

**READDRESSING
THE BALANCE:
EXPLORING
RESEARCH
TRENDS IN
CARBON DIOXIDE
SEQUESTRATION**

CAS

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American Chemical Society



Introduction

Carbon dioxide (CO₂) is a critical component for plant life and consequently all animal and human life on Earth. However, CO₂ accounts for the bulk of atmospheric greenhouse gases and these gases trap solar radiation in Earth's atmosphere, resulting in global warming. Since the Industrial Revolution, we have witnessed a rapid rise in atmospheric CO₂ emissions, which has alarming consequences for the environment.¹⁻³ This process is exacerbated by increasing populations and widespread industrialization. Global warming is now predicted to increase to 1.5°C in the period from 2030 to 2052 (**Figure 1**) (relative to pre-industrial levels).⁴

In 2015, at the 21st Conference of Parties on Climate Change (COP21), an ambitious global CO₂-emissions reduction target — “race to zero” by 2050 — was adopted by the international community.⁵ Carbon or CO₂ capture and storage

(CCS) technologies could be vital in achieving this ambitious goal; these approaches aim to reduce the amounts of CO₂ released into the atmosphere by separating it from other gases, as well as compressing, transporting and finally storing the captured CO₂ far away from the atmosphere, avoiding any leakage back into the ecosystem.^{6,7} The high costs of these technologies have limited large-scale annual capture and storage capacity to only about 0.1% of global CO₂ emissions, but this is predicted to increase to 19% by 2050.^{8,9} CO₂ sequestration research has accelerated over recent years to overcome climate-related challenges and help achieve zero overall CO₂ emissions. However, owing to techno-economical drawbacks associated with each of the technologies, only a handful of applications have been commercialized to date. Recent changes in the public perception and support of climate-change research have increased interest among the scientific community for advancing novel CO₂-capture technologies.¹⁰



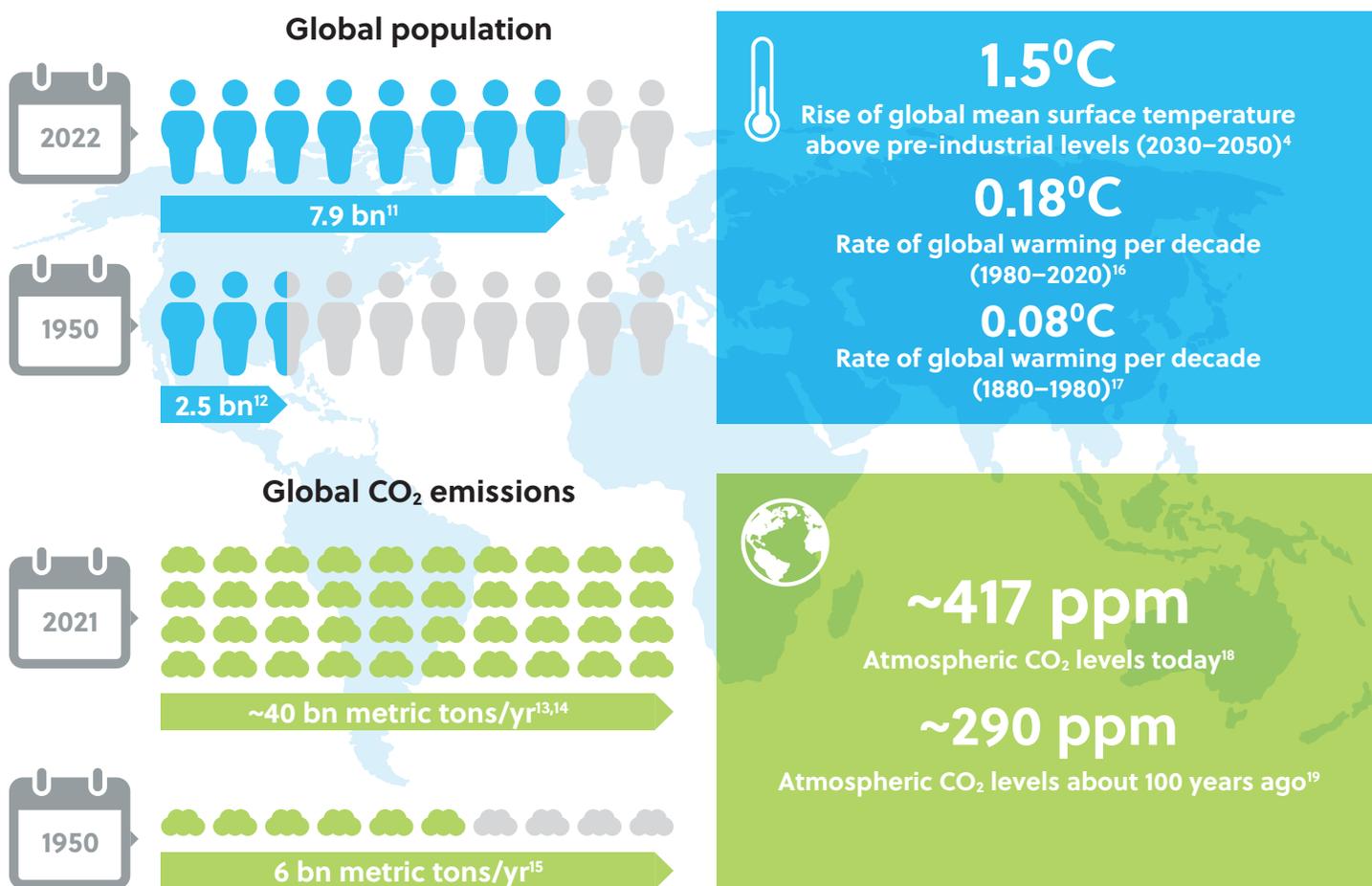


Figure 1. CO₂ in numbers: data depict global changes in population over time, accompanying trends in CO₂ emissions and projected increases in global temperature

The CO₂ sequestration approaches fall into four main categories each covering a variety of different methods as discussed in detail below. Firstly, there are **material science methods** which are used for pre- and post-combustion capture and for capturing CO₂ from flue gases or directly from the air. These are most frequently used in flues at industrial sites to prevent or limit CO₂ emissions from large scale processes such as power generation.^{20,21} **Biological methods** involve the use of biomass in which photosynthesis is exploited to fix CO₂ to create fuel; this approach encompasses the use of whole cell systems and enzymes.²² There are also **chemical methods** in which CO₂ is converted into other compounds using catalytic, electrochemical, photochemical, photothermal, photoelectrochemical, or plasma-based processes. CO₂ can be converted into various one- or two- carbon products, stored within

concrete or combined into minerals to form inorganic salts such as calcium or magnesium carbonate.^{23,24} **Geological approaches** involve the captured CO₂ being injected into specific suitable rock formations/sites such as saline aquifers, deep ocean floors, depleted oil wells or coal mines for long-term storage.²⁵ These locations, however, require careful selection and management to minimize the risks of leakage or pollution over long durations.

The CAS Content Collection™ is the largest human-curated collection of published scientific knowledge, suitable for quantitative analysis of global scientific publications against variables such as time, research area, formulation, application, and chemical composition. This white paper provides an overview of the latest trends in CO₂ sequestration research.

Research trends

Here, we summarize results of a recent analysis (~18,500 documents published between 2000 and 2021) detailing terms related to CO₂ sequestration, storage or conversion which were used in combination with terms related to atmospheric CO₂ or its environmental effect. The level of research activity related to CO₂ removal, sequestration and conversion is indicated by the annual publication volume which is summarized in **Figure 2**. It is apparent that the overall publication numbers increased rapidly during the late 2000s, these slowed down after mid-2010s but have shown fast growth again during the past few years (**Figure 2A**). The initial steady increase could reflect the perceived urgency of reducing atmospheric CO₂ levels which triggered global efforts. The absence of strong support for carbon capture and

storage projects evident in the lower investment and economic incentives given to CCS process compared with other technologies (likely due to high capital and operating costs) may have caused publication numbers to stabilize afterwards. In addition, oil prices and climate policies seem to be related. When oil prices are low, carbon capture technology appears too expensive to sustain, so to offset the operating costs, attention is focused on extracting oil in conjunction with CO₂ storage, rather than developing CO₂ capture and storage alone. A small proportion of the overall search results relate to patents (10%), suggesting a relatively small commercial interest on this research topic, although the concept count in the field has seen steep growth (**Figure 2B**), suggestive of new ideas and technologies.

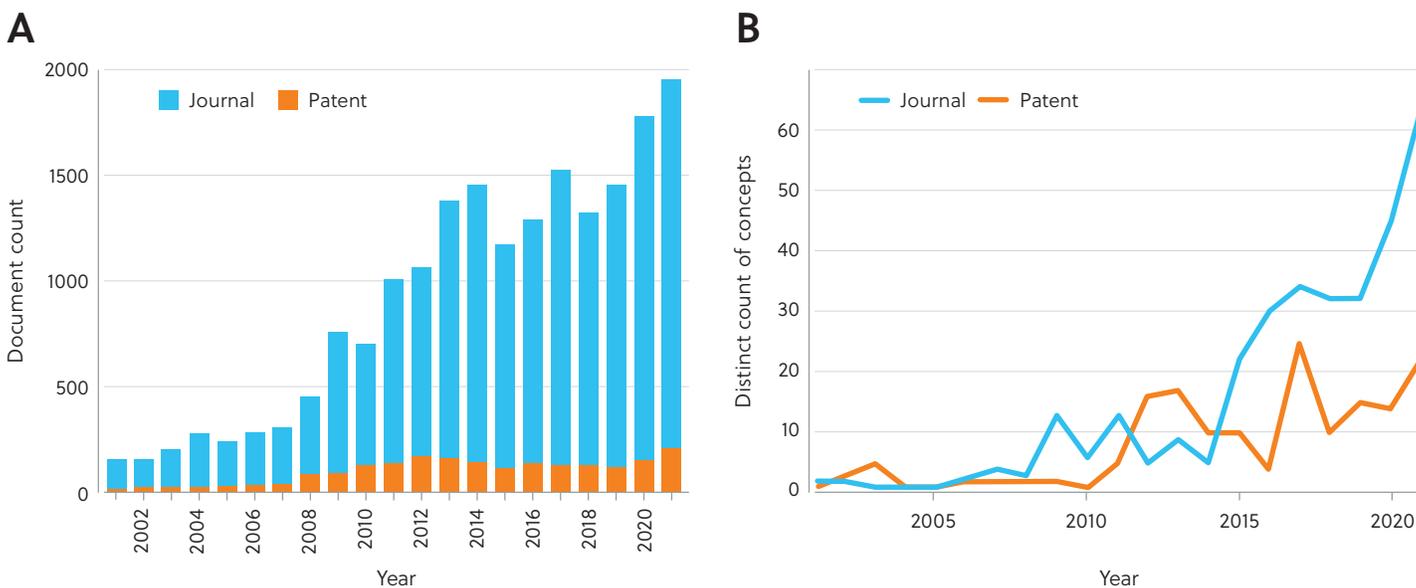


Figure 2. The overall publication trend of documents on CO₂ removal, sequestration or conversion-related research (all methods) (A) Document count. (B) Count of distinct concepts in publications



CO₂ sequestration methods

The practical methods of CO₂ sequestration fall into four main categories: material science, biological, chemical and geological, each with their relative merits and limitations. In this section progress in each of them and their current status are summarized based on publications from 2000–2021.

Material science methods

Carbon capture from flue gases: systems

The generation of power using fossil fuel combustion provides one of the largest single sources of human carbon dioxide emissions, so the removal of CO₂ from flue gases at power plants has been a major focus of carbon dioxide capture research. Depending on how the combustion is carried out and the stage at which CO₂ is captured, the three most widely studied techniques are post-combustion capture, pre-combustion capture and oxy-fuel combustion capture as outlined in **Table 1** and **Figure 3**.

The most popular method is **post-combustion capture**, which removes CO₂ from the flue gases formed from burning fossil fuels. It is the only commercial carbon capture technique and is advantageous in that it can be simply retrofitted to existing power plants. The major disadvantage of post-combustion CO₂ capture is that the flue gas, diluted with large amounts of nitrogen carried over from the air, has low pressure and low CO₂ concentration, making the separation difficult and energy intensive.

An alternative method is **pre-combustion capture**, a set of methods in which combustion is changed to make separation of CO₂ easier. Firstly, a limited amount of pure oxygen is supplied, with or without steam, to partially oxidize the fuel. The resulting hot gas (syngas), mainly carbon monoxide (CO), hydrogen and some carbon dioxide, contains thermal as well as chemical energy, which are converted to electricity via a steam turbine and a gas turbine, respectively. This process, called integrated gasification combined cycle (IGCC), is more energy efficient than direct combustion and has simpler emission control.

To capture CO₂, the cooled syngas is treated using a water-gas-shift reaction which converts CO into CO₂. The CO₂/H₂ mixture then goes through a separation unit to remove CO₂ and produce high purity hydrogen, which can be used as a storable energy source. In this method, the gas mixture has a simple composition, is at high pressure, and contains CO₂ in high concentration, making CO₂ separation much easier and less energy intensive than post-combustion capture. The drawbacks are that retrofitting power plants for pre-combustion carbon capture is much more difficult, and the production of pure oxygen for partial oxidation is energy-intensive.

Another method is **oxy-fuel combustion** in which the fuel is combusted in pure oxygen instead of air. The flue gas generated this way is predominantly CO₂ and water vapor, which are easily separated by condensation of water. The main drawback is the high energy and cost required to produce pure oxygen, which is used in much larger quantities than in IGCC.

A newly emerging technology is **chemical looping** in which the fuel is combusted in the presence of a metal oxide to generate a stream comprising CO₂, water and reduced metal oxides.²⁶ The metal oxide is regenerated by oxidation with air and returned to the fuel stream to repeat the cycle. In this process the metal oxide acts as an oxygen carrier, eliminating the need to generate pure oxygen. This method, however, is much more complicated than the combustion of gaseous fuels and requires significant optimization to reduce operating and manufacturing costs.

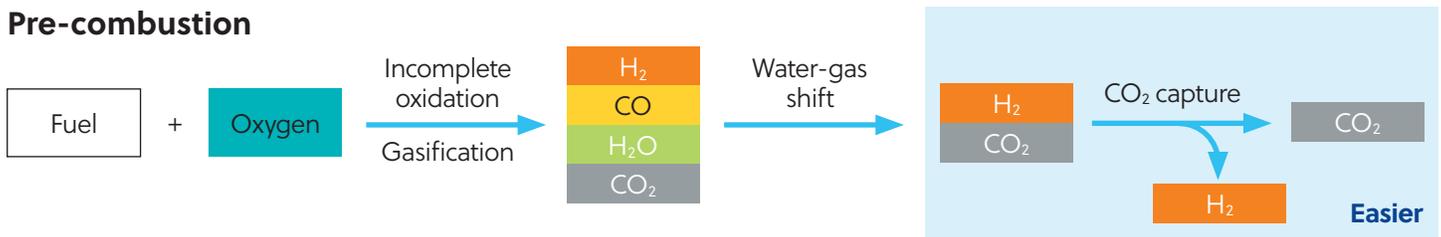
The newest form of sequestration is **direct air capture (DAC)** in which CO_2 is captured directly from the air.²⁷ Air is fanned toward filters where CO_2 is chemically absorbed or adsorbed, then pure CO_2 is released by heating the sorbent. DAC could achieve negative emissions if clean energy is used in the process without generating extra CO_2 . DAC plants are small and can be placed near carbon storage or emission sites. DAC projects have received substantial funding and so far,

19 DAC plants have been established worldwide.^{28,29} DAC is hampered by the very low CO_2 concentration found in the atmosphere (412 ppm or roughly 0.04% by volume) and the energy required is several times that of capturing it from power plant emissions in which concentrations are substantially higher (8%–10% in emissions of gas-fired power stations).^{30,31} This makes the current cost too high to make DAC profitable.

Post-combustion



Pre-combustion



Oxy-fuel combustion



Figure 3. Material science methods: simplified schematics of CO₂ capture processes

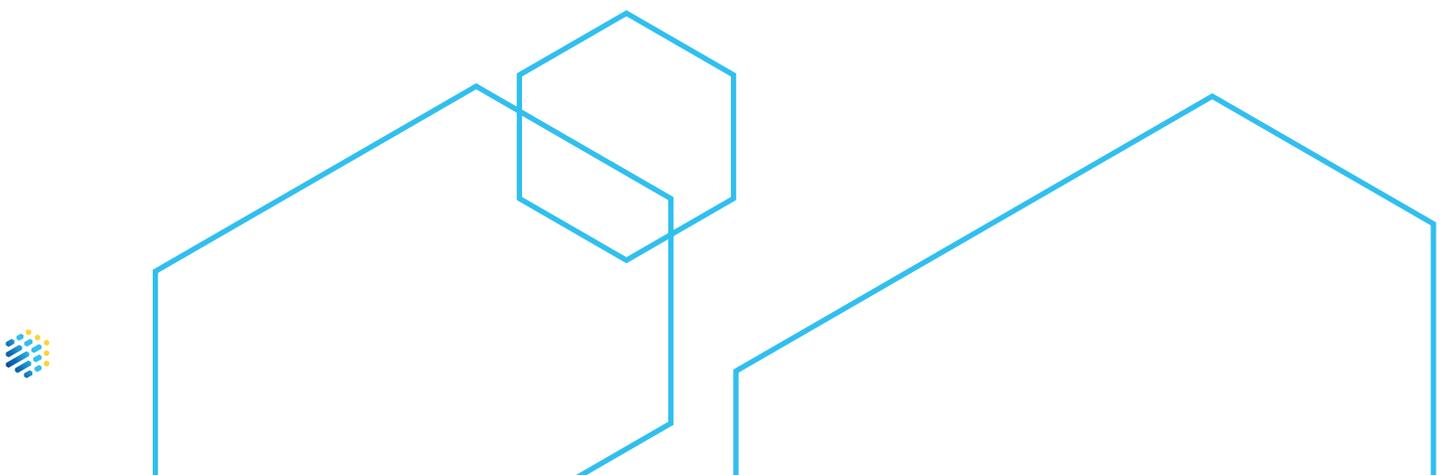


Table 1. Material science methods: comparison of CO₂ capture processes

Processes	Advantages	Disadvantages	Difficulty with retrofitting of plants
Post-combustion	More mature technology, least expensive	Low pressure stream with low CO ₂ concentration undermines separation efficiency, CO ₂ /N ₂ separation difficult	Low
Pre-combustion	High pressure stream with high CO ₂ concentration, CO ₂ /H ₂ separation easier	Only works for gasification or reforming plants, no industrial application yet, pure oxygen expensive	Moderate
Oxy-fuel	Feasible CO ₂ /H ₂ O separation	Pure oxygen production very costly	High
Chemical looping	Feasible CO ₂ /H ₂ O separation	Technology in early stage; more complicated process and equipment	High

The number of publications relating to CO₂ capture and separation were low prior to 2007 but increased sharply afterwards, peaking in the early 2010s and stabilizing after (Figure 4). Pre-combustion and oxy-fuel combustion are still in the early stages of development and produced much fewer publications most likely due to the cost of adapting current facilities. Publication volumes for

these three techniques all increased starting in the late 2000s but peaked in the early or mid-2010s, displaying a generally decreasing trend afterwards. The new and emerging technologies including chemical looping and DAC have much lower publication volumes and showed increases much later than the other three processes.

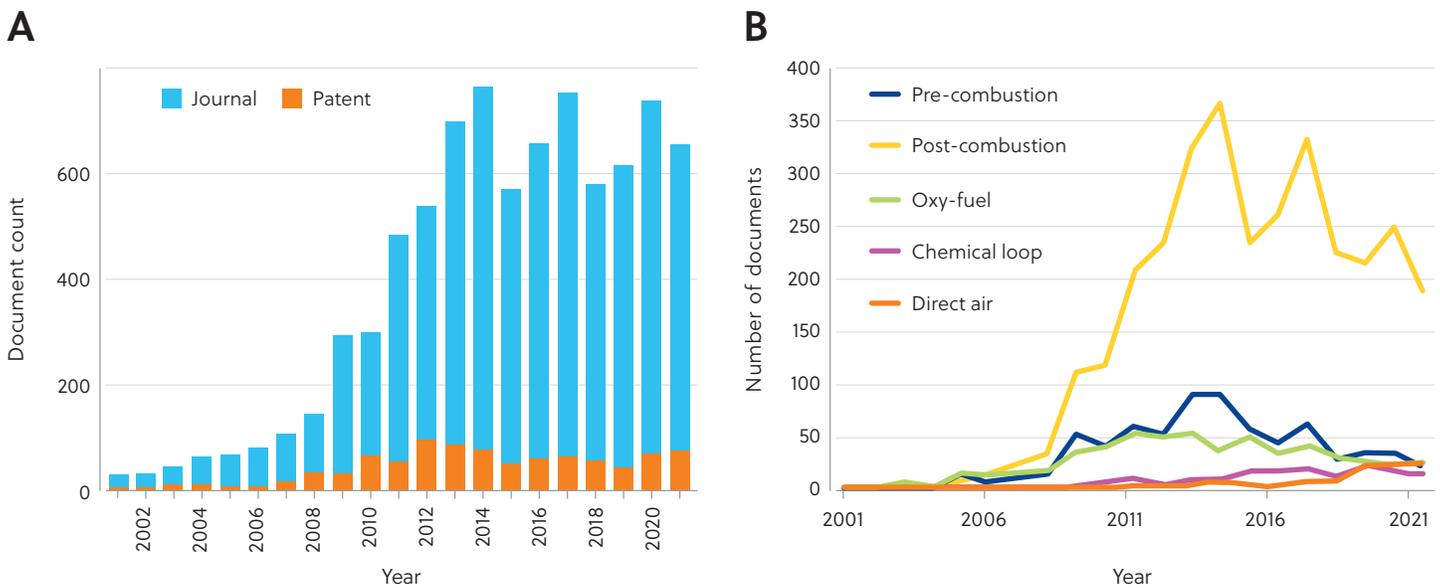


Figure 4. Material science methods: (A) Publication trend on CO₂ capture and separation between 2001-2021. (B) Publication volumes related to various CO₂ capture processes between 2001-2021

The three most studied methods for separating CO₂ from gas mixtures are described below and are summarized in **Table 2**. One method is absorption which can be carried out chemically or physically. Absorption using amine solutions is the most mature CO₂ capture method and the only one used in large scale industrial applications.

Chemical absorption takes advantage of the rapid reaction of CO₂ with bases. An alkali absorbent solution, usually with an amine, is brought into contact with the

gas mixture to neutralize CO₂ and form carbamate or bicarbonate salts.^{32,33} The resulting solution is then transferred to a regenerator (reboiler) to release the CO₂ and recover the solvent. The most common chemical absorbent (and the only one in commercial use) is monoethanolamine (MEA), but many other absorbents such as diethanolamine (DEA), methyldiethanolamine (MDEA), and piperazine have also been studied.³⁴⁻³⁷

Table 2. Material science methods: comparison of CO₂ capture methods

Methods	Most suitable process	Advantages	Disadvantages	Technical maturity
Absorption	Post-combustion	More mature technology, lower cost, simple operation	Corrosive solvent used, high solvent loss, high energy required for solvent regeneration	Moderate
Adsorption	Pre-combustion	Continuous operation, environmentally friendly	Low CO ₂ selectivity, difficult to manage solid/gas contact to maximize adsorption capacity, too many potential candidates, actual performance of adsorbents difficult to predict	Low
Membranes	Post-combustion, pre-combustion	Simple and flexible system, environmentally friendly, no regeneration needed	Low CO ₂ permeability, energy intensive, membrane material easily compromised	Very low

Physical absorption methods capture CO₂ by dissolving it on noncorrosive solvents at high pressures.³⁸ The temperatures and pressures required are more suitable for pre-combustion capture. The solvents used for physical absorption include methanol,³⁹ Selexol (polyethylene glycol dimethyl ether),⁴⁰ N-methyl-2-pyrrolidone (NMP)⁴¹ and propylene carbonate.⁴² Solvents with higher molecular weights such as Selexol generally have lower vapor pressures leading to less solvent loss but suffer from high viscosities which can impair mass transfer. Methanol is less viscous but requires refrigeration and water washing to reduce solvent loss.

Adsorption into porous solid adsorbents has also been used to capture CO₂ from flue gases. This method uses solids with large internal surface areas, such as carbon,

zeolites, and metal organic frameworks (MOFs) to hold CO₂ within their pores. Examples of adsorption approaches include activated carbon with optimized microporous/mesoporous structures derived from African palm shells using copper salt activators,⁴³ and surface modification of activated carbon using nitric acid and ammonium hydroxide, resulting in enhanced CO₂ adsorption despite reduced surface area and pore volume.⁴⁴

Recent research on adsorbents is focused on improving CO₂ uptake and adsorption kinetics, enhancing dimensional stability and reusability, as well as overcoming moisture sensitivity (for zeolites and MOFs). However, sophisticated modelling techniques are required to predict their industrial applicability.



Membrane filtration is an emerging technology for CO₂ capture; it is not yet in widespread because of the low gas permeabilities and poor separation efficiencies of current membranes.⁴⁵ Advantages of membrane filtration are that it offers lower material costs and operational simplicity and flexibility.^{46,47} Separation may occur through different mechanisms depending on the membrane material and the gas stream, including size sieving or surface diffusion (for porous membranes) and solution diffusion (only for dense membranes).⁴⁸ The most studied membranes are dense inorganic membranes (e.g. palladium and alloys), porous inorganic membranes (e.g. carbon, alumina, silica, zeolites, MOFs), and polymer membranes (e.g., polysulfones, polyimides, polybenzimidazoles). Dense inorganic and porous inorganic types are mostly used for pre-combustion applications whereas polymers are used post-combustion.

The overall publication trends for absorption, adsorption and membrane CO₂ methods over 2000-2021 are given in **Figure 5**. The number of absorption-related studies grew substantially before 2014 and then decreased, consistent with carbon capture by absorption being relatively mature and closer to industrial use. Our insights into publication trends of co-occurring topics show that absorption has been studied the most for post-combustion capture. Research interest in adsorption has continued to grow, with the related annual journal publication volume surpassing that of absorption in the past few years. Membrane separation appeared as a topic less frequently than the other two techniques. Patent publication volume was several times lower than that of absorption, consistent with it being an emerging technology.

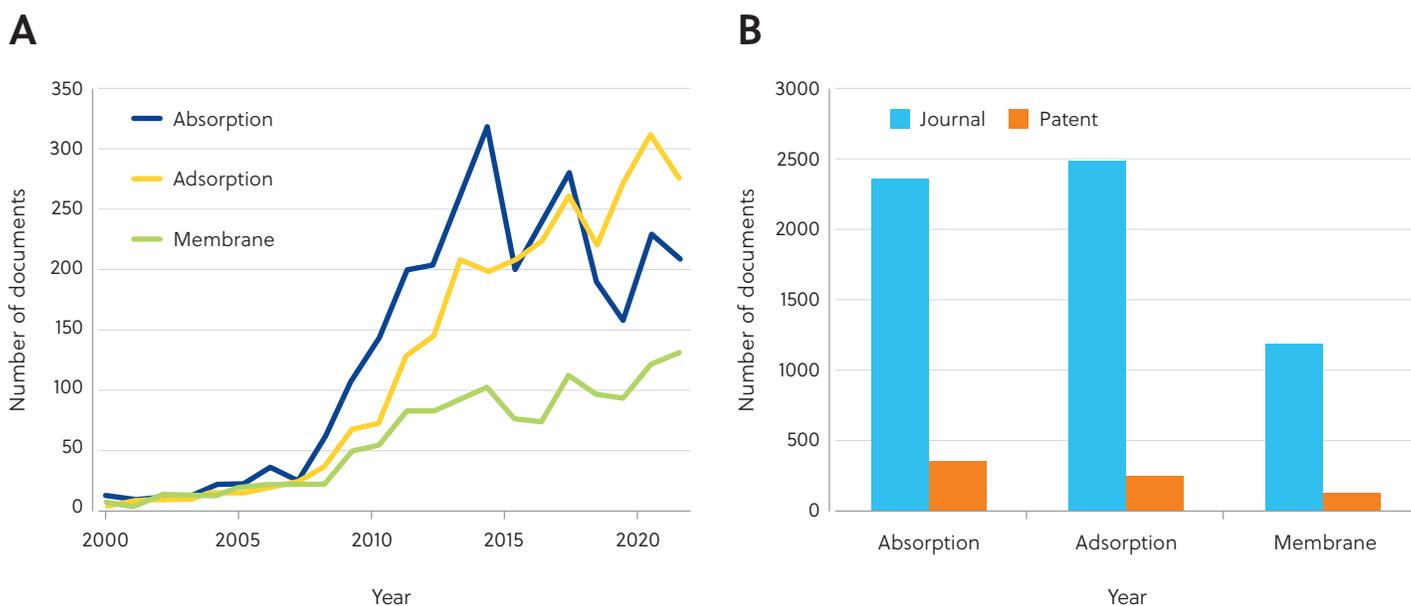


Figure 5. Material science methods: publication volumes related to different CO₂ capture methods. (A) Publication trends between 2000-2021. (B) Total publication volumes between 2000-2021

Biological methods

Organisms use photosynthesis to sequester 440 gigatons of CO₂ per year, the largest single CO₂-fixing process on earth. Native biological pathways are sustainable and can be used to either sequester CO₂ or to convert it into value-added bioproducts that can replace similar materials made from fossil fuels.⁴⁹⁻⁵¹ This carbon-neutral approach will serve the dual purpose of conserving the fast-depleting fossil fuel reserves, while also cutting down on the net increase in the atmospheric CO₂ levels, thus considered as the most sustainable approach.^{49,51} Despite scalability and efficiency limitations, biological CO₂-fixation reactions are highly selective and often require little resources, spurring interest in developing biomimetic and bio-based technologies for CO₂ capture.⁵²

Interest in biological CO₂ fixation has resulted in a rapid increase in the number of journal publications, whereas annual patent-filing activity has remained constant owing to the limited number of resultant technologies that are ripe for commercialization (**Figure 6A**). One recently emerging technology, collectively referred to as Bioenergy with Carbon Capture and Storage (BECCS), is responsible for accelerated publication activity over the past 6 years. A recent study predicts that BECCS could sequester up to 5.2 gigatons of CO₂ per year without adversely affecting land usage.⁵³⁻⁵⁵

Sequestration of CO₂ occurs in biological systems using six pathways. All organisms, including humans, are dependent on primary producers for deriving all the organic carbon to sustain life on this planet. Biological CO₂-fixing pathways are central to the existence of life. Understanding how they work is important for the application of biological systems to atmospheric CO₂ capture and to biological production of chemical feedstocks.^{50,56}

The reductive pentose phosphate pathway or the Calvin-Benson-Bassham (CBB) cycle is the most common mechanism used by plants and algae and most autotrophic bacteria for converting atmospheric CO₂ into biomass (**Figure 6B**).⁵⁷ It is also the most economically relevant pathway.⁵⁸ The other five pathways are only present in a small number of bacteria or archaea, but nevertheless provide clues regarding the unique environments in which the host organisms thrive.⁵⁹

A subset analysis of the CAS Content Collection (n=1343 journal articles and n=103 patents published between 2017 and 2021) indicates the growing use of bacteria (mostly cyanobacteria) and algae as cellular factories to sequester CO₂, because they can deliver a sustainable and renewable platform to produce biofuels and high-value products, wastewater and flue-gas remediation, and bio-mitigation of unwanted nutrients.^{60,61}

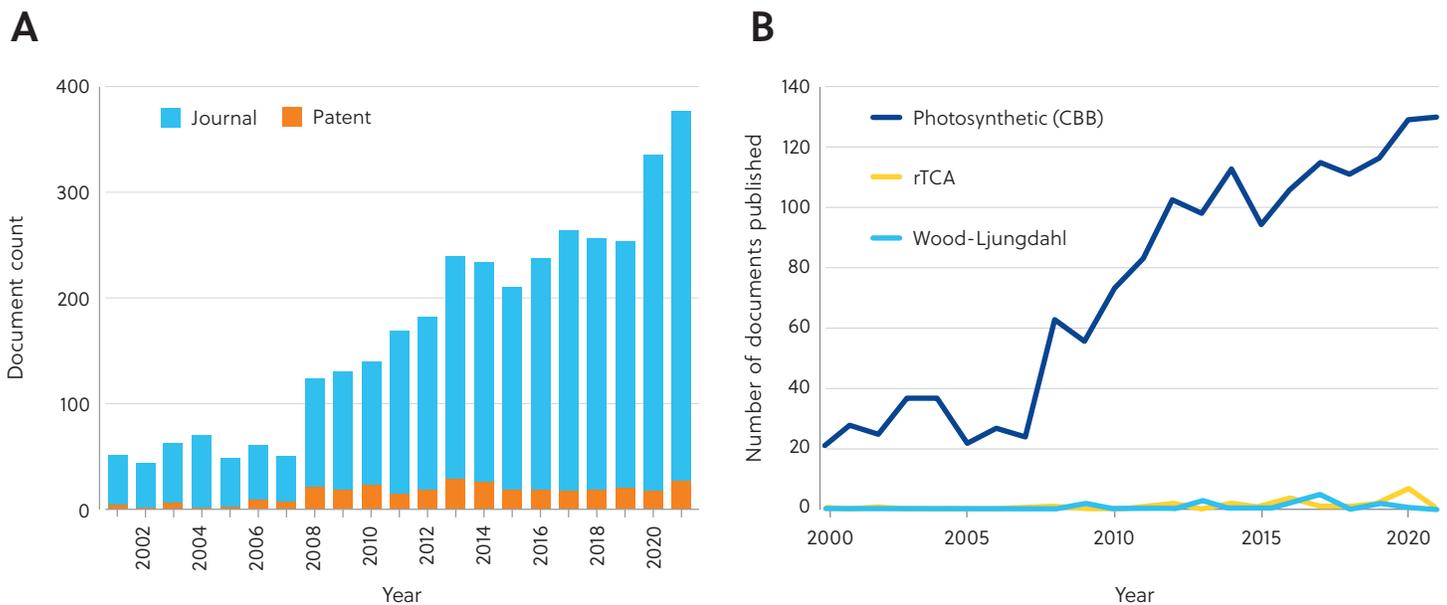


Figure 6. Biological methods: publication trends related to biological CO₂ sequestration methods. (A) Publication trends between 2001-2021. (B) Publication numbers with keywords in the abstract representing studies with host organisms containing photosynthetic CBB cycle (black line) or the rTCA cycle (orange line) or the Wood-Ljungdahl pathway (blue line) between 2000-2021



Enzyme-based technologies have been investigated as sustainable and cost-effective systems for CO₂ fixation. Many enzymes, available either from natural sources or by protein engineering, can catalyze a variety of reactions and can be used either in whole cells or as isolates, making them flexible and potentially useful tools for CO₂ capture and conversion.^{52,62}

The enzyme ribulose 1,5-bisphosphate carboxylase/oxygenase (RubisCO) is the world's most abundant and most researched protein, accounting for over 250 gigatons of CO₂ fixed annually as part of the CBB pathway, and responsible for most of the biomass present on earth.⁶³ RubisCO catalyzes the reductive carboxylation of ribulose 1,5-bisphosphate (RuBP) that ultimately leads to the assimilation of

CO₂ in the form of carbohydrates. However, the turnover frequency of RubisCO-catalyzed CO₂ fixation is low; only between 1 to 10 per second. Ongoing work aims to improve its CO₂-capture capabilities.⁶⁴ RubisCO was also the biocatalyst appearing the most frequently in the abstracts of our curated list of retrieved documents from 2017 to 2021.

The use of RubisCO variants in biochemical CO₂ capture modules may provide access to industrially valuable molecules. Combining RubisCO with other functional enzymes also offers a promising new direction to explore industrial CO₂ capture and conversion strategies.⁶⁵⁻⁶⁸



Chemical methods

Chemical methods convert CO₂ into other materials by chemical means. CO₂ can be incorporated into mineral carbonates or into concrete, which may sequester carbon for significant periods of time. It may also be converted into reduced forms that can be used either as fuels or in the manufacture of organic compounds or fuels which sequester CO₂ for a shorter time span.

The synthesis of fuels and chemicals from CO₂ requires energy and a source of hydrogen atoms. Hydrogen atoms are produced either from H₂ (which must be generated) or from protons and electrons (formally obtained from water). Four major classes of processes have been developed for CO₂ conversion, these are: **catalytic processes; electrochemical processes; photochemical, photothermal, and photoelectrochemical processes;** and **plasma-based processes** (particularly nonthermal plasma) as outlined below.

Catalytic processes use a catalyst to reduce CO₂ with a reductant such as hydrogen (H₂) or methane (CH₄) in dry reforming processes.⁶⁹ Hydrogen is obtained either from the electrolysis of water or by the reforming of natural gas.⁷⁰ Reduction of CO₂ with hydrogen (hydrogenation) generally requires elevated temperatures and pressures; to reduce overall CO₂ emissions, this energy should come from sources emitting little or no CO₂. Both heterogeneous catalysts (solid catalysts which do not dissolve or vaporize into the reaction medium) and homogeneous catalysts (catalysts which dissolve in the reaction solvent) are well-precedented and have been used on multi-ton scales.⁷¹

Electrochemical processes use energy from electricity to perform chemical reactions. Protons are used as formal hydrogen equivalents, so electrochemical CO₂ reduction does not require a source of hydrogen. In an electrochemical cell, electrons must travel on a closed circuit through the electrodes and the reaction medium, and productive reactions (for unmediated electrochemical reactions)

only occur at the electrodes. Electrochemical methods are carried out on large scales and so have the potential to be used for large-scale CO₂ reduction.⁷² The development of catalysts for electrochemical CO₂ reduction, however, is difficult. The process is constrained by the reduction potential of protons, by the electron affinity of CO₂, and by the strength of binding of CO₂ and of CO (formed as a reduction intermediate) to the catalyst.

Photochemical, photothermal, and photoelectrochemical processes use light as the source of energy for the transfer of electrons from other substances (ideally water, but also hydrogen) to CO₂. Photochemical methods can use solar energy to avoid the need for either external reductants or electricity and thus the CO₂ emissions from electricity or reductant synthesis. They can also reduce carbon dioxide at ambient pressures. The efficiency of photochemical methods is limited by the ability to transfer light energy to a substrate, and so efficient mass transfer is important for high photoreduction rates and selectivities. For these reasons the technologies for photochemical CO₂ reduction have not yet been practiced on large scale.

Plasma-based processes use strong electric fields⁷³ or microwaves that can provide sufficient energy to break bonds such as the carbon-oxygen bonds in CO₂ to yield either CO or carbon and oxygen. In gliding arc or microwave plasmas (warm plasmas), thermal energy is present but not enough to generate thermal plasma alone; these methods function at below ambient pressures and require containment and extra energy to maintain both the reduced pressures and increased temperatures.⁷⁴ Plasma methods, however, are used in the manufacture of semiconductors and have been implemented on large scale.⁷⁵

Other chemical processes include the reverse water-gas shift (RWGS), an endothermic reaction that converts hydrogen and CO₂ to CO and water (water gas).⁷⁶ Since the hydrogenation of carbon dioxide to CO is an intermediate reaction in the reduction of CO₂ to methanol, catalysts for and understanding of the RWGS may be useful. Catalysts including Cu, Fe, Ni, Pt, and molybdenum carbide have been used for the RWGS. The CO produced can also be used in the Fischer-Tropsch reaction (FTR) which converts a mixture of CO and hydrogen at 300-400 °C and elevated pressures to yield aldehydes, alcohols, alkenes, and aliphatic and aromatic hydrocarbons.⁷⁷ The FTR has been used on large scale for the generation of fuels from coal in countries lacking access to reliable or cheap oil. The selectivity of Fischer-Tropsch reactions depends both on

the catalyst (with iron, cobalt, or ruthenium complexes being the most common) and on the number of carbon atoms in the desired product.

Publication counts for chemical methods of CO₂ conversion in the CAS Content Collection have increased rapidly and all methods have shown significant increases in number of publications over the last six years (**Figure 7**). Based on publication frequency, methanation, and plasma-mediated processes have shown the greatest interest. There has been a rapid increase in the number of publications discussing RWGS. Interest in photothermal methods has increased significantly over the last five years but is still lower than that of other methods.

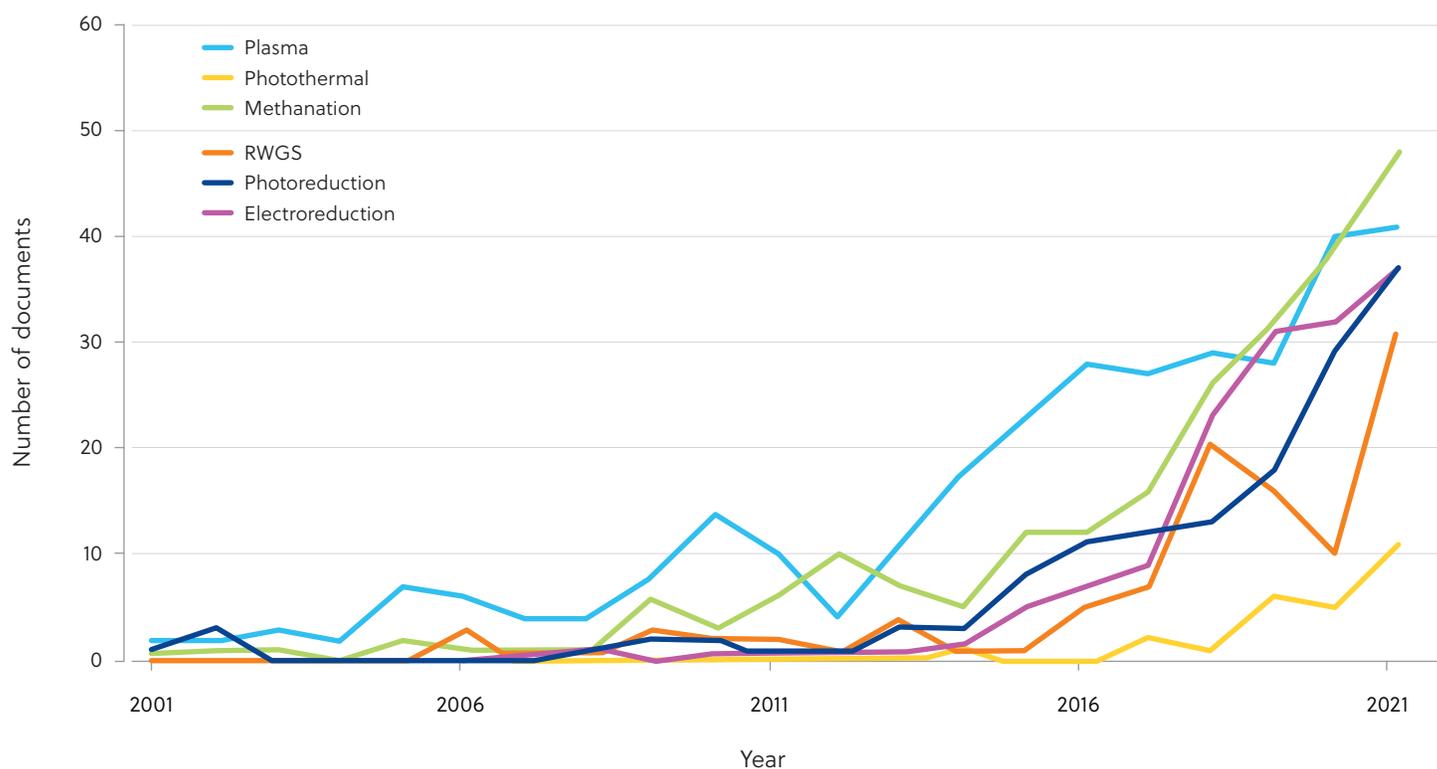


Figure 7. Chemical methods: publications containing the keywords “photoreduction”, “electroreduction”, “methanation”, “RWGS”, “photothermal”, and “plasma” in the title, abstract, or keywords of documents also discussing CO₂ capture, sequestration, or use in the CAS Content Collection between 2001-2021

Carbon products

A variety of useful one-carbon compounds can be generated from CO₂, e.g., CO,⁷⁸ methanol,⁷⁹ methane,⁸⁰ and formates⁸¹ (notably formic acid). The limited number of possible single-carbon products makes discovery of chemo-selective methods for CO₂ reduction to one-carbon compounds easier than for multi-carbon products. Multi-carbon products without carbon-carbon bonds avoid selectivity issues with generating products from CO₂ by converting single-carbon products to products with higher energy content, e.g., dimethyl ether from CO₂;⁸² other examples include dimethoxymethane,⁸³ formate esters,⁸⁴ and dimethyl carbonate.⁸⁵

A variety of two-carbon compounds can be generated from CO₂ and a number are in commercial use, e.g., ethanol,⁸⁶ ethylene,⁸⁷ and oxalic acid.⁸⁸ Ethanol is

currently used in fuel on large scale; it is a liquid at ambient temperature, has low toxicity, and can be readily converted to other useful products such as ethylene which is a high-volume commercial product with 31 million metric tons produced in 2019.⁸⁷

The trends in articles including the CAS Registry Numbers for compounds that have been investigated as potential products for CO₂ conversion are shown in **Figure 8**. The plots indicate that interest in single-carbon feedstocks is greater than that for multi-carbon feedstocks and is consistent with the relative difficulties of generating the products from CO₂. The publication count correlates with the number of methods available to prepare them. CO, for example, can be generated by catalytic, photochemical, electrochemical, and plasma-based methods.

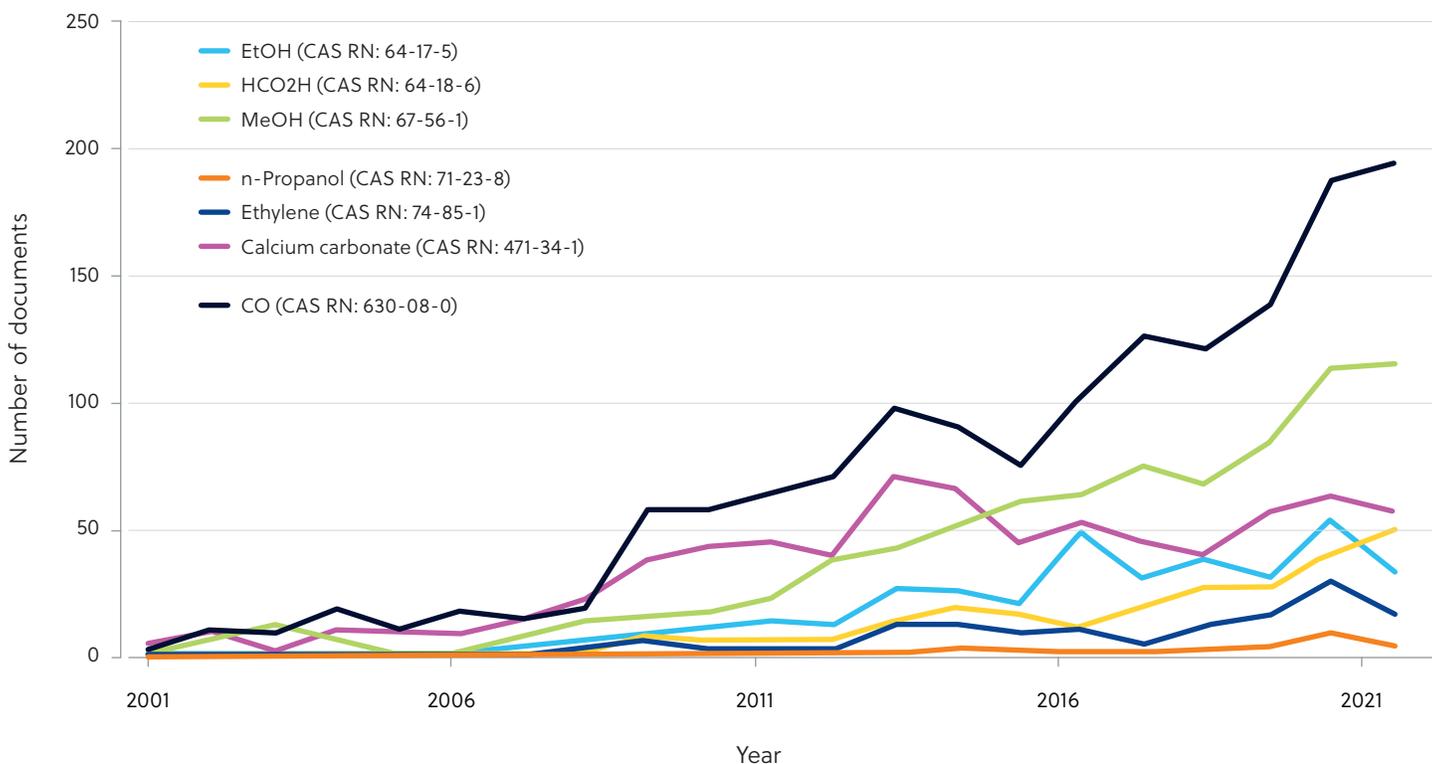


Figure 8. Chemical methods: number of documents in the CAS Content Collection discussing CO₂ capture, sequestration, or use which contain the CAS Registry Numbers for carbon monoxide, methanol, formic acid, ethylene, ethanol, 1-propanol, and calcium carbonate between 2001-2021



Concrete

Concrete manufacture is a major source of CO₂,⁸⁹ generating 7–8% of anthropogenic CO₂ emissions. Of this output, 60% comes from the decarbonation of limestone and the remaining 40% comes from the energy needed to make the cement.⁹⁰ CO₂ can also be added during concrete pouring to incorporate more CO₂ as carbonates increase concrete strength. Additionally, concrete's overall CO₂ emissions decrease 10–30% over its service life as calcium hydroxide in the cement absorbs CO₂ from the atmosphere, which also hardens and strengthens the concrete.⁹⁰ Concrete wastes also absorb CO₂ when left exposed to air, but only 1% of concrete wastes are left exposed long enough to absorb significant amounts of CO₂.⁹⁰

Mineral Carbonation

A further chemical method of CO₂ sequestration is the mineral carbonation process which forms stable metal carbonate salts such as calcium and magnesium carbonates.⁹¹ A variety of sources can be used for metal carbonates such as natural minerals containing calcium or magnesium oxides or silicates. While steel slag, mining wastes, red mud, waste ash, and alkaline paper mill waste can also absorb CO₂ and are cheap, they may require careful handling to prevent environmental contamination with materials such as asbestos, nickel wastes and red mud. Mineral carbonation can be performed directly (by treatment of the dry or slurried minerals with carbon dioxide) or indirectly (by conversion of the minerals to metal oxides or hydroxides followed by carbonation). Direct carbonation in the solid phase is limited by mass transport and is generally slow. Carbonation of minerals in aqueous solution is fast, but the dissolution of minerals in water is slow.

There are a number of ways to reduce energy consumption for cement manufacture,⁹⁰ including: improvements to the efficiency of CO₂ evolution and removal, using renewable energy sources for cement production, capturing CO₂ liberated in cement manufacture, allowing concrete wastes to remain exposed to air during demolition; recycling aggregates from demolished concrete structures which may reduce the amount of cement needed for new construction and thus the CO₂ emissions of concrete use. A recent analysis however concluded that even after implementing measures including carbon capture and using biomass fuels, it would take much of the half-life of a concrete structure to reach carbon neutrality.⁹⁰

Other materials are also used to capture CO₂ for carbonate formation and include ammonia, calcium hydroxide, calcium or magnesium brines and molten magnesium chloride. Aqueous slurry methods require large amounts of water and may require evaporation of water which may be slow or require heating. Mineral carbonation in some cases yields valuable materials such as precipitated calcium carbonate (PCC) which has been sold for \$320/ton (annual market for PCC is estimated at \$39 billion) and ultrapure calcium carbonate (profits > \$9000 / metric ton).^{91–93}

Our literature search verified that carbonation of a variety of minerals, wastes, and concrete may be a mature and cost-effective method to mitigate human CO₂ emissions. As shown in **Figure 9**, the publication pattern for calcium carbonate is consistent with that of mineralization, with a plateau in publication counts occurring after 2012 (albeit delayed from those for mineralization and carbonation). Publications involving concrete for CO₂ sequestration

follow a different pattern; the total number of articles discussing CO₂ sequestration and concrete is significantly smaller than the number of documents discussing carbonation (though some concrete articles may be included in documents discussing carbonation). We cannot yet explain the time dependence of publications discussing concrete and CO₂ sequestration.

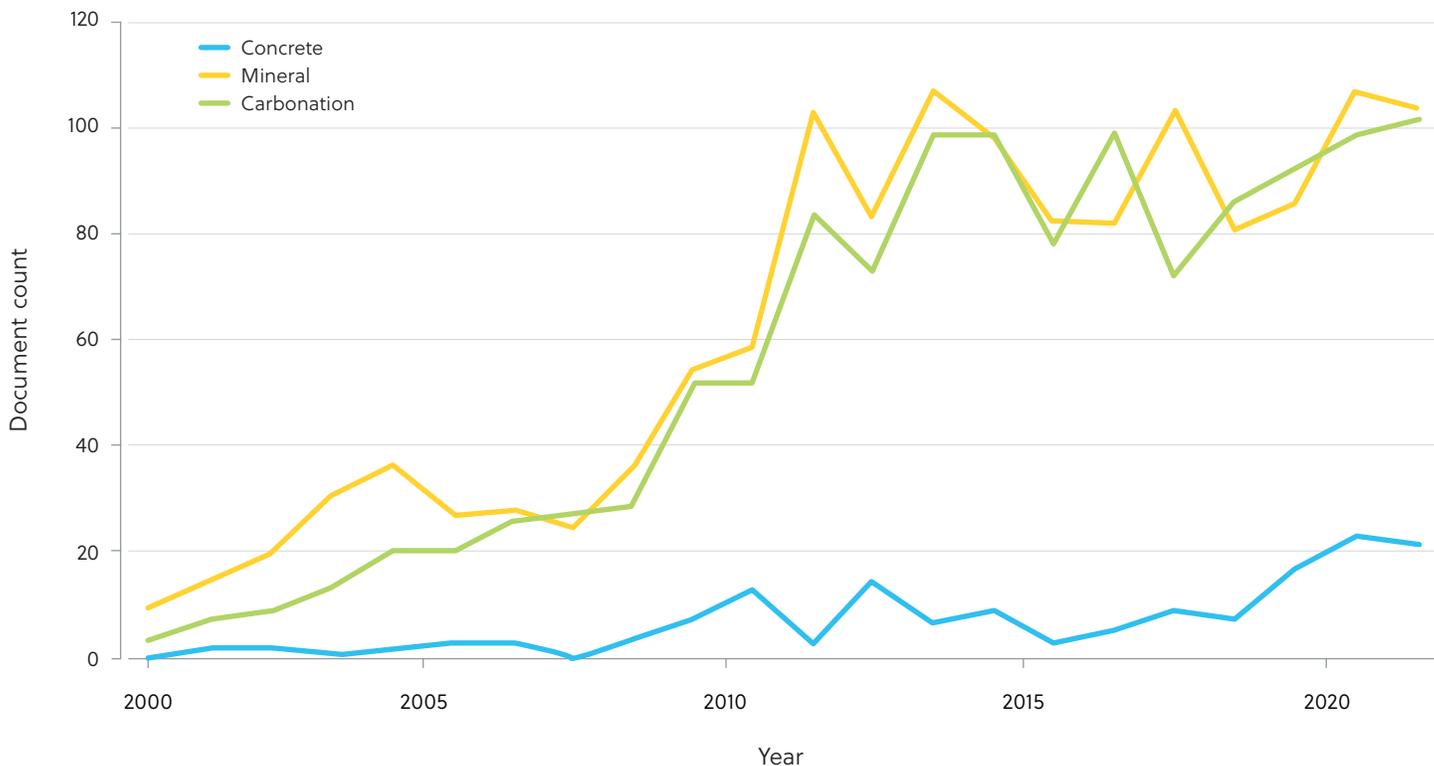
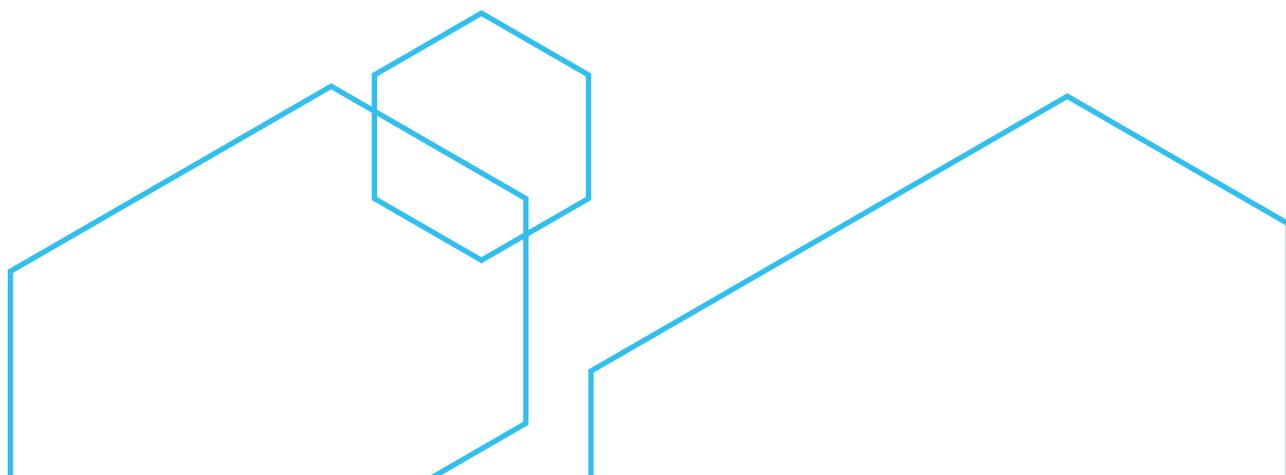


Figure 9. Chemical methods: publications discussing carbonation, concrete, mineralization in the title, abstract, or keywords of documents also discussing CO₂ capture, sequestration, or use in the CAS Content Collection between 2000-2021



Geological methods

Carbon geo-sequestration

Carbon geo-sequestration is the process of injecting captured CO₂ in deep porous geologic formations for long-term storage. Once CO₂ is captured, it is compressed to elevated pressures and converted into a supercritical fluid. The CO₂ is then transported mostly by pipelines to the injection site as this is the most cost-effective mode of transport.⁹⁴

Most estimates suggest that sufficient capacity exists to store many thousands of gigatons CO₂ with only a small risk of surface leakage in the following 10,000 years. However, there are many factors at play that could influence this: the geological formation itself (type and heterogeneity), the physical and chemical processes accompanying CO₂ storage, the method being used to determine the storage capacity and the amount of available data.^{95,96} Several assessments of regional storage capacity were conducted in Europe, China, Japan, Canada, and the United States, yet making direct comparisons of their results

Risk assessment and minimizing potential leakage

The behavior of CO₂ is influenced by many variables and thus storage sites must be assessed individually. Any method used for geological storage of CO₂ should be able to store it for a minimum of 1,000 years with a leakage rate of less than 0.1% per year. Once injected in a well, a CO₂ plume will rise via buoyant forces, since it is less dense than its surroundings. When it encounters a caprock, it will spread laterally until it finds a gap. Faults and fractures near the injection zone may all contribute to the migration and eventual leakage of CO₂ in the air or underground causing potentially devastating harm including changing the pH or contamination of groundwater.¹⁰⁸ Other risks include mobilization of environmentally challenging polycyclic aromatic hydrocarbons (PAHs) in coal seams,¹⁰⁹ and induced seismicity resulting from increased pressure underground caused by CO₂ injection.¹¹⁰

poses a problem due to their different underlying assumptions. A method to better assess the CO₂ storage capacity worldwide using globally available datasets was developed at MIT in a study that is part of a larger project to use Integrated Assessment Models (IAMs).⁹⁷

A favorable option for geological sequestration of CO₂ is saline aquifers (porous reservoirs that contain saltwater) found both onshore and offshore.⁹⁸ It is one of the best candidates owing to wide global availability, large capacity and isolation. Successful examples include the North Sea,⁹⁹ the Basal Cambrian Sands (Alberta, Canada)¹⁰⁰ and Mt Simon sandstone (Illinois, US). Other options include unmineable coal sites and shales,¹⁰¹ underground depleted oil and gas reservoirs,¹⁰² declining oil and gas fields,¹⁰³ deep ocean waters, ocean floor or sediments,¹⁰⁴ basalts or reactive rock formations,¹⁰⁵ biochar¹⁰⁶ and rock weathering.¹⁰⁷

Protective/risk management measures are essential in CO₂ storage. Monitoring of injection process and deploying surface and subsurface sensing technologies enable risk assessment and mitigation of potential release of CO₂ from wellbores, faults, and other migration pathways.⁹⁵ Monitoring allows leak detection to minimize losses, and to quantify the leak size. Simulations are also used in predicting the pressure build-up in the formation, fluid flow, and geo-mechanical and geochemical processes at the injection site. Research on improving and modeling various aspects of geological storage and monitoring of CO₂ has been conducted over the past decade.¹¹¹ No incidents of catastrophic CO₂ release from natural deposits have occurred. Reactions of CO₂ with minerals over time improve the security of geological sequestration, making it a secure, resilient, and feasible option for CO₂ storage.¹¹²

Publications in geological storage of CO₂ increased gradually up to 2013, while showing a decline in publications from that year onwards (Figure 10). The terms "aquifer", "saline", and "brine" returned more publications than the rest of the search terms used, reflecting more interest in those specific storage sites (data not shown). Individual search terms showed similar trends except for "shale" and "clathrate" that displayed an upwards movement in the past 4 years, albeit in lower

numbers. Research on CO₂ storage in the form of gas hydrates is still in development, with limited field data available, but remains promising due to its potential for high volumes of CO₂ to be sequestered. "Aquifer" was also the most common geological term appearing in a network diagram showing the top 1000 co-occurrence of concepts within documents.

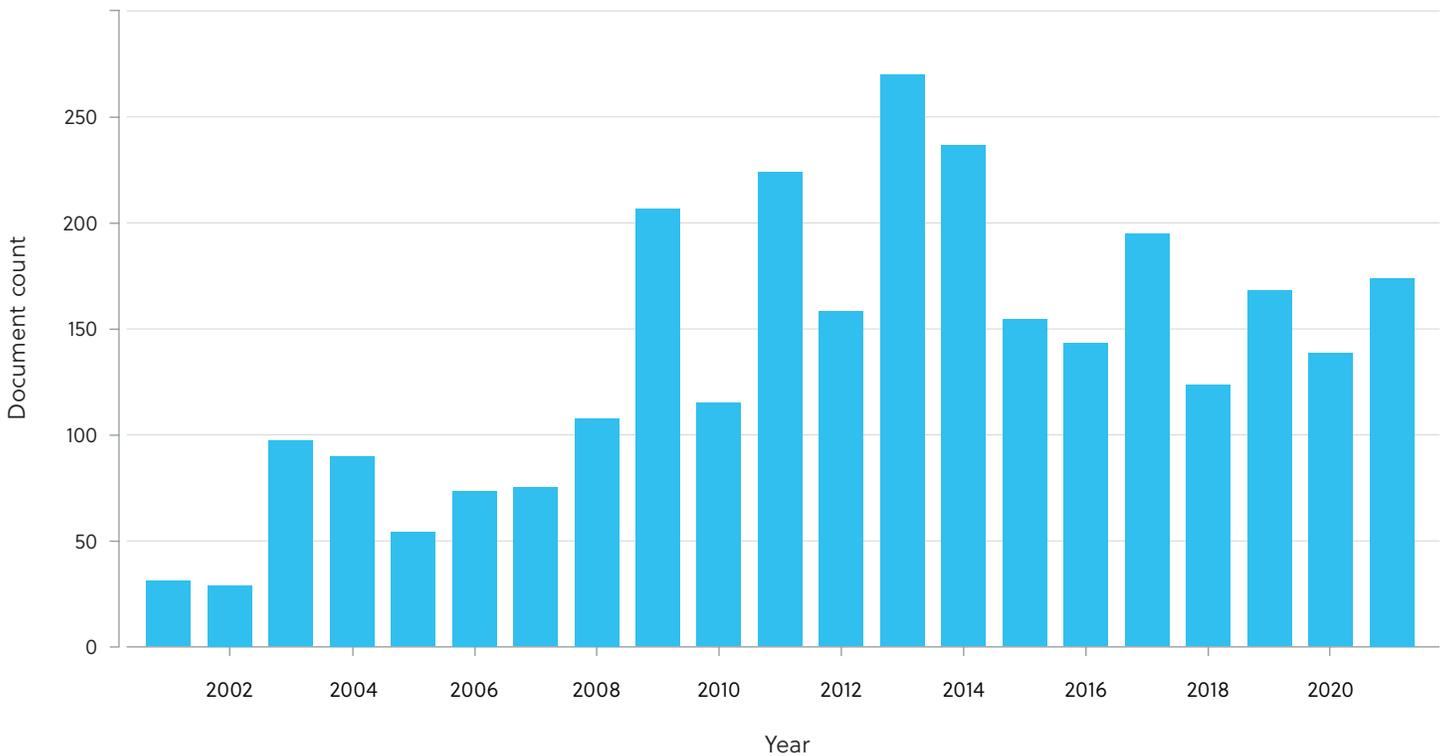
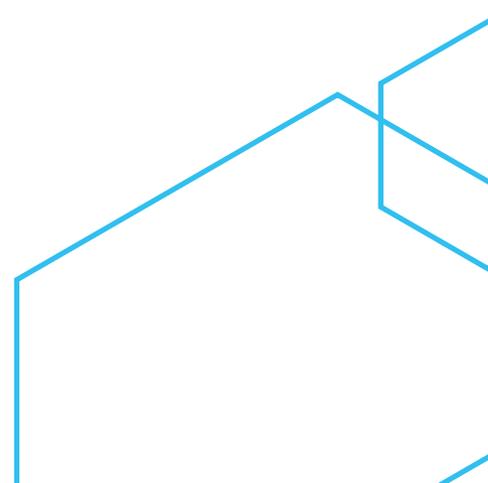


Figure 10. Geological methods: publications related to geological storage of CO₂ between 2001-2021



Conclusion

Atmospheric CO₂ is a key component of the Earth's ecosystems and vital for our existence but its overabundance in our atmosphere due to human combustion of fossil fuels is having devastating consequences. To mitigate increasing CO₂ levels, concerted efforts are underway to establish a range of cost-effective, efficacious and sustainable methods of CO₂ sequestration. The literature analysis of 18,500 publications from the CAS Content Collection has allowed us to undertake a comprehensive appraisal of publication trends in CO₂ sequestration research between 2001 and 2021. The results indicate that efforts are ongoing and in most cases are increasing to optimize multiple existing processes relating to carbon capture, biological, chemical and geological sequestration of CO₂. These trends were mainly evident in the number of scientific publications and reports but also in numbers of patents filed which is indicative of commercial interest. The rate of publications appears to be linked to prevailing economic conditions and the price of oil. The findings also suggest that the collective efforts of scientists and engineers across the globe will continue to put new technologies in the spotlight.

From the analysis it is clear that many of the numerous existing methods of CO₂ sequestration are viable. Altered land use, biomass and geological methods are likely to be inexpensive, they can be rapidly adopted and will be useful in the short term to help achieve CO₂ emission targets. Chemical methods are mostly expensive but are functional. Both chemical and many new biological

methods will require considerable technological development and sources of abundant sustainable energy (non-CO₂-producing) in order to function. The findings also indicate that worldwide interest, and consequently knowledge and expertise in CO₂ sequestration is rapidly increasing. The adoption of these technologies on scales that can have a material effect on atmospheric CO₂ levels will require government legislation and inducements. Examples of such intervention includes the US Department of Energy which has been funding CO₂ capture research for over 20 years and is enabling further development and deployment of carbon capture and storage technology.¹¹³ Currently, 12 of 24 CO₂ capture and injection projects worldwide are in the US.¹¹³ Larger adoption of such methods in the US, however, can be limited by Environmental Protection Agency and National Environment Policy Act restrictions.^{113,114} The EU has established a framework and policies to legally enable, fund and incentivize the commercial development of various methods of CO₂ capture and safe storage and overcome present barriers that prevent it.^{115,116} The UK government plans to establish carbon capture usage and storage clusters in energy-intensive industrial areas which will capture 47 million tons of CO₂ (9.4% of national output) by 2050.¹¹⁷ Taken together, this level of government planning and intervention and the findings of the literature analysis indicate that CO₂ sequestration is likely to be a significant component of the World's response to climate change in the coming decades.



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