

Advances in CO₂ capture technology: A patent review

Bingyun Li^{a,b,c,*}, Yuhua Duan^a, David Luebke^a, Bryan Morreale^a

^a National Energy Technology Laboratory–Regional University Alliance (NETL-RUA), Morgantown, WV 26505, United States

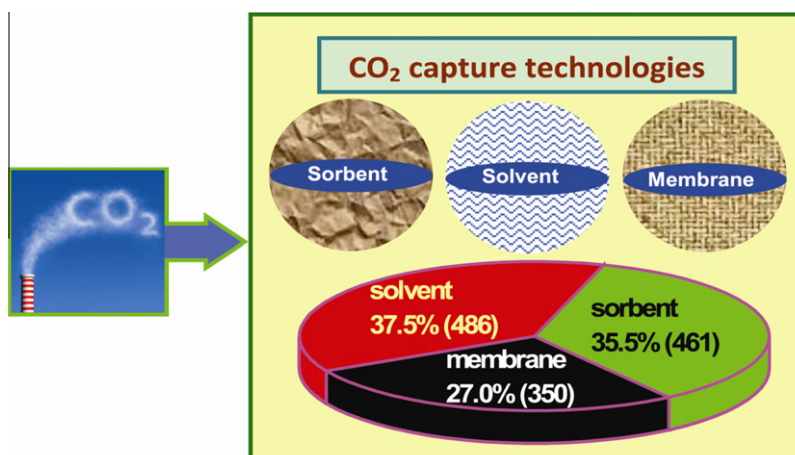
^b Department of Orthopaedics, School of Medicine, West Virginia University, Morgantown, WV 26506, United States

^c WVNano Initiative, Morgantown, WV 26506, United States

HIGHLIGHTS

- ▶ Timely updates on carbon capture technologies: More than 1000 patents on solvent, sorbent, and membrane.
- ▶ More patents on solvent and sorbent compared to membrane.
- ▶ Environmental and health concerns exist regarding carbon capture technologies.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon dioxide (CO₂) emissions are believed to be a major contributor to global warming. As a consequence, large anthropogenic CO₂ sources worldwide will eventually be required to implement CO₂ capture and storage technologies to control CO₂ emissions. In order to guide the establishment of policies for CO₂ removal, we reviewed the current status of CO₂ capture patents and technologies based on the Espacenet patent database and found that more than 1000 patents have been published on sorbent, solvent, and membrane. More than 60% of these patents were published since the year 2000, and a sharp increase in patent numbers was seen in the last several years; ~25% patents were published in the last 2 years. Substantially more patents on CO₂ removal and separation technologies are expected in the coming years. Meanwhile, the top four major types of patents, which consist of more than 2/3 of these patents, were patents granted by Japan (JP), United States (US), World Intellectual Property Organization (WO), and China (CN), and approximately half of the patents were JP and US patents. Unfortunately, no current technologies for removing CO₂ from large sources like coal-based power plants exist which satisfy the needs of safety, efficiency, and economy; further enhancement and innovation are much needed.

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* Corresponding author. Addresses: Biomaterials, Bioengineering & Nanotechnology Laboratory, West Virginia University, Morgantown, WV 26506-9196, United States. Tel.: +1 304 293 1075; fax: +1 304 293 7070.

E-mail address: bili@hsc.wvu.edu (B. Li).

URL: <http://www.hsc.wvu.edu/som/ortho/nanomedica-group/> (B. Li).

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1. Introduction

With the rapid development of modern civilization, carbon dioxide (CO₂) is produced in large quantities in industry, for instance, by the combustion of coal, coke, and natural gas, in the fermentation of carbohydrate materials and sugars, in the manufacture of cement and lime, and etc. Indeed, more than 30 billion tons of CO₂ are added to the atmosphere each year. However, the emission of CO₂, one of the major greenhouse gases, has raised great concerns about the relationship between anthropogenic CO₂ and global warming; the emission of CO₂ may have contributed to urban smog, acid rain, and health problems [1,2]. In another scenario (e.g., a space capsule, a submarine, a subterranean mining environment, or a closed-circuit respiratory apparatus), CO₂ produced by the occupants of a closed ecological system must be removed from air. Therefore, CO₂ removal is of importance. As a result, a variety of methods have been studied and patented for the removal and separation of CO₂ from industrial waste and mine gases, from the air, and from gases produced by animal metabolism, such as human respiration.

Many technical challenges, however, are facing potential large-scale implementation of CO₂ capture in power plants [3]. Fig. 1 presents the simplified pathways of CO₂ production, capture or separation, and storage or re-utilization. Among them, CO₂ capture is the key step economically and has two technology routes: (1) pre-combustion: capture from the reformed synthesis gas of an upstream gasification unit; and (2) post-combustion: capture CO₂

from the flue gas stream after combustion. Upon capture, CO₂ can be stored underground, used for enhancing oil recovery, and as carbon resources to be converted into other useful compounds [4,5] (Fig. 1). The current technologies for CO₂ capture and separation mainly include solvent, sorbent, and membrane, and the mechanisms for CO₂ capture depend on the chemistry of the capturing approaches or materials. For instance, in the monoethanolamine (MEA) approach, CO₂ is captured based on its interaction with amines to form bicarbonates or carbamates.

During the past few decades, much effort has been devoted to developing new technologies for CO₂ capture, storage, and utilization. Many reviews on this topic are already published in the literature [3–7]. However, to our knowledge, there is no report on patented innovations on CO₂ capture technology. In order to address the importance of patented innovations, in this article, the current status of patents on CO₂ capture is reviewed. It is noteworthy to mention that clean energy technologies (e.g. solar, wind, nuclear, and proton exchange membrane fuel cell, and hydrogen-based power generation) that can lower CO₂ emission are not discussed here but are very important.

2. Method for carbon capture patent search

In this study, the Espacenet website (<http://www.epo.org/searching/free/espacenet.html>) [8] was used to search for patents; Espacenet is the most comprehensive patent database available. Espacenet collects published patent applications from 1836 to today and from more than 80 countries with more than 70 million patent documents.

Accessing the Espacenet website, an advanced search using keywords in patent titles and abstracts was carried out. A search for CO₂ capture sorbent patents was conducted using (i) title keywords of CO₂ sorbent, CO₂ absorbent, CO₂ adsorbent, carbon dioxide sorbent, carbon dioxide absorbent, carbon dioxide adsorbent, and (ii) combination keywords of sorbent, absorbent, or adsorbent (in title) and CO₂ or carbon dioxide (in abstract) and vice versa. It is worth mentioning that “absorption” is the incorporation of a substance in one state into another of a different state (e.g., liquids being absorbed by a solid or gases being absorbed by a liquid), and “adsorption” is the physical adherence or bonding of ions and molecules onto the surface of another phase (e.g., amines adsorbed to a solid surface). A search for patents on CO₂ capture solvent was carried out using (i) title keywords of CO₂ solvent or carbon dioxide solvent, and (ii) combination keywords of solvent (in title) and CO₂ or carbon dioxide (in abstract) and vice versa. Similarly, patents on CO₂ capture membrane were searched via (i) keywords (in title) of CO₂ membrane, or carbon dioxide membrane and (ii) combination keywords of membrane (in title) and CO₂ or carbon dioxide (in abstract) and vice versa. Note that the

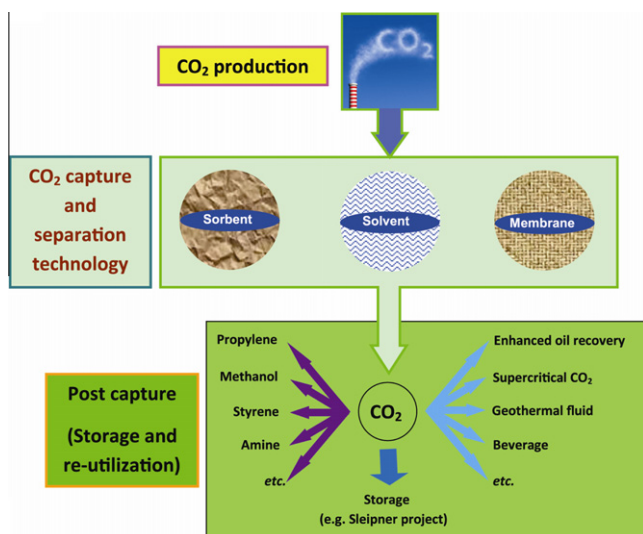


Fig. 1. Schematic diagram of CO₂ production, capture, and storage or re-utilization.

abstracts or the whole patents of all those found were carefully reviewed and were grouped into the corresponding categories.

A patent search was conducted in March 2012 and a total of 9840 patent abstracts were found. The abstracts or the complete patents (if the abstracts were not clear about the type of technology) were reviewed and those patents (a total of 1297) that belonged to CO₂ capture solid sorbent, solvent, and membrane were grouped and analyzed. No patent with the same patent number was counted more than once and patents that were filed as different patent types were counted as multiple patents.

2.1. Limitations

Patents that were not in the Espacenet database [8] were not included. Potential patents for CO₂ capture that were not mentioned in the patent title and abstract were not included; a search for full texts (claims and description) of all the patents was not possible due to limitations of the database.

3. Carbon capture patents

A total of 1297 patents on CO₂ capture solid sorbents, solvents, or membranes were found. Among them, approximately 37.5% (486 patents) belonged to solvent, 35.5% (461 patents) belonged to solid sorbent and membrane, respectively (Fig. 2). The likely reason that there were more patents on solvent and solid sorbents was because more types of materials can be used as solvent or solid sorbents. For instance, ethanolamines, ammonia, alkali metal solutions (e.g., alkali metal hydroxides, carbonates, or phosphates), amino acid salts, polyglycol ether, and ionic liquids can be used as solvents [9–33], and soda-lime, active carbon, zeolite, molecular sieve, silica gel, amine solid sorbents, metal organic frameworks, metallic compounds (e.g., metal oxides, hydroxides, peroxides, silicates, and carbonates), etc. can be used as solid sorbents [34–65]. On the contrary, relatively fewer materials have been investigated as CO₂ capture membranes. The major materials for membranes are polyimides, zeolites, and fluoropolymers [66–86]. According to the patents found, only 79 patents (~6%) were published by 1980. An increase in patents was observed from 1981 to 1989, and a more significant increase has been seen since 2008; 45 patents were published in 2007 while 189 patents were published in 2011 (an average of one patent every 2 days) (Fig. 3). Indeed, more than a quarter of the patents were documented in the last 2 years (i.e. 2010–2011). The major increase in patent applications around the 1990s was probably related to the initial adoption of the Kyoto Protocol in 1997, the realization of the Sleipner project in 1996 (environmental concern), and potential benefit of CO₂ injection for enhanced oil recovery (commercial drive). The sharp increase in patent applications since 2008 may be correlated with the more intense global focus on the potential relationship between climate change and CO₂ release, and the emphasis on reducing energy penalty, cost, and health and environmental issues relating to carbon capture technologies [1,87,88]. Every 5

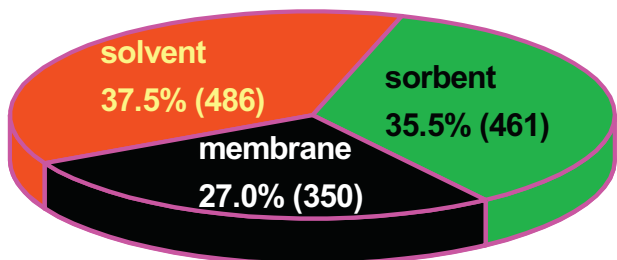


Fig. 2. Numbers of solvent, sorbent, and membrane patents through March 2012.

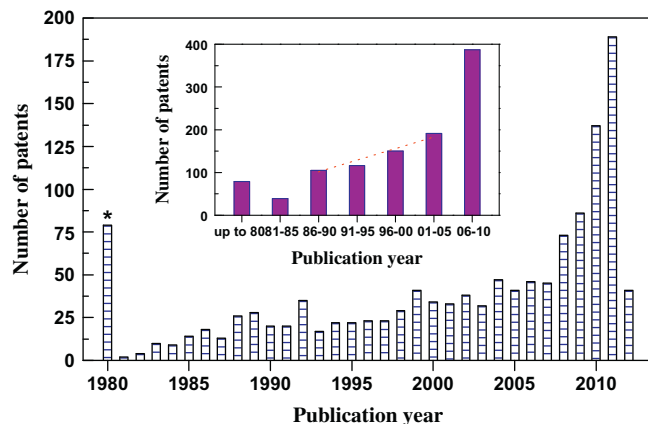


Fig. 3. Number of publications vs. publication year. *Total patents published by 1980.

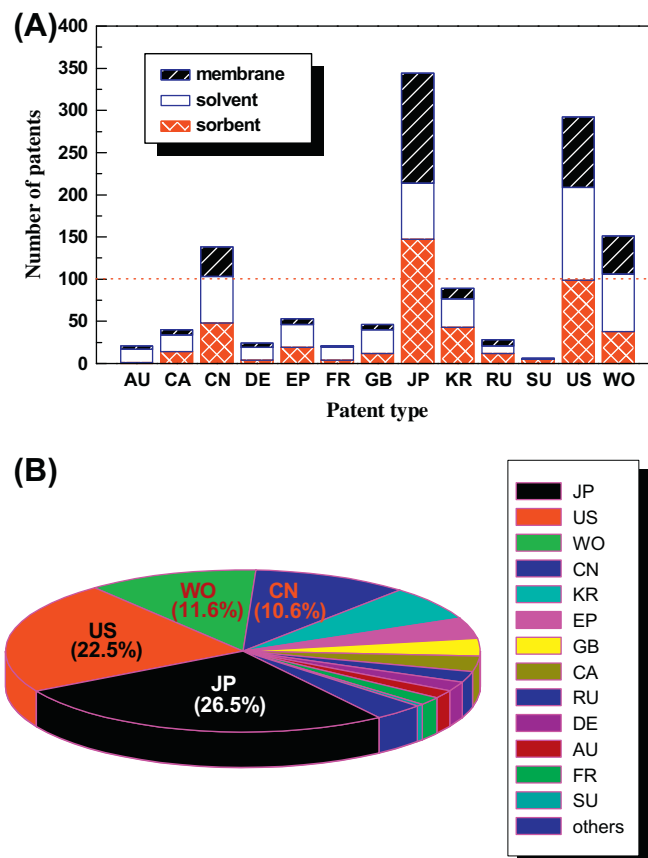


Fig. 4. (A) Number of patents in solvent, sorbent, and membrane vs. patent type. (B) Distribution of patent type. Country codes: AU (Australia); CA (Canada); CN (China); DE (Germany); EP (European Patent Office); FR (France); GB (United Kingdom); JP (Japan); KR (Korea); RU (Russian Federation); SU (Soviet Union, USSR); US (United States); WO (World Intellectual Property Organization, WIPO).

years, the number of patents increased approximately linearly during 1986–2005, followed by a sharp increase in 2006–2010 when the number of patents doubled (Fig. 3 inset). This change may indicate that a significant interest in CO₂ capture research and development has taken place from 2006 to today.

According to the patent type (i.e. the country or organization where the patent application was filed or granted), JP, US, WO, and CN are the top four types of patents found, making up approx-

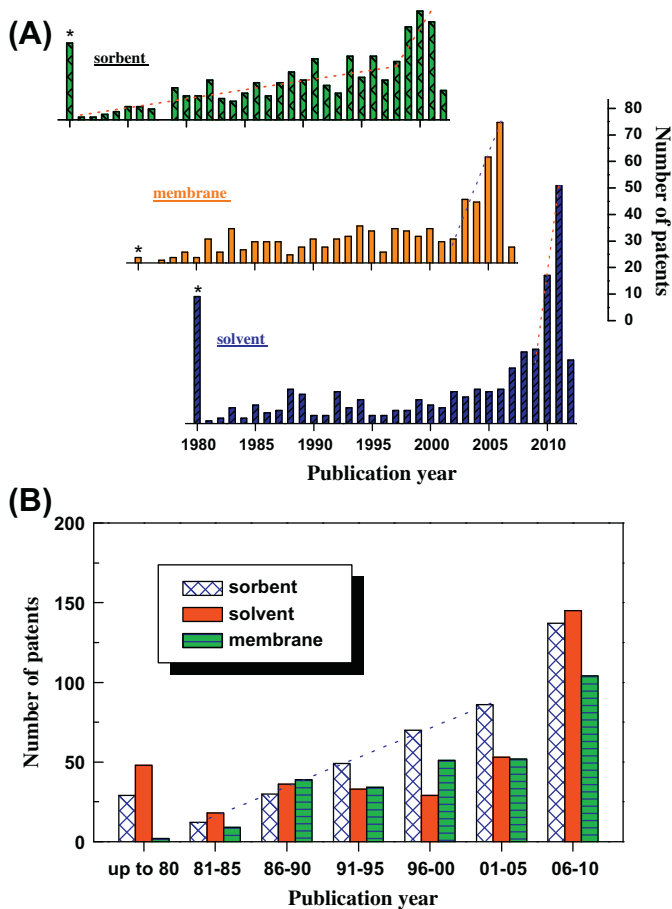


Fig. 5. Number of patents vs. publication year: (A) Yearly distribution and (B) distribution every 5 years. *Patents published by 1980.

imately 71% of patents (Fig. 4). Among them, JP has more than 344 patents alone and the US has more than 292. Each of the four types of patents (i.e. JP, US, WO, and CN) has more than 100 patents on CO₂ capture (Fig. 4A), corresponding to 26.5%, 22.5%, 11.6%, and 10.6% of the total patents, respectively (Fig. 4B). It is interesting that, for the JP patent type, substantially more technologies were patented as sorbent (192 patents) or membrane (139 patents) compared to those as solvent (53 patents). By contrast, for the Australia (AU), Germany (DE), European Patent Office (EP), France (FR), and United Kingdom (GB) patent types, solvent patents dominated (Fig. 4A).

The numbers of CO₂ capture patents on sorbent, solvent, and membrane are presented each year from 1981 to today (Fig. 5A). One can see that there was a relatively stable increase in solid sorbent patents from 1981 to 2008 followed by substantial increases in 2009 and 2010; more than 41 solid sorbent patents were documented in 2010 alone. In comparison, the number of patents on solvent and membrane has seen more ups and downs although, overall, their numbers are increasing. Before 1980, not much activity was seen in membrane patent applications and significantly more patents were published on solvent than sorbent (Fig. 5B). These numbers may explain why there were fewer membrane patents overall compared to solvent and sorbent (Fig. 2). Moreover, it seems that, from 1981 to 2005, a linear increase every 5 years in the number of patents was observed in sorbent (Fig. 5B). A substantial increase every 5 years in the number of patents was observed for sorbent, solvent, and membrane during 2006–2010 (Fig. 5B). This increase in patents during 2006–2010 may be related to an agreement among industrialized countries including the

United States and Japan. In the United Nations Conference on Environment and Development held in Rio de Janeiro, Brazil in June 1992, the industrialized countries agreed to reduce emission by 2010 of greenhouse gases by 5.2% compared with the level in 1990.

More details on representative examples of patents on solid sorbent, solvent, and membrane are discussed as follows.

3.1. Sorbent

A variety of materials have been studied as CO₂ sorbents through chemical reactions and physical absorptions. A number of patents have been published on soda-lime, active carbon, zeolites, molecular sieve, alkali metal oxides, silver oxide, lithium oxide, lithium silicate, carbonates, silica gel, alumina, amine solid sorbents, metal organic frameworks, and others. For instance, GB341748 [89] was one of the earliest sorbent patents. In this patent, solid alkali carbonates were applied to remove CO₂ in the presence of steam at ordinary or increased pressure over a temperature above the condensing point of steam. The carbonates may have been mixed with or distributed upon an inert carrier such as pumice. The sorbents were regenerated by heating to 220 °C in vacuum, in a current of air, or by passing ammonia over the mass at 180 °C where ammonium carbonate was formed and removed by sublimation from the mixture. Similarly, US4433981 [90] described a technology to impregnate alkali metal or alkali earth metal oxide or salt in an inert porous carrier (e.g., aluminum oxide) for CO₂ removal.

One of the first patents on zeolite was published as GB871750 [91], where CO₂-containing gases were separated by passing a dried or undried gaseous mixture through a zeolite material. The zeolite was activated first by heating to remove water and to produce a crystalline structure having interstitial voids at the nanometer scale. The sorbent was regenerated by passing a heated regenerating gas.

In 1951, US2545194 [92] was published and described a process for removal of CO₂ from the atmosphere of a submarine using activated carbon. This likely was the first patent on air capture although materials like lithium hydroxide, which has the limitation of lasting only a certain number of hours, were used much earlier for CO₂ removal from the atmosphere of a submarine.

In 1972, GB1283822 [93] first described the physical impregnation of CO₂-reactive polymers (e.g., tetraethylene pentamine and polyethyleneimine) inside a porous support (e.g., alumina, pumice, clay, and activated carbon) for CO₂ removal. The amine based sorbents can be easily regenerated. An improved approach was described in US5492683 [94] where a mixture of an amine compound with a polyol compound was impregnated in a porous support. The polyol compound was intended to increase the CO₂ desorption rate of the amine. The supported amine-polyol sorbent was comprised of 1–25 wt.% amine, 1–25 wt.% polyol, with the balance being support. The solid sorbent could adsorb and desorb CO₂ at relatively high rates at ambient temperatures. Enhanced CO₂ cyclic removal capacities in either dry or humid air flows was further achieved in US5876488 [95] where solid sorbent had an increased concentration of amines of 35–75 wt.%.

Solid sorbents that can selectively remove multiple gases were also described in the literature. US5779767 [96] described a mixed adsorbent of alumina and zeolite that could remove CO₂ and H₂O simultaneously from gas flows. EP0862938 [97] discussed layers of alumina and zeolite adsorbents that remove nitrogen oxides, H₂O, and CO₂ from gas streams. US6358302 [98] described the removal of H₂O, CO₂, nitrogen oxides, and/or hydrocarbons from gas streams using composite adsorbents.

It is worth noting that solid sorbents are preferred for the removal of CO₂ from manned space vehicles where there is an absence of gravity and where there are restrictions as to weight and

volume. However, caustic sorbents (e.g., alkaline hydroxides) should not be used in an undersea environment where water leakage or flooding may lead to immediate caustic injuries or damage.

3.2. Solvent

The simplest solvent approach for CO₂ removal would be water scrubbing under pressure which is based on the comparatively high and selective ability of water to dissolve CO₂ to CO, H₂, and CH₄. The water can be regenerated by pressure swing since CO₂ is driven out of the water when the pressure is lowered to ambient pressure. One of the earliest such patents was GB286622 [99] published in 1929 in which CO₂ was absorbed in water under pressure and subsequently regenerated. However, the efficiency of water scrubbing is low and numerous improved solvent technologies have been subsequently developed. For instance, technologies on alkali metal materials, sterically hindered amines, amino acids, and ionic liquids have been reported. GB1543748 [100] described a process to remove CO₂ from a cracked gas using an aqueous solution of an alkali metal salt of an N-dialkyl- α -aminomonocarboxylic acid. More recently, research about sterically hindered amines as new alkanol amines absorbents are vigorously being conducted. Among them, US4112052 [101] accomplished CO₂ removal by a process comprised of contacting the normally gaseous mixture with an aqueous amine solution, wherein at least one of the amines was a sterically hindered amine (e.g., 2-amino-2-methyl-1-propanol). EP0671200 [102] disclosed the removal of CO₂ from combustion gases at atmospheric pressure using an aqueous solution of an amino acid metal salt and piperazine. US7527775 [103] explained a process and method for separating CO₂ using a regenerable ionic liquid with an anion having a carboxylate function.

In WO2007094939 [104], a unique approach was further revealed and CO₂ was separated from flue gas using an ion pump method instead of relying on large temperature or pressure changes to remove CO₂ from a solvent. The ion pump method dramatically increased the concentration of dissolved carbonate ion in solution and increased the overlying vapor pressure of CO₂. As a result, CO₂ was removed from the downstream side of the ion pump as a pure gas. The ion pumping could be obtained from reverse osmosis, electrodialysis, thermal desalination methods, or an ion pump system having an oscillating flow in synchronization with an induced electric field.

3.3. Membrane

Membrane separation may be considered a biomimetic approach; almost all separation processes in living biological systems are performed through a membrane. Membrane separation is intrinsically energy efficient; however, challenges exist in both membrane material selection and membrane design for effective CO₂ separation. In general, polymer membranes and composite membranes have been developed. JP61133118 [105] disclosed a CO₂ separation membrane comprising a polyimide having superior heat and chemical resistance and superior performance for CO₂ separation. KR20030012224 [106] reported polyvinylidene difluoride hollow fiber membrane contactors for CO₂ separation and CA2470993 [107] described a hollow fiber membrane with crosslinkable properties. The latter had a high resistance to plasticization. US2009017514 [108] disclosed a modular membrane for CO₂ separation followed by subsequent conversion of CO₂ and H₂ into ethanol and other desirable liquid products by building a biofilm next to the membrane.

More recently, the “mixed matrix membrane” concept was developed as one type of membrane which comprised a continuous phase polymer carrier with porous particles dispersed therein. Patents such as US6503295 [109], US6562110 [110], and

Table 1
Pre-combustion technology advantages and challenges [114].

CO ₂ capture technology	Advantages	Challenges
Physical solvent	<ul style="list-style-type: none"> CO₂ recovery does not require heat to reverse a chemical reaction Common for same solvent to have high H₂S solubility, allowing for combined CO₂/H₂S removal System concepts in which CO₂ is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems 	<ul style="list-style-type: none"> CO₂ pressure is lost during flash recovery Must cool down synthesis gas for CO₂ capture, then heat it back up again and re-humidify for firing to turbine Low solubilities can require circulating large volumes of solvent, resulting in large pump loads
Solid sorbent	<ul style="list-style-type: none"> CO₂ recovery does not require heat to reverse a reaction Common for H₂S to also have high solubility in the same sorbent, meaning CO₂ and H₂S capture can be combined System concepts in which CO₂ is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems 	<ul style="list-style-type: none"> Some H₂ may be lost with the CO₂ CO₂ pressure is lost during flash recovery Must cool synthesis gas for CO₂ capture, then heat it back up again and re-humidify for firing to turbine
H ₂ /CO ₂ membrane	<p>H₂ or CO₂ permeable membrane:</p> <ul style="list-style-type: none"> No steam load or chemical attrition <p>H₂ permeable membrane only:</p> <ul style="list-style-type: none"> Can deliver CO₂ at high-pressure, greatly reducing compression costs H₂ permeation can drive the CO shift reaction toward completion – potentially achieving the shift at lower cost/higher temperatures 	<ul style="list-style-type: none"> Membrane separation of H₂ and CO₂ is more challenging than the difference in molecular weights implies Due to decreasing partial pressure differentials, some H₂ will be lost with the CO₂ In H₂ selective membranes, H₂ compression is required and offsets the gains of delivering CO₂ at pressure. In CO₂ selective membranes, CO₂ is generated at low pressure requiring compression
Water gas shift membrane	<ul style="list-style-type: none"> Promote higher conversion of CO and H₂O to CO₂ and H₂ than is achieved in a conventional WGS reactor Reduce CO₂ capture costs Reduce H₂ production costs Increase net plant efficiency 	<ul style="list-style-type: none"> Single stage WGS with membrane integration Improved selectivity of H₂ or CO₂ Optimize membranes for WGS reactor conditions

Table 2
Post-combustion technology advantages and challenges [114].

CO ₂ capture technology	Advantages	Challenges
Solvent	<ul style="list-style-type: none"> Chemical solvents provide a high chemical potential (or driving force) necessary for selective capture from streams with low CO₂ partial pressure Wet-scrubbing allows good heat integration and ease of heat management (useful for exothermic absorption reactions) 	<ul style="list-style-type: none"> Trade off between heat of reaction and kinetics. Current solvents require a significant amount of steam to reverse chemical reactions and regenerate the solvent, which de-rates power plant Energy required to heat, cool, and pump nonreactive carrier liquid (usually water) is often significant Vacuum stripping can reduce regeneration steam requirements, but is expensive
Solid sorbent	<ul style="list-style-type: none"> Chemical sites provide large capacities and fast kinetics, enabling capture from streams with low CO₂ partial pressure Higher capacities on a per mass or volume basis than similar wet-scrubbing chemicals Lower heating requirements than wet-scrubbing in many cases (CO₂ and heat capacity dependent) Dry process—less sensible heating requirement than wet scrubbing process 	<ul style="list-style-type: none"> Heat required to reverse chemical reaction (although generally less than in wet-scrubbing cases) Heat management in solid systems is difficult, which can limit capacity and/or create operational issues when absorption reaction is exothermic Pressure drop can be large in flue gas applications Sorbent attrition
Membrane	<ul style="list-style-type: none"> No steam load No chemicals Simple and modular designs 'Unit operation' vs. complex 'process' 	<ul style="list-style-type: none"> Membranes tend to be more suitable for high-pressure processes such as IGCC Trade off between recovery rate and product purity (difficult to meet both high recovery rate and high purity) Requires high selectivity (due to CO₂ concentration and low pressure ratio) Poor economy of scale Multiple stages and recycle streams may be required

US7306647 [111] described the incorporation of porous and molecular-sieving entities within a polymer matrix for improved CO₂ removal. The inclusion of highly size- and shape-selective molecular sieves (e.g., zeolite) may substantially improve overall membrane selectivity due to their ability to discriminate penetrants within a polymer matrix. As a result, the selectivity of a mixed matrix membrane may be much higher than the selectivity achievable using the neat polymer as a membrane alone.

4. Environmental and health concerns

Overall, the impact of CO₂ capture technologies on the environment and health is not well studied and comparative investigations are needed. Carbon capture sorbents, solvents, and membranes may have an unpleasant or detrimental effect on the environment and/or human health. For instance, it has long been known that the dust of certain carbon capture sorbents is harmful. Dust from sorbents such as lime and alkaline compounds can be produced during their manufacture, handling, and storage; the dust, due to its alkaline and caustic nature, may be irritating to the nasal cavity, pharynx, skin, eyes, and mucosa of humans or animals. Moreover, the dust can contaminate the environment causing damage to the surfaces with which it comes in contact. In the case of industrial applications where large quantities of sorbents, solvents, and membranes are used, or in the case of extracting CO₂ from an anesthesia gas system, the impact of carbon capture materials on the environment and health is more of a concern. Attempts have been made to reduce dust or vapor formation, for instance, by providing solid sorbents with a protective coating (e.g., US3259464 [112]); this process, however, may also impair the CO₂ capture capacity of the sorbent. Use of filters has also been studied in applications like self-contained diving gear but the filters may increase back pressure and cause a serious reduction of air flow.

In many cases, an organic solvent is used for CO₂ removal or is involved in the preparation of sorbents or membranes for CO₂ removal. In sorbents or membranes, the organic solvent must be stripped before they can be used for CO₂ removal. Obviously, solvent recovery systems are quite expensive and there is always a

possibility that the solvent will not be completely stripped. In such cases, the sorbents or membranes may be odorous. If the solvent is toxic then the prepared sorbents or membranes may not be used in applications like an anesthesia flow system or a life-supporting gas system.

In addition, CO₂ removal in applications like inhalation anesthesia or inhalation drug therapy systems may further require that the CO₂-sorbing compound within sorbents must be chemically inert (benign) to the anesthetic or drug in contact. For instance, magnesium compounds such as magnesium oxide and hydroxide are found to be more inert to inhalation anesthetic compared to calcium hydroxide (US5390667 [113]).

5. Perspective and conclusions

Carbon dioxide is an inert gas that has no heating value of combustion and it is an environmental concern since it is the major greenhouse gas. Varied technologies have been developed for CO₂ capture and separation. Each technology has its strengths and limitations. For instance, Tables 1 and 2 summarize the advantages and limitations of solvent, sorbent, and membrane as pre- and post-combustion technologies. However, there are currently no practical processes for removing CO₂ from large CO₂ sources (e.g., power plants). For example, the current MEA approach would add ~80% to the cost of electricity (COE) for a new pulverized coal plant, and ~35% to the COE for a new advanced gasification-based plant [114].

To overcome the limitations of CO₂ removal cost using current technologies, substantial improvements will have to be implemented. Fortunately, some efforts have been made to develop advanced sorbents, solvents, and membranes. One such effort is to achieve fast absorption and desorption rates by the addition of promoters/activators/catalysts. WO2006089423 [115] described a formulation that includes carbonic anhydrase in order to increase the absorption rate of CO₂ absorption solutions. US7132090 [116] disclosed a process where CO₂ enriched air was passed through a gas diffusion membrane to transfer the CO₂ to a fluid medium. The CO₂ rich fluid is subsequently passed through a matrix containing a catalyst specific for CO₂ to accelerate the conversion of CO₂ to car-

bonic acid. US2004259231 [117] reported immobilized biocatalysts that enable concentration and solubilization of CO₂ by allowing catalytic contact with water spray. WO2004028667 [118] also described the biological transformation of CO₂ into carbonated species and US2010303694 [119] told of the use of a catalyst or enzyme that promoted the transformation of CO₂ to carbonic acid. Moreover, US2010180764 [120] described the synergetic effects of an absorbent containing three or more amine compounds selected from linear or cyclic amine compounds having a primary amino group and linear or cyclic amine compounds having a secondary amino group.

Another effort has been to develop sorbents, solvents, and membranes with cost-effective materials. US7678351 [121] applied an acid treatment to eggshells, an environmental nuisance, to fabricate regenerable sorbents for CO₂ removal. JP2004261658 [122] and US2004228788 [123] disclosed the effective use of coal ashes for CO₂ fixation by subjecting flue gas to coal ash water slurry or coal ash eluate and ultimately using the coal ashes as cement or clay material. CN101804322 [124] disclosed a high-strength dry type CO₂ adsorbent for regeneration using river sediment as a carrier.

Still, future research should focus on the achievement of fast kinetics (both sorption and desorption) of CO₂ transport in sorbent, solvent, and membrane. Fast kinetics may be achieved via unique structural design (e.g. nano-layered sorbents [34,35]) and the use of effective catalysts with high stability. Moreover, focus should be directed on the potential impacts of CO₂ capture technologies on safety; detailed toxicity studies are much needed.

In summary, a significant number of patents have been published in sorbent, solvent, and membrane for CO₂ removal and separation. Approximately 50% of the patents are published as JP and US patents. Relatively more patents on solvent and sorbent are found compared to membrane. An increase in the total number of patents of every 5 years was observed, and a sharp increase in patents was seen in 2006–2010 and on in sorbent, solvent, and membrane. Future technology focuses should be on fast CO₂ transport kinetics, safety, and cost reduction. It is reasonable to believe that significant breakthroughs and a significant increase in the number of patents on CO₂ capture will occur in the coming decade.

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