubility of CO_2 in the membrane, usually using a facilitated transport mechanism, whereby the membrane includes species that preferentially interact with CO_2. Some of these species, such as poly(ethylene oxide), interact with CO_2 via physical interactions, whereas others, such as amines, interact via stronger chemical interactions. For example, Peinemann and colleagues (62, 63) have reported poly(ethylene oxide)-poly(butylene terephthalate) (PEO-PBT) multiblock copolymers with selectivities up to 50. Sirkar and colleagues (64, 65) reported poly(amidoamine) (PAMAM) dendrimer membranes with selectivities of 50–1,000. Subsequently, Kazama and coworkers (66, 67) showed that PAMAM dendrimer-poly(sulfone) composite membranes can offer selectivities of 100–200 on a practical scale. Ho and coworkers (68, 69) reported amine-containing facilitated transport membranes operating at elevated temperatures (110–180°C) with selectivities as high as 50–1,000. New polymers with intrinsic microporosity have been reported to be

S(I)LM: supported (ionic) liquid membrane

HFCLM: hollow fiber contained liquid membrane

MOF: metal-organic framework

GPU: gas permeation unit (10^4 Barrer cm^{-1}, or 10^{-6} cm s^{-1} cmHg^{-1}, or 7.5005×10^{-16} m s^{-1} Pa^{-1})

promising for these separations as well (70). Mixed-matrix membranes (71) that employ polymers containing dispersed materials that selectively permeate CO_2 such as zeolites (72–74) or MOFs (75–77) likely will also play an increased role in future methodologies for postcombustion CO_2 capture.

In addition to possible utilization of RTILs in absorption-based separations (see above), these species also can be used in membrane form. Supported ionic liquid membranes (SILMs) utilize RTILs impregnated into porous polymers or inorganic supports to solubilize and transport CO_2 through the membrane. An advantage of SILMs over SLMs with traditional solvents is the ultralow volatility of ionic liquids, which prevents loss of the fluid phase through evaporation. Because the diffusion coefficient of CO_2 is quite similar to that of N_2 in RTILs, these membranes rely on the significantly different CO_2 and N_2 solubilities in the RTIL to provide the separation. High CO_2 permeabilities (up to 1,000 Barrer) and promising ideal selectivities relative to N_2 (up to 61) have been reported (78), with these values exceeding the Robeson upper bound for typical polymeric membranes (19). Early process and economic analyses suggested that SILMs were more promising than absorption processes using RTILs and were competitive with traditional, benchmark MEA solution processes (23). SILMs also appeared promising for CO_2/H_2 separations (79). Of course, SILMs could be developed using traditional RTILs, with polymerized ionic liquids (80–82), or with task-specific, amine-functionalized ionic liquids (83). In some cases, systems including SILMs have run for months, showing their potential for stable operation (84). The role of water in SILMs varied depending on the RTIL used; the ubiquity of water in flue gas streams means that RTIL stability in the presence of water will be critical for these applications (84, 85). In addition, the thickness of typical SILMs needs to be reduced to allow for the large gas throughput required in CCS processes (19).

Facilitated transport membranes containing other CO_2-transporting media are also well-studied, including those using liquid amine solutions as active media (86, 87). Recently, the enzyme carbonic anhydrase has been targeted as a novel and efficient CO_2-solubilizing agent in facilitated transport membranes. Carbonic anhydrase first gained attention for use in CCS applications via studies that probed its ability to solubilize CO_2 in aqueous brine solutions, thereby producing $CaCO_3$ as a fixed form of carbon dioxide (88–90). More recently, the enzyme has proven useful as a solubilizing agent in facilitated transport membranes for flue gas applications, competing effectively against other traditional SLM media (91). Currently, Carbozyme Inc. is evaluating and scaling up the technology for CCS applications (92, 93). Preliminary results have been reported, and development of more sulfur-tolerant enzyme variants has been identified as a key technological need (92). Extremely high CO_2/N_2 selectivities in excess of 800 have been achieved using carbonic anhydrase-based HFCLMs (92, 94).

Overall, CO_2-selective membranes with permeabilities above 200 Barrer are still rare (54, 55), and thus a key target for future membrane materials is enhanced permeability (≥ 1000) without sacrificing selectivity (≥ 20) (55). Membranes, like all separation materials, must also be stable to CCS operating conditions, including exposure to flue gas contaminants such as O_2, NO_x, SO_x, Hg, and particulates, and relatively little work has been done to evaluate membrane materials in this regard. For polymer membranes, the materials also must have controllable plasticization properties at the CO_2 pressures of interest (82, 95). Finally, although the membrane advances described above have focused mostly on the development of membrane materials, advances in engineering modules such as those described in Merkel et al. (55) are also needed. In fact, the engineering of such advanced modules remains a major hurdle, perhaps more significant at present than the identification of new advanced materials with higher selectivities or permeances. Readers seeking more comprehensive reviews of membranes for CCS are encouraged to consult Powell & Qiao (54) or Ebner & Ritter (96).

CO₂ CAPTURE BY ADSORPTION

Adsorbents and adsorption processes are also being explored as alternative technologies for post-combustion CO_2 capture. The range of adsorbent materials (97) and the state-of-the-art in adsorption processes (96) for postcombustion CCS have been reviewed recently. The adsorbents generally can be categorized as high-temperature (98) or low-temperature. The high-temperature materials are based on reactive metal oxides such as hydrotalcites and calcium oxides, which will not be considered here. Low-temperature adsorbents are typically categorized as physisorbants (e.g., zeolites, MOFs, carbons, and related compounds) or as chemisorbants, which are based on amines supported on oxides, polymers, or MOFs (97). Recent advances in supported amine materials and MOFs are considered here.

Supported amine adsorbents have been organized into three classes (99). Class 1 adsorbents are based on monomeric or polymeric amines physically loaded onto or into a support, typically porous silica. Class 2 adsorbents are based on amines that are covalently linked to a solid support, often aminosilanes attached to silica supports. Class 3 adsorbents are based on porous supports upon which aminopolymers have been polymerized in situ, starting from an amine-containing monomer.

Class 2 amine adsorbents, which were first reported in 1992 (100, 101), are the best-studied. A wide variety of aminosilanes have been used to functionalize silica supports; the most studied moieties are based on a single primary amine [e.g., 3-aminopropyl trimethoxysilane (monosilane)] or on combined primary and secondary amines {e.g., 3-(2-aminoethyl)aminopropyltrimethoxysilane (disilane) and 3-[2-(2-aminoethyl)aminoethyl]-aminopropyltrimethoxysilane (trisilane)} (97). Sayari and coworkers (102–108) demonstrated that porous materials based on the pore-expanded mesoporous silica MCM-41 functionalized with trisilane were versatile adsorbents for CCS. These materials were highly selective for CO_2 over N_2, like all supported amine adsorbents, and stable over dozens of cycles in humid conditions (109).

Class 1 materials, originally developed by Song and coworkers (110, 111), have the advantage that large amounts of amines can be added into the pores of the supports. The most common amines used in such materials are poly(ethyleneimine)s, including low– and high–molecular weight varieties and linear and branched forms of the polymer (97). As a result, materials of this type generally had the highest adsorption capacities among supported amine adsorbents. Owing to the lack of strong interactions between the amines and the support, however, these materials appeared less stable than class 2 supported amine materials under some conditions (112). Nonetheless, the large number of weaker physisorption interactions may still prove to impart significant stability to these materials in some cases (113).

Class 3 materials are the most recent development in the area of supported amine CO_2 adsorbents. The first such material was based on a mesoporous silica support that was treated with aziridine to produce a hyperbranched aminopolymer on the solid surface (112). Subsequent work showed that key adsorption properties such as CO_2 capacity and kinetics could be tuned by controlling the polymer loading on the support (114). These materials are unique in that they combine attributes of class 1 and class 2 amine adsorbent materials, as they have the higher amine loadings of class 1 materials and the enhanced stability of class 2 materials due to the presence of covalent bonds between the amines and the support. Thus, class 3 materials can be considered a hybrid of the other two classes (109). At this stage, no class of supported amine materials has a distinct advantage over the others from the perspective of practical application, and work is needed to define costs, stability, and practical viability in real adsorption processes.

One significantly underappreciated factor in the supported amine adsorbent literature is the utility and applicability of these materials under practical operating conditions. In particular,

although there are many dozens of reports of adsorption of CO_2 from simulated flue gas (97), few reports describe amine absorbents' utility in the presence of trace amounts of common flue gas contaminants such as SO_x and NO_x (115). Furthermore, few reports examine the desorption of CO_2 and regeneration of the adsorbents under practical conditions. In this context, the first regeneration of supported amine adsorbents via steam-stripping was recently demonstrated (99). Significant future work on the long-term stability of supported amine adsorbents under practical adsorption and desorption conditions is needed to assess the role that these materials might play in future CCS processes. In addition, owing to the high heat of adsorption associated with these chemisorbent materials (50–100 kJ/mol CO_2), new process designs that allow for effective heat transfer may be required as well. Koros and coworkers (116) recently demonstrated an example of one such design based on hollow fiber adsorbent contactors.

MOFs (117–121) are also under wide consideration as mass-separating agents for CO_2 capture from flue gas (122, 123). MOFs are materials built of a crystalline network of metal centers connected by organic ligands as linkers. Many tens of thousands of MOF materials have been reported to date; a significantly smaller number of materials are being considered for applications in gas separation. A still smaller fraction of the known materials have been evaluated with regard to their gas adsorption properties in a manner relevant to CCS; the most common useful data reported are single component adsorption isotherms for CO_2 and N_2. Gas adsorption and separation using MOF materials has been reviewed recently (123, 124), and MOF materials hypothetically may be applied in practical separation devices based on cyclic adsorption cycles, which rely on quasi-equilibrium adsorption selectivity, or in kinetic separations based on membranes. The use of MOFs in kinetic separations through addition to polymeric (mixed-matrix) membranes has been mentioned (see above). Recently, Keskin et al. (123) comprehensively identified the key issues pertaining to practical use of MOFs for postcombustion CO_2 capture from flue gas. Thus, only highlights of recent work on CCS with MOFs are considered here.

MOFs have been widely touted as potential breakthrough materials for the development of processes that efficiently separate CO_2 from N_2. MOF materials have some of the highest CO_2 capacities known, although the large capacities typically reported were measured at elevated CO_2 partial pressures that are not relevant to postcombustion CCS. Similarly, many MOF materials have been reported to be selective for adsorption of CO_2 over N_2, but as Keskin et al. (123) point out, this intrinsically is not surprising, as this feature is common to essentially all microporous materials. What MOFs do offer is a near-limitless array of porous materials that can be tuned to impart desired pore sizes, pore wall functionalities, and other important factors that undoubtedly will make MOFs important materials in the future development of CCS processes.

Zhou and coworkers (124) recently reviewed the field of selective gas adsorption and separation with MOFs, with an emphasis on selective adsorption. Adsorption selectivity can be achieved in MOFs via molecular sieving or size exclusion, or via tuning the adsorbate-surface interactions within the porous solids (e.g., using the presence or absence of open metal coordination sites, incorporation of functional groups on the organic linkers). Tuning the composition of the MOF generates materials with heats of adsorption of CO_2 that vary widely, ranging from near 90 kJ mol^{-1} (strong chemisorption) to values as low as the heat of liquefaction of bulk CO_2 (17 kJ mol^{-1}) (123). Similarly, the CO_2 capacities span a broad range of approximately 8.5 to much less than 1 mol CO_2/kg at 298 K and 1 atm CO_2 pressure. Interestingly, in the data available to date, a strong correlation is not evident between CO_2 capacity and heat of adsorption (123).

In addition to the above factors, the significant framework flexibility in MOFs can be exploited to tune adsorption properties (124). Whereas other molecular sieves such as zeolites have shown only mild crystal flexibility characteristics owing to the strength and rigidity of the covalent bonds that make up their frameworks, MOF materials have been shown to be highly flexible, with

controlled dynamics in some cases. Undoubtedly, studies of the temperature and adsorption-induced flexibility of MOFs will continue to be a central scientific theme in the development of MOF materials in the coming years.

From a technological perspective, however, one may argue that the most significant impact of MOFs in the near term will be in kinetic separations (123). Kinetic separations based on MOF-mixed matrix membranes (76, 77), for example, use a much smaller volume of potentially expensive MOF materials compared with adsorption-based separation processes. For flue gas applications, temperature swing adsorption and membrane separation processes are expected to utilize MOFs most frequently. Regardless, many key issues for the application of MOFs in adsorption or membrane-based separation processes aimed at postcombustion CO_2 capture remain virtually unstudied in the literature to date. These include studies of (*a*) the stability of candidate MOF materials upon exposure to water vapor; (*b*) multicomponent adsorption of CO_2, N_2, and water; and (*c*) the stability of MOFs to wet NO_x, SO_x, and Hg (123). In addition, in membrane studies, specific attention must be focused on the use of appropriate MOFs that kinetically discriminate between CO_2 and N_2 (123). Selection of MOFs that have large differences in N_2 and CO_2 diffusion rates can be achieved through use of computational simulation (125); the evolving use of molecular simulation to characterize gas diffusion in this field has allowed for improved understanding of gas transport and adsorption in these materials (126–129). Also, in membrane studies, matching the permeation properties of the MOF material with the host polymer is important to achieving enhanced separations with MOF-polymer mixed-matrix membranes. Use of a polymer that permeates gas much more slowly than the MOF will yield mixed matrix membranes with modestly enhanced permeability but no improvement in selectivity over the host polymer. Application of polymers that permeate gases much more quickly than the MOF will result in MOF material bypass and thus little separation enhancement. Therefore, polymers with permeabilities that are appropriately matched with the characteristics of the MOFs must be used. Most MOF materials should be relatively compatible with polymers, so the surface modification that is commonly needed for zeolites (130, 131) when making mixed-matrix membranes is likely unnecessary.

DIRECT CAPTURE OF CO_2 FROM AMBIENT AIR: AIR CAPTURE

An alternative to carbon management via CCS is the direct extraction of CO_2 from the ambient atmosphere. Lackner and colleagues (13, 14) first introduced the idea of "air capture" as a means of reducing the global atmospheric CO_2 concentration in 1999. Although air capture is fundamentally different from conventional CCS, as they produce different products (air capture = negative carbon; flue gas capture = avoided carbon; **Table 1**), the approaches have important technological similarities. For example, both air capture for carbon sequestration and conventional CCS involve three steps, (*a*) separation and concentration, (*b*) compression and pipelining of CO_2, and (*c*) pumping and storage in a permanent repository such as an underground aquifer (**Figure 1**). Only the first step differs when comparing the two approaches; the costs associated with pipelining and sequestration are exactly the same in the two cases. Thus, it is worthwhile to begin a discussion of air capture by considering some of the key differences between it and conventional CCS (**Table 1**).

Although separating and concentrating a gas from an ultradilute source such as the air is more difficult than from a moderately dilute source such as flue gas (132), air capture has unique aspects that have the potential to make it more technically and economically tractable than one might initially suppose. First, air capture has the advantage of more flexible siting constraints (13, 14, 16). CCS processes, by definition, must be installed at large point sources. In contrast, air capture processes can be placed at various sites with significantly more flexibility, as the CO_2 source is almost

Table 1   Comparison of carbon capture and sequestration (CCS) and air capture constraints and opportunities

Property	Air capture	Conventional post-combustion CCS
Amount of CO_2	3 Tt	20 Gt year^{-1}
Distribution	~400 ppm, infinite, mostly uniform source	5–15% point sources at large flow rates
Temperature	10–30°C, ambient conditions	45–75°C
Contaminants	Generally low	Higher levels of SO_x, NO_x, Hg, particulates
Gas movement	Wind, fans	Fans
Energy used	Any source	Fossil fuel from point source
Product	Negative carbon,[a] lower ambient CO_2 concentration	Lower CO_2 emissions, avoided carbon[b]

[a]Avoided carbon is carbon that would be released to the atmosphere but is not. Avoided carbon technologies reduce the rate at which carbon is added to the atmosphere but leave the amount of carbon in the atmosphere unchanged.

[b]Negative carbon technologies remove CO_2 from the atmosphere, thus reducing the amount of carbon in the atmosphere.

globally uniform. Complete freedom of location is of course not possible, as sources of electrical or thermal energy are needed, and an outlet for the concentrated CO_2 is necessary (for example, access to pipelining or sequestration at the site). Furthermore, air capture processes are expected to be many times larger than CCS processes, owing to the volume of gas that must be processed to capture amounts of CO_2 comparable with a flue gas process (100–400 times higher gas volumes). Although this is disadvantageous because it makes such processes capital intensive (although conventional CCS is also capital intensive), it can lead to other advantages, as noted below.

Another advantage of air capture relative to CCS is that air capture processes are not required to have a specific throughput (13, 14, 16). Therefore, the air capture process can be optimized around process efficiency rather than around capturing a specific volume of gas. The target for most CCS processes is 90% capture of the CO_2 in the flue gas. The incremental costs associated with capturing the last 5% of the flue gas compared with the first 5% are quite significant. In contrast, it is anticipated that most air capture processes will capture significantly less than 90% of the CO_2 in the ambient air, as the process will instead be optimized for minimal cost and energy use per kilogram of CO_2 captured. To capture larger volumes of CO_2, air capture processes will simply need to be practiced on large scales.

A key technical challenge in CCS is how to handle common contaminants in the flue gas stream such as SO_x, NO_x, Hg, and particulates (**Table 1**). In general, the levels of these contaminants in air capture processes, with the possible exception of particulates, are expected to be significantly lower. Air capture will also generally be carried out on gases at lower temperatures (at ambient conditions), which is advantageous relative to CCS processes that typically operate at higher temperatures.

In principle, any energy can be used in air capture processes, including renewable energy associated with wind or solar power processes (133–137), biomass-derived energy, or nuclear energy (138) (**Table 1**). In contrast, the power plant itself, which by definition is operating on fossil fuels, nearly always will power CCS processes. A key potential disadvantage of air capture processes is the need to move massive volumes of gas without the aid of the natural draft found in flue gas stacks (**Table 1**). To this end, air capture processes require designs that allow for effective movement of the air at low cost; using the wind could decrease air movement costs.

In considering hypothetical processes for air capture, two potentially costly aspects are immediately apparent. First, the discussion above suggests that systems will need to be large to process

huge volumes of air, at least 100–400 times greater than in typical CCS processes, to capture the same amount of CO_2. This figure may be larger in practice, as only a fraction of CO_2 moving through the process likely will be captured, as noted above. Thus, researchers must develop designs for air-sorbent or air-solution contactors that are low cost and can be produced on a large scale. Large pressure drops also must be avoided. Second, for a sorbent or solution to effectively extract CO_2 from the air (at ~400 ppm CO_2), very large heats of reaction with CO_2 would be advantageous to allow for high ad/absorption capacities. A similar or larger amount of energy must be input to regenerate the adsorbent or solution, and thus the sorbent or solution regeneration step is expected to be a significant process cost, as it is in conventional CCS technologies.

Following Lackner's suggestion to develop air capture technologies as a mode of combating climate change, several groups evaluated potential air capture processes. Initial attempts centered on known, existing technologies for CO_2 removal from air. The older literature dating back to the 1940s and 1950s describes numerous studies evaluating the extraction of CO_2 from dilute gases such as the air via aqueous, basic absorption processes (139–141). In 1977, Steinberg & Dang (142) evaluated eight methods for the extraction of CO_2 from the atmosphere for the purpose of converting the CO_2 into fuels or chemicals. These methodologies included various forms of absorption and stripping (five different modes), removal of water vapor by adsorption with molecular sieves and subsequent extraction of CO_2 by refrigeration, removal of water vapor by compression refrigeration and subsequent extraction of CO_2 by refrigeration, and removal of water vapor by adsorption on molecular sieves and adsorption/desorption of CO_2 from dry air by molecular sieves (142). Of the eight processes, absorption and stripping of air by a dilute aqueous potassium carbonate solution required the least energy. To this end, many of the air capture processes evaluated since 1999 have been based on absorption in aqueous solutions of alkaline bases.

Zeman & Lackner (143) described a hypothetical process based on absorption of CO_2 in aqueous sodium hydroxide solutions to form sodium carbonate. The resulting solution was then causticized using calcium hydroxide to produce calcium carbonate, a process known since 1884 and widely used in the paper industry (the Kraft Process). The calcium hydroxide was recovered by calcination as calcium oxide, followed by rehydration, driving off a concentrated CO_2 stream for recovery (**Figure 2**). This initial study identified calcination, which is typically carried out at 700–1,000 K, as the most energy-intensive and expensive step (143). Subsequently, Keith and coworkers (16) followed up with a basic economic analysis of a similar air capture process along with an air capture policy discussion.

In 2006, Mazzotti and coworkers (144) reported a more detailed process design as well as an energetic and economic analysis of a hypothetical air capture process based on a sodium/calcium cycle, as described above, using packed column contactors. Again, the calcium carbonate calcination, requiring a 900°C temperature in the calciner, proved to be the most energy-intensive
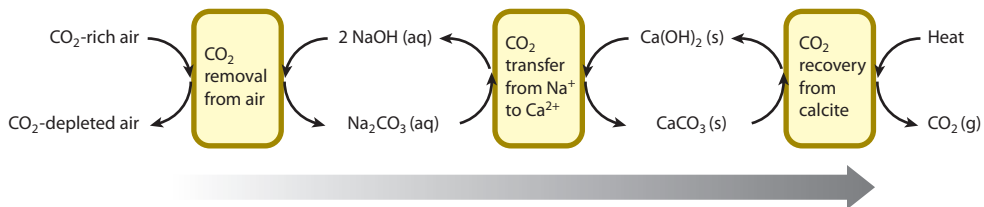

Figure 2

The first process proposed for air capture, which includes CO_2 absorption by sodium hydroxide to produce sodium carbonate, causticization with calcium hydroxide to produce calcium carbonate, and calcination to recover CO_2.

step. An overall energy balance estimated that the real energy demand for such a process ranged between 12 and 17 GJ tCO_2^{-1} captured, depending on the mode of calcium carbonate precipitation used. The authors pointed out that the energy released by combustion of coal and methane is 9 and 20 GJ tCO_2^{-1} emitted, respectively. They thus argued that the removal of CO_2 from the atmosphere using such a process based on Kraft-inspired technologies was questionable (144) and suggested the need for processes that used low-cost energy (133–138).

Shortly thereafter, Zeman (145) followed up with an economic analysis of a similar process and compared the energetic costs of the three processes side by side. The three Kraft-inspired processes had minor variations in calcium carbonate drying, CO_2 purification, and other steps, but the overall scope of each process was similar. The results showed a significant variation in total energy requirements; the average was 546 kJ/mol CO_2^{-1} captured, with a high of 679 and a low of 442 kJ/mol CO_2 captured. These energy requirements were quite significant, as the carbon intensity of electricity production varies from 190–1,900 kJ/mol CO_2 around the world (see below) (146). Thus, in many areas of the world, the energy required for capturing CO_2 via this air capture process would produce more CO_2 than would be captured.

Recognizing that these energy costs were quite large, at this stage the field began to move toward new or modified designs that offered lower energy consumption and hypothetical process costs. A series of papers appeared describing processes similar to those mentioned above, but the designs utilized waste heat from nuclear reactors (138, 142) or energy from solar radiation (only a calcium hydroxide–calcium carbonate loop was proposed, removing the sodium component) (135). Seeking to improve the basic design and reduce costs, Keith and coworkers (147) reported a prototype air capture system that used a spray tower rather than a packed column contactor. An energetic and economic analysis showed it to be a viable alternative to the traditional packed column design, and the CO_2 capture process (without solution regeneration considered) was estimated to cost approximately \$100 tCO_2^{-1} captured (compared with ∼\$50 tCO_2^{-1} total for modern CCS processes using MEA absorption cycles). Given that the solution regeneration and sequestration steps are likely to be at least equally expensive, the overall cost of the process was expected to be quite large (147). Thus, the estimated cost of air capture via this process was approximately four times the cost of a modern MEA-based CCS process. Later, Mahmoudkhani & Keith (147) suggested the adoption of a direct sodium tri-titanate causticization process, originally developed in the pulp and paper field, as a replacement for the conventional lime causticization approach (148). This alternative methodology was reported to reduce energy consumption during sodium hydroxide regeneration by half. Although the suggested fourfold higher cost of alkali-absorption-based air capture processes relative to conventional amine absorption-based CCS may be striking considering the 100–400-fold reduction in inlet CO_2 concentration and considering that only a few process design iterations occurred, such an alkali-based absorption process is unlikely ever to compete directly with conventional CCS on an energy or cost basis.

In 2008, the first analyses of adsorption-based approaches for air capture were reported. Steinfeld and coworkers (149) completed a thermodynamic and thermogravimetric analysis of the adsorption of CO_2 from the air using a sodium hydroxide–sodium bicarbonate–sodium carbonate adsorption cycle. They showed that the slow carbonation rate of the solids was a significant technical challenge that led to slow adsorption rates and inefficient use of the sorbents; less than 10% carbonation had occurred after several hours of air treatment. Such inefficiencies would lead to enormous solid inventories in the hypothetical process, making the approach infeasible. Steinfeld then considered the use of a calcium oxide–calcium carbonate adsorption cycle similar to those studied in high-temperature CCS processes for years (97). Adsorption was evaluated at temperatures of 290–390°C with adsorbent regeneration via decarbonation at 875°C. Use of a solar-driven fluidized bed reactor was suggested to offset energy costs (134, 137).

In 2009, Lackner & Brennan (15) first reported an alternative air capture design based on adsorption using weakly basic, quaternary ammonium ion-exchange resins. In this initial report, they suggested that commercial resins such as Marathon A (Dow Chemical) could be used to achieve CO_2 uptake rates similar to those of sodium hydroxide solutions when the resins were swung between the bicarbonate and carbonate forms, and that simple exposure to moisture could remove the CO_2. This report marks a noteworthy move away from processes based on absorption or adsorption steps with a significant heat of reaction with CO_2. Past designs had used sodium or calcium hydroxides as the reacting species in solid forms or in solution. These highly exothermic reactions required substantial heat input to regenerate the sorbent or solution, leading to significant energy costs. On the contrary, the suggested regeneration of the quaternary ammonium resins, requiring only water, implies that the bicarbonate-carbonate capture swing in the adsorption step is unlikely to be very exothermic. Thus, the adsorption capacity of the adsorbent materials could be quite small, and therefore large masses of adsorbent may be needed, although the authors report rather high capacities (0.25–0.85 mol CO_2/kg).

In a follow-up narrative report with few experimental results or details, Lackner (146) described the Marathon A–based process in slightly more depth. He suggested the creation of low pressure drop contactors using woven filters, akin to household furnace filters, made from the adsorbing resin (60%) in an inert polypropylene matrix (40%). The resin reportedly cycled between the carbonate and bicarbonate forms upon exposure to air and was regenerated by exposure to aqueous carbonate solutions, water, or water vapor. Exposure to water vapor at 45°C was sufficient to desorb CO_2 from the resin and convert it back to the carbonate form (146). The desorption of CO_2 from a bicarbonate-loaded resin upon exposure to water is a curious finding, as it goes against the typical law of mass action, as noted by the author, but it was reported to be highly reproducible. The counterintuitive chemistry in this process warrants more detailed investigation to understand the molecular-level details.

The suggested adsorption-desorption process then involved adsorption on a (mostly) dry resin in the carbonate state to generate bicarbonate, followed by exposure to significant humidity from a sodium carbonate brine to generate a CO_2 and water vapor mixture, from which the CO_2 could be recovered easily via compression. An operating process would utilize multiple filters, with one in adsorption mode and the others in various stages of regeneration using either water vapor or liquid water to induce desorption (146). The authors stated that the entire process could be operated via mechanical energy with no need for heat. An overall energy consumption of 50 kJ/mol CO_2 captured (1.1 MJ/kg CO_2 captured) was reported, which would make the process energetically tenable in nearly any environment. For instance, the authors reported that the carbon intensity of energy varied considerably by region, ranging from 190 kJ/mol CO_2 released in a heavily carbonized economy such as China, to 230, 290, 1,700, and 1,900 kJ/mol CO_2 in the United States, Germany, Brazil, and France, respectively. Thus, even in China, nearly four times as much CO_2 would be captured by such a process than would be generated to provide the power for the process. The authors suggested that the first prototypes should break even at a carbon cost of $200 $tCO_2{}^{-1}$, with process improvements and economies of scale pushing this cost of capturing carbon much lower over time (146). These results appear quite promising, but in the absence of a detailed quantitative process description and account of experimental results, including details of the intriguing moisture-swing approach, the literature will remain filled with more detailed reports of other processes that suggest air capture is too costly for large-scale deployment (144, 149).

Other groups are also pursuing novel air capture materials and processes that are based on adsorption at ambient temperatures. In 2009, Jones and coworkers (150) described the use of oxide-supported amine materials, namely hyperbranched aminosilicas, as adsorbents for the extraction of CO_2 from simulated air (400 ppm CO_2 in an inert gas). In 2010, Sayari and coworkers

(151) provided the first detailed report of the use of silica-supported amines for the extraction of CO_2 from ambient air. Clearly, supported amine adsorbents are promising materials for use in potential air capture processes, as they are potentially regenerable by treatment with low-cost waste heat in the form of steam (99). Undoubtedly, the scale-up and demonstration of additional designs for air capture will be reported in the coming years.

In closing this section, it is important to mention that much of the work on air capture has not been completed by chemical engineers. As a result, peer-reviewed reports of detailed chemical engineering process designs, including complete mass and energy balances, are relatively rare. Indeed, most of the reports currently in the peer-reviewed literature are general and descriptive, or offer detailed, rigorous analyses of small parts of an overall process (several reports cited in this section are not peer-reviewed publications in archival journals). Until more quantitative analyses are completed on the newer designs (other than the sodium hydroxide–calcium carbonate absorption cycle, which appears energetically too expensive) (132, 145), it is difficult for a reader to independently assess the practical utility of many of the new process designs that are partially described in the literature. Thermodynamics suggest that air capture likely will be more energetically costly compared with conventional CCS, but the degree of difference depends on how closely air capture processes can approach perfect thermodynamic efficiencies. The ratios of the minimum work required for conventional CCS with 90% capture versus air capture with 25–90% capture range from 2.65–2.86 (132). Only with detailed accounts of air capture process designs can policymakers, scientists, and engineers compute the true costs for air capture processes and then weigh the appropriate levels of investment in CCS, which can only slow the rate of increase of the global atmospheric CO_2 concentration, and air capture, which can actually reduce the global CO_2 concentration in the atmosphere.

In that context, it is worth discussing the propensity for some to consider conventional CCS and air capture as "either or" options to mitigate anthropogenic carbon emissions. In the short term, conventional CCS should be practiced to limit emissions from large point sources. But successful development of conventional CCS in no way removes the need for development of air capture technologies. Its ability to account for emissions from mobile sources and other advantages with regard to siting and throughput make it an interesting partner for conventional CCS in global carbon management. Many detractors of air capture technologies routinely point to the energy costs associated with stand-alone air capture facilities in comparison with conventional CCS. But, as noted above, air capture and CCS deliver different products. Initial air capture developments will likely focus on smaller-scale applications such as CO_2 production for food processing (146) or for feeding to algae farms (where concentration to high purity CO_2 is not needed). Furthermore, the possibility of coupling modern cogeneration processes with technologies that utilize the cogenerated low-temperature heat to drive the CO_2 capture process offers the potential to use fuels more efficiently while simultaneously removing carbon from the atmosphere. The field of air capture is still in its infancy, but more detailed analyses of various process designs and additional, low-cost processes are clearly needed, which provides many opportunities for chemical engineers to play a crucial role in the development of the field.

SUMMARY POINTS

1. The most mature technologies for postcombustion CO_2 capture use aqueous amine absorption processes. They have already been demonstrated on a moderate scale and will likely become the dominant first-generation CCS processes.

2. Second-generation CCS processes may ultimately compete with amine absorption; alternative absorption, adsorption, and membrane processes are under study.

3. Recent advances in separation materials include the development of CO_2-selective adsorbents, membranes, and solvents based on (*a*) supported amine materials, (*b*) MOFs, (*c*) polymeric membranes, (*d*) mixed-matrix membranes, (*e*) facilitated transport membranes, and (*f*) RTILs.

4. Research on novel solvents, adsorbents, and membrane materials has not yet sufficiently considered the long-term stability of these materials in the presence of flue gas components such as H_2O, NO_x, SO_x, O_2, Hg, and particulates. For adsorbents, practical and scalable regeneration processes have not been widely described.

5. Removal of CO_2 from the ambient air via air capture is under consideration as a complementary technology to conventional CCS and could ultimately reduce the concentration of CO_2 in the atmosphere.

6. Several air capture processes are at various stages of development, but the literature currently lacks detailed, quantitative reports of hypothetical air capture processes, which leaves an unclear picture of the utility and viability of air capture as a technology.

DISCLOSURE STATEMENT

ACKNOWLEDGMENTS

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146. A narrative description of a quaternary ammonium resin–based air capture process with humidity swing regeneration.

Contents

Errata

An online log of corrections to *Annual Review of Chemical and Biomolecular Engineering*
articles may be found at http://chembioeng.annualreviews.org/errata.shtml