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Cost Analysis of Adsorption based Air Capture of CO2

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Preface

Carbon dioxide (CO2) capture and conversion to value added products, such as chemicals, polymers, and carbon-based fuels represents a promising approach to transform a potential threat to the environment into a value-added product for long term sustainability. Emerging Carbon Capture Technologies: Towards a Sustainable Future provides a multidisciplinary view of the research that is being carried out in this field, covering materials and processes for CO2 capture and utilization and including a broad discussion of the impact of novel technologies in carbon capture on the energy landscape, society and climate. Of interest to students, researchers and professionals in industries related to greenhouse gas mitigation, post-combustion CO2 capture processes, coal-fired power plants, environmental sustainability, green solvents, green technologies, and the utilization of clean energy for environmental protection, this book covers both the experimental and theoretical aspects of novel materials and process development providing a holistic approach toward a sustainable energy future.

Cost Analysis of adsorption based direct air capture of CO_2 using porous sorbents, especially porous polymer networks(PPNs) provide a thorough, non-specialist introduction to technologies aimed at reducing greenhouse gas emissions from burning fossil fuels during power generation and other energy-intensive industrial processes, such as steelmaking. Extensively revised and updated, this second edition provides detailed coverage of key carbon dioxide capture methods along with an examination of the most promising techniques for carbon storage.

The book opens with an introductory section that provides background regarding the need to reduce greenhouse gas emissions, an overview of carbon capture and storage (CCS) technologies, and a primer in the fundamentals of power generation. Chapters focus on key carbon capture technologies, including absorption, adsorption, and membrane-based systems, addressing their applications in both the power and non-power sectors.

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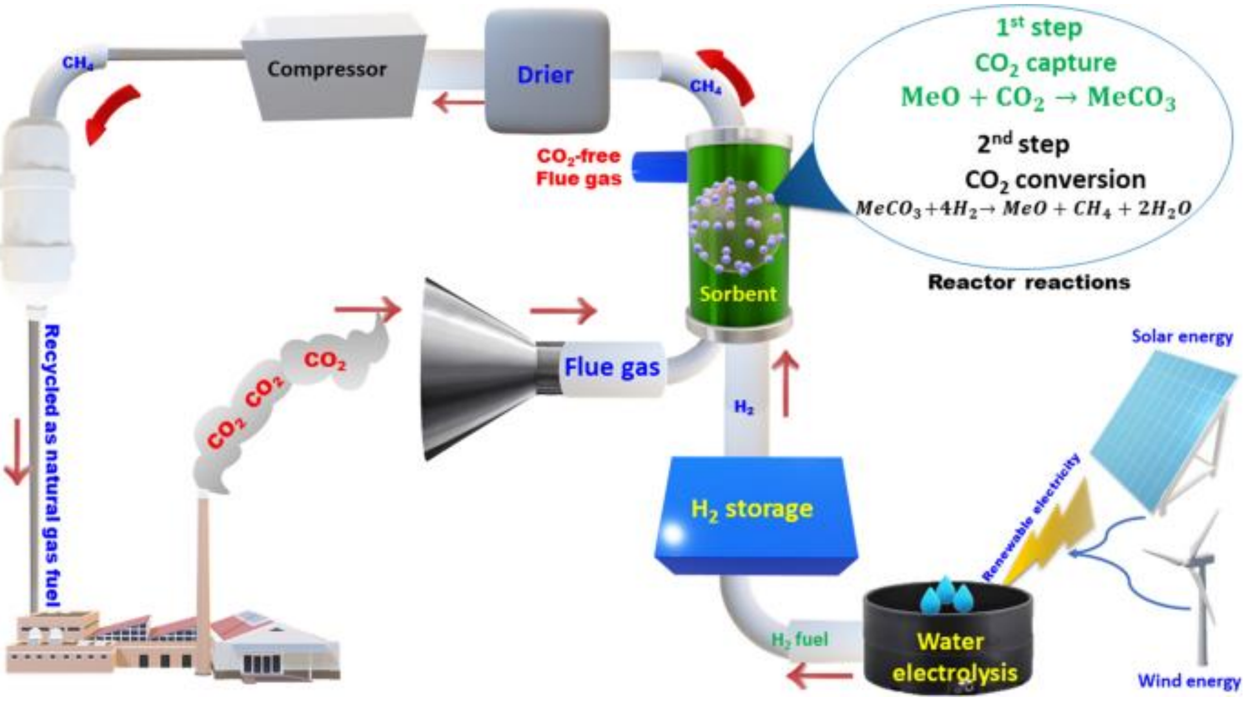

CH_4
Compressor
Drier
CH_4
1st step
CO_2 capture
$MeO + CO_2 \rightarrow MeCO_3$
2nd step
CO_2 conversion
$MeCO_3 + 4H_2 \rightarrow MeO + CH_4 + 2H_2O$
Reactor reactions
CO_2-free Flue gas
Sorbent
Recycled as natural gas fuel
CO_2 CO_2 CO_2
Flue gas
H_2
Solar energy
H_2 storage
Renewable electricity
Water electrolysis
H_2 fuel
Wind energy

Chapter 1

Capture from Industrial Sources

Carbon capture

We believe carbon capture utilization and storage (CCUS) will play a key role in global efforts to reduce emissions, while ensuring the world can continue to thrive.

Carbon capture, utilization, and storage (CCUS) is a technology approach to the management of anthropogenic carbon dioxide gas emissions to the atmosphere. By injecting CO_2 into host rocks, or by employing an ex-situ application step, geological formations can react with and store huge volumes of CO_2 as carbonate minerals. An alternative mineral feedstock material is the Gt of industrial process wastes that are often disposed to landfill. By applying an accelerated carbonation step to solid waste, there is potential to sequestrate meaningful quantities of CO_2 in carbonate-cemented products that have reuse potential. The manufacture of carbonated aggregates is commercially established in Europe, and recent advances in technology include a mobile plant that directly utilizes flue-gas derived CO_2 in the mineralization process. The present work discusses the basis for mineralization in geologically derived minerals and industrial wastes, with a focus being on the manufacture of products with value. An assessment of mineralized construction aggregates suggests that carbon capture, utilization, and storage technology can manage significant quantities of this CO_2

How does CCUS work

CCUS technologies capture CO_2 emissions at source or directly from the air.
CO_2 emissions are then transported away and stored deep underground or turned into useful products.

Capturing carbon has been used for decades to help improve the quality of natural gas, but pioneering new technologies mean we can now remove and sequester CO_2 indefinitely. Moreover, we are exploring new ways to add value to waste CO_2 by turning the gas into marketable industrial and commercial products.

Uthmaniyah is one of the Middle East’s largest carbons enhanced oil recovery initiatives, which sees carbon captured and reinjected back into an oil reservoir.

What CCUS technologies are available?

- **Capture** technologies take CO_2 from exhaust or reformed gases or stationary sources using pre-combustion, post combustion, or oxy-combustion techniques
- **Sequestration** technologies deposit captured CO_2 in geological formations
- **Enhanced Oil Recovery** involves extracting oil from oil fields by changing the original properties of oil, such as chemical flooding, carbon dioxide injection, or thermal recovery
- **Utilization** means using captured CO_2 directly for example in manufacturing cement or converting captured CO_2 and other gases into useful industrial products like chemicals or fuels
- **Mobile Carbon Capture** technologies capture CO_2 from mobile sources and store the gas on board, ready for sequestration or utilization.
- **Direct Air Capture** processes capture CO_2 directly from the atmosphere (rather than at source), to be sequestered or utilized.
- **Bio Energy Carbon Capture and Storage** technologies extract and store CO_2 from biomass, itself a renewable energy source.
- Finally, **nature** can act as a natural carbon sink. Mangrove trees, for example, sequester carbon far more effectively and permanently than terrestrial forests. Alternatively, CO_2 can be sequestered by cultivating algae, which can be harvested and processed to produce useful products like biofuel and protein-rich animal feed.

What are we doing to implement CCUS?

As the world's largest integrated energy and chemicals company, we believe Aramco is uniquely qualified to drive the technology and collaboration needed to address the global emissions challenge. Our innovative low-carbon practices and technologies already position us as one of the lowest carbon emitters in our industry, and we have the brightest minds working on carbon capture and sequestration.

Some of our latest projects in this field are as follows:

Pioneering enhanced oil recovery

Carbon capture and sequestration is the process of capturing waste CO_2 from large sources, such as power plants, before depositing it underground to prevent it from entering the atmosphere.

At one of the Middle East’s largest CO_2 capture and storage demonstration projects, we’re proving it’s possible to capture CO_2 , inject it in our reservoirs, and test the feasibility of enhancing oil recovery in the process.

Every day, we have the capability to capture and process 45 million standard cubic feet of CO_2 at our plant in Hawiyah. The captured CO_2 is piped 85 kilometers and pumped into the Uthmaniyah oil reservoir, sequestering the gas while also helping to maintain pressure in the reservoir and recover more oil. Since the initial injection of CO_2 in 2015, we have doubled oil production rates from four of our wells.

We are currently evaluating the scheme for potential future applications at other facilities and oil fields in the Kingdom. This pioneering work in carbon capture and sequestration is just one element of our Corporate Carbon Management Technology Roadmap, guided by our Advanced Research Center of our Exploration and Petroleum Engineering Center (EXPEC ARC) in Dhahran, Saudi Arabia.

Driving technological change in transport

Aramco is working with a number of partners to develop Mobile Carbon Capture and storage technologies for cars and trucks. Today, the latest variant of the technology can capture and store up to 25% of the CO_2 in their exhaust omissions on-board, before unloading the gas at fuel stations for sequestration or recycling into other forms of material or energy.

Our efforts to reduce CO_2 emissions in the automotive sector are further evidenced by the work of our global research network. For example, we are also advancing automotive technologies that, in combination with innovative new fuels, can substantially reduce emissions and improve efficiency for light-duty vehicles, while maintaining expected performance.

While others view CO_2 and other GHG emissions as waste products, we see them as useful materials to create potential additional value streams for our company, such as manufacturing feedstock.

Harnessing nature’s power

Nature-based solutions also play an important role in removing carbon as part of the Circular Carbon Economy (CCE) the framework promoted by the Kingdom and adopted by the G20 member states during Saudi Arabia’s presidency of the G20.In line with CCE, Aramco’s initiative to protect, plant and restore millions of mangrove trees inside and outside the Kingdom will absorb carbon and enhance biodiversity, while also prioritizing water conservation, treatment, and reuse.

Mangrove trees act as an effective, natural carbon sink. Our mangrove plantation initiative to restore lost mangrove habitats in the Kingdom’s coastal areas is a voluntary sustainability community initiative to protect the natural habitats and ecosystems our company relies on.

In addition to our mangrove initiative Aramco is working on other nature-based solutions such as developing algae ponds and photo bioreactors that are expected to reduce thousands of tons of CO_2 emissions from across our operations.

As a founding member of the Oil & Gas Climate Initiative (OGCI), Armco work with many of the world's leading energy companies to find practical solutions to climate change. A key focus is on injecting momentum into a global CCUS industry, using our collective expertise to support shared infrastructure and operations, and implement CCUS at a lower cost. With OCCGI partners Armco recently spearheaded an OGCI report 'CCUS in Saudi Arabia: the value and opportunities for deployment' to bring focus to the challenges and opportunities of scaling this technology.

Reaction of Carbon Dioxide with Mineral Systems

Mineralization is nature's way to sequester CO_2, but it is a slow process. The hydrolysis of CO_2 in moist air or water is a major driver of rock chemical weathering. The geological record indicates that tectonic forcing exposes large rock masses to the atmosphere and subsequent weathering occurs at a rate that can markedly reduce atmospheric. Notwithstanding that natural weathering can remove some 30 Gt of CO_2 from the atmosphere each century, it is this natural process that has the potential to be accelerated and, therefore, industrialized. In this way, anthropogenic CO_2 can combine with a reactive substrate to form a mineralized product carbonate salt, for ultimate disposal or conversion into valorized products. Mineralized products have the potential to be beneficially utilized in quantities that can ultimately reduce the effects of global warming.

Carbon Capture, Utilization, and Storage

The concept of managed mineralization offers an environmentally sustainable opportunity that can work in synergy with carbon capture and storage. By incorporating a "utilization" option within a "storage" concept, captured CO_2 can be used as a feedstock for making products, products in which CO_2 gas is sequestered permanently. This unison is known as carbon capture, utilization, and storage (CCUS).

It is not widely appreciated that CO_2 gas has been used for centuries as a feedstock in industrial processes. Uses extend from carbonating beverages (18th Century) to the application of supercritical CO_2 in the manufacture of instant coffee, pharmaceuticals (20th Century), or construction materials (21st Century).

CO_2 gas-enhanced curing chambers have been utilized for conditioning and accelerating the hardening of cementitious materials since the 19th century ,as alkaline materials tend to be very CO_2 reactive. The tendency of minerals to react with CO_2 under the right conditions can be harnessed for CCUS, using both in situ and ex situ processing methods. The application of in situ mineralization technology has been described as mineral trapping or managed weathering and is simply an accelerated weathering step. Silicate rocks are the most suitable host rock formations for mineralized carbon, with the rate of carbonate mineral production being kinetically controlled . As mineral carbonation is an analog of natural weathering, the reaction between CO_2 and suitable silicate rocks can be summarized as (Equation 1):

$$\text{(Ca,Mg)SiO3(s) + CO2(g)} \rightarrow \text{(Ca,Mg)CO3(s) + SiO2(s)(Ca,Mg)SiO3(s) + CO2(g)} \rightarrow \text{(Ca,Mg)CO3(s) + SiO2(s)}$$

If we consider the course of natural weathering of olivine (Mg_2SiO_4) or serpentine [$Mg_3Si_2O_5(OH_4)$], it is the dissolution and ionization of CO_2 in the rain or groundwater that produces carbonic acid. This, in turn, dissociates into H^+ and $HCO3^-$ or bicarbonate. As bicarbonate is conjugate acidic, it can chemically degrade susceptible minerals, liberating calcium and magnesium, which then bind with the bicarbonate to form solid carbonates.

Potential geological storage “reservoirs” for mineralized CO_2 involve igneous (flood basalts, pillow lavas, and ultramafic rocks, such as peridotite), metamorphic (serpentinites and ophiolites), and perhaps, surprisingly, sedimentary rock formations, such as glauconitic and hematite-cemented sandstones. In respect of the latter, hematite has the potential to form siderite ($FeCO_3$) or ankerite ($CaCO_3$, $MgCO_3$, and $FeCO_3$), when Fe^{3+} is reduced to Fe^{2+}. Arkosic sandstones, containing feldspar, are also a potential target host rock formation. Plagioclase (anorthite) found in igneous rocks and arkose may be a mineral suitable for carbonation; its reaction with CO_2 gas is summarized below (Equation 2):

$$CaAlSi2O8 + H2CO3 + H2O \rightarrow CaCO3 + Al2Si2O5(OH)4 \quad (2)$$

$$CaAlSi2O8 + H2CO3 + H2O \rightarrow CaCO3 + Al2Si2O5(OH)4 \quad (2)$$

Of particular interest are flood basalts with high porosity and a linked vesicular structure. These potential host rocks extend to thousands of cubic kilometers but can be geographically isolated, as are pillow lavas. Where basalt formations are saline, stable carbonates, including calcite, magnesite, and siderite, may be expected to form on contact with H_2CO3 Groundwater permeation through ultramafic rocks, such as dunnite, is accompanied by the dissolution of alkali and precipitation of carbonate

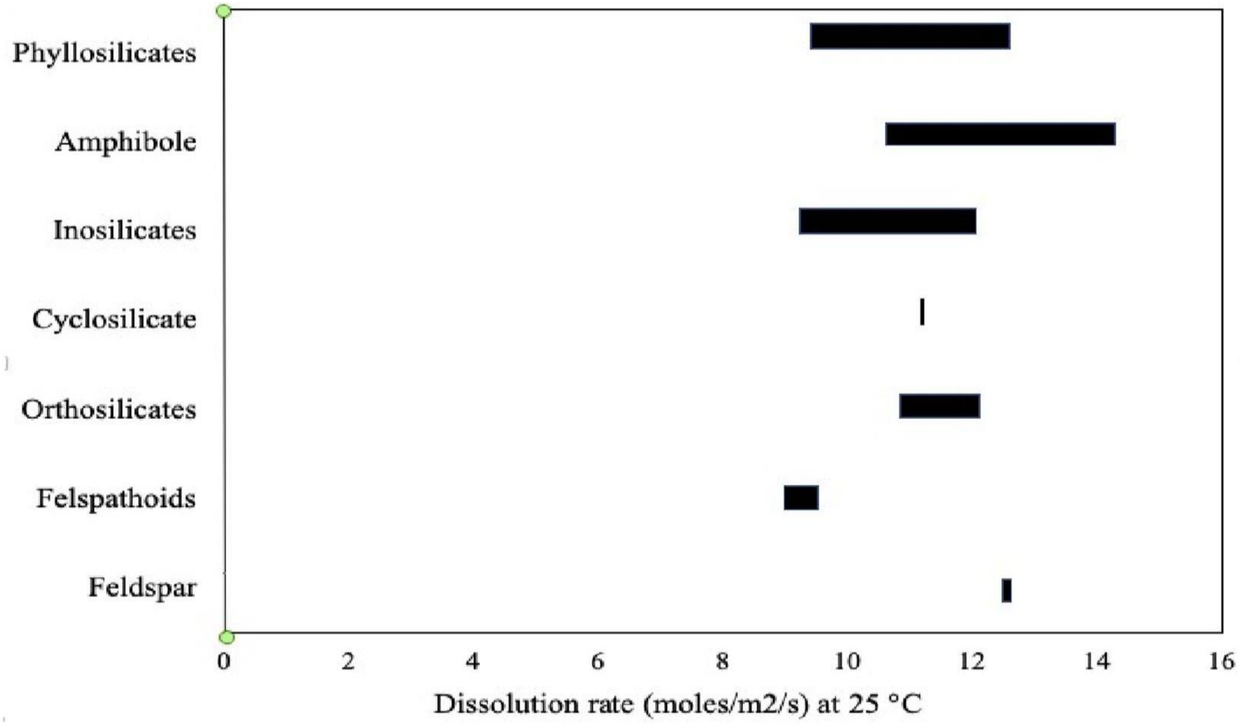


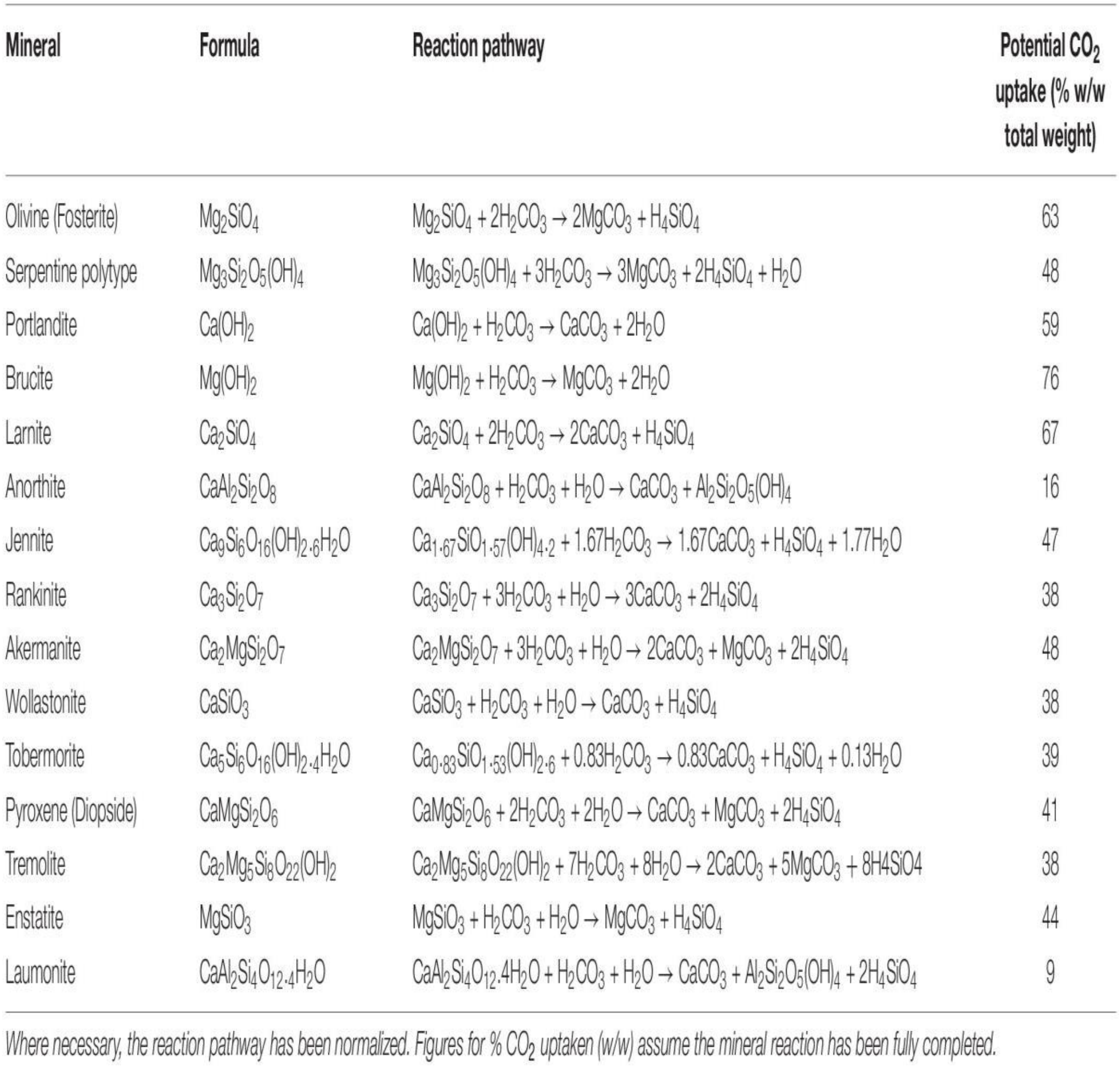
Figure 1. Dissolution rates for major rock-forming minerals at 25°C and pH

The injection of CO_2 into the vicinity of active spreading ridges, where new oceanic crust is being formed, has been suggested as suitable host rocks, as they are characterized by saline hydraulic gradients . Seawater flows into pelagic sediments towards the spreading ridge itself, and injection of CO_2 would promote the formation of Mg and Ca carbonates. Estimate that there is a capacity to store 8–40,000 Gt of CO_2 worldwide in the vicinity of spreading ridges.

Wherever suitable rock formations exist, their physical and chemical characteristics, including interlinked void space, pore solution chemistry, and temperature are key considerations for suitability for large-scale mineralization.

As such, one of the issues to be faced is the reaction yield, that is, how much CO_2 is mineralized per unit of mass of target mineral. Rarely is a target mineral reacted with CO_2 as predicted on stoichiometry grounds, meaning that in ex situ applications, high temperatures and pressures and the use of chemical reagents are required to achieve an acceptable yield in a short time. This will inevitably have an impact on cost, as the amount of target mineral required to trap 1 t of CO_2 (the R_{CO_2}) already varies widely; for example, the feedstock requirement for olivine, wollastonite, basalt, and magnetite is 1.6, 2.6, 4.9, and 5.3 t, respectively

The reaction of CO_2 with olivine and serpentine in the presence of water is given in Table 1,. Thus, a 100% reaction condition is rarely achieved.



Mineral	Formula	Reaction pathway	Potential CO_2 uptake (% w/w total weight)
Olivine (Fosterite)	Mg_2SiO_4	$Mg_2SiO_4 + 2H_2CO_3 \rightarrow 2MgCO_3 + H_4SiO_4$	63
Serpentine polytype	$Mg_3Si_2O_5(OH)_4$	$Mg_3Si_2O_5(OH)_4 + 3H_2CO_3 \rightarrow 3MgCO_3 + 2H_4SiO_4 + H_2O$	48
Portlandite	$Ca(OH)_2$	$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O$	59
Brucite	$Mg(OH)_2$	$Mg(OH)_2 + H_2CO_3 \rightarrow MgCO_3 + 2H_2O$	76
Larnite	Ca_2SiO_4	$Ca_2SiO_4 + 2H_2CO_3 \rightarrow 2CaCO_3 + H_4SiO_4$	67
Anorthite	$CaAl_2Si_2O_8$	$CaAl_2Si_2O_8 + H_2CO_3 + H_2O \rightarrow CaCO_3 + Al_2Si_2O_5(OH)_4$	16
Jennite	$Ca_9Si_6O_{16}(OH)_{2\cdot6}H_2O$	$Ca_{1\cdot67}SiO_{1\cdot57}(OH)_{4\cdot2} + 1.67H_2CO_3 \rightarrow 1.67CaCO_3 + H_4SiO_4 + 1.77H_2O$	47
Rankinite	$Ca_3Si_2O_7$	$Ca_3Si_2O_7 + 3H_2CO_3 + H_2O \rightarrow 3CaCO_3 + 2H_4SiO_4$	38
Akermanite	$Ca_2MgSi_2O_7$	$Ca_2MgSi_2O_7 + 3H_2CO_3 + H_2O \rightarrow 2CaCO_3 + MgCO_3 + 2H_4SiO_4$	48
Wollastonite	$CaSiO_3$	$CaSiO_3 + H_2CO_3 + H_2O \rightarrow CaCO_3 + H_4SiO_4$	38
Tobermorite	$Ca_5Si_6O_{16}(OH)_{2\cdot4}H_2O$	$Ca_{0\cdot83}SiO_{1\cdot53}(OH)_{2\cdot6} + 0.83H_2CO_3 \rightarrow 0.83CaCO_3 + H_4SiO_4 + 0.13H_2O$	39
Pyroxene (Diopside)	$CaMgSi_2O_6$	$CaMgSi_2O_6 + 2H_2CO_3 + 2H_2O \rightarrow CaCO_3 + MgCO_3 + 2H_4SiO_4$	41
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	$Ca_2Mg_5Si_8O_{22}(OH)_2 + 7H_2CO_3 + 8H_2O \rightarrow 2CaCO_3 + 5MgCO_3 + 8H4SiO4$	38
Enstatite	$MgSiO_3$	$MgSiO_3 + H_2CO_3 + H_2O \rightarrow MgCO_3 + H_4SiO_4$	44
Laumonite	$CaAl_2Si_4O_{12\cdot4}H_2O$	$CaAl_2Si_4O_{12}.4H_2O + H_2CO_3 + H_2O \rightarrow CaCO_3 + Al_2Si_2O_5(OH)_4 + 2H_4SiO_4$	9

Where necessary, the reaction pathway has been normalized. Figures for % CO_2 uptaken (w/w) assume the mineral reaction has been fully completed.

Table 1. Common minerals and their reactivity with carbon dioxide.

As the rate of reaction between rock and bicarbonate is slow, a managed mineralization step requires a high-energy environment and complex reaction conditions to overcome kinetic constraints . Thus, until mineralization technology advances, the in-situ injection of CO_2 into a rock for storage (as opposed to the utilization of sedimentary formations found in depleted oil wells) is unlikely to be widely adopted.

Accelerated Carbonation of Mineral Systems

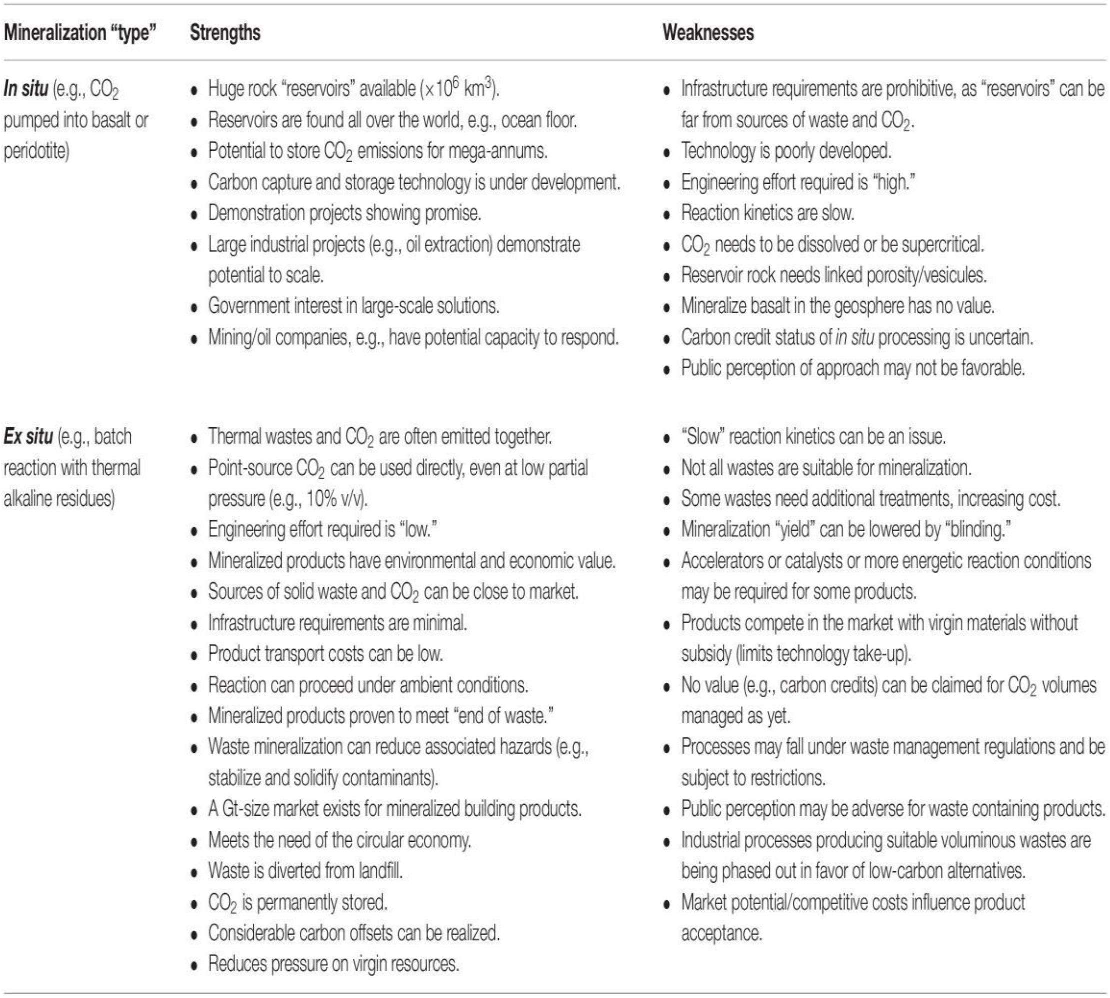
The mining and fine grinding of basaltic or other rocks have been investigated for ameliorating soil to enhance mineral weathering and produce bicarbonate . Notwithstanding, the impacts on the chemistry of the oceans, the logistics involved in mining, processing, transporting, and widely applying this technology are likely to be prohibitive.

It is often assumed that the use of *ex situ* treatments may overcome many of the issues associated with the costs and technical complexity of the in-situ mineralization of CO_2 in host rocks. An advantage of ex situ processing is the ease of auditing and confirming the permanence of carbon stored in the mineralized product(s). The drawbacks in respect of the energy requirement associated with processing and subsequent carbonation are augmented by one issue not receiving much attention to date, and that is the disposal of the mineralized media back into the geosphere. As mineralized products occupy significantly more volume than the originally excavated rock as it now contains carbonate, the environmental impacts associated with "landfilling" more rock that was excavated must be fully costed, as environmental harm will undoubtedly arise. Geologically derived feedstock materials for mineralization, such as olivine and serpentine, are abundant, and mining technologies are mature enough to handle appropriate quantities of processed mineral media for carbonation.

The high costs of intensive reaction conditions can, to a certain extent, be mitigated if commercially attractive mineral products, such as silica or magnesia, can be made available for sale.

For the industry to apply mineralization technology, changes in commercial and regulatory operating environments are needed. This is particularly important if the mineralization processes used manufacturing products that are suitable for reuse or sale into the market. Unless facilitating tax, regimes are in place to support processing and the disposal of mineralized products to land, the cost involved can only be mitigated by the manufacture of products for sale, such as silica or finely divided calcium carbonate.

Table 2 gives a general comparison of the strengths and weaknesses of in situ and ex situ mineralization technologies. There are benefits from both approaches; however, technology readiness and the investment involved are important impediments, especially where *in situ* technologies are concerned.



Mineralization "type"	Strengths	Weaknesses
In situ (e.g., CO_2 pumped into basalt or peridotite)	• Huge rock "reservoirs" available (×10^6 km^3). • Reservoirs are found all over the world, e.g., ocean floor. • Potential to store CO_2 emissions for mega-annums. • Carbon capture and storage technology is under development. • Demonstration projects showing promise. • Large industrial projects (e.g., oil extraction) demonstrate potential to scale. • Government interest in large-scale solutions. • Mining/oil companies, e.g., have potential capacity to respond.	• Infrastructure requirements are prohibitive, as "reservoirs" can be far from sources of waste and CO_2. • Technology is poorly developed. • Engineering effort required is "high." • Reaction kinetics are slow. • CO_2 needs to be dissolved or be supercritical. • Reservoir rock needs linked porosity/vesicules. • Mineralize basalt in the geosphere has no value. • Carbon credit status of *in situ* processing is uncertain. • Public perception of approach may not be favorable.
Ex situ (e.g., batch reaction with thermal alkaline residues)	• Thermal wastes and CO_2 are often emitted together. • Point-source CO_2 can be used directly, even at low partial pressure (e.g., 10% v/v). • Engineering effort required is "low." • Mineralized products have environmental and economic value. • Sources of solid waste and CO_2 can be close to market. • Infrastructure requirements are minimal. • Product transport costs can be low. • Reaction can proceed under ambient conditions. • Mineralized products proven to meet "end of waste." • Waste mineralization can reduce associated hazards (e.g., stabilize and solidify contaminants). • A Gt-size market exists for mineralized building products. • Meets the need of the circular economy. • Waste is diverted from landfill. • CO_2 is permanently stored. • Considerable carbon offsets can be realized. • Reduces pressure on virgin resources.	• "Slow" reaction kinetics can be an issue. • Not all wastes are suitable for mineralization. • Some wastes need additional treatments, increasing cost. • Mineralization "yield" can be lowered by "blinding." • Accelerators or catalysts or more energetic reaction conditions may be required for some products. • Products compete in the market with virgin materials without subsidy (limits technology take-up). • No value (e.g., carbon credits) can be claimed for CO_2 volumes managed as yet. • Processes may fall under waste management regulations and be subject to restrictions. • Public perception may be adverse for waste containing products. • Industrial processes producing suitable voluminous wastes are being phased out in favor of low-carbon alternatives. • Market potential/competitive costs influence product acceptance.

Table 2. Example strengths and weaknesses of mineralization technologies

Treatment of Industrial Process Waste

The mineralization of CO_2 in waste has been variously demonstrated in the laboratory and commercially, including at ambient temperature and pressure conditions. The mineralization reaction primarily involves metal/mineral oxides, hydroxides, and silicates with CO_2 gas. Mineralization can be achieved (in minutes), but the reactions concerned are rarely fully completed. Calcium and magnesium carbonates, on account of the environmental impact and stability, are the favored reaction products and are simply represented as M^+ (Equations 3 and 4):

$$M+O + CO2 \rightarrow M+CO3(3)M+O + CO2 \rightarrow M+CO3(3)$$

$$M+(OH)2 + CO2 \rightarrow M+CO3 + H2O(4)M+(OH)2 + CO2 \rightarrow M+CO3 + H2O(4)$$

A “world-first” long-term study on the sequestration of CO_2 in soil via field-scale carbonate-based solidification treatment of contaminated soil in Southeast England was carried out in 2000.

Wastes included air pollution control residues (APCr), which were mineralized with CO_2 derived from a landfill flare. The aggregated products were found to comply with construction material standards, and the approach was further developed and scaled up and commercialized in the United Kingdom .

Figure 2. Manufactured carbonated aggregate <14 mm (courtesy of Carbon8 Systems, Ltd.).

The mineralization of CO_2 in waste is attractive, as it is a circular economic approach that can be achieved via direct use of available point-source CO_2. Potential carbonate-able wastes and CO_2 sources are generally co-located, and this provides a unique opportunity to strip the CO_2 gas directly from a flue to manage both solid- and gaseous-waste streams efficiently.

The formation of carbonates is an energetically downhill process, with the chemical reactions (e.g., as shown in Equations 3 and 4) being highly exothermic. The heat generated by a managed mineralization process can be recovered and reused. Important circular economic considerations related to mineralization include:

- Availability, location, and source of both solid waste and CO_2 gas.
- Optimal handling of feedstock solid and gaseous waste.
- Use of renewable energy in processing; and
- Facilitating standards for the use of the mineralized products.

The waste materials that have the right chemistry, mineralogy, and physical properties can react with CO_2 under ambient temperature and pressure conditions. The carbonate-cemented products can have the potential for reuse in engineering applications. However, as many industrial waste streams contain priority metals, there is a possibility of pre-processing to extract and recover the valuable metals before carbonation is carried out.

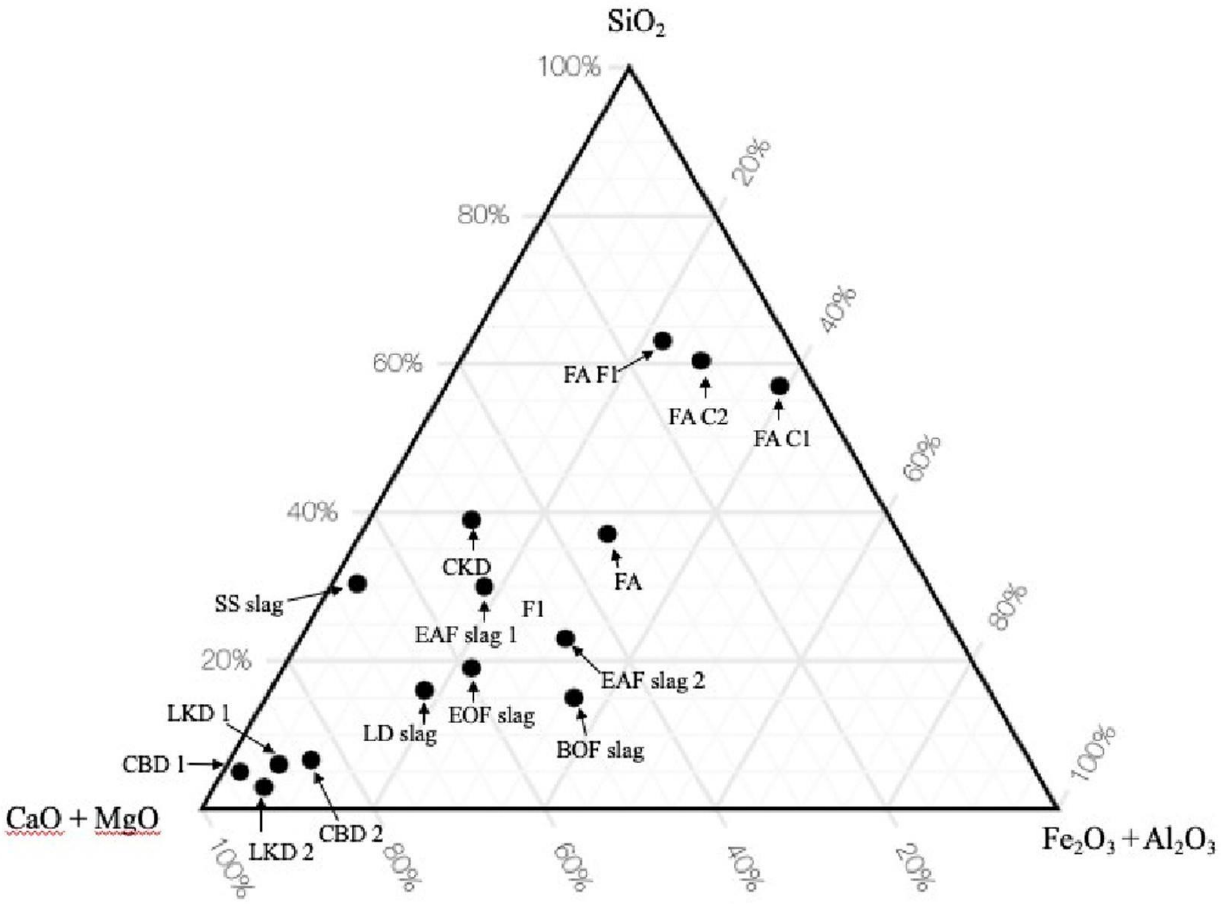


Figure 3. Normalized phase diagram showing the variability in chemistry of industrial process wastes

There are several technical issues that potentially negatively impact the versatility of mineralization as a mechanism to carbonate wastes. One of those to avoid is the use of pure CO_2, supplied as a process gas as the costs involved in compressing and transportation being relatively high. Thus, by capturing CO_2 directly from a flue gas without purification and liquefaction, costs are kept to a minimum as, for example, thermal residues can be reacted readily with the CO_2 released during their combustion without the need for transportation to a mineralization plant for onward processing. However, the amount of CO_2 in a flue gas can be low, and 10% v/v is not untypical. A point source with a low pCO_2 will necessitate extended reaction times and higher processing costs.

One approach to overcoming the kinetic constraints of flue gas with a low pCO_2 is the use of accelerators, and several homogeneous catalysts are available. These include

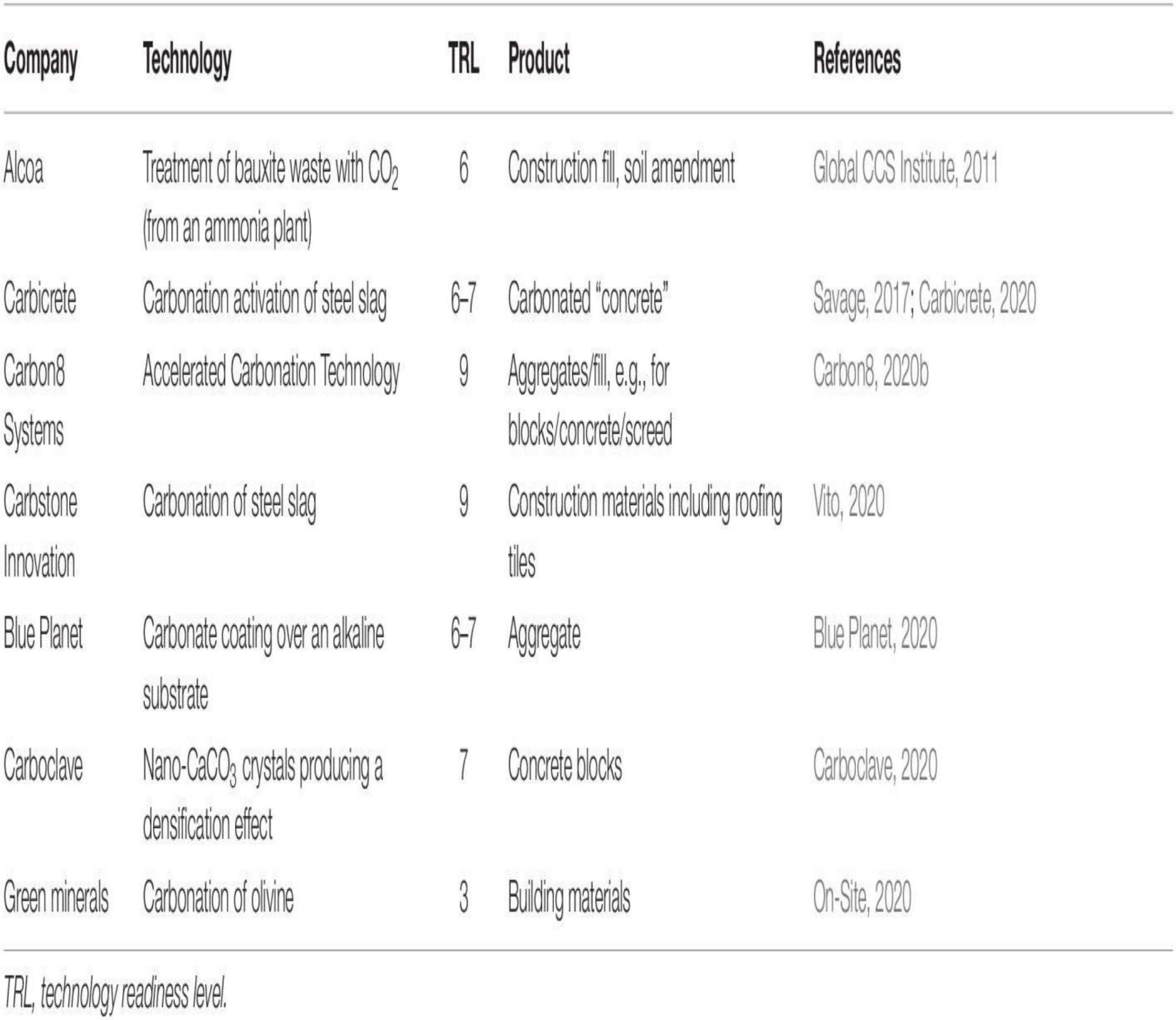
inorganic oxyanions (e.g., hypochlorite or sulfite), organic solutes (e.g., sugars and polyhydric alcohols), and amines and alkanolamines (which produce carbamates with CO_2) for the solvation and hydration of CO_2 in water that are available
It is important, however, to ensure that the presence of residual catalysts in the mineralized product does not affect reuse as might happen with enhanced sulfate or chloride leaching.

Legacy Wastes

Legacy residues, such as mine tailing, have the potential to be passively carbonated or mined as a feedstock for CCUS. This approach is sometimes called surficial carbonation, and tailings arising from mafic and ultramafic rock sources are candidate
wastes suggests that 10× Mt/year CO_2 can be readily sequestered in mine tailings this way investigates the carbonation of alkali earth silicate and hydroxide-containing minerals.

Carbon Dioxide Mineralization in the Construction Industry

As mentioned, CO_2 has been long used to accelerate the curing of concrete and mortar. However, this application has rarely, if at all, been used to achieve a high degree of carbonation (i.e., where carbonate phases are responsible for hardening, rather than “normal” hydrated phases).



Company	Technology	TRL	Product	References
Alcoa	Treatment of bauxite waste with CO_2 (from an ammonia plant)	6	Construction fill, soil amendment	Global CCS Institute, 2011
Carbicrete	Carbonation activation of steel slag	6–7	Carbonated "concrete"	Savage, 2017; Carbicrete, 2020
Carbon8 Systems	Accelerated Carbonation Technology	9	Aggregates/fill, e.g., for blocks/concrete/screed	Carbon8, 2020b
Carbstone Innovation	Carbonation of steel slag	9	Construction materials including roofing tiles	Vito, 2020
Blue Planet	Carbonate coating over an alkaline substrate	6–7	Aggregate	Blue Planet, 2020
Carboclave	Nano-$CaCO_3$ crystals producing a densification effect	7	Concrete blocks	Carboclave, 2020
Green minerals	Carbonation of olivine	3	Building materials	On-Site, 2020

TRL, technology readiness level.

Table 3. Selected mineralization processes yielding construction products.

A notable recent development is a mobile carbonation plant producing construction aggregates, which is a flexible alternative to fixed plants using liquid CO_2 supplied by a road tanker. The mobile plant has a capacity of approximately 12 kt/year of manufactured carbonated aggregates using CO_2 directly stripped from a point source. This enables both gaseous and solid-waste streams to be economically captured and combined at relatively small emission locations or industrial plants with limited access. Figure 4 shows the "CO2ntainer, which has been deployed at two cement plants, one in the United Kingdom and another in Ontario, the latter as a demonstration project funded under the Ontario Centers of Excellence Solutions 2030 initiative.

Figure 4. Mobile plant for manufacture of carbonated aggregates (courtesy of Carbon8 Systems, Ltd).

The capacity of the plant is designed to match the quantity of reactive waste residues generated by an industrial plant (e.g., 6–7,000 t for cement plants and 10–12,000 t for energy from wastes), removing the need to transport the waste residues for treatment at a central site and removing the need to purify the CO_2 for transport for use elsewhere. The containerized plant can be rapidly deployed and directly connected into the flue stack to extract the CO_2, with the remaining flue gas being returned to the stack.

Life Cycle and Techno-Economic Assessments of Carbon Dioxide Mineralized Products

As we move to a circular economy as part of our wider sustainability efforts, the potential of mineralized CO_2-based products entering the marketplace mean the accounting of carbon is required. The key considerations concern the net carbon emissions of the process, materials processing/handling and transport, and energy requirements. At a system/sectoral level, the mineralization of CO_2 in wastes allows for the application of CCUS across a range of different industrial settings within an economy, making sure the varied inputs into the process are considered.

New technologies for CCUS are emerging, and their economic and environmental viability, and economic and environmental trade-offs must be carefully analyzed. This involves a combination of life cycle assessment (LCA) and techno-economic assessment (TEA) and is key to informed decision-making and a standardized assessment. Several regulatory bodies of the European Commission (e.g., the Scientific Advice Mechanism, EIT Climate-KIC) have recognized the need of a common assessment guidelines involving LCA and TEA to enhance reliability, transparency, and compatibility of CCUS technologies and their technology readiness

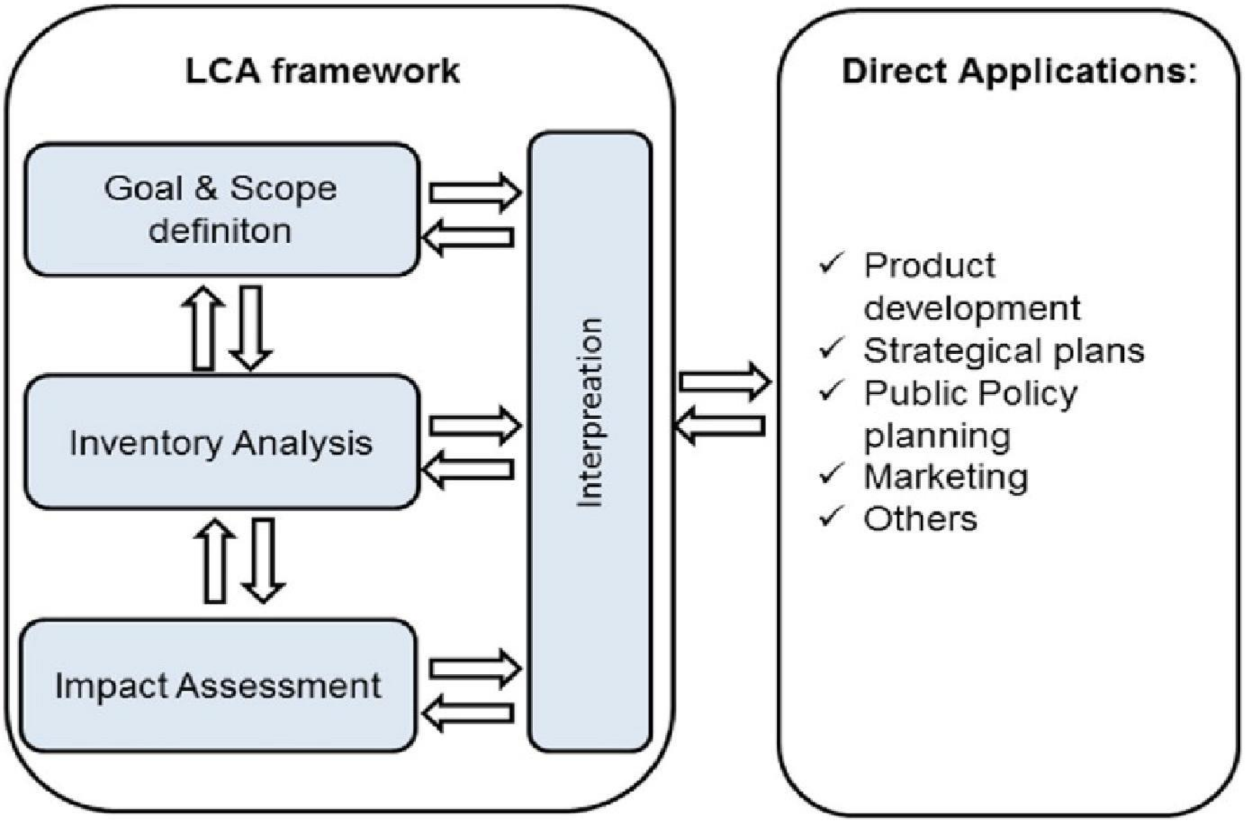
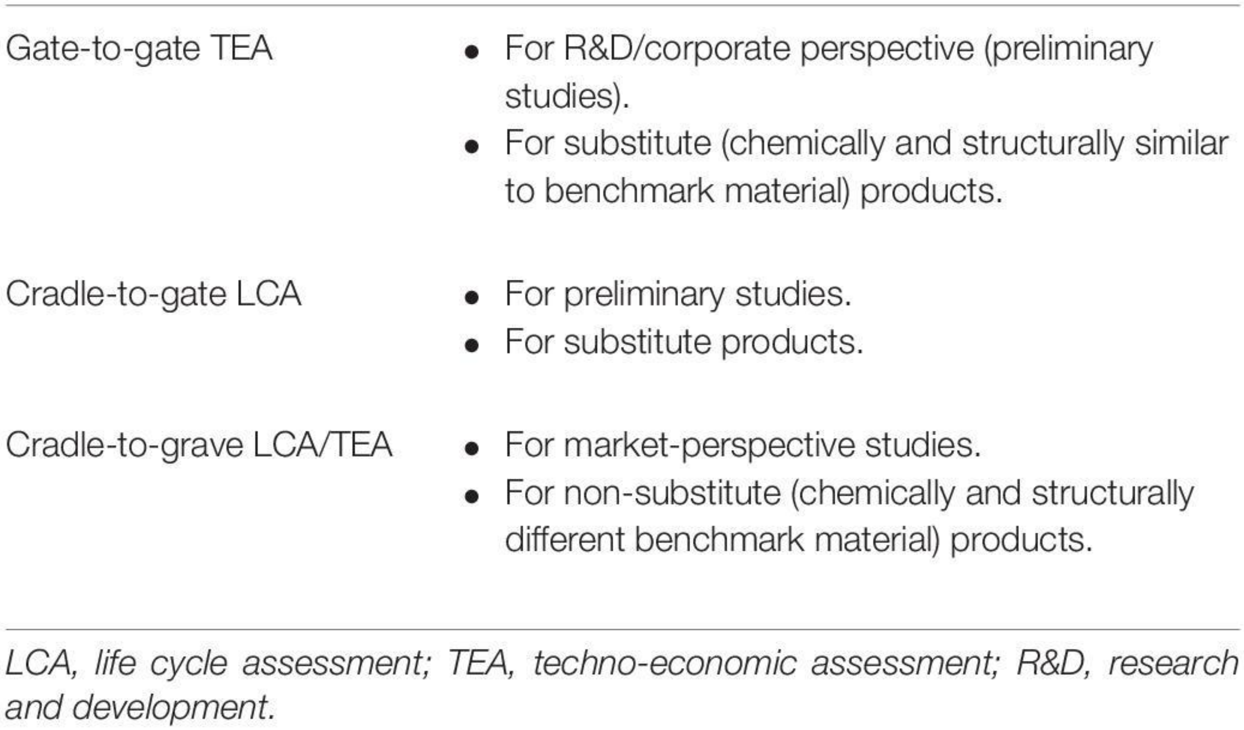


Figure 5. General framework for life cycle assessment .

The TEA is a widely used tool that considers several perspectives (e.g., research and development, corporate, and market) and varying guidelines according to application, technology development, and stakeholder needs .



Gate-to-gate TEA	For R&D/corporate perspective (preliminary studies). For substitute (chemically and structurally similar to benchmark material) products.
Cradle-to-gate LCA	For preliminary studies. For substitute products.
Cradle-to-grave LCA/TEA	For market-perspective studies. For non-substitute (chemically and structurally different benchmark material) products.

LCA, life cycle assessment; TEA, techno-economic assessment; R&D, research and development.

Table 4. The scope of LCA and TEA in CCU-based products.

Future Developments for Carbon Dioxide Mineralization

Within the United Kingdom, the right commercial environment exists to produce manufactured accelerated carbonated aggregates that are cost-competitive to natural stone and are market accepted. Acknowledging that the United Kingdom situation may be fortunate, in which aggregate sources are dwindling, landfilling of waste is subject to rising prices, and the market is amenable to new products.

However, as it currently stands, the general development of mineralization processes is largely held back by a mix of technical and economic reasons Current hurdles to overcome and their likely solutions are given in Table 5.

Problem	Solution	Timescale
Carbonation is kinetically controlled	Catalysts to increase efficiency of mineralization processes are required	Medium
Higher energy processing to increase “yield” is costly	Ensure renewable energy systems employed with catalysis	Medium
The cost of accessing and securing CO_2 is too high	Develop processes or sorbents that directly strip CO_2 from flue gas	Short
Regulation is immature and lacking for capture of CO_2 in waste	Revise waste regulations to allow combining of gaseous and solid emissions	Short
Investment is hard to obtain/too costly, so business-related risk is not low enough	Government to underwrite and reduce risk profile for CCUS technologies	Medium
Materials standards do not recognize mineralized products	Ensure materials standards are cross-cutting and do not rely on virgin feedstock	Medium-long
Value for mineralized products has to be created	Government to provide incentives (e.g., tax breaks) for CCUS-derived products	Short-medium
Public acceptance needs to be improved	Implement a public awareness campaign of benefits of the circular economy	Medium
Government incentives are not available to grow a “mineralization” industry	Ensure climate change mitigation and CCUS is central to fiscal policy	Medium
Infrastructure remains lacking	Ensure *trans*-boundary infrastructural systems is built and available for use	Medium-long

Table 5. Problems and solutions for the development of mineralization technologies.

The mineralization of CO_2 in geologically derived and solid process wastes is attractive, not least that the quantities of mineral feedstock available are suitable for sequestering Gt of carbon each year. As the technology and infrastructure required develop, the associated costs will decrease. How this will be paid for and by whom is a matter of current debate. In the meantime, efficiency measures, renewable energy sources, and other measures will go some way to limit emissions to the atmosphere.

The appeal of wastes as a feedstock for mineralization is promising, as the technology for manufacturing mineralized products is already commercially established and is being further developed (e.g., mobile carbonation plant directly using CO_2 from point-source emissions). In addition, the following advantages may also apply:

- Solid waste and point-source CO_2 are commonly co-located,
- Many solid process wastes are alkaline in nature, and
- Being often located close to the market is an added advantage, as proximity to the market is critical if valorized products are to be cost-competitive with virgin products.

An important implication of mineralization of CO_2 in waste to produce construction materials is the environmental and economic benefits accrued via direct and indirect CO_2 emissions offset. The direct offset is achieved via permanently sequestering CO_2 in waste-based products, whereas indirect offsets can be realized by:

- Direct replacement of cement with carbonated materials made from waste,
- Replacement of hydraulic cement by carbonate-able binders,
- Reduction of transport involved in landfilling of waste,
- Replacement of quarried virgin stone,
- Reduced transport/materials handling, where solid waste and point-source CO_2 are co-located close to the market.

As the emphasis moves further towards low-carbon construction and wider certification of products becomes firmly established, the carbon offsets achieved by the manufacture and use of mineralized construction products will become more important.

The requirements for entering the “market” with a mineralized waste-based product involve complying with relevant regulatory instruments. In the European Union, this is governed by the Waste Framework Directive. However, the laws of a particular territory sometimes preclude compliance, as the framework cannot be enacted. Furthermore, the needs and perceptions of the market and the supply chain in place may be an issue. In the United Kingdom, the Environment Agency is receptive to landfill avoidance strategies through the “end of waste” process and provides objective guidance. Thus, there are several technical and non-technical challenges involved, not least securing long-term contracts for waste feedstock and product offtake and the impact these “hurdles” have on investment confidence.

A consideration not widely reported is the public perception of using wastes in products, including those for construction. Industrial by-products have been widely used in construction, such as coal fly ash (pulverized fuel ash) and steel slag (ground-granulated blast-furnace slag). These materials are wastes but have legal status as by-products. With many alkaline wastes falling under waste management regulations and remaining as wastes until they are sold to the market, a contradiction based on labeling emerges. As such, there is a need to address this either by legally changing the “label” or by educating stakeholders that mineralized products meeting “end of waste” are indeed products and not wastes by another name.

There are many considerations involved, and one might be to focus on:

- The embodied carbon within the mineralized product,
- Its fitness for purpose including meeting internationally accepted material standards
- An accentuation of the sustainability gains, including protection of virgin resources.

Also, the move by the construction industry to carbon neutrality was an important consideration to the successful entry of manufactured carbonated aggregates into the United Kingdom market. With competitive pricing and technical advantages, such as lighter weight, augmented by carbon negativity, the United Kingdom construction block industry has been receptive. Furthermore, these benefits have also been somewhat recognized by the wider stakeholder community. Thus, inward investment supporting innovation and rising industry buy-in of the sustainability gains add strength to this CCUS approach.

Currently, in Europe, there is pressure for mineralization technologies to be included in the European Union ETS along with the generation of e-fuels, to avoid the release of fossil carbon. The mechanism being proposed is via the Emissions Monitoring and Reporting Regulation and relates to the ability of industrial flue gas to be transformed into useful materials, including mineralized building products. Changes to emission trading regulations, as proposed, will be a significant stimulus to help meet innovation challenges for the circular economy, the avoidance of CO_2, protection of natural resources, and the creation of wealth.

The world market for construction aggregates is in the order of 50 Gt/year and rising, so it is well placed to receive manufactured carbonated aggregate products. The total value of aggregate sales is projected to be US$547 Bn by 2025 , highlighting that value-added mineralized product can benefit from a growing global market. With the right incentives within emerging circular economies, such as those anticipated in Europe and Asia, sustainable mineralized products can play an increasingly important role in the building materials supply chain.

Chapter 2

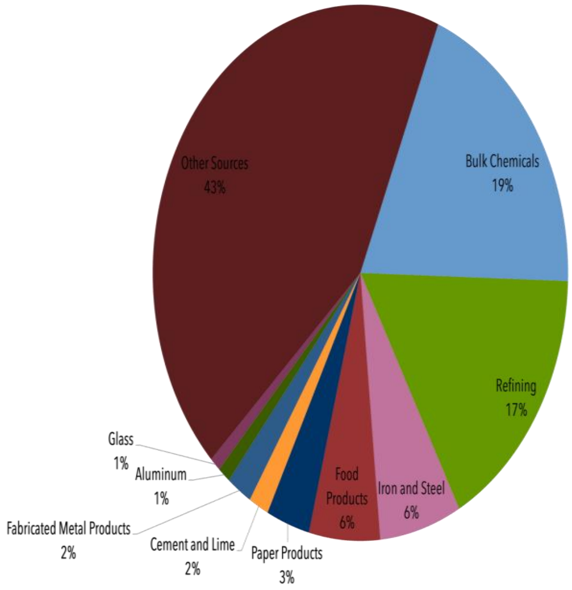
CO_2 Emission

Almost a quarter (23 percent) of U.S. greenhouse gas emissions come directly from industrial sources, such as manufacturing, food processing, mining, and construction. These direct emissions result from diverse processes, including the on-site combustion of fossil fuels for heat and power, non-energy use of fossil fuels, and chemical processes used in iron, steel, and cement production.

In addition, industry generates indirect emissions from the centrally generated electricity it consumes. The industrial sector makes up about one quarter of total U.S. electricity sales. If direct and indirect emissions are combined, the industrial sector is the largest emitting sector in the U.S. economy, responsible for 29.6 percent of total emissions

- Nearly 30 percent of U.S. greenhouse gas emissions come from industry, including indirect emissions from the sector's electricity consumption.
- Oil and gas production is the largest manmade source of methane in the United States.
- In January 2021, President Biden issued an Executive Order directing federal agencies to review actions taken during the previous administration.

Energy-related carbon dioxide emissions from industry, 2020



Source (U.S. Energy Information Administration, 2021)

Reducing Industrial Emissions

There are many ways to reduce greenhouse gas emissions from the industrial sector, including energy efficiency, fuel switching, combined heat and power, use of renewable energy, and the more efficient use and recycling of materials. Many industrial processes have no existing low-emission alternative and will require carbon capture and storage to reduce emissions over the long term.

HFCs

Hydrofluorocarbons (HFCs) — chemicals widely used in refrigeration, air conditioning, foam blowing, and other applications are the fastest-growing greenhouse gases. With a global warming potential thousands of times greater than carbon dioxide, HFCs can have a significant impact on climate change. Given their high emissions rates and relatively short atmospheric lifetimes (compared to carbon dioxide), efforts to reduce HFC emissions in the near term will significantly reduce projected temperature increases over the coming decades.

The American Innovation and Manufacturing Act of 2020 directs EPA to implement an 85-percent phasedown of the production and consumption of regulated HFCs over a 15-year period, manage these HFCs and their substitutes, and facilitate the transition to next-generation technologies. EPA is required to issue regulations for the HFC phasedown within 270 days after enactment (by September 16, 2021).

Oil and Gas Production

Oil and gas production is the United States' largest manmade source of methane, the second biggest driver of climate change. In the production process, methane can leak unintentionally. It also can be intentionally released or vented to the atmosphere for safety reasons at the wellhead or to reduce pressure from equipment or pipelines.

In January 2021, President Biden issued Executive Order 13990, Protecting Public Health and the Environment and Restoring Science to Tackle the Climate Crisis, directing federal agencies to review actions taken in the last four years. Among many other things, the Executive Order calls on the EPA to consider suspending or revising a 2020 technical amendment to the new source performance standards (NSPS) for the oil and gas sector by September 2021. In addition, the Executive Order calls on EPA to consider proposing regulations for methane and volatile organic compounds (VOCs) from existing operations in the oil and gas sector by September 2021.

In June 2021, Congress voted to repeal the 2020 methane rule under the Congressional Review Act and the resolution was signed into law by President Biden. The measure restores the more stringent 2016 methane rule.

In August 2020, EPA issued two amendments (i.e., the 2020 methane rule) that effectively rescinded the 2016 oil and gas new source performance standards (NSPS) under Section 111(b) of the Clean Air Act. These amendments removed transmission and storage segments from covered oil and gas source categories, rescinded NSPS applicable to those sources, and rescinded methane-specific requirements for the production and processing segments under Section 111(b) of the Clean Air Act. In the amendments, EPA declared that there are no emissions impacts or potential costs from removing the methane requirements for new, reconstructed, and modified sources in the production and processing segments. The EPA justified the amendments with the claim that the current methane limits are redundant with the NSPS volatile organic compounds (VOCs) requirements in the production and processing segments (e.g., fugitive emissions, pneumatic controllers, pneumatic pumps, and compressors).

Operators new oil and gas wells must now follow the 2016 methane rule, which required them to find and repair leaks and capture natural gas from the completion of hydraulically fractured oil and gas wells. They must also limit emissions from new and modified pneumatic pumps, and from several types of equipment used at natural gas transmission compressor stations, including compressors and pneumatic controllers. When it issued the rule in 2016, EPA estimated it could prevent the emission of 510,000 short tons of methane in 2025 (the equivalent of 11 million metric tons of carbon dioxide) in addition to reducing other harmful air pollutants such as volatile organic compounds (VOCs, which are ozone-forming pollutants).

Regardless of the regulatory approach, EPA continues to work with industry and states through its voluntary Natural Gas STAR program to reduce methane from existing oil and gas operations.

In addition, Executive Order 13990 would require the Department of Interior to review a 2018 rule that rescinded the 2016 methane emissions rule from wells on lands managed by the Bureau of Land Management and Indian lands. The 2016 rule placed the first limits on flaring natural gas and increased disclosure requirements. Furthermore, it prohibited venting except in specified circumstances, required pre-drill planning for leak reduction, and increased use of leak-detection technology.

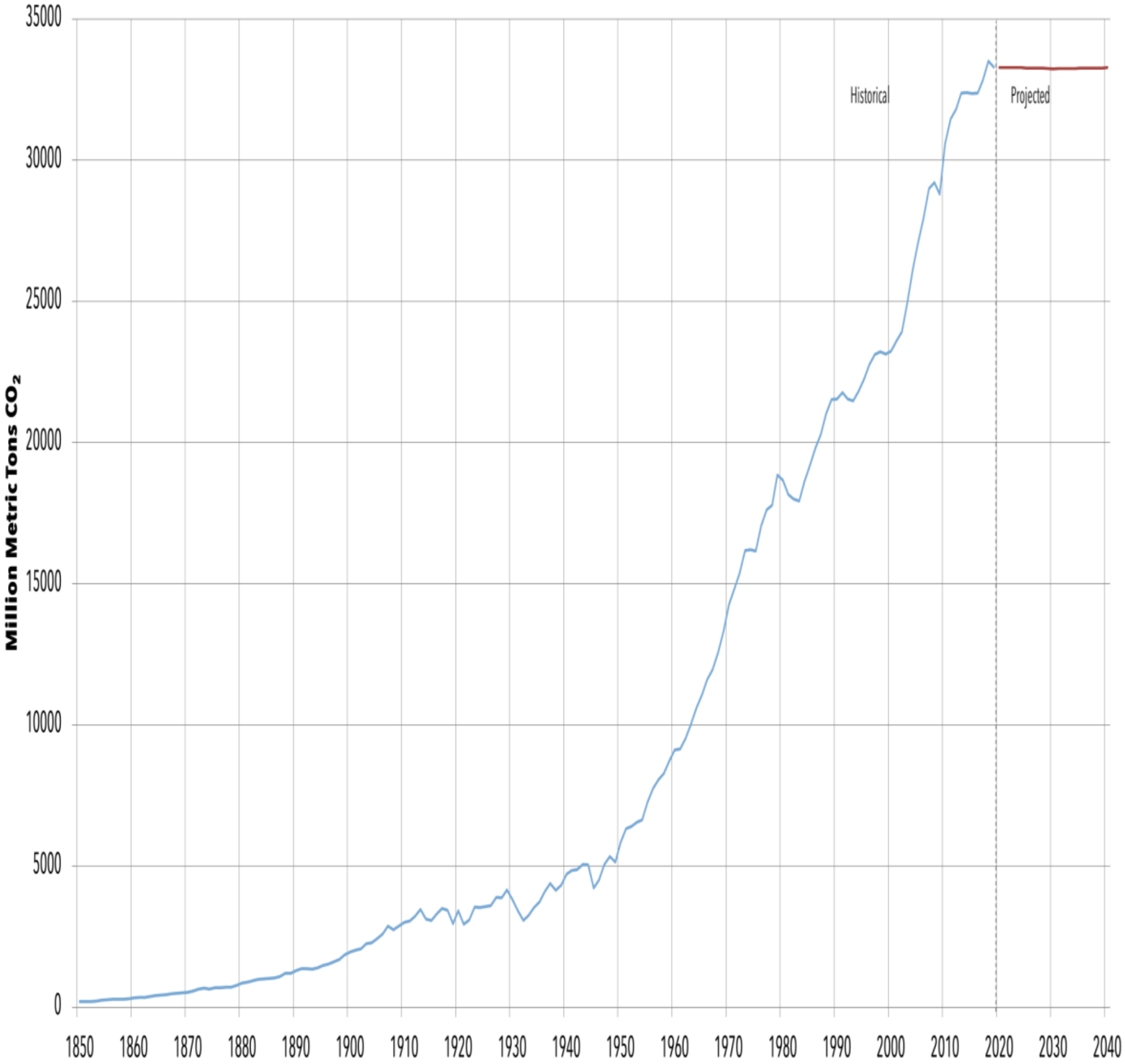
Other Industrial Sources

Other industrial sectors, such as refineries and cement kilns, have been regulated for certain pollutants, including particulate matter (PM), sulfur dioxide (SO2), and dioxides of nitrogen (NOx), since the Clean Air Act became law in 1970.

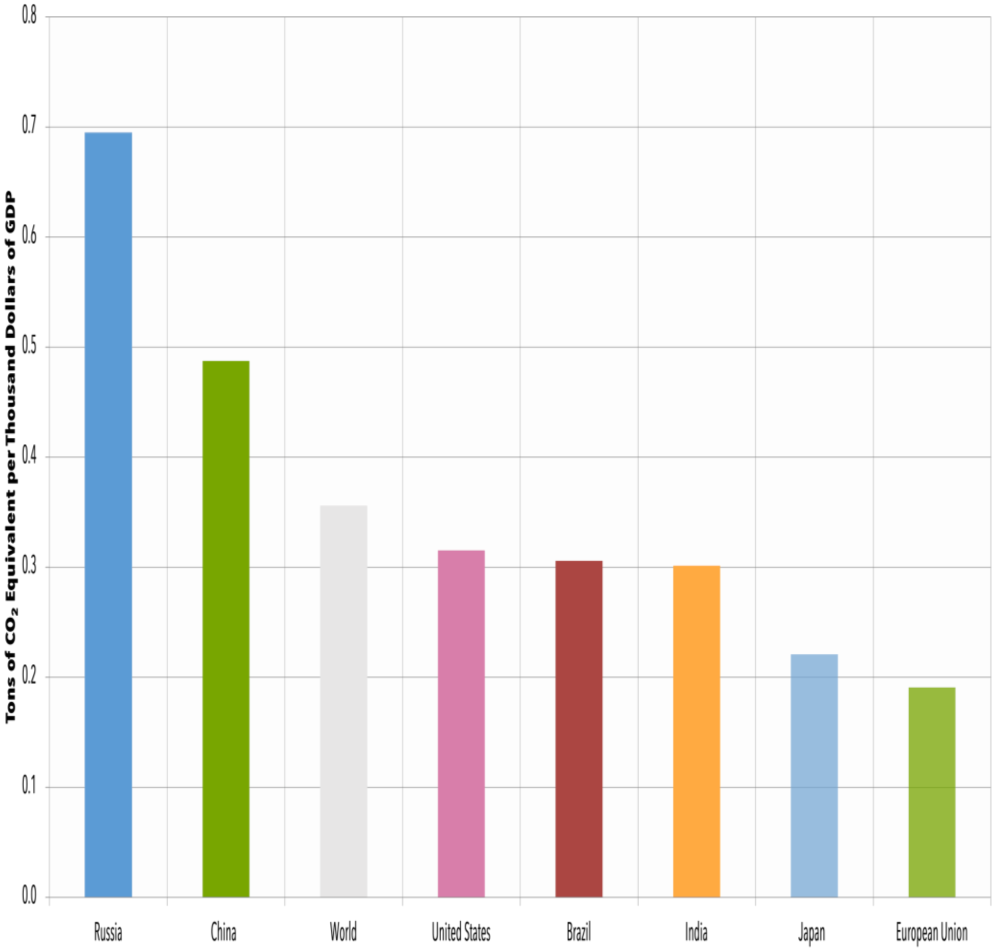
Section 111 of the act requires the regulation of pollution from new, modified, and reconstructed facilities through the New Source Performance Standards (NSPS) program. NSPS are technology-based standards that apply to specific categories of stationary sources. NSPS for pollutants are regularly strengthened by EPA to safeguard human health and the environment as technology advances and new pollution controls become more economically feasible. The Clean Air Act requires EPA to establish New Source Performance Standards for greenhouse gas emissions from all significant emitting subsectors, as clarified in the U.S. Supreme Court case *Massachusetts v. EPA*.

Global Emissions

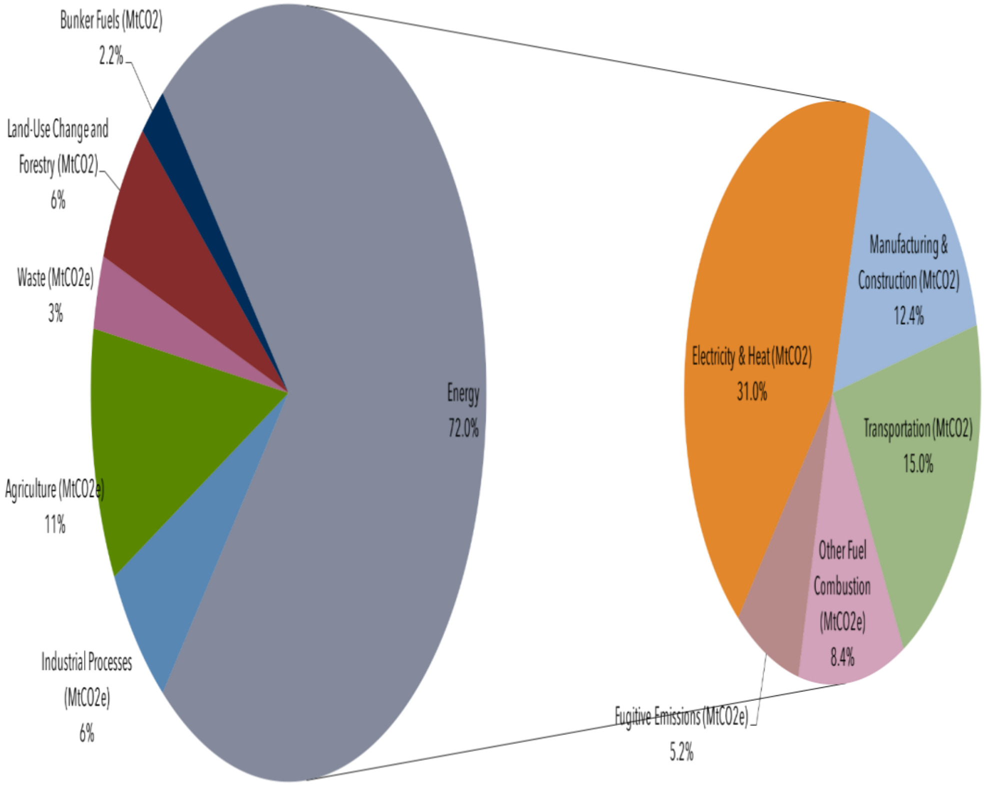
Carbon dioxide emissions, primarily from the combustion of fossil fuels, have risen dramatically since the start of the industrial revolution. Most of the world's greenhouse gas emissions come from a relatively small number of countries. China, the United States, and the nations that make up the European Union are the three largest emitters on an absolute basis. Per capita greenhouse gas emissions are highest in the United States and Russia.



Global Carbon Dioxide Emissions,1850-2040

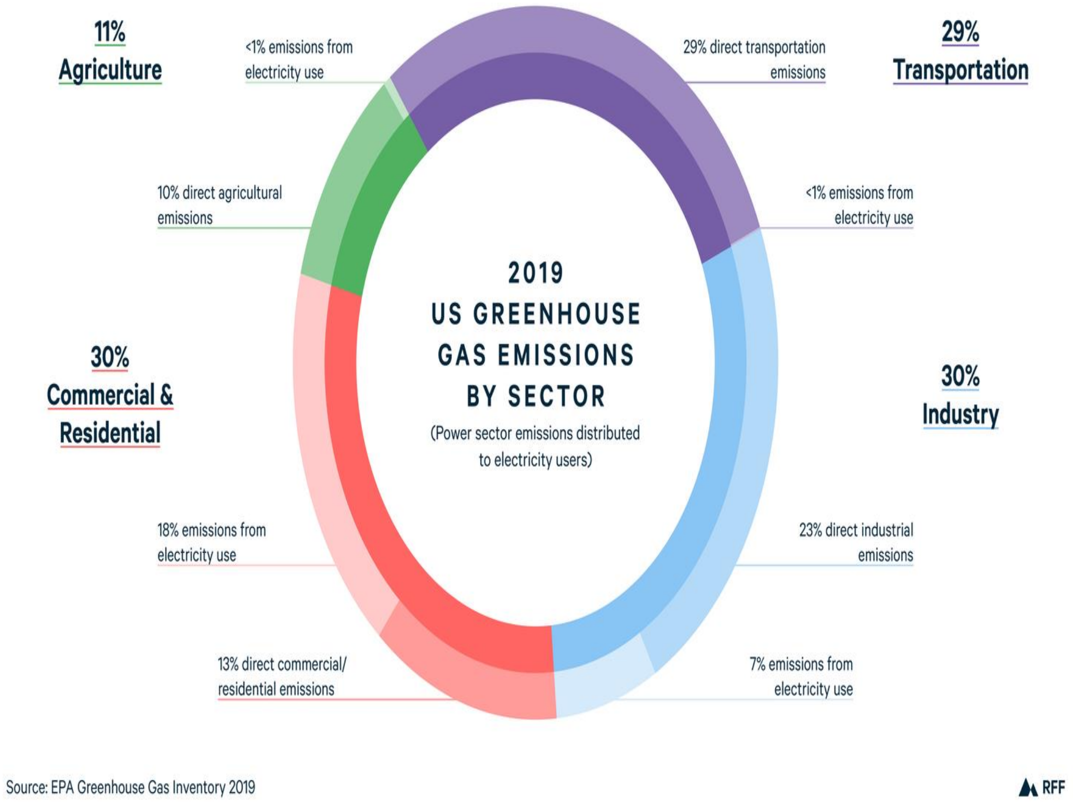


Per Capita greenhouse Gas Emissions,2018



Global Manmade Greenhouse Gas Emissions by Sector,2013

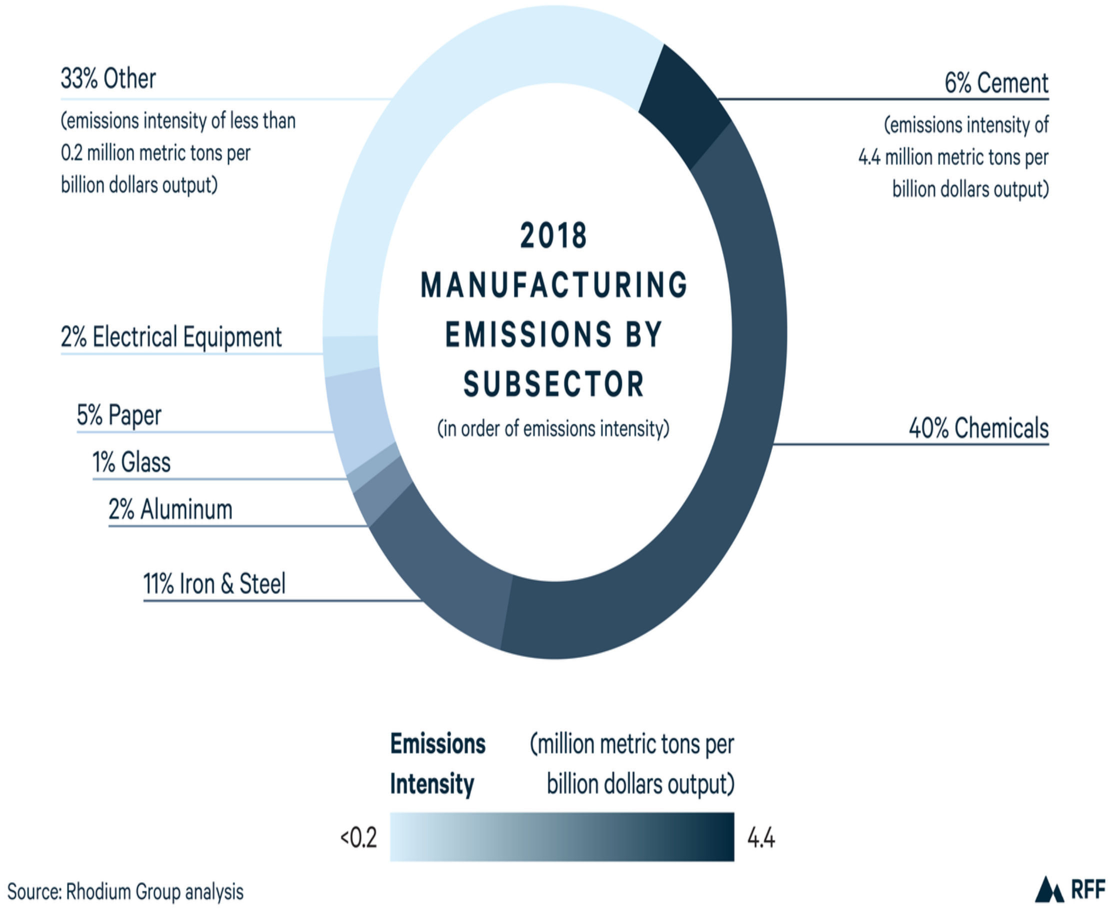
Reducing industrial emissions of greenhouse gases (GHGs) primarily carbon dioxide (CO2), but also some nitrous oxide and methane has received little policy attention compared to the power and transportation sectors, in spite of industry's large and growing carbon footprint. In 2019, the industrial sector produced 29.6 percent of all GHG emissions in the United States, when including emissions from generating electricity used by industry (Figure 1).



Source: EPA Greenhouse Gas Inventory 2019

Figure 1: US Greenhouse Gas Emissions by Sector in 2019

The majority of industrial emissions (78 percent) comes directly from industrial processes, heating, and other uses, while about 22 percent are emissions that arise indirectly from the use of electricity within the sector. The industrial sector includes a diverse set of activities, such as manufacturing goods and producing materials like steel and cement.



Source: Rhodium Group analysis

Figure 2. 2018 GHG Emissions and Emissions Intensity of Manufacturing

Given the characteristics of the industrial sector, several mitigation pathways are possible and likely necessary to reduce industrial emissions:

1. Incentivizing a shift away from high-carbon energy sources and high-carbon manufacturing processes toward lower-carbon energy sources and processes (e.g., low-methane-emissions natural gas, decarbonized hydrogen, biogas, and electrification of production processes and heat sources).
2. Encouraging industrial sources to capture the CO2 they generate
3. Reducing energy use by increasing the energy efficiency of production processes and heat systems.
4. Cutting material use and planning for the “circular economy” through product designs and manufacturing standards that reduce waste and one-time use.
5. Decarbonizing the grid. Reducing the emissions associated with generating and transmitting electricity will lead to industrial emissions reductions, particularly if the industrial sector becomes more electrified. While this pathway would not directly involve the industrial sector and would increase electricity costs, no changes in industry investments, fuel use, or production processes would be necessary.
6. Accelerating technological development that reduces costs or increases the efficacy of the other five pathways.

Policies can target one or more of these pathways—and some policies can operate on all six at once. For example, a carbon price applied to all industrial sources of CO2 would encourage factory managers and company owners to find the cheapest ways of reducing emissions and avoiding carbon fees, thereby indirectly stimulating innovation. However, sufficiently high carbon prices to decarbonize the industrial sector may be politically infeasible. Also, most emissions policies operating directly on the industrial sector cannot sufficiently incentivize innovation, so policies promoting research, development, and demonstration still would be needed.

Energy Efficiency Standards

The Basics

Improving energy efficiency is a proxy, albeit imperfect, for reducing CO2 emissions in the industrial sector. Energy-efficient technologies have promise for reducing the costs and environmental damages associated with energy use, but these technologies are not being leveraged to their full economic benefit by businesses or consumers. Policies that encourage the adoption of energy-efficient technologies can both benefit the industrial sector and reduce emissions. Note that the private energy-efficiency gap is generally smaller than the social energy-efficiency gap, which considers the broader societal damages associated with energy use.

Two types of energy efficiency standards are commonly discussed:

- Prescriptive standards (also known as technology standards) typically require a particular energy-saving technology or process to be installed or used. Historically in the environmental field, prescriptive standards have been applied most often for reducing pollutants—but they could be applied to the industrial sector, as well.
- Performance standards generally limit the emissions or energy consumption per unit of product (e.g., amount of GHGs emitted per ton of cement manufactured). Unlike prescriptive standards, performance standards do not specify the technology or design details of the process.

Benefits and Challenges

The principal advantage of energy efficiency standards is the reduced use of energy as well as generally lower GHG emissions (and conventional pollutant emissions). Lower energy use often reduces operating costs as well, which can offset some or all of the higher capital costs. The standards are also generally transparent, which simplifies enforcement.

The principal disadvantage of energy efficiency standards is the increased capital costs of the products or processes covered by the policy, or potential reductions in performance. Further, prescriptive standards do not allow much flexibility for producers and can lock technologies, which can forestall technological innovations.

Tradable performance standard

The Basics

A **performance standard** is a policy that sets a benchmark that firms must meet, without specifying how the benchmark should be achieved (for example, a limit on the emissions that result from manufacturing each ton of cement). A **tradable performance standard** (TPS) sometimes referred to as a "clean energy standard" for industry is a flexible mechanism that encourages firms to use less carbon-intensive materials and employ production techniques that lead to lower emissions.

The "tradable" aspect of a TPS refers to the ability of firms to buy and sell credits with one another. This can improve overall cost-effectiveness and encourage innovation that in turn leads to lower emissions, as companies can make money from selling excess credits.

In principle, a TPS could be set for each industrial category or sub-category, requiring firms to meet emissions or other benchmarks based on the quantity or dollar value of product sold. Depending on the design of the system, a TPS for industry might allow trading within each sector and/or across sectors. Certain elements of existing cap-and-trade programs are carried over to TPSs. A TPS can create incentives for firms to reduce emissions, like a cap-and-trade program that allocates emissions allowances in proportion to a facility's output. Examples include California's economy-wide cap-and-trade program and the European Union Emissions Trading System.

Benefits and Challenges

Compared to an energy efficiency standard, a TPS is more flexible and is almost always more cost-effective.

A major advantage of a TPS is that this policy rewards innovative firms for emissions reductions because reducing emissions generates compliance credits that can be sold to firms whose performance would otherwise fall short of the standard.

A second advantage is that a TPS is less likely than a carbon price to harm industrial sector employment or cause **emissions leakage**. (Leakage happens when a regulation in one jurisdiction raises costs enough to shift economic activity and corollary emissions from a regulated area to an unregulated area.) The emissions leakage and adverse employment effects that do occur depend on the magnitude of the cost increase caused by regulation. A TPS raises costs only for businesses that use inputs with higher emissions intensity than the industry benchmark. Consequently, a TPS causes a smaller overall cost increase by reducing emissions leakage and employment losses, compared to other potential policies such as a carbon price.

A key disadvantage of a TPS, compared to a carbon price, is that the smaller product price increases provide less incentive for consumers to substitute shift away from emissions-intensive products and toward more environmentally friendly products. Applying multiple industry- or product- specific standards can further increase costs.

Chapter 3

Physical adsorption of CO_2

1. Climate change

Emissions of greenhouse gasses particularly CO_2 is the main contributor to climate change. This undesired impact considers serious challenging and urgent environmental problems facing the world. Increasing the population around the world results in rising the demand for energy which tuns in continuous emissions of carbon dioxide. The main reason behind the carbon dioxide emissions is human activities such as post/pre-combustion of fuels, agriculture practices, transportation, and industrial operations . Many possible consequences can be presented such as ecosystems, floods, and droughts that will negatively impact future generations. The highest recorded amount of the released carbon dioxide to the environment was during the years of 2000–2010 0f 49 Gt; 78 % of this amount is from industry and the combustion of fossil fuels

Many studies have stated that carbon dioxide concentration in the environment should be alleviated in a range of 350 ppm–450 ppm . Researchers presented many different technologies to capture CO_2 from other gases mixtures such as absorption, membranes, cryogenic carbon dioxide, and adsorption.

The main drawbacks of employing absorption technology for carbon dioxide removal are the extensive energy demand especially in the regeneration stage and the corrosion issues of the plant facilities . On the other hand, carbon dioxide removal using solid adsorbents exhibit advantages like high carbon dioxide uptake, high recovery and stability materials, efficient under humid conditions, and low cost in contradiction to absorption processes (See Fig. 2) .

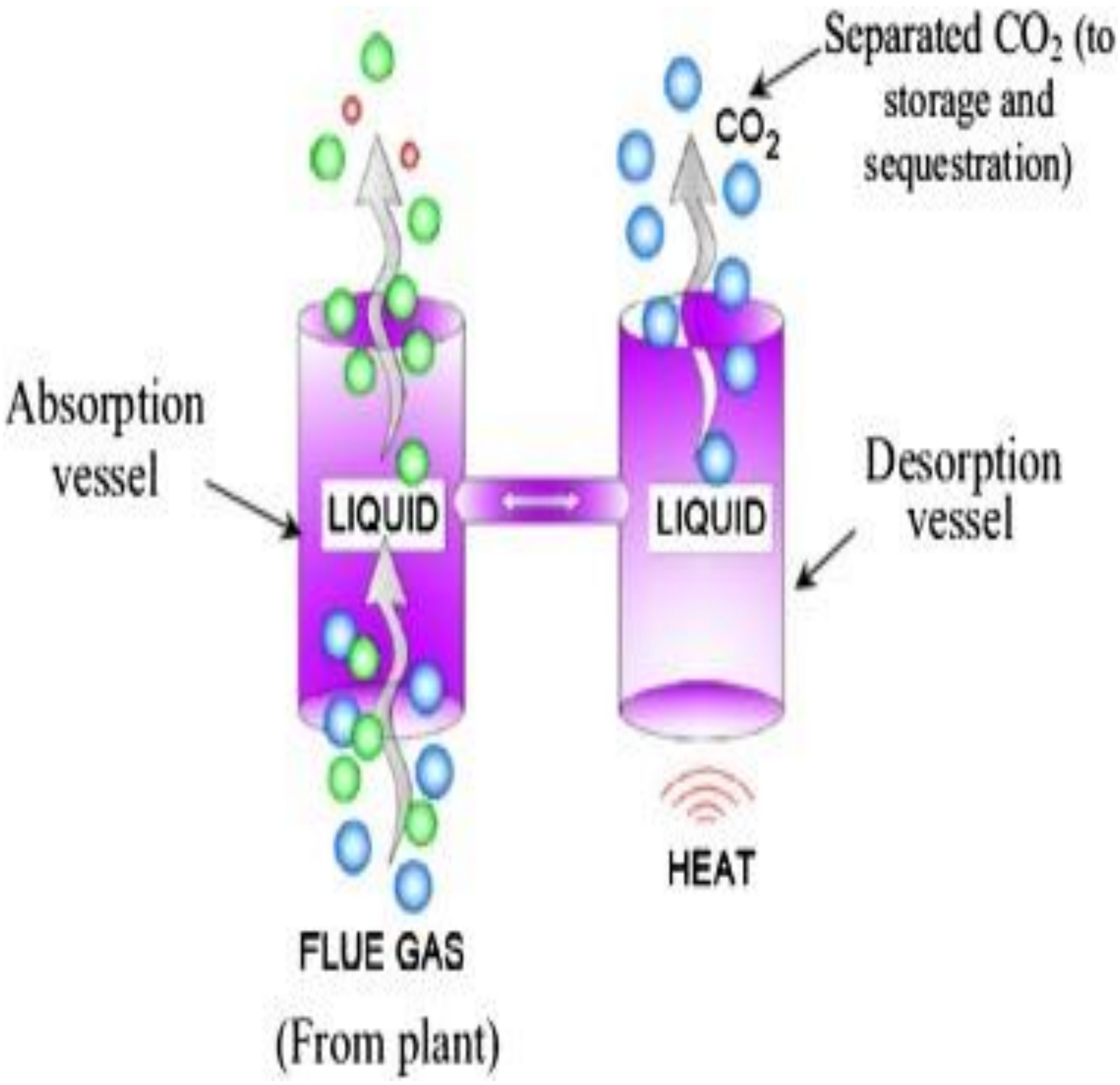


Fig. 1. Graphical diagram of carbon dioxide capturing by Absorption.

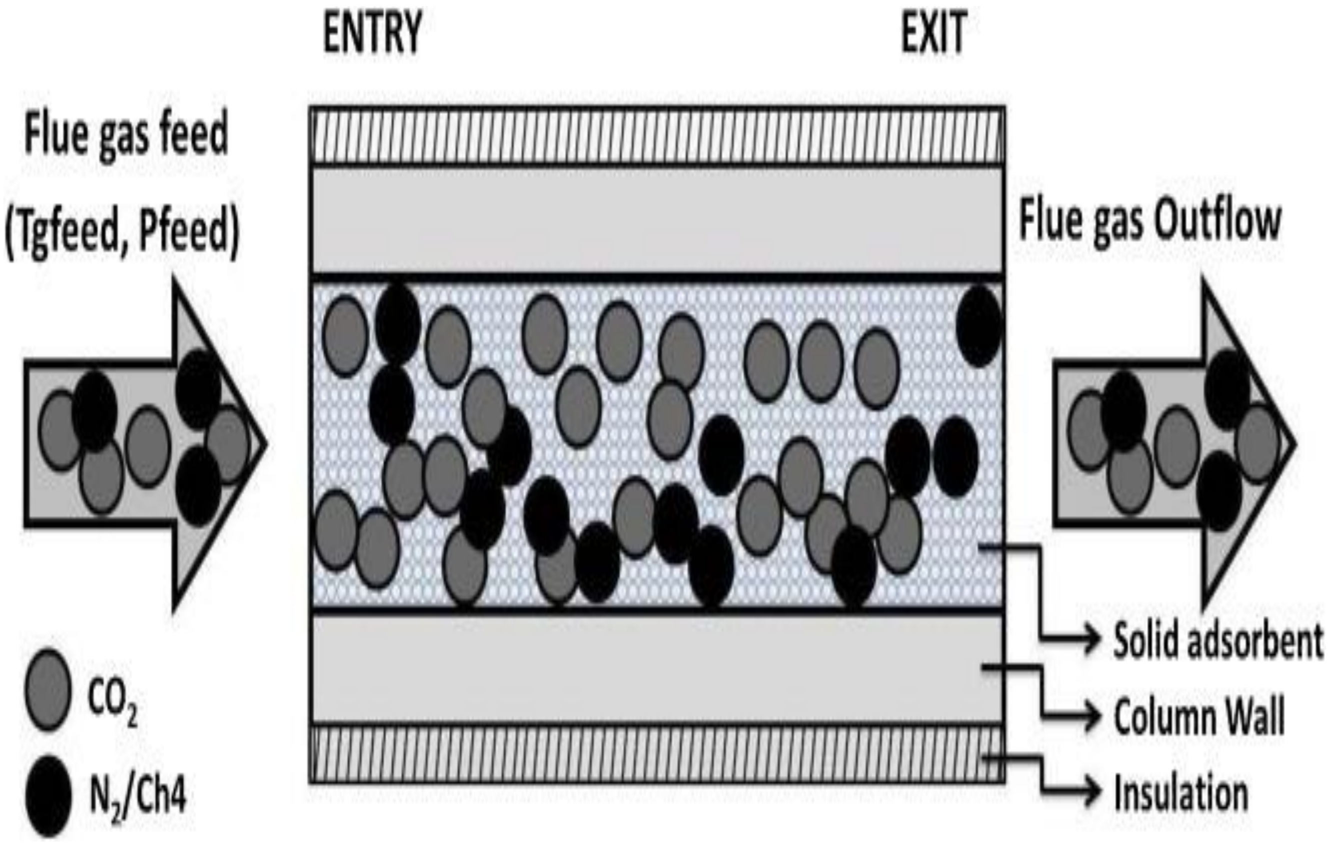


Fig. 2. Graphical diagram of carbon dioxide separation by Adsorption.

Adsorption technology types

Once the adsorbent is approved, the adsorption/desorption cycling procedures can be almost specified based on the maximum equilibrium cyclic capacity, which is estimated using the isothermal model as temperature and/or pressure swing. In addition, the distinctive property of adsorbents like electric-thermal property can also estimate the regeneration method. Typical adsorption technologies for carbon dioxide include pressure swing adsorption (PSA), temperature swing adsorption (TSA), moisture swing adsorption (MSA), and electric swing adsorption (ESA) or the incorporation of those technologies like temperature vacuum-pressure swing adsorption (TVPSA) . Out of the mentioned technologies, two efficient methods have been reported compatible for carbon dioxide capturing at an industrial scale:

> (1) Pressure/Vacuum swing adsorption (PSA/VSA) : carbon dioxide removal performance in this technology is influenced mainly by two parameters: selectivity and adsorption capacity. For PSA, the adsorption process exists at a pressure higher than 1 bar, while VSA is done around 1 bar pressure or lower.
>
> (2)Temperature swing adsorption (TSA) : In TSA, the bed of adsorbents is heated via hot gas or stream to elevating the adsorption temperature. The desorption stage is done by cooling the adsorbents bed using cold steam.

Of these two technologies, pressure swing adsorption is a more feasible option due to easy operation over a large range of temperatures and pressures.
low energy penalty
3) lower operation cost. Mainly, the adsorption/desorption is classified into two types namely moving and fixed bed.

In the moving adsorbents bed, the adsorbents bed moves from the adsorber to the regenerator cyclically and continuously.

While, in the fixed adsorbents bed, the adsorbents bed fixes, and the change exist on the operating parameters such as the temperature, pressure, and moisture.

2. Physical adsorbents

carbon dioxide adsorption via physical adsorbents (carbonaceous and non-carbonaceous materials) requires low energy demand with reference to the chemical adsorbents. The reason is no new bonds are generated between the carbon dioxide and the surface of adsorbent which turns in less energy penalty for carbon dioxide regeneration. However, classes of the well-known physical adsorbents like activated carbon come with the disadvantage of low carbon dioxide/nitrogen selectivity and the successful overcoming of this issue will dominate the amines absorption technologies and saving energy . Some types show good selectivity for carbon dioxide like zeolites; however, they suffer from low CO_2 loading in humid conditions. In all, the design of new materials of adsorbents with high CO_2 adsorption performance and high selectivity is a serving issue. Good stability, high affinity for CO_2, acceptable scalability, and low energy requirements are the major research activities of solid adsorbents for carbon dioxide removal. It is crucial to develop and modify potential materials for carbon dioxide removal that will challenge the known separation technologies. As well as attention should be paid to a better evaluation of molecular-level gas-sorbent synergy. Fig. 3 summarized the most popular physical solid adsorbents materials that used for carbon dioxide capture.

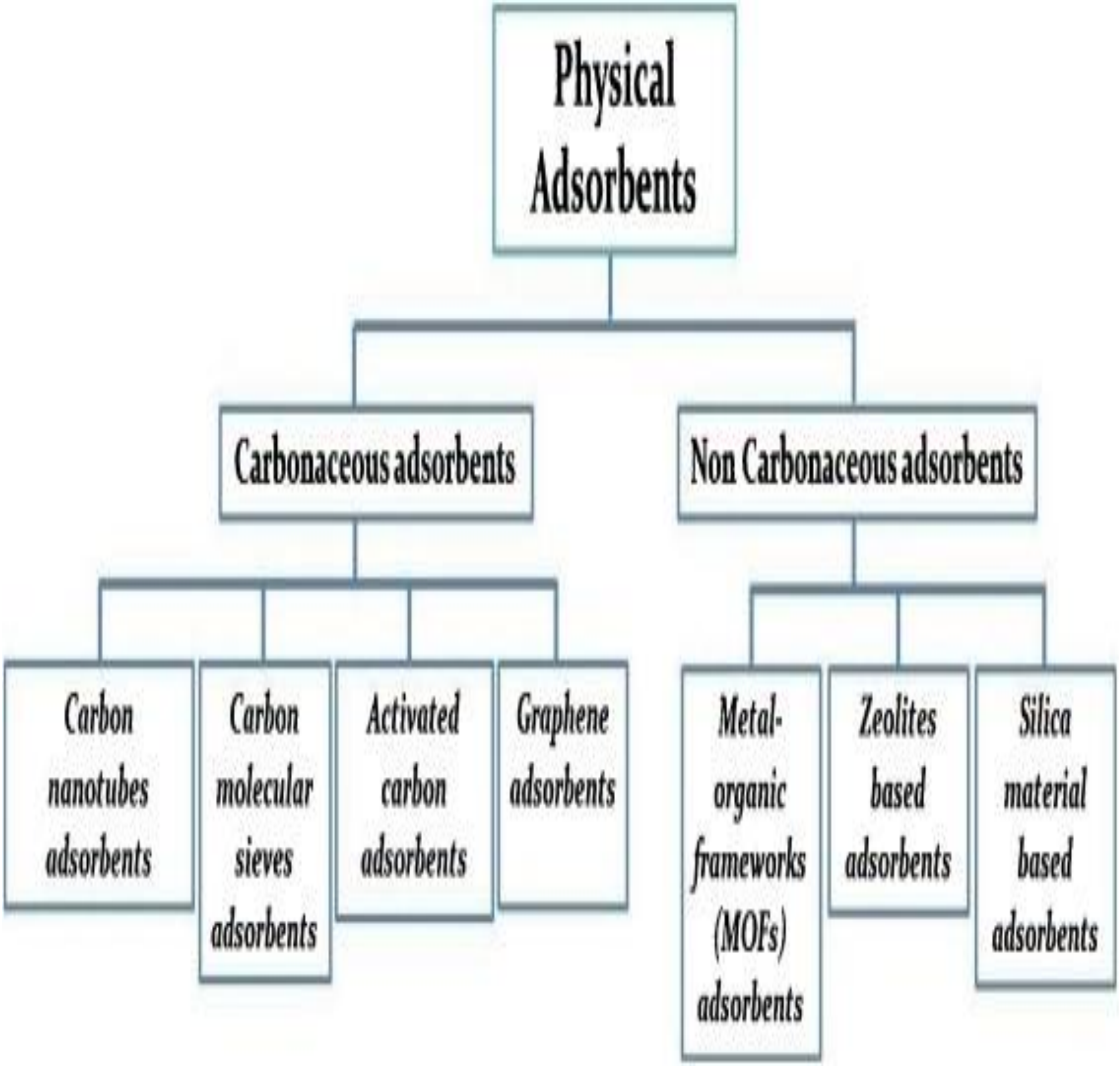


Fig. 3. Physical solid adsorbents for carbon dioxide adsorption.

1 .Adsorbent's selection

When the carbon dioxide molecules come close to the adsorbent surface will reach reduced free energy, where the gas molecules will attract to the electronic environment of the adsorbent surface. The interactions of the gas molecules–solid surface and the associated reduction in entropy turns in increasing the number of CO_2 molecules at the adsorbent surface. Adsorption could exist physically as it will follow van der Waals forces. As well as it could exist chemically which involve the formation of chemical bond between the adsorbent surface and the adsorbate. Various materials describe portraying dissimilar chemisorption mechanisms in the adsorption process. For example, MOFs adsorbents, the mechanism of the chemical reaction exists by uncoordinated metal sites and the functional groups form on the surface of the MOFs, while the biomass adsorbents, the interaction process exists by the intermolecular forces .

Carbon dioxide adsorption can exist with/without the consistence of chemical bonds. For the physisorption of carbon dioxide, the electric quadrupole moment-electric field gradient interaction often dominates the interactions of carbon dioxide with the adsorbent surface. The value of the electric quadrupole moment (EQM) is the main factor behind the limitation of the interaction of the gas molecules and the surface of the adsorbent. Graham et al. mentioned that the EQM magnitude of the carbon dioxide is more than the EQM of nitrogen by three times which tuns in more partitioning of CO_2 on the adsorbent surface than that of nitrogen. The number of gas molecules entrapped increases as the operating pressure increases up till reaching the maximum capacity.

Whereas the number of entrapped gas molecules increases as the temperature decreases by reason of the exothermic nature of the adsorption process. The operating temperature and pressure consider important parameters in the management of the uptake gas molecules; for example, in the TSA process, the desorption process allocated by elevating the operating temperature. While in the PSA, the capturing process exists at high pressure and the regeneration process occurs by decreasing the operating pressure. Solid adsorbents are grouped into three different levels according to their pore sizes. The International Union of Pure and Applied Chemistry defined the three types based on the pore size as

1) micropores ≤ 2 nm,
2) mesopores in-between 2 and 50 nm,

3) macropores ≥ 50 nm. Overlapping of volume filling and surface coverage for extremely small pores and their impacts on the adsorption capacity. The study concluded that besides the pore size, the shape of pores like silts, cylinders and/or cages linked via pore windows is another valuable factor to manage the adsorption performance. The adsorbent material should achieve some necessary criteria to be satisfied in both economical and operational for carbon dioxide removal which is illustrated in this section:

3. Adsorption Performance

The adsorption performance is of essential significance to the capital cost of the adsorption process because it determines the required amount of adsorbent which turns in estimating the volume of the adsorption column. That is, the high uptake of carbon dioxide minimizes both adsorbent amount and process equipment size. The adsorption can be considered competitive in comparison to other existing technologies, when the process achieves a carbon dioxide loading in a range of 3–4 mmol/g of adsorbent.

Selectivity

Selectivity defined as the ratio of carbon dioxide capacity to another gas capacity which has a direct impact on the entrapped carbon dioxide. Efficient adsorbent should show high carbon dioxide selectivity, as well as the adsorbents must offer high capacity for CO_2 in humid conditions.

The adsorption/desorption kinetics are another important factor in rating the efficiency of the adsorbents, where the adsorbents need to have fast adsorption /desorption kinetics for carbon dioxide. The kinetics of the adsorption and the regeneration processes control the cycle time where fast kinetics produce a sharp carbon dioxide breakthrough curve, whereas the slow kinetics yield a distended breakthrough curve. The carbon dioxide adsorption kinetics on the porous adsorbents influenced by the reaction kinetics of carbon dioxide with the functional group on the adsorbent surface, besides the mass transfer through the adsorbent surface.

Mechanical Strength

The mechanical strength of the adsorbent is crucial to maintain high kinetics. The selected adsorbent should show adequate mechanical strength to reduce the adsorbents makeup amount and to keep the capturing plant cost-effective.

Heat of Absorption

The heat of adsorption is the measurement of the required energy for adsorbents regeneration which should be as low as possible. For physisorption cases, the heat of adsorption is ranging between −25 to −50 kJ/mol, whereas from −60 to −90 kJ/mol for chemisorption cases

Adsorbent Cost

The adsorbent cost is the major subtle characteristic. A sensitivity economic analysis to reach a baseline of 10$ for one kg of the adsorbent.
The mentioned characteristics are desirable for a typical adsorbent; however, scarcely single adsorbent will include all the mentioned attributes.

The mechanism of carbon dioxide removal on the adsorbent surface can be envisaged as:

$$CO2+Surface \rightleftharpoons (CO2).(Surface)$$

The process of selection for carbon dioxide is obtained based on van der Walls attraction of carbon dioxide molecules and the adsorbent surface, as well as, via pole/ion and pole/pole interactions between the quadruple of carbon dioxide and the ionic and polar sites of the solid adsorbent surface.

Carbonaceous materials adsorbents

These materials usually consist of carbon and other associated material that can estimate excellent properties such as eco-affinity, thermal and chemical stability, heat and electrical conductivity, or high strength . Carbonaceous materials are available in different classes such as porous activated carbons, molecular carbon sieve, carbon nanotubes, and graphene. Generally, they are cheap, easily consisted of natural sources, high specific surface area, large pore volume, and lightweight.

1. Activated carbon materials (ACs)

The ACs have been widely reported as efficient adsorbents in the removal of CO_2 because of their high specific surface area, and thus have large adsorption ability. In the formation of activated carbons, any carbonaceous material shows high carbon and low ash contents, inexpensive sources, and low volatiles matters can help in the formation of the activated carbons pores . Besides, the raw material should be easily activated and comes with a low degradation rate to maintain the physiochemical properties . Therefore, the selection of proper raw sources in the formation of activated carbons is important where the compositions of the raw material like C, N_2, O_2, H_2, and S will impact the properties of the produced activated carbons. Activated carbons synthesize from carbonaceous materials via pyrolysis at elevated temperature and specific pressure through the activation furnace where high surface area and complex pore structure are formed. The carbonization stage employs inert gas like nitrogen or argon to remove the volatile matters and/or impurities and produce enriched carbon samples. Afterward, the formed sample will pass through the activation process in the presence of oxidizing gas like CO_2, steam or O_2 at a temperature between 800 ℃ to 1000 ℃℃ which is called the physical activation process.

Extensive research has been conducted using carbon dioxide via a single or dual stage activation process (see Table 1).

Table 1. Displays selected physically activated carbons for carbon dioxide adsorption.

Source	Surface Area (m^2/g)	Uptake (mmol/g)	Type of oxidant
Coconut shell	371	1.8 at 298 k	CO_2
Almond shell	862	2.7 at 298 k	CO_2
Olive stone	1215	3.1 at 298 k	CO_2
Coffee residue	593	2.4 at 298 k	CO_2
Nutshell	573	3.48 298 k	CO_2
Cotton stalk	610	2.3 at 293 k	CO_2
Almond shell	557	2.1 at 298 k	O_2 (3%)
Olive stone	697	2 at 298 k	O_2 (3%)
Palm activated carbon	167.08	7.32 at 303k	CO_2

The endothermic reaction in the activation process between the carbonaceous materials and the oxidizing gases (i.e., CO_2) are illustrated in Eqs 1

$$C+CO2\rightarrow 2CO\Delta H=+173kJ/molC+H2O\rightarrow CO+H2\Delta H=+132kJ/mol$$

The employing of carbon dioxide as activation agent rather than steam is because of its ability to create narrow micropores which match carbon dioxide molecules, while steam is prone to produce mesopores . Therefore, activation using carbon dioxide is suitable for gas adsorption, as it is prone to produce micropores activated carbons that strongly matches the adsorption of small carbon dioxide molecules, stated the importance of the formation of narrow micropores (pore size ≈ 0.55 nm) for the carbon dioxide adsorption at low pressures, where the pore size presents amble spaces for carbon dioxide molecules to allocate themselves in the pore walls as shown in Fig. 4.

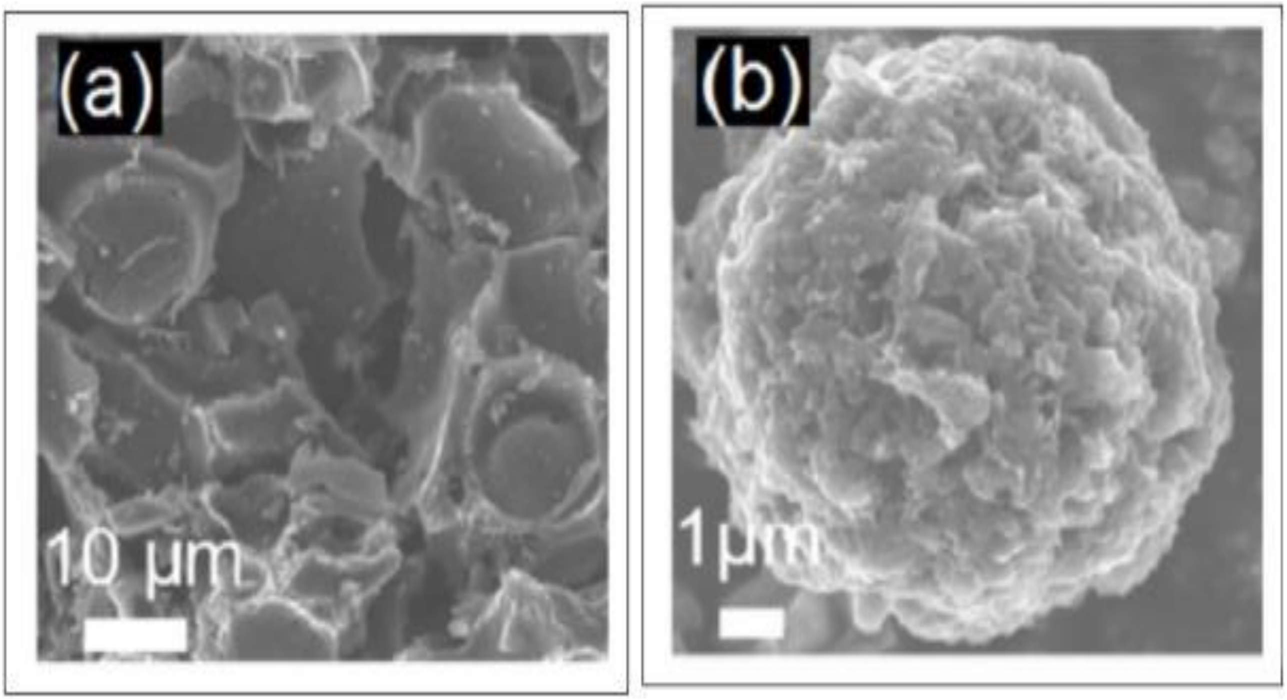


Fig. 4. SEM image of the surface of two different activated carbons.

Whereas the chemical activation process involves impregnation of raw materials with a dehydrating agent before the carbonization/activation process. The dehydration agents that are usually used include alkaline, acidic, and salt mediums such as KOH, NaOH, ZnCl2, H3PO4, etc.

Extensive studies have been acknowledged that the chemical activation process requires lower energy in view of the temperature of activation which is ranging 400–800 °C°C that will improve the carbon yield and reduce the required time of the process (see Table 2). Besides, the chemical activation process is completed in a single step, where both carbonization and activation have existed simultaneously with help of chemical activator, which will create porosity via dehydration and oxidation reactions .Though, the chemical activated carbons normally require to undergo a bushy washing step to eliminate the chemicals waste and impurities from the designed surface, and thus turn into secondary pollution issues, caused by the corrosiveness of dehydrating chemical agents and inefficiency in chemical recovery during the washing stage . The activated carbons formed via chemical activation process have a large specific surface area which can be reached more than 3000 m^2/g . The activation agent is strongly impacting the formation of the adsorbent surface in terms of pore structure and specific surface area.

Table 2. Displays selected chemically activated carbons for carbon dioxide adsorption.

Source	Surface Area (m^2/g)	Uptake (mmol/g)	Activator
Cellulose	2370	5.8 at 273 k	KOH
Starch	2190	5.6 at 273 k	KOH
Algae	1940	7.4 at 273 k	KOH
Celtuce leaf	3404	6 at 273 k	KOH
Fungi	1479	5.5 at 273 k	KOH
Bamboo	1846	7 at 273 k	KOH
Yeast	1348	4.8 at 298 k	KOH
Coffee ground	831	4.9 at 273 k	KOH
Sludge	179	1.3 at 298	NaOH
Bean dreg	1060	4.2 at 298 k	KOH
$SBAT_{16}$	179	56 mg/g	NaOH
Palm stone	1320	3.1 at 273 k	(48 %) H_3PO_4
Wood	1889	2.9 at 303 k	H_3PO_4
Poly- aniline	1695	7.6 at 273	
Sawdust	1643	8 at 273 k	KOH
Pitch	1770	3.8 at 298 k	KOH
Pine	1486	7.7 at 273	KOH
Peanut shell	956	5.4 at 273 k	KOH
Sunflower seed	1790	7.1 at 273 k	KOH

Source	Surface Area (m^2/g)	Uptake (mmol/g)	Activator
MCC-K1	916	3.82 at 273 k	KOH

Isosteric heat of ACs can present data about the mechanism of carbon dioxide adsorption which may be physisorption or chemisorption. The results presented in Fig. 5 is observed that the isosteric heat of the prepared activated carbon were ranging 22–37 kJ/mol which much lower than that of chemisorption of 60–90 kJ/mol. Thus, the adsorption of CO_2 on the surface of modified activated carbon is physical adsorption. As well as the Isosteric heat decreased as the carbon dioxide uptake increases which proved that the adsorption sites on the surface of the activated carbons adsorbents are heterogeneous.

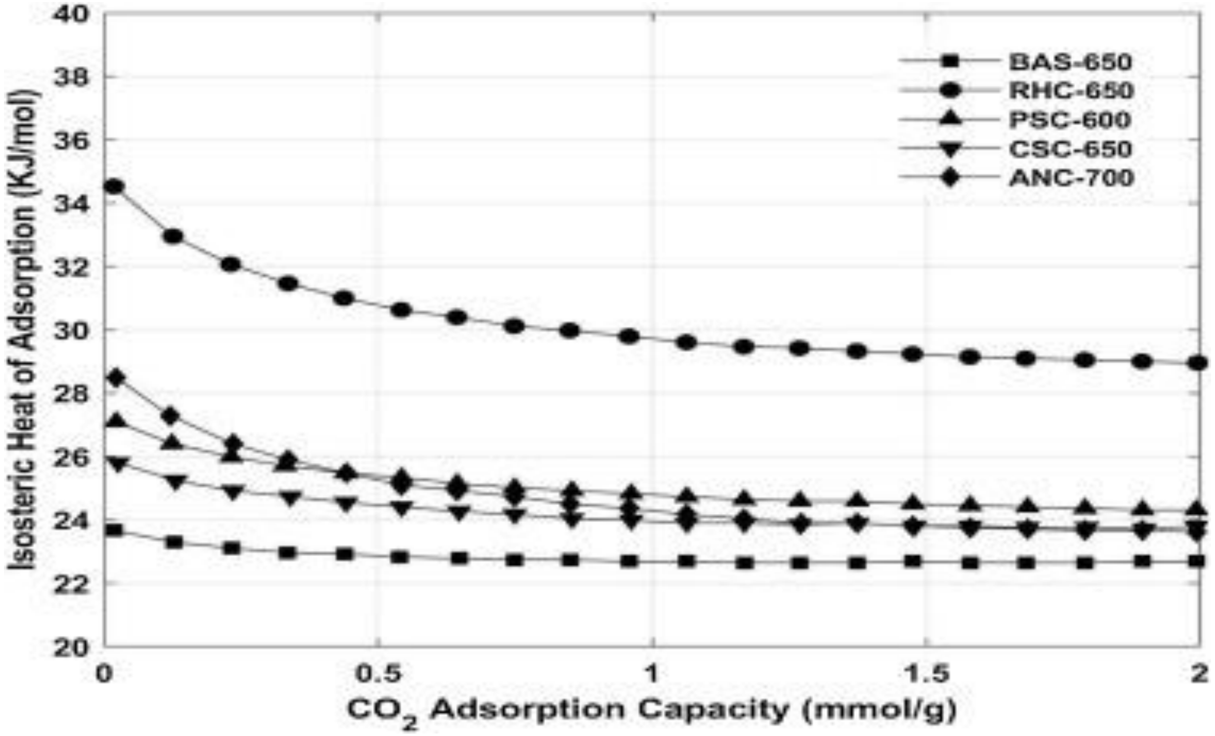


Fig. 5. Heat of carbon dioxide adsorption of different ACs.

Generally, the textural properties of the ACs materials mainly relate to the raw materials, activation process, and the preparation processes .They reached 68.4 % carbon dioxide recovery, from a gas mixture consists of 17 % CO_2, 4% O_2, and 79 % N_2 at 298 k, whereas the percentage of carbon dioxide contaminant in the adsorbent was 6.3 %. In the same context, they stated that the equilibrium separation of CO_2 from the gas mixture via activated carbons is better than the kinetics separation via CMS. The same researchers extended the study to report that zeolite 13X is better than ACs in case of equilibrium separation.

The operating temperature is one of the factors that has direct impact on the adsorption performance and the impact degree different form one adsorbent to another. studied the impact of temperature on the adsorption capacity of F30/470 activated carbon adsorbent. They reported that the carbon dioxide uptake decreases at the time that the temperature reduced (See Fig. 6).

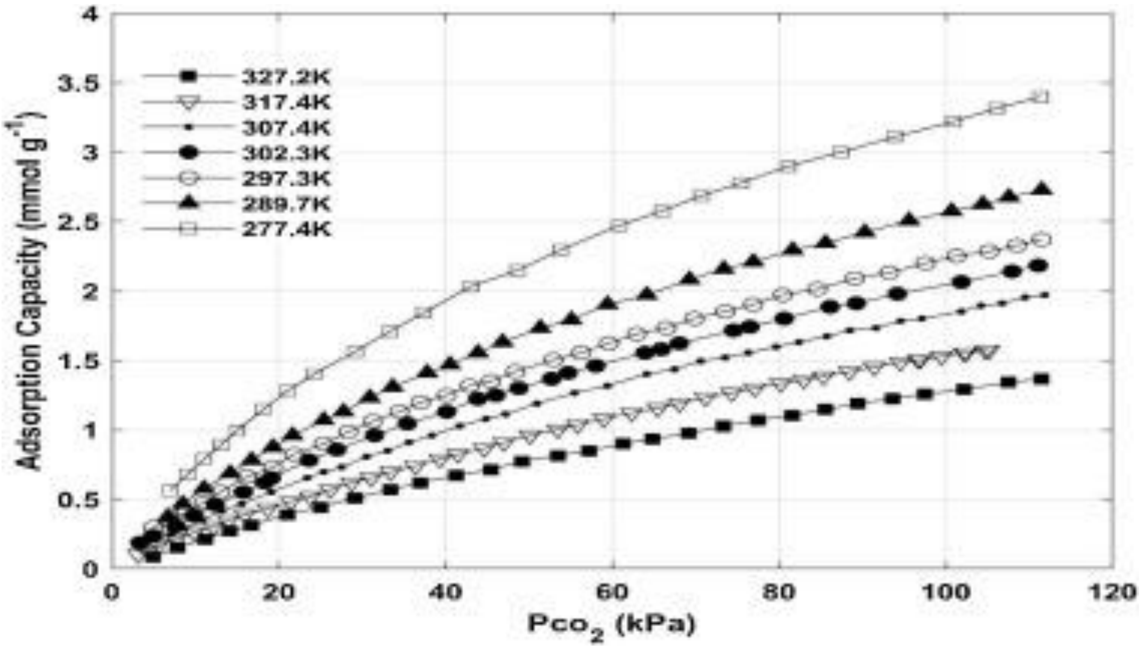


Fig. 6. Impact of temperature on the CO_2 uptake using activated carbons.

Another activated carbon **as** shown in Fig. 7. This impact can be attributed to the increase of the surface energy and molecular diffusion which results in elevated the adsorption temperature. The consequence of elevating adsorption temperature is that the entrapped carbon dioxide molecules on the adsorbent surface become unsteady and desorption of captured molecules.

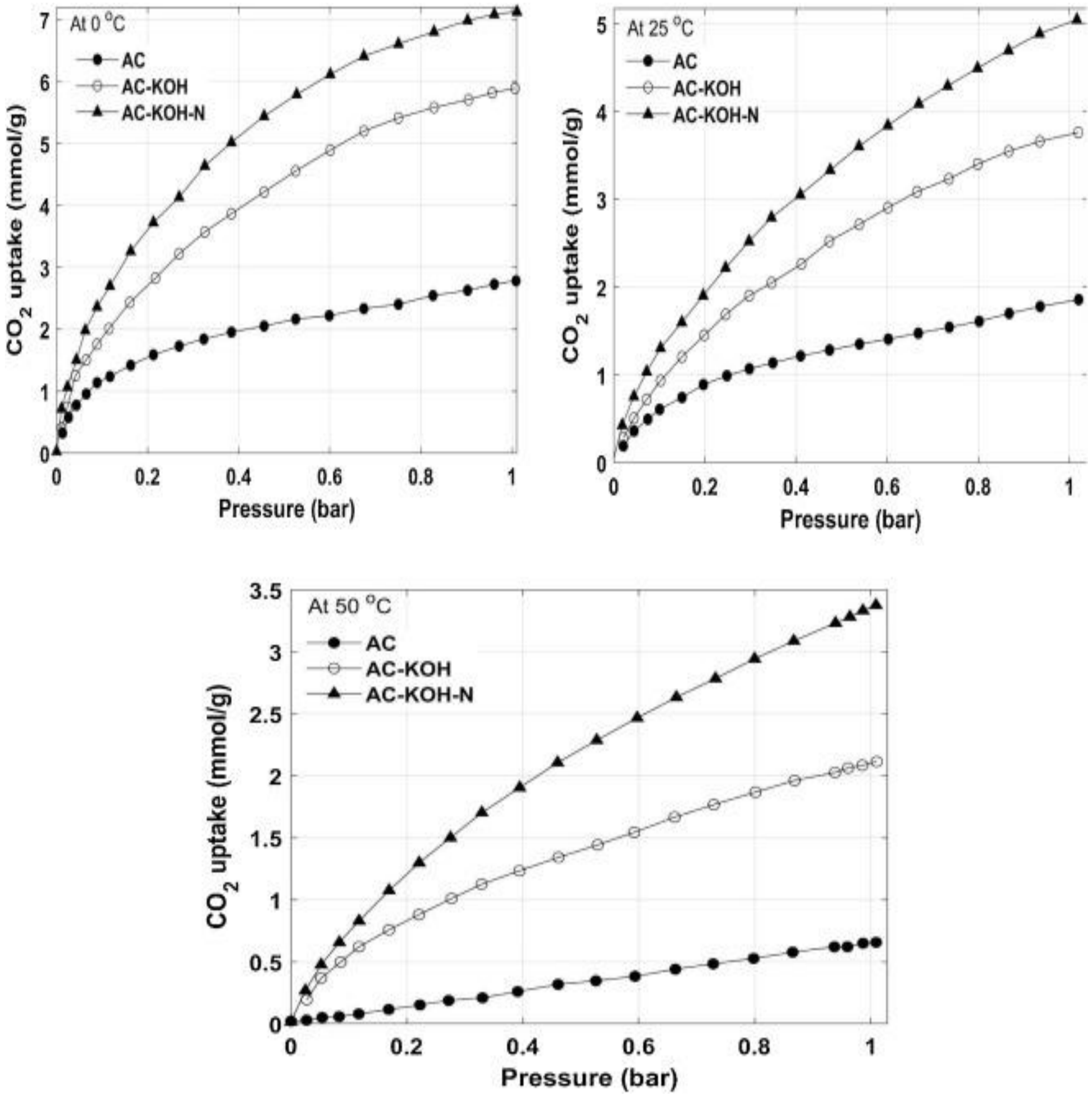


Fig. 7. Comparison of the carbon dioxide uptake for three activated carbons materials at different temperature.

Activated carbons are low-cost adsorbents with a fast adsorption process and low desorption energy penalty. However, the main dominances of the activated carbons are highly sensitive for moisture and low selectivity. CO_2 uptake on activated carbons adsorbents produced from bamboo chips and coconut shell, in humid conditions, they stated that water negatively affected the carbon dioxide adsorption at low pressure. compared the adsorption performance and selectivity of G-32H activated carbon, zeolite 13X, and 14A molecular sieves for carbon dioxide. They conducted that the adsorption capacity of X13 is relatively better than the ACs adsorbents and the CO_2 adsorption was not influenced by the adsorption capacity of the other mixture gases like N_2 and H_2.

Recently, activated carbon fibers have been taken much more attention as an efficient adsorbent owing to its high surface area and narrow pore size distribution . Different from the known activated carbons, activated carbons fibers is a modified generation of carbon-based materials full of micropores. modified activated carbon fibers adsorbents via chemical activation using KOH for carbon dioxide adsorption at atmosphere pressure.

In conclusion, the activated carbon adsorbents present some advantages like low regeneration energy, easy to regenerate, low regeneration temperature, raw materials availability and high thermal stability; mainly the adsorption performance enhances when the partial pressure of carbon dioxide increases . While the adsorption capacity decreases as the partial pressure of carbon dioxide decreases due to the impact of the presence of impurities such as NO_x, SO_x, H_2O, and Hg. Besides, the ACs materials are soft and may cause high attrition in the bed and more adsorbents replacement. Recently, the research on activated carbon materials is mainly exploring the improvement of CO_2 adsorption performance and selectivity at low carbon dioxide partial pressure. The major research lines include deploying novel raw sources to produce materials that have high active surface area and compatible pore size.

2. Carbon molecular sieves adsorbents

CMSs are a special member of microporous carbon adsorbents with molecule-sized pores. The preparation process of carbon molecular sieve adsorbent includes four steps
1) carbonization of raw material,
2) surface activation,
3) deposition usually via chemical vapor, and
4) subsequent carbonization of aromatic molecules.

A porous monolithic carbon fiber composite molecular sieve with carbon dioxide adsorption capacity more than 2.27 mmol/g at 303 k and atmosphere pressure; this carbon dioxide uptake decreased as the temperature increased. CMSs adsorbents in the form of particle and monoliths and tested full study about the impacts of pore blockage to conclude that the decomposition of the surface during the carbonization process results in the formation of narrow micro-porosity which is compatible for CO_2 molecules.

This method can be deployed for providing more opportunities for synthesis novel carbon molecular sieve adsorbents of carbon dioxide.
Carbon molecular sieve adsorbents consider as promising adsorbents and can improve the selection of carbon dioxide over methane which is worthy of more detailed studies.

3. Carbon nanotubes adsorbents

Carbon nanotube materials are a new member of the carbon group which is aroused high attention as a novel type of adsorbents. Many theoretical and experimental studies dedicated to examining the adsorption performance of CO_2 on the carbon nanotubes adsorbents. Carbon nanotubes can act as an efficient adsorbent for carbon dioxide separation.

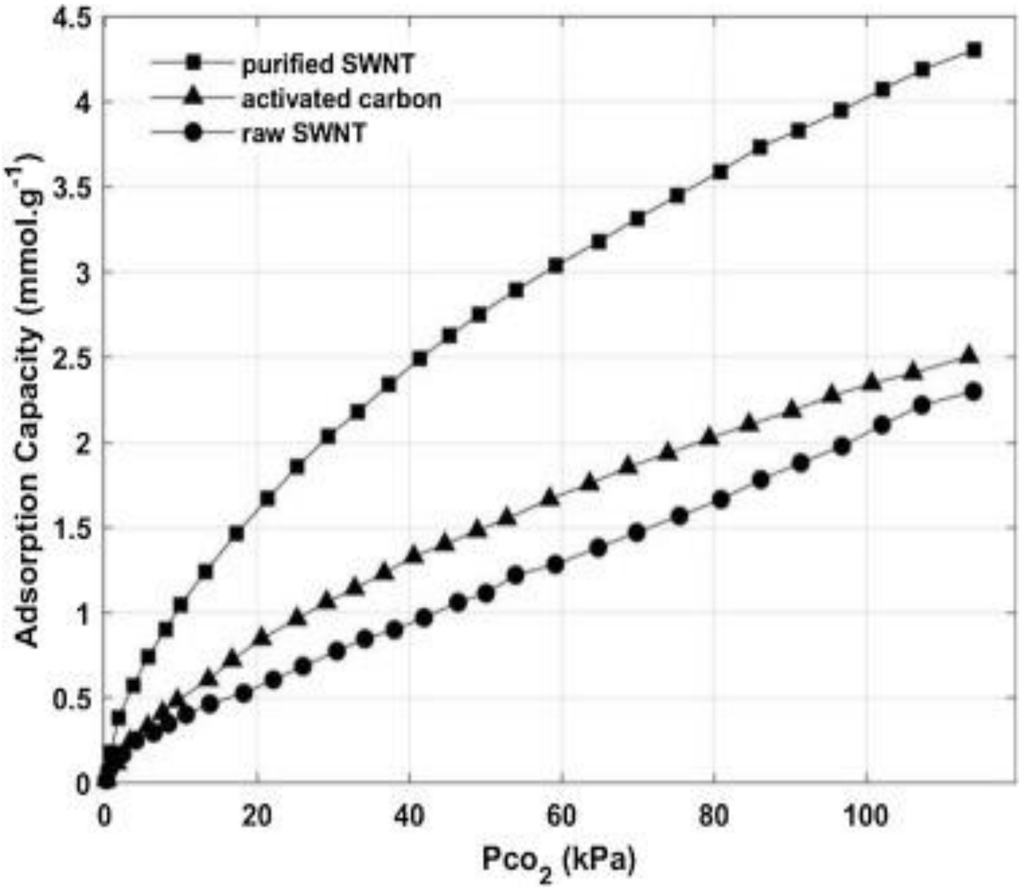


Fig. 8. Comparison of carbon dioxide uptakes of activated carbon and carbon nanotubes adsorbents at 308 k.

The carbon nanotubes materials are promising adsorbent for carbon dioxide and many surface modifications that can be employed to enhance the surface area and tunable the pore size.

4. Graphene

Graphene is a new class of carbonaceous materials with acceptable adsorption capacity and recently taken massive attention. It is basically a flat single layer of sp^2 hybridized carbon atoms, densely packed into an ordered two-dimensional honeycomb network. Before 2011, as far as I can tell, there are no research about the deployment of graphene/graphite as carbon dioxide adsorbents. However, since 2012, much papers research has been offered to investigate the employing of graphene/ graphite as carbon dioxide adsorbent owing to the large active surface area and low preparation cost. The investigations are generally in three research directions

1) proposing new structures
2) surface modifications
3) synthesized hybrid materials. Several studies employed various treatments to modify the graphene surface and propose a high surface area and tunable pore volume.

They stated that the carbon dioxide adsorption as a reversible physisorption mechanism, where the carbon dioxide uptake increases linearly with the pore size. As well as the CO_2 uptake of the proposed adsorbent was 1.275 mmol/g at 273 k with good carbon dioxide/nitrogen selectivity and recyclability.

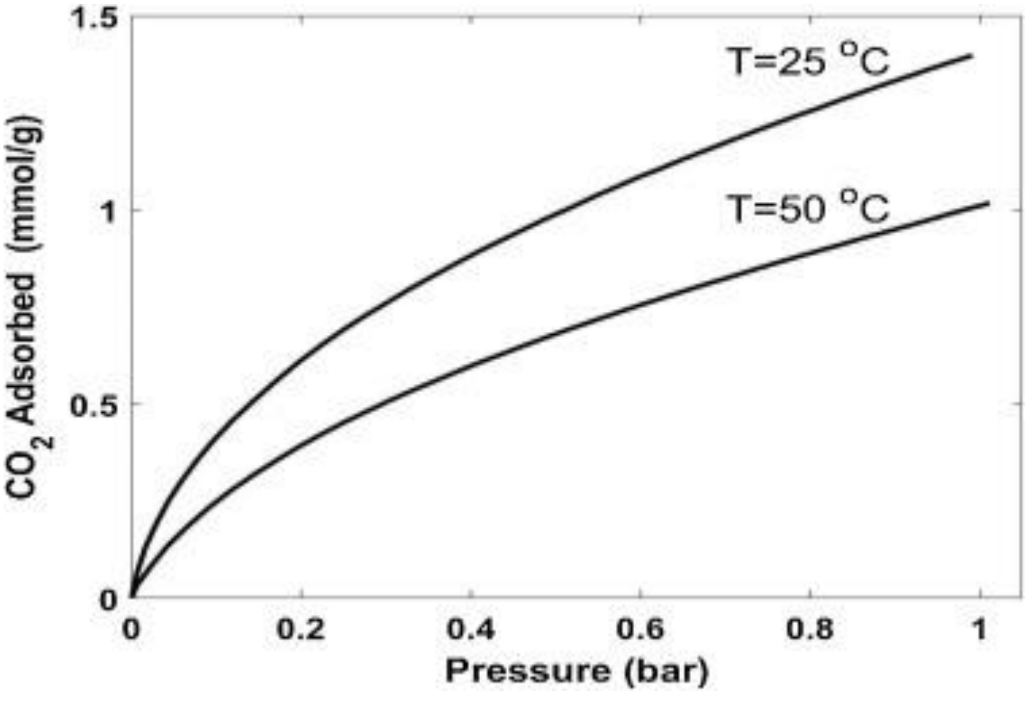


Fig. 9. Impact of temperature on the uptake of HGF-III for carbon dioxide.

Table 3 illustrates the most highlighted graphene-based adsorbents in terms of specific surface area and carbon dioxide loading. Researching the utility of graphene-based adsorbents technology for carbon dioxide removal is an ongoing endeavor, with challenges remaining in improving the adsorption rate and selectivity for CO_2.

Table 3. Various selected graphene-based adsorbents for carbon dioxide.

Adsorbent	**Surface area ($m^2\ g^{-1}$)**	**uptake (mmol g^{-1})**
3D Graphene	477	0.7
a-PPy/Rgo	1360	4.3
PANI/HEG	–	75
Graphene/Mn_3O_4	541	2.59
graphene nanoplates	480	56.4
Nano-MG	1480	31.1
PIG6 hybrid	534	3
3D-GO	700	2.7
PIG6 hybrid	534	3
ZIF/GO	1120	16.36
GEPMs	253 ± 22	2.54
B-rG-O	514	1.82
Fe3O4/HEG	98.2	60
GTCF	440	2.65
SAGA	1230	2.45
HPGCs	459	1.76
PGFs	825	25.45
HRGO	530	2.40

Non-carbonaceous dry adsorbents

1. Zeolites

Zeolites are microporous crystalline framework materials that exist naturally and can be synthesized in the research laboratory. Zeolites possess regular pore sizes ranging from 0.5 to 1.2 nm, consisting of a chain of channels to capture the gas molecules . It has been therefore widely deployed in the gas separation technologies. Zeolites have been broadly studied for carbon dioxide removal in the interest of their molecular sieving impact and the robust dipole–quadrupole (electrostatic) interactions between carbon dioxide and alkali metal cations in the zeolite frameworks. The efficiency of Zeolite adsorbents relates to several parameters like structure and composition of the framework, cationic shape, purity, size and shape of the molecules, and molecular polarity. There are several common types of zeolites for carbon dioxide adsorption such as zeolite A, X, and Y or natural zeolite like chabazites, clintopiles, ferrierites, and mordenites . Their results showed that the adsorption capacities enhanced in the act of increasing the pressure as shown in Fig. 10, where 13X zeolite reached the highest carbon dioxide adsorption followed by NaY, HZSM-5−30, HiSiV-3000, HY-5 respectively. This is by virtue of the low ration of Si/Al of 13X with the cations that cause a strong reaction with carbon dioxide molecules.

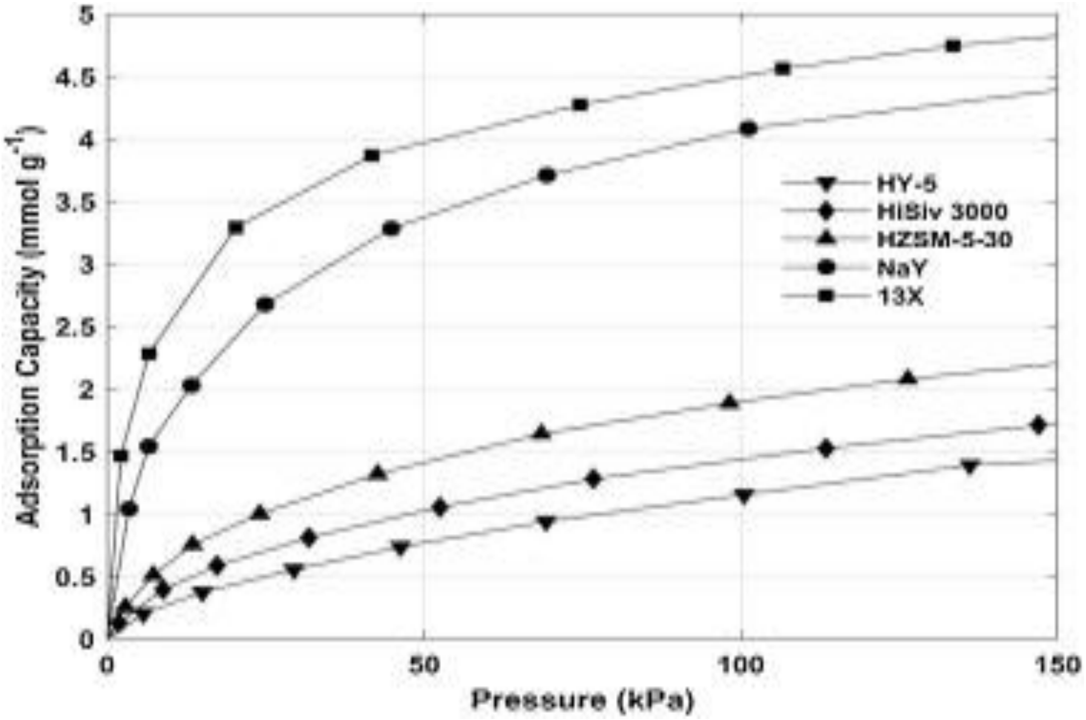


Fig. 10. Comparison of carbon dioxide adsorption isotherms for fresh zeolite at 22 °C°C based on ZSM-5 structure with (Si/Al > 1000).

Recently, studies investigated on the modifications of the structure of zeolites by the deployment of large and electropositive polyvalent cations to improve the CO_2 loading. NaX zeolite (Si/Al = 1.21) exchanged with more cations of Ni^{+2} and Cr^{+3} can reduce the CO_2 NaX and NaY zeolites that resulting from the process of ions exchanged with Cs.

In recent times, binderless zeolite NaX microspheres for carbon dioxide removal were synthesized using chitosan-assisted synthesis. The modified zeolite had a regular particle size of around 1.3 mm and an active surface area of 931 m^2/g . Fig. 11 displays the cations of K^+ and Cs^+ residing in the surface pores on ZK-5, where increasing K^+ ions can block the entry of large gas molecules like methane and nitrogen whilst permitting the smaller gas molecules like carbon dioxide to enter. Their results improve the adsorption selectivity's of CH_4 and N_2 to CO_2 were improved by 10^5 times.

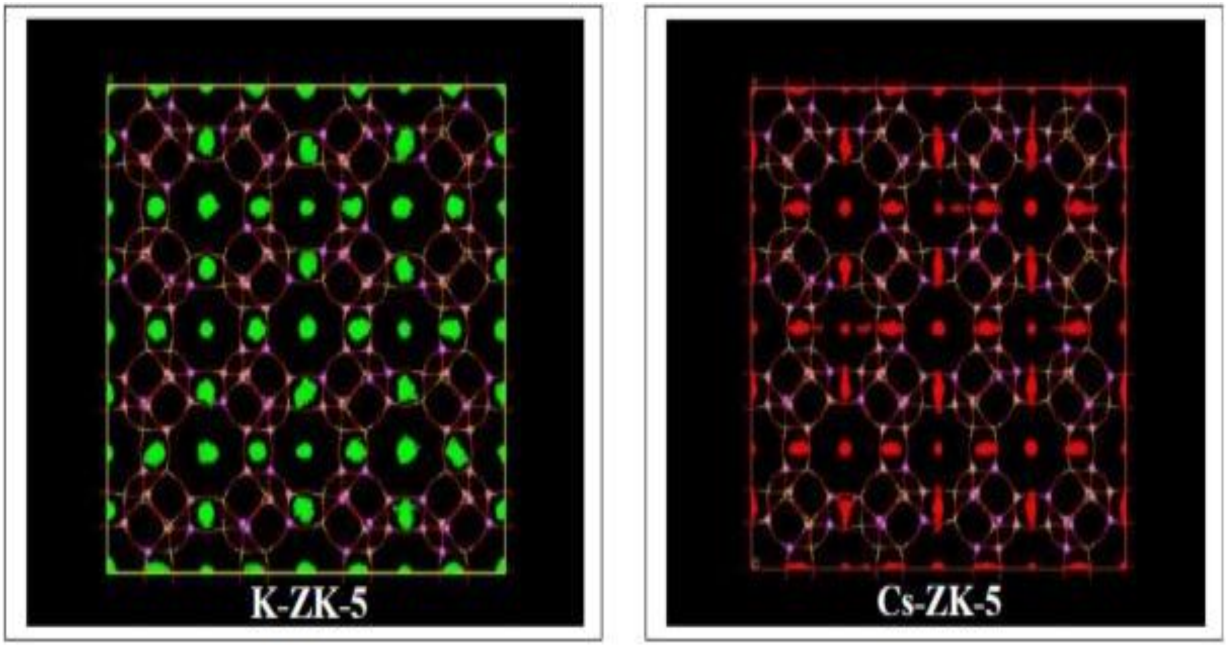


Fig. 11. The location of K and Cs ions in K-ZK-5 and Cs-ZK-5 predicted using GCMC simulation.

The carbon dioxide removal performance of zeolite adsorbents is strongly affected by the operating temperature and pressure. Zeolite's adsorbents are typically employed at pressures more than 200 kPa with high regeneration temperature might reach 573 k; it has been therefore carbon dioxide regeneration turns in huge energy loss . As well as the adsorption capacity of zeolites adsorbents decreases due to the high affinity to adsorb moisture. Small content of moisture could greatly reduce the CO_2 loading, which

adsorbed on the surface of zeolites and form a film to block the access for carbon dioxide molecules . To tackle this issue, many studies were performed to use amines additives on the surface of zeolites to produce efficient composite materials. impregnation by mixing of amines with a solvent at a specific ratio as showing in Fig. 12.

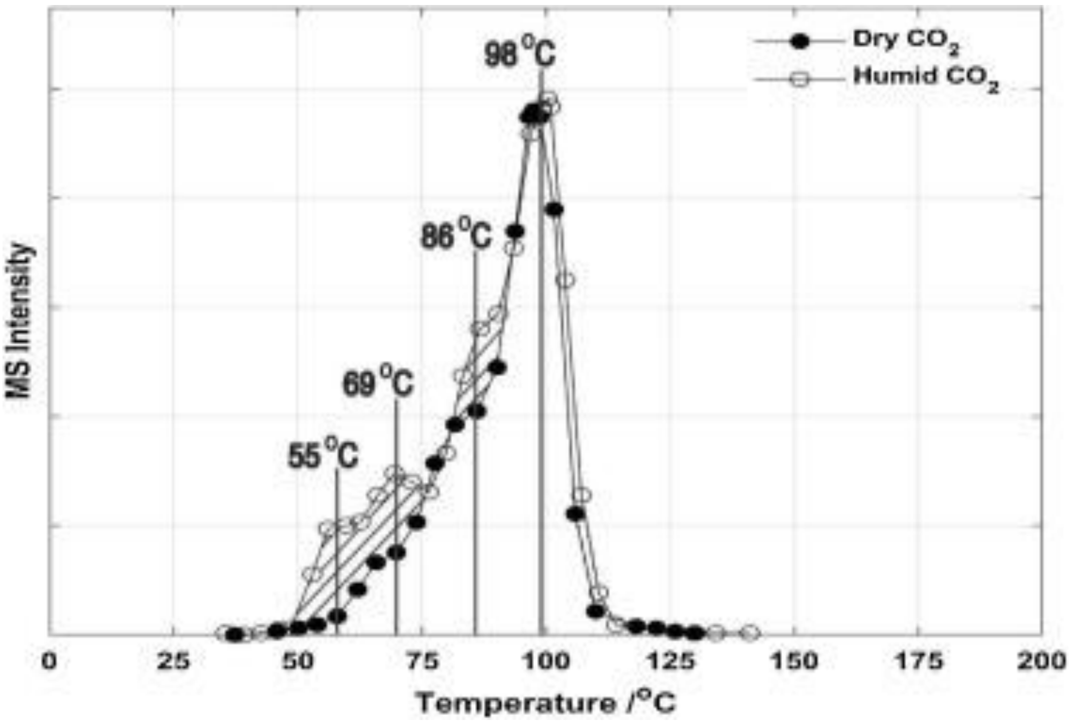


Fig. 12. Carbon dioxide adsorption in dry and humid for 40 % aminopropyltriethoxysilane/β-25 on temperature-programmed desorption profiles.

Later, the solvent removes by either evaporation or filtration. The synthesized adsorbent showed excellent performance for carbon dioxide adsorption/desorption with adsorption capacity up to 4.705 mmol/g and the desorption presenting at 333 k. The nonviability with the mentioned adsorbent is the presence of moisture can help in enhancing the adsorption capacity by 19 % as shown in Fig. 13 commonly exits in the cationic zeolites. zeolites with small micropores shown good carbon dioxide/nitrogen selectivity, however the carbon dioxide diffusion into the material was limited. On the other hand, zeolites with large micropores have higher carbon dioxide adsorption and low carbon dioxide capturing performance. Some research activities of modifications of selected types of zeolite-based adsorbents for carbon dioxide removal are summarized in Table 4.

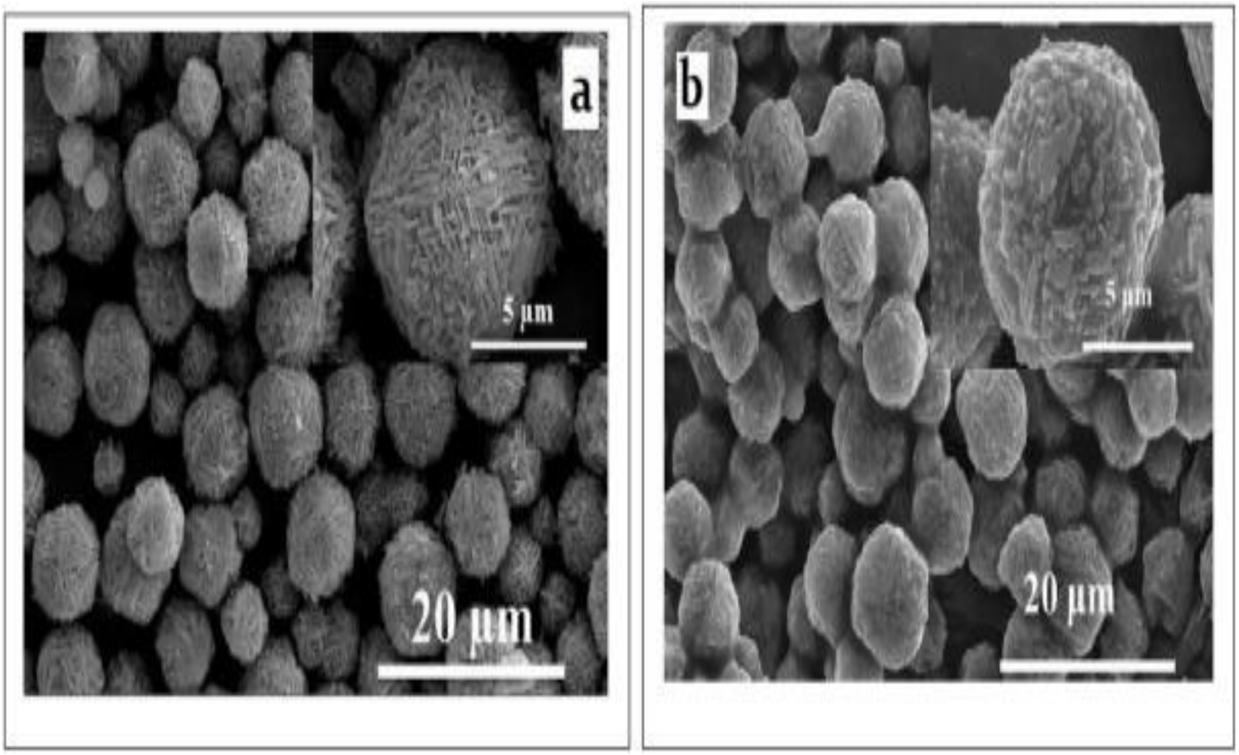


Fig. 13. SEM pictures of (a) 13X, (b) Meso-13X and (c) Meso-13X-PEI.

Table 4. Carbon dioxide adsorption capacity of zeolites-based adsorbents

Adsorbent	**Temperature,** ℃℃	pco2	**Adsorption Capacity (mmol/g)**
Zeolite X13	**20**	0.152 bar	2.63
	22	1 bar	4.61
	25	1 bar	4.66
NaX	32	1 bar	5.71
NaY	**32**	1 bar	5.5
	22	1 bar	4.06
NaM	25	1 bar	2.95
Silicalite	30	15.2 bar	0.48
erionite (ZAPS)	17	1 bar	2.8
mordenite (ZNT)	17	1 bar	1.8
clinoptilolite (ZN-19)	17	1 bar	1.7
Na-ZSM-5	30	1 bar	0.75
ZSM-5	40	1 bar	0.32
HZSM-5−30	22	1 bar	1.9
HiSiv 3000	22	1 bar	1.44
HY-5	22	1 bar	1.13
Cs-X-c	100	1 bar	1.15
Cs-X-h	50	1 bar	2.42
ZIF-69	0	1 bar	2.5
ZIF-70	0	1 bar	3.1

2. Silica materials

Based materials are another generation of non-carbonaceous dry adsorbents for CO_2 capture which characterize a high surface area, large pore size, and great mechanical stability . Silica is generally employed as support on which other materials added for carbon dioxide removal. Therefore, most of the research efforts on silica-based adsorbents are mainly interested in modifying various types of silicas and deploying appropriate amine types. Heretofore, many studies reported the use of silica materials-based adsorbents for carbon dioxide. Three driving aspects should be taken in process of production of silica-based material adsorbent:

1) using new preparation technologies to design amine-modified silica materials
2) advancing new surface structure
3) evaluating carbon dioxide adsorption performances of various silica composites.

There is a wide range of silica-based adsorbents and the recent studies interest on the development of mesoporous silica materials for effective carbon dioxide removal. Modifying of mesoporous silica-based materials with amines can efficiently enhance the adsorption capacity for CO_2 by virtue of the primary and secondary amines have a high affinity for carbon dioxide and react strongly by hydroxyls on the surface as following

$$\mathrm{CO2+2RNH2 \rightarrow RNHCOO\text{-}+RNH3+CO2+2R2NH2 \rightarrow R2NHCOO\text{-}+R2NH2+}$$

They modified the hyperbranched amino silica carbon dioxide adsorbents using the ring-opening polymerization of aziridine from mesoporous silica and amines. The modified adsorbent presents more stability of the organic groups covalently bound to the silica support in comparison to those made by physiosorbed processes. They prepared modified SBA-15 adsorbents using co-condensation, chemical grafting, and physical impregnation. The results stated that the synthesized adsorbents using co-condensation and physical impregnation resulted in poor carbon dioxide adsorption capacity.

This adsorbent offered good carbon dioxide loading (2.75 mmol/g at 358 k) and acceptable stability. To create molecular basket adsorbent, it is sterically branched polyethyleneimine with many carbon dioxide affinity pores and low adsorption heat loaded into the large-pore-volume mesoporous molecular support. Fig. 14 displays the graphical process of polyethyleneimine loaded in the mesoporous molecular sieve of MCM-41. The modified adsorbent selects carbon dioxide in condensed form in the mesoporous molecular sieve, then forming a carbon dioxide molecular basket, it is therefore showing high carbon dioxide adsorption capacity and acceptable selectivity.

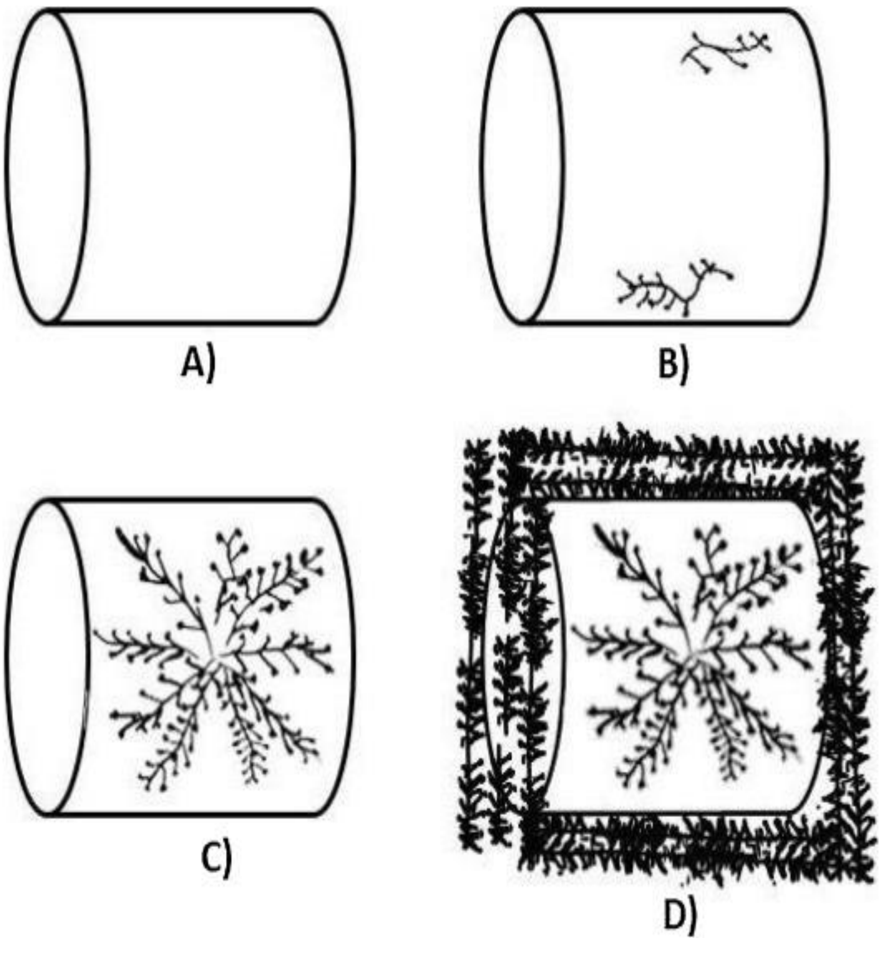


Fig. 14. Graphical process of PEI loaded on MCM-41. (A) MCM-41 support; (B) low- (C) high- (D) extremely high-PEI loading.

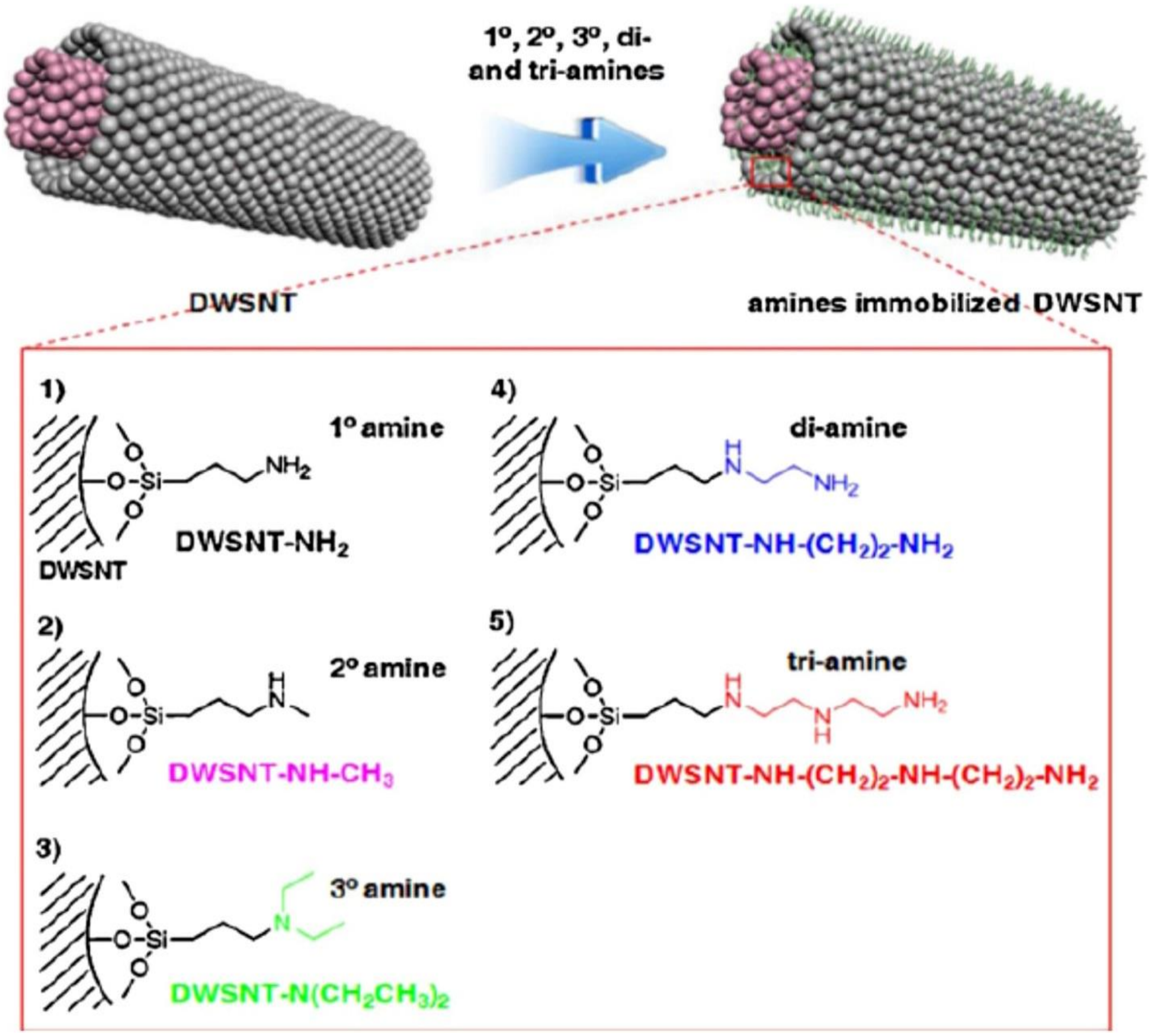


Fig. 15. Graphical diagram of primary, secondary, tertiary, di-, and tri-aminosilanes DWSNTs.

The carbon dioxide adsorption capacities of four types of modified adsorbents remained stable and the masses of adsorbents decreased by 5.1 %, 0.6 %, 0.2 %, and 0.1 %; they concluded that PIE modified adsorbent shows excellent thermal stability.

The results showed that the large pores can elevate the grafting degree of organ silane, whilst the narrow pores enhance the physical adsorption capacity by improving the interaction between carbon dioxide and adsorbent surface. Macropores adsorbents recorded the highest amines loading on the pore structure, highest CO_2 uptake, high carbon dioxide/nitrogen selectivity, and shortest adsorption time. Finally, silica materials have been reported as efficient adsorbents for CO_2 with a low regeneration energy penalty. The amine-based silica adsorbents are stable and the presence of some impurities such as SO_2 and NO_x do not have a significant impact on the carbon dioxide adsorption performance . However, many issues might take place by the cause of the hydrolysis of Si-o-Si bonds.

Future research is to create amine synthesized silica composites adsorbents that can turn in increasing the surface area and result in a compatible pore size for carbon dioxide molecules. Table 5 summarized some efficient silica-based adsorbents for carbon dioxide in terms of specific surface area and adsorption performance.

Table 5. Carbon dioxide adsorption capacity of common silica-based adsorbents.

Silica-based Adsorbent	**Uptake, mmol/g**	**Pressure**	**Temperature, K**	**Surface Area m^2/g**
AMD16	1.4	1 bar	298	199
MSPs (NaSi)	2.92	1 bar	273	908
NH2-HNs-0.88	1.7	1 bar	273	332
MSPs (TEOS)	3.57	1 bar	273	1012
SiO2–PAA (3000)– PEI (10,000)	3.8	1 bar	313	–
aminosilanes immobilized DWSNTs	2.3	1 bar	298	348
DIPA/silica fume	1.3	1 bar	303	271.2
MSPs (HNO3)	5.01	1 bar	273	776
FS-PEI-50	3.016	1 bar	298	27.2
BMSHS	4.4	1 bar	383	923
MCFs-PEI modified	6	1 bar	358	942

Silica-based Adsorbent	Uptake, mmol/g	Pressure	Temperature, K	Surface Area m²/g
APMS grafted	2	1 bar	333	650
MPS-LA-120	3.86	1 bar	323	56
HMS-12c	0.56	1 bar	318	1181
XG00−4.5a	1.8	1 bar	273	674
Ti/M1/PEHA	2.34	1 bar	273	1387
P-MCM-41	3.67	1 bar	308	372
SBA-AE-ev	4.1	1 bar	303	572

3. Metal organic framework adsorbents

Metal-organic frameworks (MOFs) materials are a new generation of solid adsorbents materials that are produced by the combination of metal ions linked by coordination bonding as shown in Fig. 16.

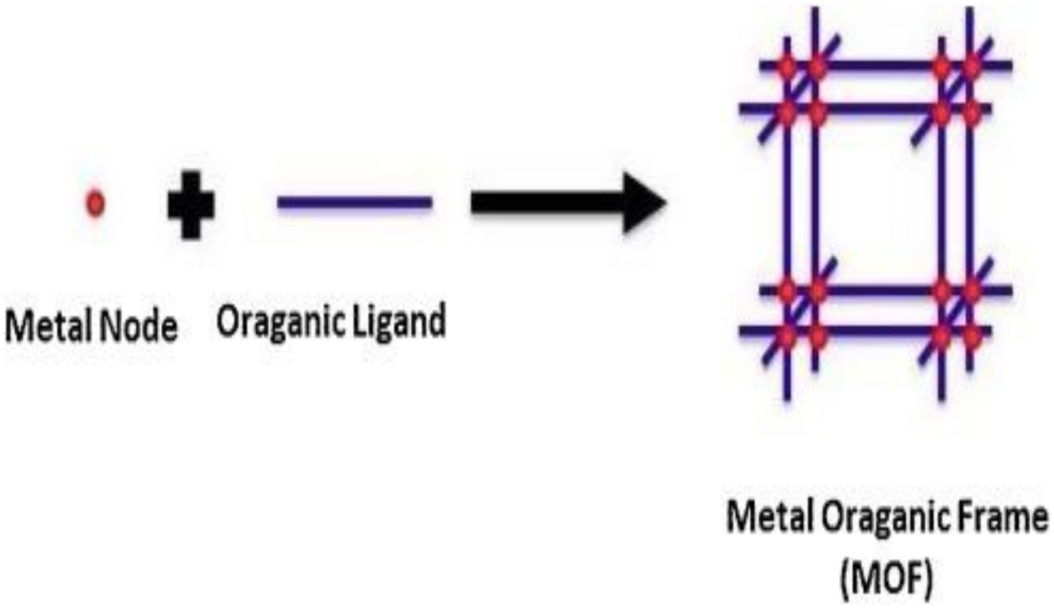


Fig. 16. Graphical diagram of producing MOFs materials.

The flexibility of manipulation of both metal ions and the organic linkers offers copious options to manage the pore size, shape, and the potential of the adsorbing surface, which improves the selectivity, CO_2 loading, and adsorption/desorption kinetics .All the mentioned features nominate MOFs adsorbents ideal for CO_2 capture. Almost, all the metals and a large range of organic species can be deployed to produce metal-organic frameworks. Two important criterions keys for selecting a proper MOFs adsorbent for CO_2 removal are that the adsorbent pores must be harmonious with the carbon dioxide molecules diameter. Besides, the adsorbent should come with polar (−OH, N = N-, -NH_2, and -N = C (R) -), where pores have a larger CO_2 loading owing to quadrupole moments of carbon dioxide molecules. Therefore, considering these criterions in the design of the MOFs adsorbents can turn in a huge improvement of the carbon dioxide adsorption. The rigid metal-organic frameworks have strong frameworks that create permanent pores similar to zeolite materials, while the dynamic type has soft frameworks whose structures change by external impacts like pressure, temperature, and guest molecules. The most common approach is to create a bare-metal site lining the pore by liberation of a coordinating solvent area, the modified adsorbent has acceptable carbon dioxide loading of 2.9 mmol/g at 0 °C°C.

Adsorption of carbon dioxide using solid materials is a promising technology that can minimize the energy requirements for the regeneration process compared to the other commonly used capturing technologies. This review concludes the recent state of knowledge on the physisorbents adsorbents that can be employed to remove carbon dioxide. Various modifications methods like amine functionalization and enhancing the textural properties improve the carbon dioxide adsorptive performance. Porous materials with narrow pores doped with carbon di oxide-philic heteroatoms are compatible with carbon dioxide removal technologies. The efficient adsorbent materials for adsorption technology should offer high thermal stability, good mechanical strength, high selectivity, low synthesis cost, resistance in humid conditions that can be necessary to compete with other capturing methods.

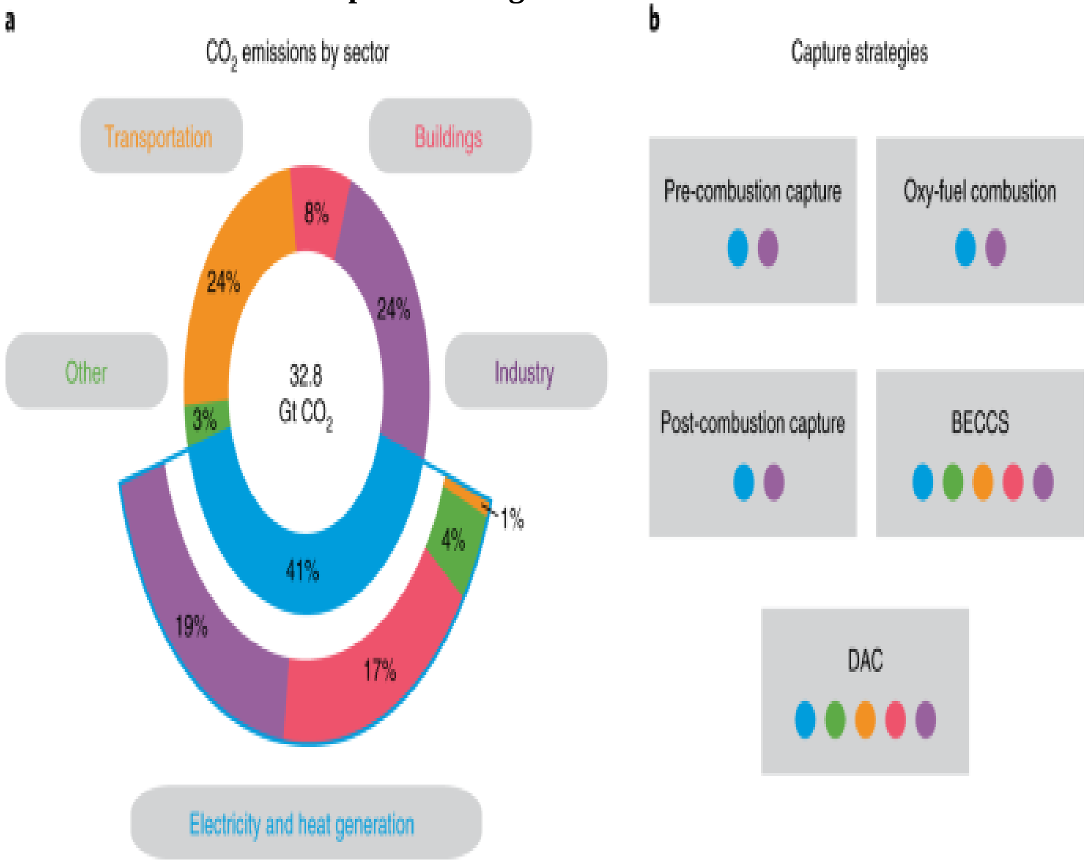
Chapter 4

Porous Material for CO_2 separation

Carbon capture and sequestration (CCS)in which CO_2 is selectively captured and permanently stored underground has been recognized as a vital component of strategies to limit warming below 2 °C . Industrial development of carbon capture technology dates to the 1930s, when aqueous amine scrubbing was first patented for the selective removal of CO_2 from crude natural gas. Supported largely by economic incentives related to enhanced oil recovery, CO_2 transport, and storage have also already achieved commercialization. However, deployment of commercial-scale CCS projects specifically for the purposes of emissions mitigation has been slow. At the time of writing, the Global CCS Institute lists 65 commercial CCS facilities, with 26 in operation. These facilities can currently capture and sequester approximately 40 million tons per annum (Mtpa) of CO_2, with the potential for an ultimate combined capacity of >100 Mtpa. Although this ultimate capacity addresses a modest 0.3% of global annual emissions, the contributions of these established commercial-scale operations can catalyze broader adoption of CCS during this critical period of accelerated decarbonization. For an excellent broader discussion of the current status of CCS, including remaining commercial and political barriers, we refer readers to a recent comprehensive review.

Research efforts towards CCS have largely focused on post-combustion capture from fossil fuel-fired power plants, which are attractive targets due to their emission of large quantities of CO_2 at relatively high concentrations (~4–15%). Indeed, in 2017, the production of electricity and heat generated 41% of global CO_2 emissions (Fig. 1), and thus decarbonization of the power sector is critical to mitigating emissions. Beyond fossil fuel sources, CCS can additionally be coupled with bioenergy production, potentially enabling the net removal of CO_2 from the atmosphere (‘negative emissions’) in a process termed bioenergy with carbon capture and sequestration (BECCS). Furthermore, CCS can support the production of renewable or lower-carbon fuels. The industrial sector, which contributes 24% of global CO_2 emissions (Fig. 1) also offers a number of opportunities for decarbonization in cement production, oil refineries, iron and steel mills, and the pulp and paper industry. Finally, direct air capture (DAC) of CO_2 can provide an additional strategy for negative emissions

Fig. 1: Emission sources and capture strategies.



a, Global CO_2 emissions by sector in 2017, with emissions due to electricity and heat generation further reallocated by end-use sector (purple, pink, orange and green represent industry, buildings, transportation and other sectors, respectively). Emissions from the industrial sector also include energy industry own-use emissions resulting from the extraction, refining, mining or manufacture of fuels. The ‘other’ sector encompasses emissions from commercial and public services, agriculture and forestry, and fishing.

b, Capture strategies suitable to target emissions from each sector. BECCS and DAC processes can indirectly target emissions from all sectors through net CO_2 removal from the atmosphere.

Aqueous amine solutions, which capture CO_2 through the reversible formation of carbamate or bicarbonate species, remain the most technologically advanced capture systems. Despite their proven performance at commercial scale, amine solutions suffer from volatilization and oxidation as well as corrosivity, which necessitates dilute Solutions that require energy-intensive regeneration due to the large volume of inert water that must be thermally cycled. As a result, the capture step in an aqueous amine-based CCS process at a coal-fired power plant currently comprises 60–80% of the total cost of CCS, which encompasses capture, compression, pipeline transport and underground storage of CO_2 . Ongoing research in amine absorption has led to energy savings using new amines or blends of amines, corrosion inhibitors, promoters or catalysts to enhance the absorption rate, and thermal integration within a plant; nonetheless, only incremental improvements in overall process efficiency are anticipated for solvent-based processes moving forward. To overcome these limitations, several new capture technologies have been reported for CCS in recent years. Although at an earlier stage of development, water-lean solvents, membranes, metal oxides and encapsulated liquid sorbents may offer means to increase the efficiency of CCS. As another alternative, porous materials have received growing attention due to their potential to achieve intrinsically lower energy consumption than amine solutions in CO_2 capture processes, with a reduction of up to 30–40% in parasitic energy projected for adsorptive versus absorptive carbon capture processes at coal-fired power plants. Adsorbents offer several other potential advantages in carbon capture processes: pore size and shape act as additional handles to fine-tune capture chemistry in the solid state; adsorbents and cycling configurations can be varied to target a wide range of thermodynamic conditions; and toxic or corrosive volatiles emitted from amine absorption units can be avoided with dry capture systems. In this Review, we discuss the state of the art in CO_2 capture with porous materials, beginning with an overview of the primary adsorbent classes. We then examine individual target separations with a focus on remaining technological barriers to deployment, such as contaminants that can act as adsorbent poisons. Throughout the latter section, we highlight recent developments in materials design towards overcoming stream-specific CCS challenges. We then conclude with a discussion of critical needs from the materials community to drive continued progress in this area.

The role of CCS in cross-sector decarbonization

The start of the 2020s has led to a flurry of decarbonization activity as parties within the Paris Agreement execute their nationally determined contributions. China, the world’s largest greenhouse gas emitter, has committed to reaching peak emissions before 2030 and carbon neutrality by 2060. The United States, the second-largest emitter, has rejoined the Paris Agreement and committed to decreasing overall greenhouse gas emissions to 50–52% below 2005 levels by 2030, while targeting 100% carbon-free electricity by 2035 and economy-wide net-zero emissions by 2050. Roadmaps to meet these commitments focus heavily on massive mobilization of renewable energy technologies coupled with rapid electrification of transport, buildings and industry. What is the outlook for carbon capture within this fast-moving transition?

The power sector is the crux of the net-zero transition, and recently plunging costs of wind and solar energy have shifted the economics of decarbonized electricity. In the

United States, an illustrative recent report outlined a path to 90% carbon-free electricity by 2035 that would reduce wholesale electricity costs by 10% versus 2020 levels while supporting a greater number of jobs versus a business-as-usual case. Such a plan would require strong policy—which the authors advocate for in the form of a staged federal clean electricity standard as well as a highly aggressive build-out of 1,100 GW (70 GW per year) of new wind and solar capacity. (Comparatively, ~34 GW of wind and solar capacity was installed in the United States in 2020.In China, the record one-year capacities for wind and solar expansion sum to 84 GW; While US utility companies have begun making net-zero pledges, current resource plans from utility companies are largely not keeping pace with the necessary shift away from fossil energy. A recent study of 79 US operating companies that generate 43% of US electricity found that these companies plan to add over 36 GW of new gas capacity by 2030 while retiring only 25% of their coal generation. This energy system inertia follows from the >100 GW of new gas capacity added in the United States in the past decade. Policy shifts could dramatically alter this trajectory, but even plans with aggressive deployment of wind and solar often lean on existing natural gas assets to smooth periods of high demand or low renewables output, particularly in the near term. New technologies, such as long-duration storage, could help bridge the gap to 100% carbon-free electricity while reducing curtailment of intermittent energy sources. However, CCS can provide a tool to address both the inertia of the current energy system and the final gap to a fully carbon-free grid. Given the scale of power plant emissions and the compressed timeline needed for carbon-free electricity, widespread CCS in the power sector would require well understood, inexpensive and imminently scalable materials.

Considering decarbonization of transport and buildings, rapid electrification will lead the transition to net-zero emissions: electric vehicles, electric heat and hot water, and electric appliances must replace fossil fuel-consuming counterparts. However, certain subsets of these sectors will prove more difficult to decarbonize, such as aviation, shipping and heavy-duty trucking. Carbon capture could contribute to decarbonization in these sectors with DAC- or biomass-sourced CO_2 for carbon offsets (via sequestration) or carbon-neutral fuel production, or through the production of ‘blue hydrogen’ via steam reforming of natural gas coupled with CCS. (‘Green hydrogen’, generated by renewable-powered electrolysis of water, is a cleaner alternative when and where it can be produced cost-competitively.) The smaller niche, more limited optionality and longer projected transition timeline for difficult-to-electrify subsectors may support earlier-stage materials development for CCS in these areas.

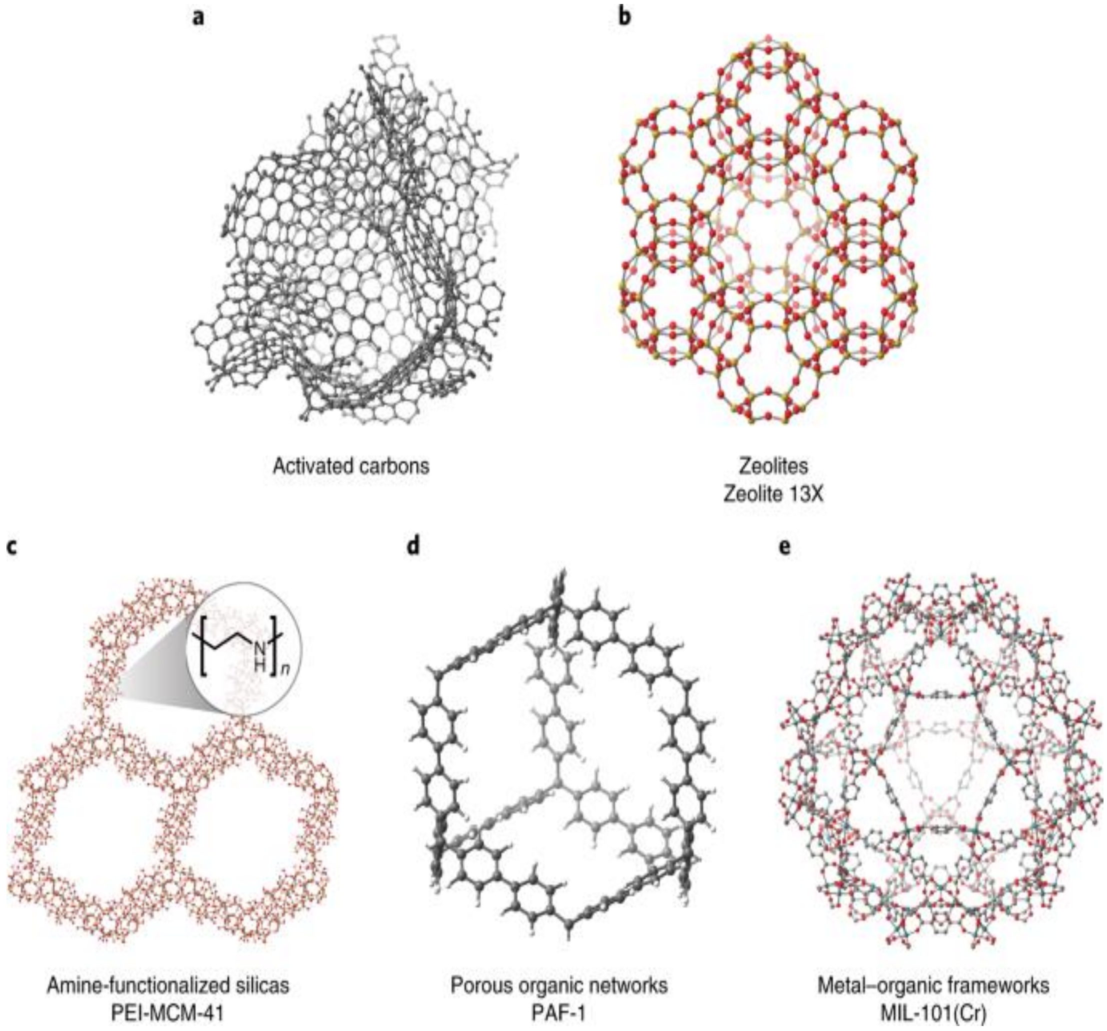
Several areas of industry will also likely prove difficult to abate with electrification alone. In contrast to the power sector, which operates within controlled regional markets, heavy industry must compete in global commodity markets with extremely thin margins. Industrial facilities require large capital investments with decades-long lifetimes, and profitability hinges on maximizing capacity factors and minimizing downtime. As a result, fossil energy is abundant in heavy industry due to its ability to provide high-temperature and high-flux heat with both a steady supply and low cost. Low-carbon replacement options are limited, particularly for the highest-temperature (≥1,200 °C) processes in the steel and cement industries, and the path to net-zero is not yet clear. In a recent evaluation of decarbonization strategies for heat in heavy industry, CCS was generally found to hold the greatest technical and economic feasibility compared with alternatives such as blue or green hydrogen, electrification via resistive heating, biomass or advanced nuclear processes. In addition, CCS will likely be favored to address emissions generated as by-product streams within industrial processes. While alternative processes that minimize liberated carbon are under development, producers of structural materials are extremely conservative when considering any changes that could impact the physical properties of their products. Overall, given the large abatement potential, concentrated CO_2 point sources, limited optionality and earlier stage of decarbonization, the industrial sector is a particularly promising area for adsorptive CCS. Growing investment from the materials community is needed in this area.

Beyond these sectors, negative emissions technologies, such as DAC, remain at the forefront of decarbonization discussions. The technological challenges associated with CO_2 capture from ultra-dilute streams are discussed in the main text, but non-technological factors are also shaping the future of DAC. In recent years, the negative emissions space has seen an outpouring of public and private sector support, including government research and development funding, tax credits, venture capital, and voluntary financial commitments from large multinational corporations. Furthermore, negative emissions approaches are featured prominently in the recent IPCC report outlining pathways to keep warming below 1.5 °C . In addition to financial and policy incentives, the greater flexibility in deployment timeline and scale for negative emissions technologies makes DAC amenable to exploratory materials research and commercialization of new breakthrough technologies.

Adsorbent classes

A wide array of porous inorganic, organic and inorganic–organic hybrid structures have been proposed for adsorptive CO_2 capture (Fig. 2). Key metrics for evaluating the utility of an adsorbent include; the CO_2 selectivity of the adsorbent in the presence of all mixture components, the CO_2 swing capacity of the adsorbent in adsorption–desorption cycling, the kinetics of adsorption and desorption, the energy required to cycle or regenerate the adsorbent, the stability of the adsorbent to chemical and mechanical stresses during extended cycling, and the economic and environmental viability of the adsorbent in a cradle-to-grave lifecycle assessment. Ultimate evaluation of an adsorbent requires analysis of a structured material (for example, pellets, fibers, monoliths) within a full-scale process, with several possible cycling configurations (for example, temperature swing, pressure or vacuum swing, concentration swing) and adsorption unit configurations (for example, fixed bed, fluidized bed, rotating bed). Although these engineering considerations are critical to the overall process efficiency, we focus here on recent developments in the optimization of the fundamental adsorbent design for carbon capture. The primary adsorbent classes evaluated for carbon capture so far are reviewed below

Fig. 2: Illustrative examples of adsorbent classes discussed in this work.



a, Activated carbons

b, Zeolites, represented by zeolite 13X (base faujasite cage structure shown; Na^+ ions omitted for clarity)

c, Amine-functionalized silicas, represented by PEI-MCM-41 (PEI, polyethylenimine; MCM, Mobil Composition of Matter)

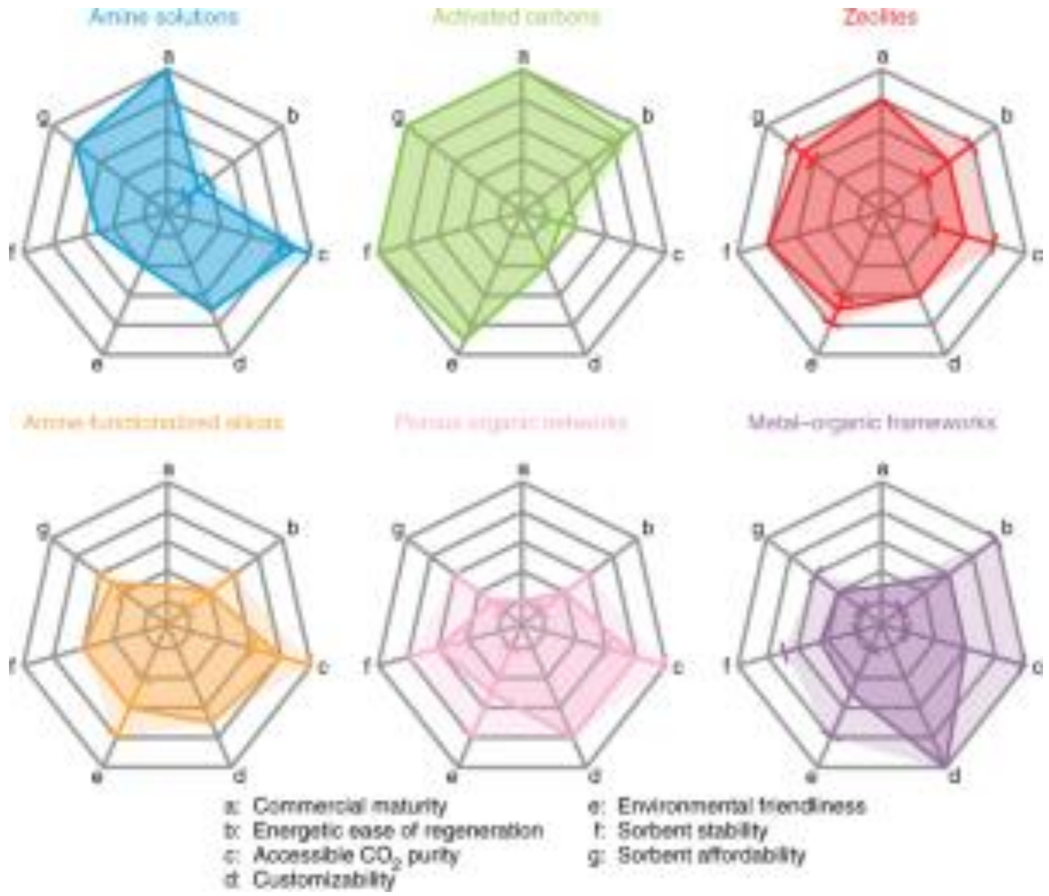
d, Porous organic networks, represented by PAF-1 (also known as PPN-6; PAF, porous aromatic framework; PPN, porous polymer network). The structure depicts one possible local environment within the amorphous material

e, Metal–organic frameworks, represented by MIL-101(Cr) ($Cr_3O(bdc)_3F$; MIL, Matérial Institut Lavoisier; bdc^{2-}, 1,4-benzenedicarboxylate)

In **a–e**, yellow, red, grey, green and white spheres represent Al/Si, O, C, Cr and H atoms, respectively.

Sorbent selection considerations

The choice of adsorbent strongly influences both capital and operating costs in a carbon capture process. Considering capital costs, adsorption columns and associated equipment will be sized according to gas equilibria and kinetics within the material: adsorbents that bind and release greater quantities of CO_2, and at faster rates, may enable smaller columns. However, for materials with high sorption enthalpies, additional capital investment may be required to ensure that the capture equipment can effectively control thermal excursions. High enthalpies may likewise drive operating costs by requiring time- and resource-intensive heating and/or cooling. The stability of an adsorbent can also influence capital and operating costs by driving investment in pretreatment technologies and dictating adsorbent replacement rates. More expensive materials may be justified if a long sorbent lifetime can be achieved without extensive pretreatment. Nonetheless, given the sorbent quantities needed to achieve impactful emissions mitigation, every effort must be made to minimize the cost, deployment timeline, and environmental footprint of large-scale synthesis, shaping and end-of-life processes for any CCS material. Trade-offs in key sorbent selection criteria are captured in the figure for various sorbent classes.



Qualitative assessment of key metrics for materials selection in carbon capture applications. Bold lines indicate average values for each property within a materials class, with error bars indicating typical variability for a given property within that class.

Examining the strengths and weaknesses of various carbon capture sorbents raises key questions towards resource allocation in deploying emissions mitigation technologies. Given the broad range of capture conditions for different CO_2-containing streams, and even within a single class of emissions or process streams (Table 1), should researchers optimize capture processes around a limited set of materials, or rather optimize individual materials for each process, or even each plant? Greater process efficiency may be possible with sorbents purpose-built for specific CCS separations. However, the high cost to de-risk the production, use and disposal/recycle of new materials at CCS-relevant scales favors a focus on a minimal number of inexpensive, well understood sorbents. In practice, viable solutions will require a degree of versatility in both the materials and process design. Close collaboration between materials scientists and process engineers will accelerate identification of optimal paths forward.

The scale and urgency of each carbon capture opportunity should also drive decision-making in the CCS community. Average annual CO_2 emissions per sector and source are provided in the table below. At present, fossil fuel-fired power plants are the largest point-source emitters of CO_2 and have thus attracted the majority of CCS research attention. The scale of these emissions would need to be met with a proportionate response in materials production. For example, a 2013 study projected that capturing 90% of the CO_2 from all coal-fired power plants in the United States (annual emissions of 1.97 $GtCO_2$) with a metal–organic framework would require production of 1.5 million tons of adsorbent per year. The authors demonstrate the high sensitivity of their estimates to the adsorption/desorption cycle time (taken as 60 min) and the lifespan of the adsorbent (taken as 8,000 cycles), with a projected consumption rate of 0.7 kg adsorbent per tCO_2 captured. (Comparatively, solvent consumption rates for absorptive CCS processes are estimated as 0.2–1.6 kg per tCO_2, with the Mitsubishi Heavy Industries hindered amine KS-1 at the low end, and Fluor's ECONAMINE at the high end. Production and disposal or recycle of materials at this scale would require rapid, massive mobilization if adsorptive CCS efforts are to contribute to keeping warming below 2 °C.

As decarbonization efforts in the power sector accelerate, unavoidable industrial emissions, such as those from cement production, will assume a greater proportion of overall emissions. The adsorption community will therefore benefit from increased investment in these enduring yet understudied CCS challenges. Likewise, CCS opportunities in BECCS and DAC will persist as well.

Global annual total emissions and average emissions per source for CO_2-containing stream

Process	Global emissions ($MtCO_2\ yr^{-1}$)	Average emissions/source ($MtCO_2\ yr^{-1}$)
Power sector (as of 2017)		
Coal	9,761	3.94
Natural gas	2,975	0.77–1.01
Industry (as of 2014)		
Cement	2,545	0.79
Refineries	950	1.25

Process	Global emissions (MtCO$_2$ yr^{-1})	Average emissions/source (MtCO$_2$ yr^{-1})
Iron and steel	3,487	3.67

1. annual average sub stream emissions within a representative refinery or 2 Mt integrated steel mill, see ref.

Activated carbons

Activated carbons (Fig. 2a) are among the most industrially mature adsorbents, with applications in air and water purification, solvent recovery systems, and decolorization of sugar and other products through the removal of trace organic species. Preparation of activated carbon involves pyrolysis of biomass followed by high-temperature activation (typically at 700–1,100 °C) using physical agents including steam, CO_2, O_2 or other gases. Alternatively, chemical activation agents can be used to access higher surface areas or incorporate specific surface functionalities, such as nitrogenous groups to increase basicity. Porosity in activated carbons is generated through random stacking of microcrystalline graphite domains and can be controlled through modulation of the pyrolysis and activation conditions. Because they can be prepared from low-cost, environmentally benign feedstocks, such as waste biomass. these materials are attractive candidates from an adsorbent lifecycle perspective. Furthermore, given their generally non-polar, hydrophobic surfaces, activated carbons can capture CO_2 in the presence of moisture and minimize regeneration energy costs associated with adsorption–desorption cycling of water. However, the non-polar adsorbent surface also limits the equilibrium CO_2/N_2 selectivity and CO_2 capacity of typical carbons at conditions relevant to CO_2 capture from flue gases ($\leq$15% CO_2) As a result, cost savings achieved with inexpensive, low-enthalpy carbonaceous adsorbents must be balanced with the potential requirements of increased adsorbent bed size and/or shorter cycle times.

Zeolites

Zeolites have likewise reached a state of maturity for industrial separations. The commercialization of these aluminosilicate materials has been facilitated by their high degree of stability, a result of their strong constituent tetrahedral Al–O and Si–O bonds. This stability has in turn supported the processing of zeolites into industrially viable structured forms, such as pellets. Furthermore, the crystalline nature of zeolites has enabled computational screening of known and predicted structures to identify optimal architectures for specific separations. Zeolites for carbon capture often achieve equilibrium selectivity for CO_2 through the interaction of the CO_2 quadrupole moment with exposed metal cation sites within the pores. While such equilibrium selectivity is effective for the removal of CO_2 from dry emission or process streams, this selectivity is often lost in the presence of water, which outcompetes CO_2 in coordinating exposed metal sites. Because gas streams of interest for CCS are often saturated with water, continued development of zeolites for CCS will benefit from new design motifs, such as amine-impregnated organic/inorganic hybrids, that preserve CO_2 capacity and selectivity in its presence. Alternatively, while pre-drying CCS process streams is likely to be cost prohibitive other innovative process configurations, or separations leveraging differences in mass transport of guest species through the pores, may afford viable engineering solutions for CO_2 capture from humid streams.

Amine-functionalized silicas

As with amine solutions, polyamine-functionalized silicas (Fig. 2c) leverage the selective acid–base chemistry of amines, enabling effective CO_2 capture from humid streams[11,30]. Using a solid support in place of an aqueous solvent medium, energetic costs associated with heating the solvent can be avoided, potentially enabling more efficient capture processes. Polyamines can be physically impregnated (class 1) or covalently grafted (class 2) to the silica support[30], and selectivity is achieved through the formation of ammonium carbamate, carbamic acid or bicarbonate species, with the product distribution varying as a function of amine identity, amine proximity to adjacent amine groups and water content[31]. To achieve full-scale CCS processes with amine-functionalized silicas, chemical or engineering solutions are needed to overcome common limitations of amine chemistry, such as leaching of amines from class 1 materials and amine deactivation via oxidation or urea formation.

Porous organic networks

Purely organic porous networks, such as amorphous porous polymers (Fig. 2d) or crystalline covalent organic frameworks, can be synthesized from multitopic organic monomers. Although these materials are at an earlier stage of development, they afford a high degree of chemical tunability, as well as the potential for high gravimetric and volumetric capacities due to the use of light constituent elements. Covalent linkages within these frameworks can further provide a high degree of hydrothermal stability and CO_2-targeting functional groups such as amines can be incorporated directly into the polymer backbone, thereby mitigating volatilization concerns. Advances in the technology readiness of this class of materials will require greater characterization of stability and CO_2 selectivity under simulated process streams, as well as the development of scalable syntheses and structured forms suitable for commercial use.

Metal–organic frameworks

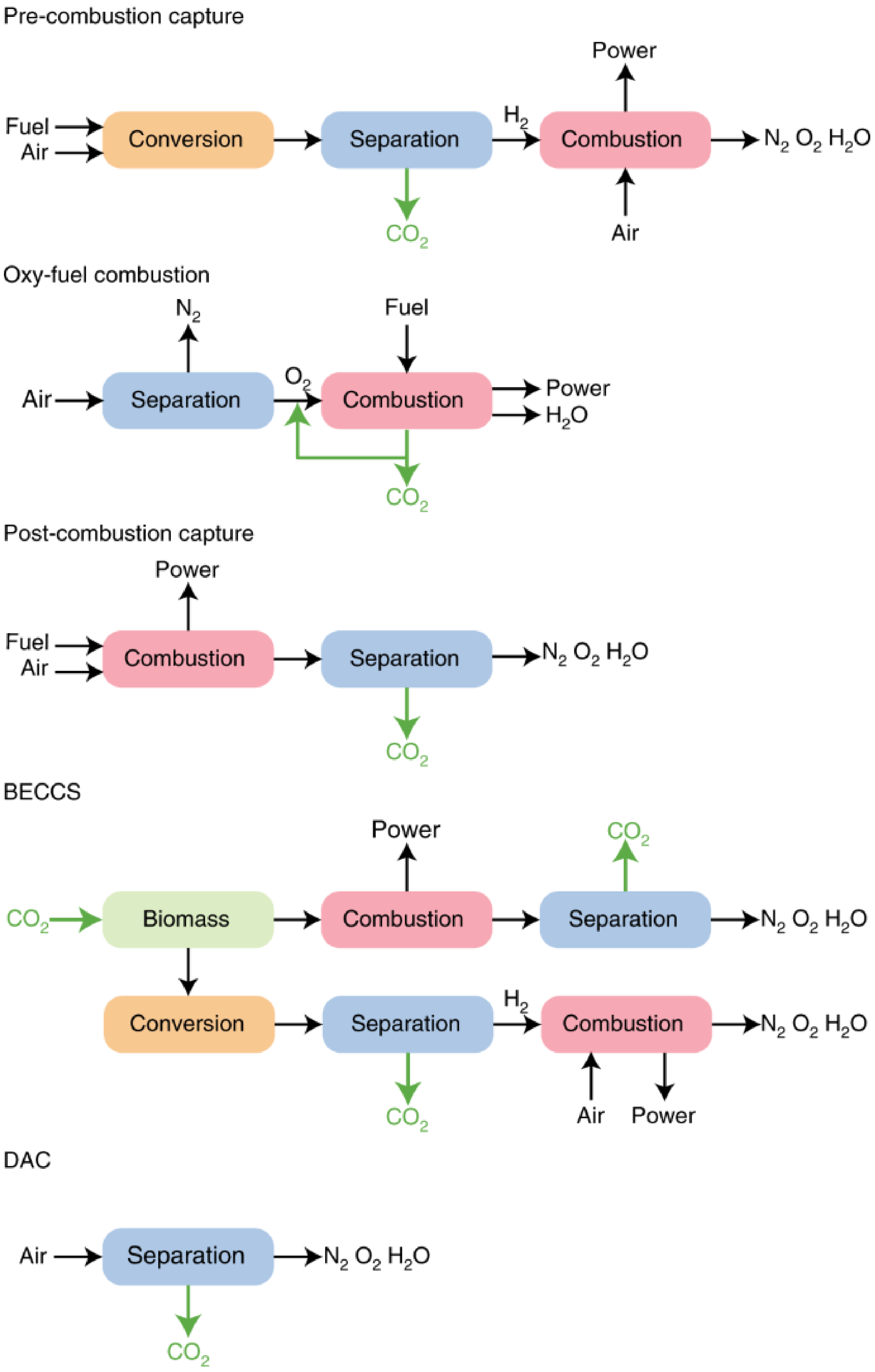
Metal–organic frameworks (Fig. 2e) are a class of crystalline, porous materials constructed from inorganic ions or clusters joined by multitopic organic ligands Through pre- or post-synthetic modification, a high degree of control can be exerted over the pore size, shape and surface chemistry. The development of metal–organic frameworks for CO_2 capture applications has largely focused on the use of charge-dense adsorption sites, such as coordinatively unsaturated metal cations, to select for CO_2. However, as with cationic binding sites in zeolites, these adsorption sites are prone to water passivation in carbon capture applications involving humid process or emission streams. Accordingly, frameworks with CO_2-binding functionalities, such as amines, have gained increasing attention in recent years. Alternatively, stable and scalable frameworks that maintain partial CO_2 capacity following water adsorption may offer a rapid pathway to commercialization. Functionalization with hydrophobic groups can likewise improve capture performance from humid streams. The success of metal–organic frameworks in commercial carbon capture applications further necessitates a focus on materials with earth-abundant constituent metals and scalable synthetic routes. In addition, candidate materials must have suitable hydrothermal stability of the labile metal–ligand coordination bonds, as well as oxidatively robust metal nodes and organic constituents. Ongoing work is needed to evaluate these materials under more realistic process conditions and to develop pellets, monoliths, fibers or other industrially viable structured forms.

Target separations and case studies

The power sectors

The production of electricity and heat is responsible for 41% of global annual CO_2 emissions (Fig. 1) and is therefore a primary focus of CO_2 emission mitigation efforts. A number of potential separation strategies may be used to reduce or eliminate CO_2 emissions from thermal power plants, such as pre-combustion, oxy-fuel combustion and post-combustion capture, as well as BECCS and DAC (Fig. 3). In pre-combustion capture, synthesis gas (or syngas, consisting of a mixture of H_2 and CO) is produced from gasified fuel and sent to a shift reactor, which oxidizes CO to CO_2 and reduces H_2O to produce additional H_2. The resulting CO_2/H_2 mixture is then separated into H_2 for fuel and CO_2 for subsequent compression and sequestration. In oxy-fuel combustion, pure oxygen is used in place of air during the combustion of a hydrocarbon fuel, resulting in a flue gas containing only CO_2 and easily condensable H_2O. In the latter scenario, most of the energy is consumed in the initial separation of O_2 from N_2 in air. Here we focus on post-combustion CO_2 capture, in which CO_2 is removed from a flue gas containing primarily N_2, O_2, H_2O and CO_2.

Fig. 3: Carbon capture configurations.


Pre-combustion capture
Fuel
Air
Conversion
Separation
H_2
Combustion
Power
Air
N_2 O_2 H_2O
CO_2
Oxy-fuel combustion
N_2
Air
Separation
O_2
Fuel
Combustion
Power
H_2O
CO_2
Post-combustion capture
Power
Fuel
Air
Combustion
Separation
N_2 O_2 H_2O
CO_2
BECCS
Power
CO_2
CO_2
Biomass
Combustion
Separation
N_2 O_2 H_2O
Conversion
Separation
H_2
Combustion
N_2 O_2 H_2O
CO_2
Air
Power
DAC
Air
Separation
N_2 O_2 H_2O
CO_2

Strategies for carbon capture in the power sector include pre-combustion, oxy-fuel combustion and post-combustion capture from fossil fuel-fired power plants, as well as BECCS and DAC. Processes for BECCS are further subdivided into pre- and post-combustion strategies.

Coal-fired power plants

Although coal is the second-largest fossil fuel energy source after crude oil, it is the largest contributor to global CO_2 emissions as a result of its heavy carbon intensity (87–109 tCO_2 TJ^{-1}, versus 54–58 tCO_2 TJ^{-1} for natural gas). For example, in 2017, coal supplied 27% of global primary energy while generating nearly 50% of global CO_2 emissions. Accordingly, coal-fired power plants have garnered considerable attention in the CCS community. A typical coal-fired power plant emits a flue gas stream at ambient pressure that can be cooled to ~40–60 °C and contains 70–75% N_2, 10–15% CO_2, 8–10% H_2O, 3–4% O_2, and trace SO_x, NO_x and other impurities. The relatively high concentration of CO_2 in the flue gas stream is favorable for adsorptive CO_2 capture. Importantly, the primary challenge for adsorptive post-combustion carbon capture from coal-fired plants is not typically separation of CO_2 from N_2, but instead the selective capture of CO_2 in the presence of H_2O and other contaminants. As mentioned above, water has long been known to outcompete CO_2 to coordinate at exposed metal cations, which are often the primary adsorption sites in zeolites and metal–organic frameworks with equilibrium selectivity for CO_2 over N_2.

In a recent evaluation of 15 activated carbons, zeolites, mesoporous silicas and metal–organic frameworks, only adsorbents functionalized with alkylamines maintained appreciable CO_2 capacity in ternary ($CO_2/N_2/H_2O$) equilibrium experiments simulating a coal flue gas. Of these adsorbents, the metal–organic framework mmen–Mg_2(dobpdc) (mmen, *N*,*N*′-dimethylethylenediamine; dobpdc^{4-}, 4,4′-dioxidobiphenyl-3,3′-dicarboxylate) was identified as particularly promising. This material features step-shaped CO_2 adsorption isotherms resulting from cooperative, reversible insertion of CO_2 into the metal–amine bonds to form chains of ammonium carbamate along the pore axis. Incorporation of the diamine 2,2-dimethyl-1,3-diaminopropane (dmpn) in place of mmen was subsequently found to shift the cooperative adsorption pressure to an optimal range for coal flue gas capture and to improve the stability of the material substantially. In a related approach, the metal–organic frameworks $M^{II}M^{III}(OH)Cl_2$(bbta) (M, Mn, Co; H_2bbta, 1*H*,5*H*-benzo(1,2-*d*:4,5-*d*′)bistriazole) were found to capture large quantities of CO_2 under simulated coal flue gas conditions through the reversible formation of metal-bound bicarbonate at surface sites bearing monodentate hydroxide ligands. Likewise, incorporation of amines within the organic linkers of metal–organic frameworks has been demonstrated as an effective strategy to achieve selective CO_2 capture under humid conditions. Furthermore, amine-functionalized silicas have long been valued for their ability to bind CO_2 selectively in the presence of water, and these materials often exhibit improved CO_2 capture performance under humid conditions due to bicarbonate formation. Amine-functionalized zeolites have also been demonstrated to enable CO_2 capture from humid streams. As a notable recent example, a chemically grafted ethylenediamine-Y zeolite was shown to have high thermal stability to 180 °C, resistance to urea formation and CO_2 selectivity in the presence of water. As water-tolerant adsorbents advance towards commercialization, the most efficient materials must not only maximize the quantity of CO_2 cycled but also minimize the energetic sink of any co-cycled water.

In tandem with experimental efforts, computational approaches have become increasingly powerful screening tools. A recent survey of 325,000 hypothetical metal–organic framework structures led to the identification of a physisorption binding pocket for CO_2, consisting of aromatic rings 6.5–7.0 Å apart, that minimizes the binding energy of water by hindering the formation of hydrogen-bonding networks. Indeed, two aluminum-based frameworks synthesized with the computationally identified binding pocket showed modest, stable CO_2 working capacities from humid simulated coal flue gas over ten cycles. Continued partnership between computational and experimental researchers will accelerate sorbent development and can potentially unlock new advantageous CO_2 binding modes.

Another key challenge for post-combustion capture from coal-fired power plants is the presence of SO_x, NO_x, Hg and particulate matter in the flue gas stream. In a comprehensive two-part investigation, class 1 and class 2 amino silica materials were found to be unaffected by NO but irreversibly bound NO_2 at high concentrations (200 ppm, 35 °C) to form nitrates, resulting in a dramatic loss of CO_2 capacity. Similarly, exposure of aminosilicas to 20 ppm of SO_2 at 35 °C led to a loss in CO_2 uptake from dry 10% CO_2 streams, a result ascribed to the formation of sulfates and/or sulfites on the adsorbent surface. Further research is needed to determine the influence of water on the competitive adsorption of CO_2, SO_x and NO_x in these materials, as well as any degradation resulting from combined exposure to water and SO_x. Critically, deactivation of amine-based binding sites by SO_x and NO_x has also been observed for other amine-based capture materials, including amine solutions, which form heat-stable salts.

Limited experimental data have been reported regarding the effect of other flue gas contaminants, such as particulate matter and Hg, on the performance of CO_2 capture materials. However, the degradative nature of these contaminants on adsorbent structure is likely to be minimal compared with the degradation risks associated with O_2 and acid gases. Nonetheless, characterization of accumulated toxic metals within the adsorbent bed will be necessary in the ultimate safe disposal of spent material. Notably, beyond CO_2 capture, adsorbents may also play a role in Hg emission control efforts in processes such as activated carbon injection, in which vapor-phase Hg is captured by activated carbon dispersed in the flue gas ductwork.

Natural gas-fired power plants

Adsorptive, post-combustion CO_2 capture from natural gas-fired power plants is also poised to become a critical strategy to reduce emissions in the power sector. Indeed, due to increasingly available reserves and its lower CO_2 emissions footprint among fossil fuels, natural gas is anticipated to surpass coal in its contribution to global primary energy by 2030 (new policies scenario, IEA) or 2032 (EIA). The flue gas of natural gas combined cycle (NGCC) power plants contains lower levels of SO_x, particulate matter and Hg compared with coal flue gas and therefore may be more readily treated in an adsorptive post-combustion capture process. However, NGCC flue gas contains lower CO_2 concentrations (~4%) and higher O_2 concentrations (~12%) compared with coal flue gas (~10–15% CO_2, 3–4% O_2), as well as similar water concentrations (~8% H_2O). Consequently, adsorbents for carbon capture from NGCC power stations must have strong oxidative stability as well as binding sites capable of selective CO_2 uptake from more dilute, humid streams. While amine-based capture materials have suitable chemical selectivity to achieve this separation, the high oxygen content of NGCC flue gas is likely to lead to deleterious reaction pathways. For example, solution-phase amines tend to generate soluble iron and copper species through equipment corrosion, and these trace metals act to catalyze oxidation reactions of the mobile amine species.

Biofuel-fired power plants

BECCS has been proposed as another necessary technology to meet climate targets and is included in several of the IPCC integrated assessment models. In BECCS, biomass is cultivated both to sequester CO_2 and generate energy. If the CO_2 generated during energy production from biomass is subsequently captured and sequestered, net removal of CO_2 from the atmosphere can be achieved. The composition of the target stream in a BECCS process can vary widely based on the fuel composition, but post-combustion streams will typically contain SO_x, NO_x, particulate matter, and trace alkali and transition metals. Considering adsorptive capture from a willow wood-fired BECCS plant (flue gas properties in Table 1), a recent report highlighted the criticality of a long adsorbent lifetime (>2 years) and slow capacity fade (half-life ≥1.3 years), as well as a moderate CO_2 working capacity (≥0.75 mol kg^{-1}) and heat of adsorption (optimally –40 kJ mol^{-1}).Overall, BECCS remains an underexplored area for adsorbents, and additional research is needed to accelerate the deployment of this important technology. With greater BECCS adoption, careful decision-making will be required in designating land for the cultivation of food versus biomass fuel and in management of water resources.

Biomethane

Adsorptive CO_2 capture can also contribute to the production of renewable or low-carbon fuels. Notably, biomethane, a renewable natural gas equivalent, can be produced by removing CO_2 contamination from crude biogas (~25–50% CO_2 in CH_4) generated through the anaerobic digestion of plant or animal waste. Biomethane production offers the dual environmental benefits of harnessing otherwise harmful methane emissions from organic waste for energy production, while also supporting intermittencies of other renewable sources, such as wind and solar power. Further emissions reductions can be achieved if biomethane consumption is coupled with CCS, an example of BECCS, as mentioned above. Considerable precedent exists for industrial removal of CO_2 from CH_4 in the processing of fossil-derived natural gas, although adsorptive CO_2 capture remains at an earlier stage of development compared with well-established amine absorption technologies. Natural gas-processing facilities have provided much of the early support for commercial CCS demonstrations and will probably remain major contributors to long-term CCS efforts.

Industrial CO_2 streams

Beyond gas processing, several industrial CO_2-containing streams are candidates for CCS The iron and steel industry generates the largest fraction of industrial emissions (31%), but deployment of CCS in this sector is complicated by the large number of CO_2-emitting processes within each mill. Removal of CO_2 from the blast furnace, the largest source of CO_2 in an integrated steel mill, is under active investigation, and adsorbents could play a role in reducing the costs of capture compared with traditional liquid amine scrubbers. In the refining industry, CCS deployment may be favored due to the considerable relevant expertise in this sector, as well as the relatively small cost of CCS compared with typical price differentials routinely managed by the industry in the cost of crude oil.

The cement industry, a particularly attractive target sector, generates approximately 5% of global CO_2 emissions that result from both fuel consumption to power the kiln (40% of cement industry emissions) and unavoidable emissions associated with production of lime from limestone ($CaCO_3 \rightarrow CaO + CO_2$). Many process configurations have been proposed for carbon capture from cement plants, including post-combustion capture, with research efforts largely focused on aqueous amine technology thus far. However, a pilot-scale demonstration incorporating PEI-functionalized silica was undertaken in a collaboration between RTI and Norcem at the first cement plant CCS test Centre in Brevik, Norway.

Direct CO_2 capture from air

Along with BECCS, DAC has received growing attention in recent years as a potential negative emissions technology. Proponents highlight the necessity of DAC for CO_2 removal if warming overshoots target limits. In the near term, DAC may accelerate the development of CCS by circumventing technical challenges associated with integration of capture systems within power plants or other industrial facilities. To achieve net negative emissions, DAC facilities must be coupled with transport and storage infrastructure, and the energy consumed to power DAC systems must emit less CO_2 than is sequestered. A primary technical challenge in DAC arises from the low concentration of CO_2 in air (414 ppm at the time of writing), which is over 100 times more dilute than the exhaust streams of fossil fuel-fired power plants (4–15%). As a result, the theoretical minimum work to separate CO_2 from air (19–21 kJ mol^{-1} CO_2) is two to four times greater than that required for CCS from the emissions of power plants fired by gas (6–9 kJ mol^{-1}) or coal (5–7 kJ mol^{-1}) (Fig. 4. While cost estimates for DAC vary over orders of magnitude, scaling the average cost of CO_2 captured from a coal-fired power plant (roughly US$100 per tCO_2) by the minimum work suggests a cost of US$300 per tCO_2 for DAC. However, the power and industrial sectors are obligated to focus not on minimizing the cost of captured CO_2 but instead on the cost of decarbonized product (MWh, cement, steel) while maintaining consistent quality and meeting demand. In contrast, DAC researchers can work to minimize capture costs without these additional constraints.

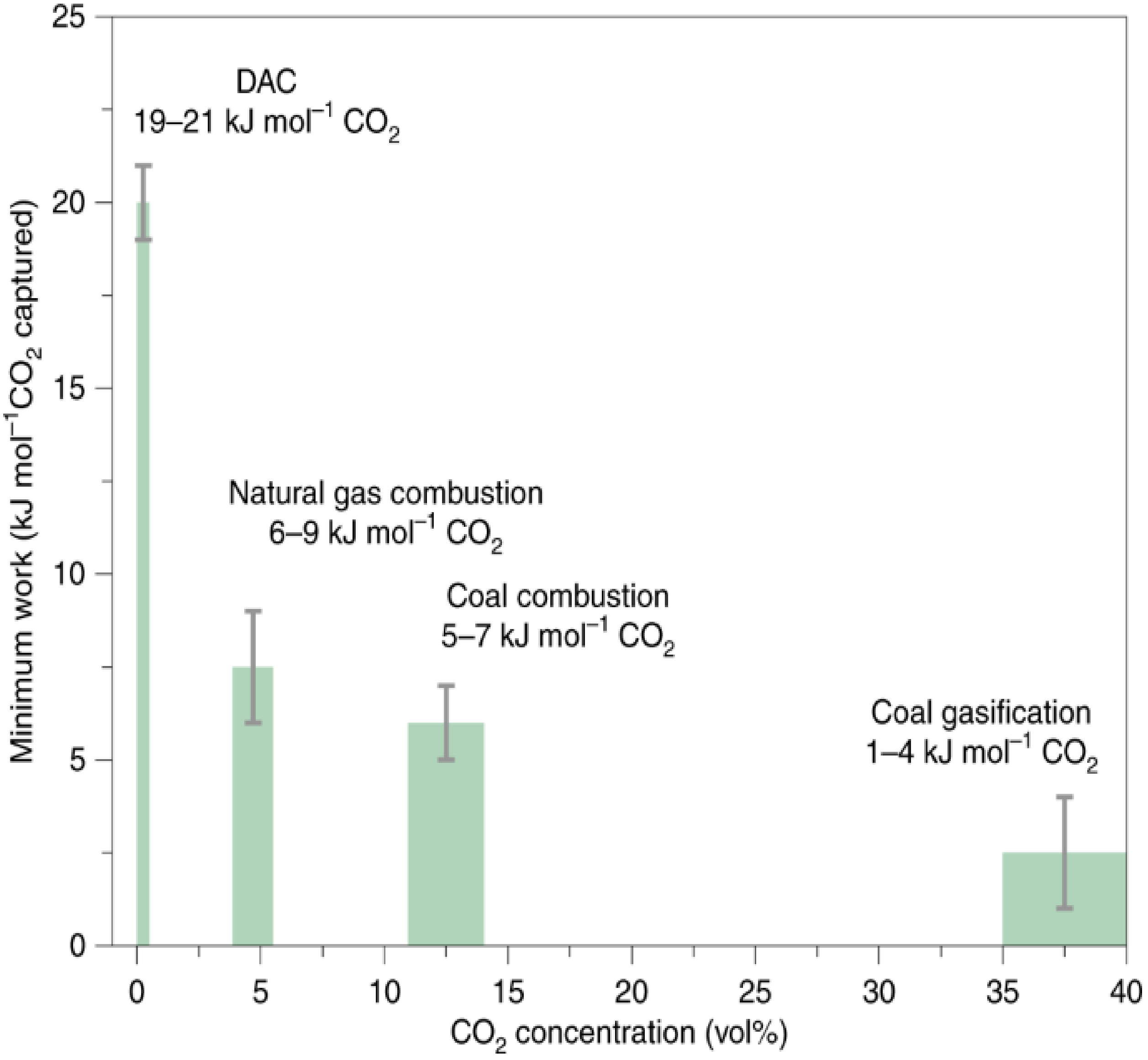


Fig. 4: Minimum work versus CO_2 concentration

Theoretical minimum work required for CO_2 capture in different applications as a function of CO_2 concentration. Grey bars and ranges indicate the variation in minimum work anticipated for 50% CO_2 capture at 80% purity (lower bound) to 90% CO_2 capture at 99% purity (upper bound).

Outlook and key needs from the materials community

The materials community has advanced substantially towards deploying adsorbents for carbon capture. Nonetheless, continued investment is needed to address several key needs on the path to commercialization. In general, greater attention is needed towards lifecycle considerations, with increasingly rigorous analyses performed as materials advance along the development pipeline Specifically, starting materials must be viable at the target scale (particularly for metal–organic frameworks, given limited extraction rates and reserves of certain metals and proposed synthetic routes must be safe and scalable, with minimal steps and high space–time yields. Recyclability and management of waste streams must likewise be considered. For materials that meet these criteria, computational efforts will remain essential in supporting adsorbent down-selection by elucidating key adsorbent–adsorbate interactions and by predicting competitive adsorption behavior for increasingly realistic mixtures. From experimentalists, as promising materials are identified, additional research is needed to illuminate adsorbent deactivation mechanisms and rates in the presence of humid streams containing O_2, SO_x, NO_x, H_2S and other stream-specific contaminants. These data can in turn guide pretreatment options and inform adsorbent replacement rates in techno-economic models, while facilitating the development of next-generation materials with enhanced stability. In addition, continued experimental efforts are needed to quantify the energetic impact of co-adsorbed and co-cycled species, particularly water.

Beyond fundamental adsorbent development, the expertise of the materials community is also needed in the production of adsorbents at large scale and in structured forms such as pellets, monoliths, films or fibers Industrial-scale formulation is well understood for traditional adsorbents such as zeolites, but continued development is still needed for newer materials, such as porous organic networks and metal–organic frameworks. The ultimate structure of a commercial material will strongly influence the pressure and thermal gradients across the adsorption unit, which in turn will dictate factors such as the bed size, cycle times and overall energy demand. Process design efforts therefore require expanded characterization of the thermal properties, mechanical stability and volumetric capacities of both powdered adsorbents and structured forms.

In addition, the materials community can support process engineering efforts to enhance the efficiency of CCS systems. For example, combining materials within multi-adsorbent systems or hybrid processes, such as adsorption–membrane systems, could facilitate carbon capture by coupling technologies at their peak efficiencies. Aligning materials and engineering solutions may additionally offer opportunities to leverage existing, inexpensive and easily scaled adsorbents across a broader range of process conditions, and with shorter commercialization timelines. As another opportunity area, materials scientists can develop solutions to mitigate sorption enthalpy. Notably, in a recent report, microencapsulated phase-change materials were incorporated in fiber sorbents to dampen thermal excursions via adsorption–melting/desorption–freezing cycles. New materials have also enabled alternative cycling configurations that expand the mechanisms and thermodynamic space under consideration for adsorption–desorption cycling. For example, composites of metal nanoparticles and metal–organic frameworks have been used to demonstrate magnetic induction swing adsorption, and large-pore adsorbents have been proposed for use in a sub ambient pressure swing process to yield ultrahigh CO_2 swing capacities. In an even greater deviation from traditional adsorptive approaches, carbon nanotubes have been decorated with quinones as redox-active species capable of electrochemically mediated capture and release of CO_2 . Ongoing innovation at this nexus between materials science and process engineering will continue to improve CCS technologies.

Increased dialogue between materials scientists and power plant or industrial personnel will likewise aid in accelerating CCS deployment. Carbon capture test centers, such as the Technology Centre Mongstad (Norway), the National Carbon Capture Center (United States) or the Pilot-Scale Advanced Capture Technology facility (United Kingdom), can serve as a bridge between these groups. While these centers are largely focused on de-risking technologies beyond the laboratory scale, we propose that test centers could also play a key role in early-stage materials development by providing experimentalists with access to real flue or process gas to conduct small-scale stability tests. Led by these facilities, standardization of analysis conditions and reporting metrics will enable the field to converge on the most promising materials more rapidly.

Meeting ambitious decarbonization targets will require political, economic and technological alignment at an unprecedented global scale to deploy a suite of mitigation solutions while balancing allocation of intertwined energy, water, land and food resources. Carbon capture and sequestration is widely recognized as a vital component of the least-cost pathways to limit warming below 2 °C, and porous materials are strong contenders to form the basis of next-generation capture technologies. Continued research by the materials community will accelerate the deployment of CCS within the power and industrial sectors and for negative emissions technologies. Together with strong investment in renewable energy, rapid cross-sector electrification and ongoing efficiency improvements, CCS can help secure a cleaner future for generations to come.

Chapter 5

CO_2 capture adsorbents functionalized by amine – bearing polymers:

Efforts to capture CO_2 from anthropogenic sources as well as from the air are being continuously intensified as to battle the greenhouse gas effects and climate change. Capture by liquid solvent absorption, mainly involving amines, is the common industrial practice, yet capture relying on solid adsorbents is increasingly gaining interest due to its potential for less energy-demanding and more efficient operation. Despite the large variety of porous adsorbents being explored, such as zeolites, carbons, mesoporous silicas, graphene and related structures, polymers, and metal-organic frameworks, it remains challenging to find a proper material to cover all the critical specifications, i.e., with respect to CO_2 capacity, selectivity, chemical and thermal stability, fast kinetics, cyclability, low energy consumption, low manufacturing cost, and mechanical robustness.

To this end, combining highly CO_2-phylic amines with the most robust of the developed solid porous materials through functionalization of the latter is a highly promising approach. Consequently, particular emphasis is given to increase the number of amine functional groups per unit of support area, enhance CO_2-phylicity of the amines, and provide suitable diffusion pathways to enhance CO_2 capacity. Towards achieving this goal, use of amine-bearing polymer functionalities is being highly investigated. This work critically and comparably reviews current progress on polymeric amine - functionalized solid adsorbents and their performance in CO_2 capture.

It examines works based on various polymers, including polyethylenimine, polypropylenimine, polyallylamine, polyaniline, amino dendrimers, and hyperbranched polyamines. Based on the extracted comparisons, optimal systems are proposed and envisioned, and future trends and directions are stated.

Because of the increasing environmental impact related to climate change and global warming, which is mainly the result of the escalating fossil fuel consumption and associated combustion products emission, research community has put immense attention in limiting the release of the carbon dioxide, as the main greenhouse gas (GHG) contributor, to the atmosphere. The affect can be limited by either applying highly efficient capturing and storage techniques or introducing more environment-friendly (green) energy resources.

Among the major combustion flue gas constituents, namely CO_2, SO_2, N_2O, N_2, and unburned fuel, CO_2 is observed to be abundantly present in the atmosphere in continuously increasing concentrations that currently exceed the 400 p. In addition to fuel combustion, such increase in CO_2 concentration has also been contributed by industrial chemical processes, gas and oil treatment, as well as naturally occurring volcanic eruptions. Capture and sequestration currently constitute the most prominent options to reduce the atmospheric CO_2 accumulation and its negative effects, often offering attractive combination of performance and cost. Notably, CO_2 capture from ambient air or direct air capture (DAC) is an emerging technology, which can achieve point-source capture through the capture from inaccessible as well as distributed sources, and address residual emissions. DAC has the potential to contribute in various ways to suppress atmospheric CO_2 levels, such as compensation of emissions from mobile sources, suitability at remote storage sites, re-capturing of leaked CO_2, feedstock contributor for synthetic fuel production, and help towards realization of negative emission levels .The immense attention for CO_2 capture is also related to the appearance of CO_2 as one of the major impurities in the shale gas .

Several studies have been reported supporting that the capture of CO_2 can be effectively undertaken through absorption, adsorption, membrane separation, or cryogenic distillation processes .CO_2 capture by aqueous amine scrubbing is a traditional technology widely accepted by the industry owing also to its applicability in industrial processes such as syngas purification, H_2S removal, and various other process schemes such as in steel industry. However, the regeneration and desorption of captured CO_2 from these liquid amine systems is an energy intensive process because of the high heat of sorption with the CO_2, high heat capacity of water, and the associated requirement of high regeneration temperatures. This substantially high regeneration energy requirement adds significant operating cost to the CO_2 capture process and leaves a considerable carbon footprint itself. In addition, drawbacks such as corrosion of equipment, limited capability for increasing amine concentration, heavily diffusion-limited process, and amine leakage to the environment often take place in these classical aqueous amine schemes. Notably, the environmental impact of CO_2 capture systems based on amines is crucial due to amine release, the photo-oxidation of amines in the influence of atmospheric oxidants, and the resultant generation of products, such as nitrosamines, nitramines, amides, etc. These compounds can affect health and pose environmental risks. For instance, nitrosamine is toxic at very low concentrations, and it may cause carcinogenicity, mutagenicity and reproductive effects .To alleviate the above issues, intense research efforts are focusing on developing novel solvents and solvent combinations exhibiting lower volatility, better thermal stability, lower corrosive characteristic, lower degradation rate, and reduced regeneration cost.

Adsorption constitutes an attractive solution owing to minimal utilization of regeneration energy, high capture capacity and selectivity, processing convenience, cost effectiveness, and reduced environmental. Adsorption is a surface-dominated capture mechanism taking place when CO_2 meets a solid adsorbent material through weak physical interactions or stronger chemical bonding. The former is named physisorption or physical adsorption and mainly occurs via electrostatic or van der Waals forces, whereas the latter is called chemisorption or chemical adsorption . The captured CO_2 can be then desorbed in the regeneration step and become available for underground sequestration, enhanced oil recovery, utilization by conversion to fuel and chemicals, and more . One of the drawbacks of use of adsorbents is their poor performance in terms of adsorption capacity and selectivity at low partial pressure conditions , which becomes more severe in the presence of moisture, where water can occupy active sites or compromise the stability of the adsorbent materials . To overcome these issues, adsorbent functionalization has been received considerable attention . The introduction of various amine-containing basic moieties for instance into porous solid sorbents is found advantageous to markedly strengthen their capture capacity through interaction with CO_2 *via* chemical means leading to the formation of carbamates and bicarbonates when CO_2 meets amine in anhydrous and hydrous conditions, respectively, as shown below

(1) $R\text{-}NH_2 + CO_2 \rightarrow R\text{-}NHCO_2^{-} + H^{+}(2)R\text{-}NH_2 + CO_2 + H_2O \rightarrow R\text{-}NH_3^{+} + HCO_3^{-}$

Amine-functionalized adsorbents

comprise a support, typically porous, with weakly bonded (impregnated) pre-made polymeric amines or small amine molecules or with covalently bonded (grafted) small amine molecules or *in situ* formed polymeric amine. Impregnated systems are developed through the rather facile impregnation into the support, i.e., by physical adsorption of amines. On the other hand, amine - grafted/covalently bonded systems are prepared through chemical tethering of amines to support surface upon synthesis (*in situ*) or post-synthesis modification. Amine impregnated CO_2 sorbent systems often exhibit high capture capacity, yet shortcomings such as stability lack due to the leaching of amines over capture/regeneration cycles and limited transport of CO_2 to active support sites due to the diffusion hindrance pose challenges associated to these systems.

In order to overcome these issues and improve performance and long-term sustainability, amine - grafted/covalently bonded CO_2 sorbent systems are being explored. The grafted/covalently bonded amines on these sorbents can grant stability over many regeneration cycles, whereas challenges associated to controlled grafting and optimization need to be given emphasis. Polymeric amines, i.e., polymers with amine moieties in their backbone or side chains, are receiving immense attention for design of supported amine-based sorbent systems due to their higher content of amine groups

Fig. 1 schematically portrays the introduction of polymeric amines into porous structures and the resulting CO_2 capture possibilities. Because of their ability to capture CO_2 effectively in dry as well as wet environments, polymeric amines containing more primary and secondary amine moieties are preferred for the design of supported amine capture applications . Primary amines for instance typically display higher enthalpy of adsorption, which makes them suitable for direct CO_2 capture in ultra-dilute ambiances .

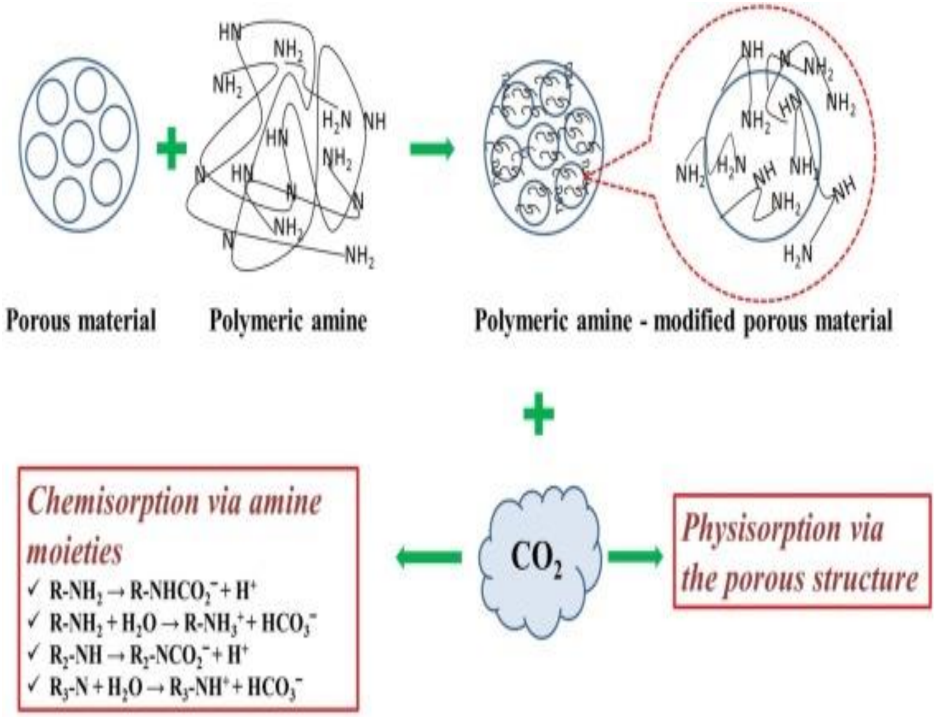


Fig. 1. Schematic of functionalization of porous materials with polymeric amines and their CO_2 capture action.

Cost of Polyamine functionalized solid adsorbents

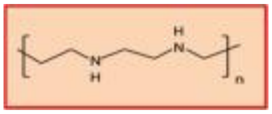
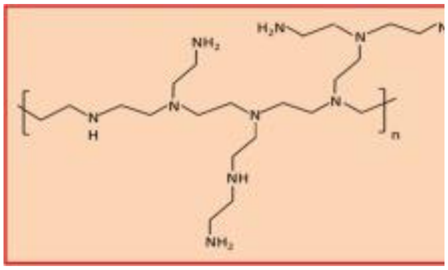
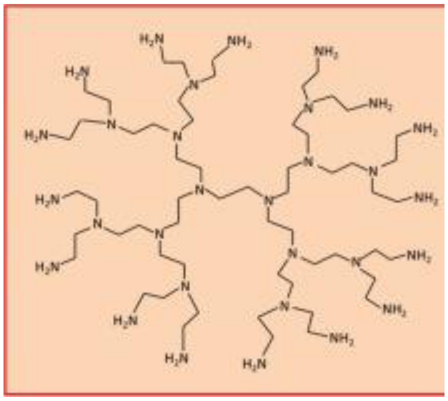
Regarding the cost of polyamine-functionalized solid adsorbents, in order to link-up the targets of low-cost capture, one should target a reasonable cost of sorbent manufacturing. To this extent, a proper balance between selected amine functionalities, support selection, and preparation/functionalization procedure should be kept. Most of the supports used are relatively non expensive, e.g., silica, carbons, zeolites, and clays, as are most of the used amines, e.g., polyethylenimine (PEI). Also, the properties of the developed sorbents should be maintained after several adsorption-desorption cycles as to reduce the need for adsorbent replacement. Regarding operating cost, the main contributor comes from the substantially high regeneration energy required. For example, in the case of aqueous amines, the regeneration of absorbed CO_2 is an energy intensive process owing to the high regeneration temperature, cycle duration, and heat capacity of water, while solid supported amine sorbents have the potential to alleviate these issues. In comparison to aqueous amines, the lower heat capacity and facile regeneration of solid sorbents can contribute to reduce the energy consumption and thereby CO_2 capture cost. Furthermore, the corrosion issues associated with liquid amines, which elevate the need and associated cost for equipment maintenance and replacement, can be alleviated through the application of solid-supported amine sorbents because only solid-solid contact with equipment surface takes place in such systems.

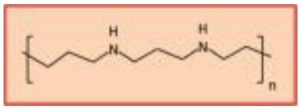
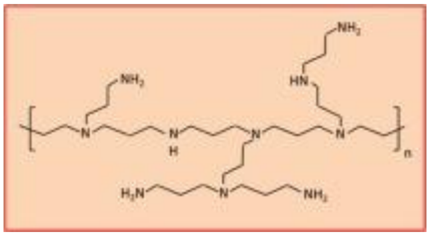
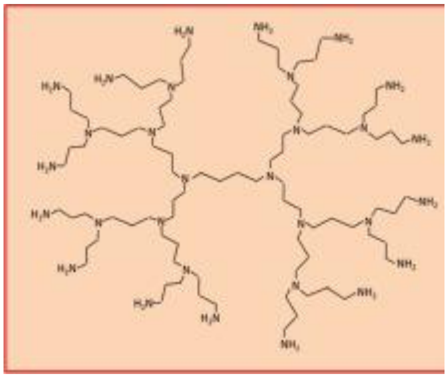
Critical parameters such as adsorption capacity, selectivity, kinetics, renderability, stability, mechanical robustness, cost, and energy consumption need to be considered when it comes to selecting adsorbent materials for effective CO_2 capture application. Thus far, various supported polymeric amine-based CO_2 adsorbents have been designed through the combination of various support materials and polymeric amines.

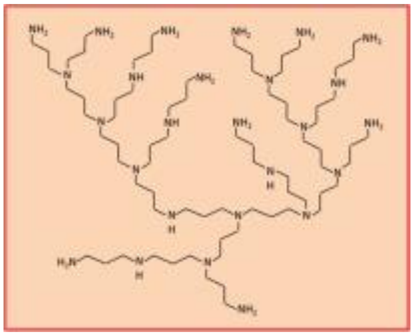
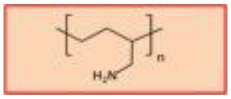
In this chapter , we are reviewing studies reported on polymeric amine - functionalized solid adsorbents for CO_2 capture, including involvement of polyethylenimine, polypropylenimine, polyallylamine, polyaniline, amino dendrimers, and hyperbranched polyamines.

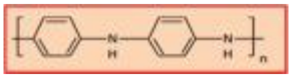
An overview of these polymeric amines is summarized in Table 1. For emphasizing on the technological scope, we would like to point out that the examined parameters throughout the review are tightly connected to the potential capture performance at large scale, and without such characteristic's examination, successful scaled up process cannot be realized. Specifically, developments/advancements of systems based on various support materials, i.e., silica (SBA-15, MCM-41, fumed silica, precipitated silica, silica foam, silica gel, and more), different clays, graphene and related structures, carbon nanotubes, fullerene, mesoporous carbon, carbon spheres, alumina, metal-organic frameworks, zeolites, porous polymers and more, with the various polymeric amines are reviewed, compared and summarized. It is noteworthy to mention that such valuable feedback on the current status of various supported polymeric amine - based CO_2 sorbents is inevitable in order to effectively choose and further optimize the developed systems as to accomplish the required performance goals at the large-scale process level. In this review article, the performance of the studied sorbents was compared in connection to capture capacity, selectivity, kinetics, heat of adsorption, renderability, cyclic stability, oxidative stability, thermal stability, stability in various conditions like moisture and steam, and amine efficiency, based on data availability, properties that are of critical importance for large scale implementation.

Table 1. Details of polymeric amines reported for CO_2 capture applications.

S.No.	**Polymeric amine**	**Chemical structure**	**Remarks**
1.	Polyethylenimine (or polyaziridine)		- Wide availability in various structural forms and molecular weights.
1.a.	Linear polyethylenimine		- Secondary amines on the backbone.
1.b.	Branched polyethylenimine		- Primary, secondary, and tertiary amines at respective chain ends, back bone, and branch points.
1.c.	Polyethylenimine dendrimer		- Primary and tertiary amines at respective chain ends and branch points. - Regularly ordered highly branched repeating units around a central core. - Size, chemical functionality, and molecular weight can be tuned on demand.

S.No.	**Polymeric amine**	**Chemical structure**	**Remarks**
2.	Polypropylenimine (or polyazetidine)		- High amine or nitrogen density. - Better oxidation stability than that of polyethylenimine. - Challenges associated to monomer synthesis and polymerization time.
2.a.	Linear polypropylenimine		- Secondary amines in the backbone.
2.b.	Branched polypropylenimine		- Primary, secondary, and tertiary amines at respective chain ends, back bone, and branch points.
2.c.	Polypropylenimine dendrimer		- Primary and tertiary amines at respective chain ends and branch points. - Regularly ordered highly branched

S.No.	Polymeric amine	Chemical structure	Remarks
			repeating units around a central core. • Size, chemical functionality, and molecular weight can be tuned on demand. • High amine or nitrogen density.
2.d.	Hyperbranched polypropylenimine		• Primary, secondary, and tertiary amines at respective chain ends, back bone, and branch points. • Irregularly ordered, highly branched macromolecular structure. • High amine or nitrogen density.
3.	Polyallylamine		• Primary amine at the side chain.

S.No.	Polymeric amine	Chemical structure	Remarks
			- Better thermal and oxidation stabilities. - Capable to bind strongly with other material surfaces.
4.	Polyaniline		- Secondry amines in the backbone. - Superior thermal stability.

2. Polyethylenimine – based CO_2 adsorbents

Polyethylenimine, also named as polyAziridine, is one of the most highly investigated aliphatic polymeric amines for CO_2 sorption due to its availability, high CO_2 capture capability, increased amine density, primary amine chain ends, and stability as it can maintain CO_2 sorption capability up to 90 °. PEI grants versatility in customized functionalization as it is available in linear, branched, or dendrimer structural forms, at 300–750,000 molecular weight range and can contain primary, secondary, and tertiary amines at respective chain ends, back bone, and branch points (Table 1). For CO_2 capture applications, the role of PEI was recognized in 2001 by Satyapal et al. through its introduction in space applications. Thereupon, PEI is intensively investigated for various supported amine related CO_2 capture applications, as reviewed in the following sections.

1. Siliceous adsorbents with PEI

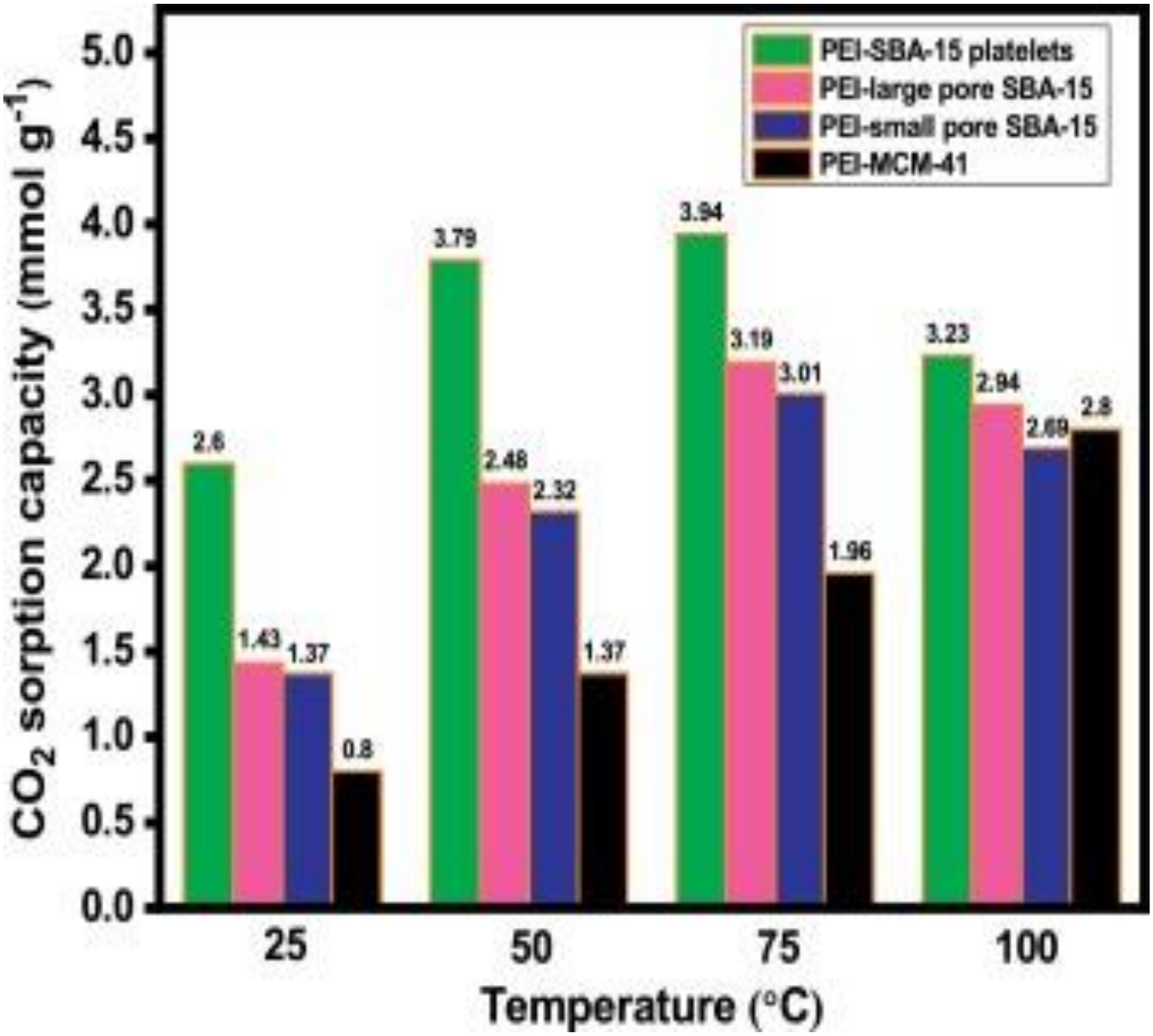
By virtue of their well-ordered porous nature and pore distribution or of their amorphous nature, large specific surface area, and appreciable amine holding capability, various siliceous materials are receiving interest for designing diverseamine - supporting CO_2 sorbents including, SBA-15, MCM-41, fumed silica, precipitated silica, mesoporous siliceous foam, and silica gel.

1.1. SBA-15 – supported PEI

SBA-15 (SBA standing for Santa Barbara Amorphous) is an attractive mesoporous silica material having well-ordered and relatively large hexagonal pores in the range of 4.6−30 nm. This siliceous material was a research contribution from University of California, Santa Barbara in 1997 . Due to its promising features as support and CO_2 capture medium, several works have been reported that design effective SBA-15 supported PEI adsorbents.
CO_2 adsorbents based on SBA-15 - filled with PEI with the aid of wet impregnation by varying the filling amount of linear polyethylenimine (LPEI). The mesoporous nature of SBA-15 was shown to be well preserved after the infusion of LPEI. Adsorption studies in a fixed-bed system at 75 °C and atmospheric pressure revealed that the 60 wt% LPEI ($M_w = 423$) system exhibited a maximum adsorption capacity of ca. 3.51 mmol g^{-1}.

PEI - functionalized SBA-15 and revealed the effectiveness of pore filling from N_2 adsorption-desorption at 77 K. In this study, PEI - functionalized mesoporous silica exhibited a CO_2 capacity of ca. 0.81 mmol g^{-1} at 25 °C and 1 atm, which was almost analogous to that of neat mesoporous silica at the same conditions. The capacity increased with increase in temperature and a maximal value of ca. 1.55 mmol g^{-1} was observed at 75 °C.

PEI with M_n of 600 for the modification of SBA-15. At 273 K and 800 mmHg, an adsorption capacity of more than 1.8 mmol g^{-1} was realized for 20 wt.% PEI - modified SBA-15 reported higher adsorption capacities of ca. 2.60 and 3.94 mmol g^{-1} at 25 and 75 °C, respectively and 1 atm, for 55 wt% PEI - impregnated in SBA-15 platelets in comparison to SBA-15 possessing small and large pores and MCM-41 (Fig. 2).PEI dispersion on the SBA-15 pore walls paying attention to coating formation at initial composition and then deposition upon increase in PEI amount. Effective anchoring of PEI into mesoporous SBA-15 was possible by means of amine-silanol interactions.



The CO$_2$ adsorption performance of PEI - modified SBA-15 in simulated post-combustion ambiances. The adsorption capacity of 50 wt.% PEI - modified SBA-15 remained almost unaffected for up to 10 adsorption/desorption cycles in diluted CO$_2$ gas mixtures, whereas some reduction was noticed for tetraethylenepentamine - modified SBA-15. Under the presence of 1000 ppm SO$_2$, the adsorption capacity of the adsorbents was considerably decreased. Additionally, owing to the substantial amount of nitrogen occupancy, PEI - modified SBA-15 displayed an increase by ca. 60 % in adsorption capacity under moisture influence (5 %). the reusability of PEI - impregnated SBA-15 based CO$_2$ adsorbents. For this, the authors followed repeated calcination/re-functionalization cycles. After 7 such cycles, PEI - impregnated SBA-15 was found to maintain to a good extent its initially obtained adsorption capacity (1.72 mmol g^{-1} under 1 bar and 45 °C). This observation was related to the amine efficiency, typically defined as the moles of CO_2 adsorbed normalized by the moles of amine present in the material, after each PEI loading cycle. capability of SBA-15 supported PEI based solid CO_2 adsorbents to maintain their adsorption capacity upon cyclic adsorption-desorption operation.

The introduction of phosphate ester surfactants such as bis(2-ethylhexyl)phosphate and tri(2-ethylhexyl)phosphate (TEHP) was beneficial to enhance the CO_2 adsorption of SBA-15 supported PEI. Indeed, the CO_2 capture capacity for SBA-15 with 45 % PEI and 5 % TEHP at 75 °C and 1 atm was 1.89 mmol g^{-1}, which was ca. 19 % higher compared to the same adsorbent without the added surfactant. Liu et al.propanesulfonic acid surface treatment enhanced the performance of SBA-15 after PEI - loading by improving dispersion and increasing CO_2 diffusion. Adsorption studies in a gravimetric analyzer revealed an optimal capacity of ca. 2.30 mmol g^{-1} at 75 °C and 1 atm, for SBA-15/PEI composite sorbent treated with 5 % propanesulfonic acid.

The increased acidity of the support surface and stronger interaction with the amines, resulted in enhanced flexibility in adsorbent regenerability compared to the unmodified material.

The influence of various heteroatoms such as Al, Ti, Zr, and Ce on the CO_2 adsorption of SBA-15 supported BPEI ($M_w = 800$). The maximal CO_2 adsorption capacities of ca. 1.56 and 1.68 mmol g^{-1} was observed for the Zr containing sorbent in dry and humid conditions, respectively, for 10 % CO_2 at 25 °C. Investigating the effect of Zr loading, 7 mol% Zr showed an optimal performance in terms of adsorption capacity and amine .Zr infusion in enhancing the CO_2 performance of PEI - impregnated SBA-15. Indeed, an increase of ca. 60 % in adsorption capacity was obtained by Zr doping of SBA-15, though, Zr doping had no significant influence on the adsorption performance of SBA-15 with large pores.

According to above results, a capture capacity of SBA-15 platelets - supported PEI sorbent is highlighted, i.e., 3.94 mm as well as of conventional SBA-15 - supported LPEI of 3.51 mmol g^{-1} together with good conservation of mesoporosity. Moreover, propanesulfonic acid - treated SBA-15 - supported PEI sorbent presents improved regenerability and capacity maintenance (2.3 mmol g^{-1}) on account of increased surface interaction with the amines. It has also been observed that dual amine modification of pore-expanded SBA-15 by APTES and BPEI is beneficial to enhance amine efficiency and, as a result, an improved capacity was reported (e.g., 2.8 mmol g^{-1}) accompanied with a reduction of sorption kinetics. It is evident from these observations that more attempts are needed to precisely optimize the performance of SBA-15 supported PEI CO_2 capture sorbents by studying different systems based on SBA-15 with varying morphological and surface features, PEI with varying concentration, molecular weight and structural features, combination or blending with other amines, and doping or incorporation of other additives. Moreover, the effect of in situ PEI functionalization on the performance of SBA-15 could be explored as well.

1.2. MCM-41 – supported PEI

Since its development in 1992 by Beck et in Mobile Research and Development Corporation, MCM-41 (Mobil Composition of Matter No. 41, also known as Mobil Crystalline Material No. 41) has received considerable attention in various applications with focus on catalysis, as it constitutes a structure of the class of ordered mesoporous silica materials with uniformly ordered honeycomb like pores with diameter in the range of 2–6.5 nm. Interestingly, the size and distribution of the mesopores can be tailored by demand . Due to these features, MCM-41 is extensively being investigated for CO_2 capture applications as well.

The preparation of CO_2 adsorbent by means of effective BPEI loading into mesoporous MCM-41. Of the various compositions studied, 50 wt.% BPEI loading demonstrated the maximum adsorption capacity of ca. 2.26 mmol g^{-1} at 1 bar and 100 °C. The authors also studied the effect of increase in pressure until 20 bar, and found an increased capacity of ca. 3.55 mmol g^{-1}, as portrayed in Fig. 3. High CO_2/N_2 and CO_2/H_2 selectivity's were also reported for this adsorbent. A reduction in adsorption capacity after 3 and 6 cycles by ca. 9.29 and 21.68 %, respectively, was also observed.

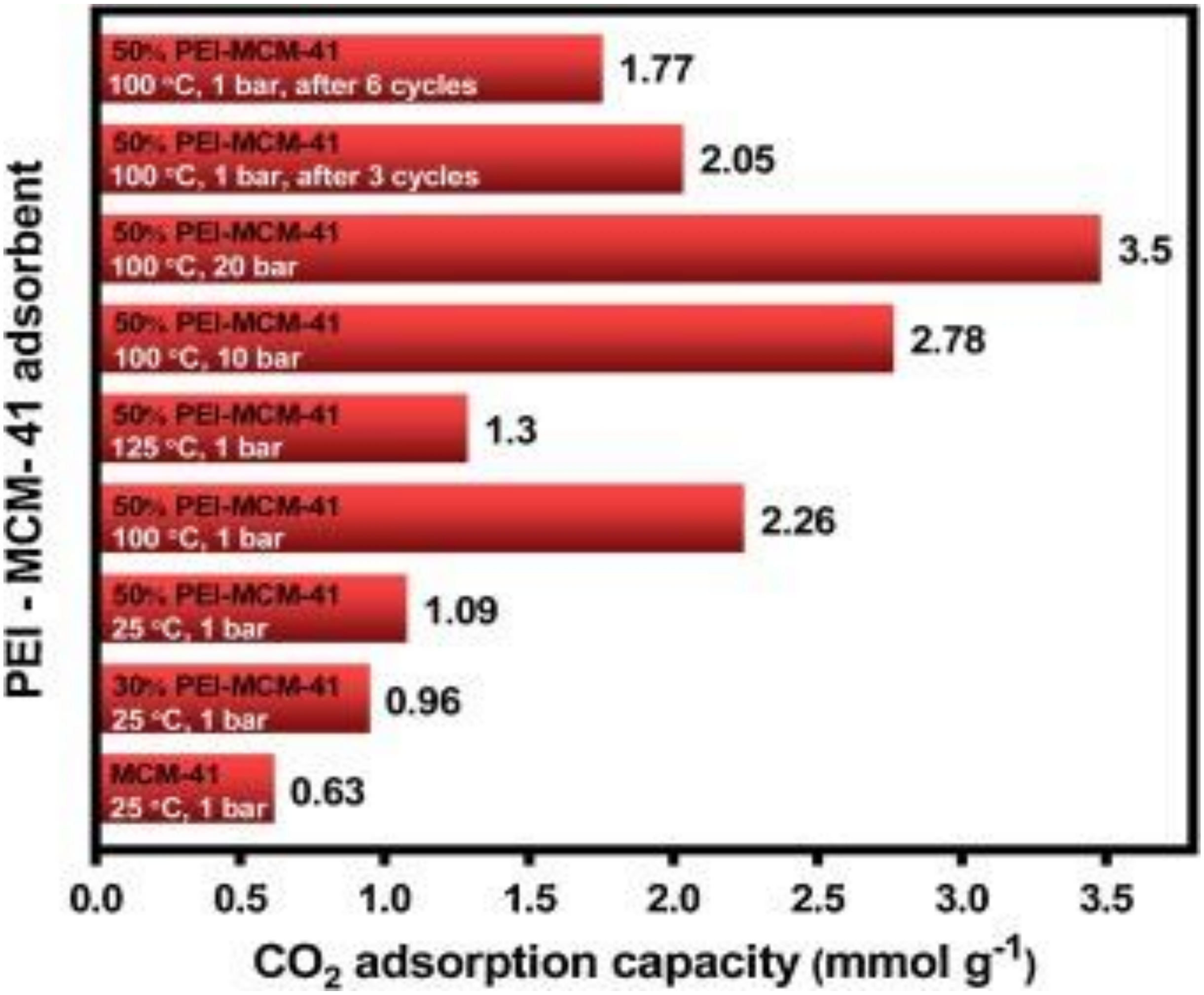


Fig. 3. CO_2 adsorption capacity for PEI - impregnated MCM-41 in varying conditions.

An optimal CO_2 adsorption capacity of ca. 0.57 mmol g^{-1} was discerned for 50 wt% PEI ($M_w = 25{,}000$, as revealed by gravimetric adsorption studies at 40 °C. The aforesaid result was related to the influence of higher N content by ca. 17 %, which offered improved acid-base reaction with CO_2. In addition, X-ray diffraction (XRD) underlined the PEI dispersion in the MCM-41 framework by displaying a downshifting of the characteristic diffraction peak corresponding to (110) plane. Concerning the pore volume and surface area of MCM-41, a decreasing trend was observed with increase in PEI loading.

PEI functionalization on rice husk sourced MCM-41 and compared its performance with aniline- and monoethanolamine - modified systems. Of the studied adsorbents, PEI - functionalized MCM-41 showed better CO_2 capture performance, namely, a capture capacity of ca. 1.70 mmol g^{-1} was obtained for 50 wt.% PEI loading at 75 °C. Liu et al. compared two different PEI molecular weights i.e., 600 and 1800, on the modification of MCM-41. In this study, the modified material with lower molecular weight PEI displayed superior adsorption capacity in comparison to one with higher molecular weight. Specifically, adsorption capacities of ca. 1.6 and 1.3 mmol g^{-1} were obtained at 35 °C and 10 % CO_2 for low and high molecular weight PEI - impregnated systems, respectively, with a loading amount of 40 wt.%.

In order to ensure effective post-combustion CO_2 capture, research performed accounted the dual amine modification of pore-expanded MCM-41. Dual amine modification was found to exhibit enhanced amine efficiency and adsorption capacity. Indeed, adsorption studies performed at 45 °C and 1 bar revealed adsorption capacities of 1.39 and 1.80 mmol g^{-1} and amine efficiencies of 0.35 and 0.30 mol CO_2/mol N for aminopropyl/PEI- and diethylenetriamine/PEI - modified MCM-41, respectively. The modified adsorbent comprising 55 wt.% of PEI ($M_n = 423$) showed a CO_2 adsorption capacity as high as 4.69 mmol g^{-1} at 75 °C and 1 atm.

A higher CO_2 adsorption capacity for cetyltrimethylammonium - treated pore-expanded MCM-41 after PEI impregnation by virtue of increased amine efficiency. Specifically, adsorption capacities of ca. 2.2 and 2.9 mmol g^{-1} were observed at 25 °C and ambient pressure for 40 wt.% PEI - loaded support after cetyltrimethylammonium treatment in dry and humid conditions, respectively. Furthermore, the adsorption capacity was found to decrease by 4.6 % after 20 adsorption-desorption cycles under dry conditions, whereas a 2 % decrease was noted under humid environment.

It is worth noting that cetyltrimethylammonium modification of conventional as well as pore-expanded MCM-41 is beneficial to enhance the performance of MCM-41 supported PEI CO_2 sorbents, and indicatively a capacity of 4.69 mmol g^{-1} was . It is evident that more surface modifications of MCM-41 need to be realized as to optimize performance, while the practicability of *in situ* synthesis of PEI over MCM-41 support can be considered in future activities.

1.3. Fumed silica – supported PEI

Fumed silica (SiO_2, also named as pyrogenic silica) is a class of nonporous pure silica possessing large surface area of ca. 600 m^2 g^{-1} and particle size range of 5−50 nm. For CO_2 capture, fumed silica based supported adsorbents have displayed promising performance as a result of the relatively large surface area in combination with good adsorption capacity and selectivity, but also with superior mechanical performance.

The generation of LPEI - coated fumed silica-based CO_2 adsorbents using the wet impregnation approach. The resulting adsorbent displayed high selectivity even in dry air condition. An optimal CO_2 adsorption capacity of ca. 3.53 mmol g^{-1} was reported for this system at 25 °C. In addition, LPEI - coated fumed silica offered benefits in terms of faster desorption potential in the temperature range of 50−100 °C. Interestingly, the adsorption capacity of this adsorbent remained stable even after > 100 adsorption-desorption cycles. As compared to BPEI - coated system, LPEI - coated fumed silica displayed substantially lower values of heat of adsorption.

CO_2 adsorption behavior of BPEI - functionalized fumed silica. An adsorption capacity of 1.74 mmol g^{-1} at 25 °C and 1 atm, was observed in humid conditions after impregnation using 33 wt.% BPEI. This material also offered reasonable regenerability over repeated adsorption-desorption cycles a capture capacity of 2.57 mmol g^{-1} at 80 °C, for 10 % CO_2/N_2 mixture by using fumed silica supported PEI ($M_w = 800$) with 40 wt.% of PEI loading.

Effect of moisture on the adsorption performance of PEI - loaded fumed silica. From the experimental data, it was clear that the influence of up to 11.5 mg H_2O g^{-1} specific humidity had a positive effect on the adsorption capacity for both BPEI- and LPEI - loaded systems at a temperature of 25 °C. Further increase of specific humidity had no significant effect on the adsorption capacity of LPEI based systems, whereas a reversing effect was observed in the case of BPEI. An optimal adsorption capacity of ca. 4.1 mmol g^{-1} was reported for 44.5 wt.% LPEI - loaded fumed silica under the influence of 15.3 mg H_2O g^{-1}, as compared to ca. 1.4 mmol g^{-1} in dry CO_2.

CO_2 adsorption capacity of PEI - loaded fumed silica with that of PEI - loaded 3D TUD-1 and 2D SBA-15. Gravimetric adsorption at 95 °C and atmospheric pressure revealed that the maximum value of adsorption capacity of ca. 3.07 mmol g^{-1} was recorded for 40 wt.% PEI - loaded fumed silica. Interestingly, the addition of PEG into the aforesaid molecular basket CO_2 sorbent further strengthened its capacity through the increase of amine efficiency by causing stronger inter-molecular affinity with bulk PEI. As a result, PEI layer separation was increased thus facilitating diffusion, as depicted schematically in Fig. 4.

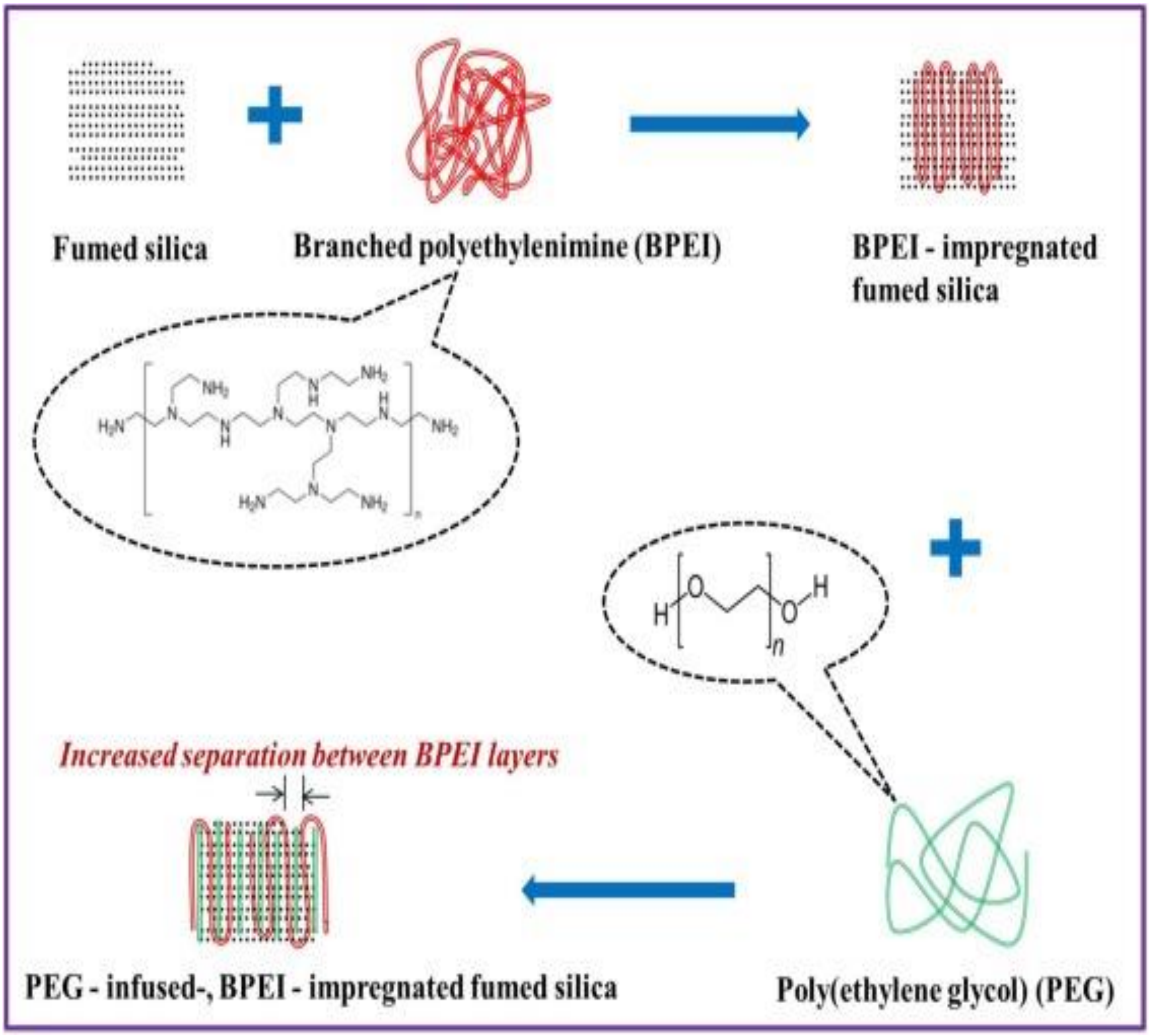


Fig. 4. Schematic representation of the role of PEG addition on the structure of PEI - impregnated fumed silica.

PEI functionalization of poly(acrylic acid) (PAAcid) - modified fumed silica. In this system, PAAcid functioned as multifaceted bridge where the attached carboxylic acid groups were effectively reacted with amine groups from PEI. The effect of molecular weights of PEI and PAAcid on the CO_2 uptake of the resultant sorbent system was evaluated, and the results indicated superior performance for fumed silica - modified with higher molecular weight PEI and PAAcid. A CO_2 capacity of 3.8 mmol g^{-1} at 40 °C and 1 atm, was realized for the adsorbent containing PAAcid and PEI with molecular weights of 3000 and 10,000, respectively.

Three different modifiers based on Lewis-base polymers on the adsorption behavior of BPEI ($M_w = 25{,}000$) - functionalized fumed silica. Gravimetric adsorption studies at 45 °C and 1 bar revealed that PEG had a positive effect on the adsorption capacity in comparison to other modifiers such as poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAC), while PMMA and PVAC modifiers offered advantages in terms of desorption kinetics and regenerability.

The above studies pointed out that PAAcid modification of fumed silica is a promising approach to enhance the performance of fumed silica supported PEI CO_2 sorbent and indicatively a capacity of 3.8 mm was observed, whereas the highest capacity for conventional fumed silica supported PEI was 3.53 mmol g^{-1}among the various studies. Available reports show that more attempts must be generated to precisely study adsorption properties other than capacity, as well as effectiveness of *in situ* synthesis of PEI over fumed silica support.

1.4. Precipitated silica – supported PEI

Precipitated or amorphous silica is an interesting class of mesoporous silica having particle sizes in the range of 5−100 nm and specific surface area in the order of 100 m^2 g^{-1}. Its large pores with > 30 nm pore diameter, increased surface area, and comparatively low cost make it suitable for large scale applications related to CO_2 capture .

The BPEI - modified material exhibited a higher CO_2 capacity than that of the LPEI - modified one. A capacity of ca. 4.60 mmol g^{-1} was realized for precipitated silica functionalized using BPEI with a molecular weight of 800 at 105 °C, though, LPEI - modified precipitated silica displayed a superior adsorption-desorption cycling stability. Additionally, with increase in PEI molecular weight, the adsorption capacity was decreased. In another work, the same team also studied the impact of differing adsorption conditions and BPEI amounts on the CO_2 capacity. Specifically, observed CO_2 capacities included ca. 3.05 mmol g^{-1} at 0.15 bar and 75 °C and 3.64 mmol g^{-1} at 1 atm and 90 °C for 50 wt.% BPEI, and 3.01 mmol g^{-1} at 0.15 bar and 75 °C and 4.24 mmol g^{-1} at 1 atm and 105 °C for 60 wt.% BPEI.

A reduced regeneration energy for precipitated silica - supported BPEI ($M_w = 1300$). For such sorbent with 50 wt.% BPEI, a reduction of ca. 46.7 % was accomplished as compared to a 30 % methanolamine aqueous solution to silica materials that were discussed in the previous sections, precipitated silica supported PEI CO_2 sorbent showed enhanced performance in its conventional form, with indicatively a capture capacity of 4.60 mmol g^{-1} . The limited reports on precipitated silica supported PEI sorbents directs for more detailed investigations by exploring various key parameters such as support material pre-modification approaches, incorporation of different modifiers and dopants, in situ generation of PEI, effect of various PEI materials and concentrations.

1.5. Mesoporous siliceous foam – supported PEI

For CO_2 capture applications, mesoporous siliceous foam can be considered as one of the strong candidates from the family of porous siliceous materials. Mesoporous siliceous foam is a hierarchical interconnected cellular nanostructured version of silica with pore diameters in at least 2–3 different scales in the range of 0.2−50 nm. In addition to this, the presence of large surface area, and tailorable pore and window dimensions by varying the synthesis approach, make such material suitable as support for effective CO_2 capture.

For a 70 wt% BPEI - impregnated system, the observed adsorption capacity values were ca. 3.44 mmol g^{-1} at 105 °C and 3.03 mmol g^{-1} at 115 °C in a gas mixture of 50 % CO_2-Ar. The observed values were higher compared to a system based on same amount of BPEI - impregnated in SBA-15. Moreover, with increase in temperature, the adsorption-desorption kinetics improved, whereas the capacity was decreased. Effect of PEI impregnation on the CO_2 adsorption capacity of mesoporous siliceous foam. The porosity of the siliceous foam was observed to be within the range of 1.12-1.64 cm^3 g^{-1} after impregnation of PEI. A maximum adsorption capacity of ca. 4.11 mmol g^{-1} was acquired at 75 °C after impregnation of 50 wt.% of BPEI with M_w of 600 in comparison to BPEI and LPEI with M_w of 25,000.

The generation of CO_2 adsorbents based on mesoporous siliceous foam with PEI impregnation using different molecular weights and amounts. According to the obtained results, the designed adsorbents corresponding to 50 % BPEI loading and M_w of 800 exhibited large pore volume (ca. 4.17 cm^3 g^{-1}) and an optimal value of CO_2 uptake of ca. 6 mmol g^{-1} at 85 °C. Interestingly, the adsorption kinetics was high for the adsorbent comprised of PEI with M_w of 25,000 compared to PEI with M_w of 800. Considering regenerability, the resulting adsorbents possessed superior stability independently of PEI molecular weight for more than 100 consecutive adsorption/desorption cycles at 75 °C.

The optimal PEI loading was found to be 71.2 wt.% with an adsorption capacity of 0.9 mmol g^{-1} at 105 °C, which was found to be maintained upon regeneration. To enhance uptake, the positive effect of sonication upon synthesis of BPEI ($M_w = 1200$) - impregnated mesocellular silica foa.by means of improvement in PEI dispersion and infiltration. A CO_2 capacity of 1.94 mmol g^{-1} was recorded at 46 °C and atmospheric pressure, whereas the respective value without sonication was 1.29 mmol g^{-1}. the existence of a higher CO_2 uptake capacity for mesocellular siliceous foam functionalized using LPEI ($M_n = 423$) in comparison to BPEI ($M_n = 10{,}000$), though, the observed thermal stability was superior for the BPEI - based system.

Effectiveness of PEI filling of very large mesopores (> 40 nm) of structured silica foam. In this study, low molecular weight PEI ($M_w = 423$) was more efficient in terms of adsorption capacity, whereas high molecular weight PEI ($M_w = 10{,}000$) displayed more regeneration stability upon repeated adsorption/desorption cycles. Specifically, a high adsorption capacity of ca. 5.8 mmol g^{-1} was achieved at 1 atm and 75 °C for 80 wt.% low molecular weight PEI in dry CO_2 environment, with the adsorbents exhibiting also fast adsorption/desorption kinetics.

The increased number of research activities on silica foam supported PEI CO_2 sorbents indicates the superior properties of this material leading to high-capacity values (6 mmol g^{-1} indicatively .Effective tuning of textural features of a silica foam support may lead to further optimization. Furthermore, precise investigation on surface pre-modification of silica foam is needed, whereas only few studies reported the role of pluronic P123 involvement. The role of different modifiers and dopants as well as addition of other amines on the final performance needs to be studied in detail. Also, it would be appreciable to compare the performance of silica foam supported PEI sorbent with that of an analogous adsorbent synthesized and functionalized in situ.

1.6. Silica gel – supported PEI

Silica gel is an amorphous form of silica with irregular pattern of nanopores in the range of 2.4−7 nm. Due to its pore structure along with relatively large surface area of ca. 800 m^2 g^{-1} and low cost, silica gel has been investigated as support for CO_2 sorption application.

Cost effective adsorbent composed of PEI - impregnated silica gel, who observed higher CO_2 uptake when compared to SBA-15 supported PEI. Accordingly, a mass-based uptake of 3.14 mmol/g and a volume-based uptake of 83 mg/cm^3 were obtained at 75 °C for silica gel - loaded by 50 wt.% of PEI. also reported the preparation of silica gel/PEI adsorbent and achieved a CO_2 uptake of ca. 2.13 mmol g^{-1} at atmospheric pressure and 70 °C, for 30 wt.% LPEI ($M_w = 423$) using a 15.1 % CO_2/N_2 mixture. The capacity remained almost unchanged for > 5 cycles of operation. For 20 wt.% PEI - impregnated silica gel, observed an uptake of 4.69 mmol g^{-1} in 99.99 % CO_2 at 275 K and 3.5 MPa. The authors also made a comparison with the APTES - modified system and found a higher performance for the PEI based system due to the higher amine density.

PEI functionalization of silica gel for CO_2 capture. Among the modified systems obtained using differing amounts of BPEI ($M_w = 600$), the one with 40 wt.% polymer demonstrated optimal performance in terms of adsorption capacity, i.e., ca. 2.44 mmol g^{-1} at 65 °C in simulated flue gas passing through a packed bed reactor. In addition, high stability was observed over repeated adsorption-desorption cycles for this adsorbent in a fluidized bed reactor. modified fly ash sourced silica gel. At a pressure of 0.5 bar, the resultant PEI - modified silica gel displayed good adsorption capacities of ca. 3.18 and 3.30 mmol g^{-1} at 75 and 90 °C, respectively. This system exhibits good potential in terms of stability, cost effectiveness, and waste management

Thermal degradation behavior of silica gel - supported PEI CO_2 adsorbents. It was found that the thermal stability of these adsorbents was increased with PEI molecular weight. According to the observations, after 10 cycles of operation at 105 °C, the CO_2 uptake capacity of the studied samples remained almost unaffected. In addition, the observed thermal stability of such CO_2 sorbents was higher in a fluidized bed in comparison to gravimetric mode of operation.

The application of diethanolamine together with PEI into silica gel enhanced CO_2 performance. Accordingly, a capacity of 2.93 mmol g^{-1} along with an amine efficiency of 0.40 mol CO_2/mol N were reported at 35 °C for 50 wt.% PEI ($M_w = 800$)/diethanolamine (1:1) - loaded silica gel. In the case of neat PEI-silica gel, the respective values were 1.92 mmol g^{-1} and 0.17 mol CO_2/mol N. The observed performance of the developed adsorbent was maintained to a good extent over two cycles of adsorption/desorption.

It has been recognized from above reports that appreciable performance for conventional silica gel - supported PEI CO_2 capture sorbents can be achieved (indicative capacity value of 4.69 mmol g^{-1} and stability over cyclic operations, in comparison to conventional SBA-15 and MCM-41 based sorbents. The scope of silica gel pre-modification as well as mixed amine infusion on the performance of the sorbents needs to be investigated. Moreover, the subject of in situ polymerization of ethylenimine over silica gel support must be considered.

The performance with respect to capture capacity of clay-supported PEI sorbents is observed to be lower than the conventional silica-based systems, whereas higher in terms of regenerability. Additional efforts must be generated for effective tuning of textural features of clay materials and subsequent PEI attachment.

2.3. Carbonaceous materials with PEI

Carbonaceous materials are widely used for CO_2 capture applications in account of their advantageous features that include high specific surface area, tunable porosity, flexibility in surface modification, superior chemical and thermal stability, appreciable mechanical features, availability in various forms, and cost-effectiveness originating mainly from the low cost of the raw materials used to produce carbonaceous adsorbents . This sectiodeals with various carbonaceous materials such as graphene oxide/graphene, activated carbon,

carbon spheres, carbon nanotubes, and fullerenes, used as PEI supports to yield CO_2 sorbent systems. .

2.3.1. Graphene oxide/graphene – supported PEI

Graphene oxide (GO) is one of the major graphene-based products with a graphite atomic sheet structure composed of sp^2 and sp^3 hybridized carbons holding various surface oxygen functionalities like carboxyl, carbonyl, hydroxyl, and epoxy. The porosity of the material lies on the few layers, intercalated/exfoliated forms as well in the interconnectivity of the graphene flakes upon growth, which leave a porous configuration to the final material. Due to the availability of the functional groups on the surface, GO can be successfully functionalized with other moieties by chemical means and be thereby tuned for targeted sorption applications. In addition, the influence of the layered morphology and associated porous nature opens numerous perspectives for CO_2 capture. Fig. 5 demonstrates the mechanism of interactions upon PEI functionalization of graphene oxide.

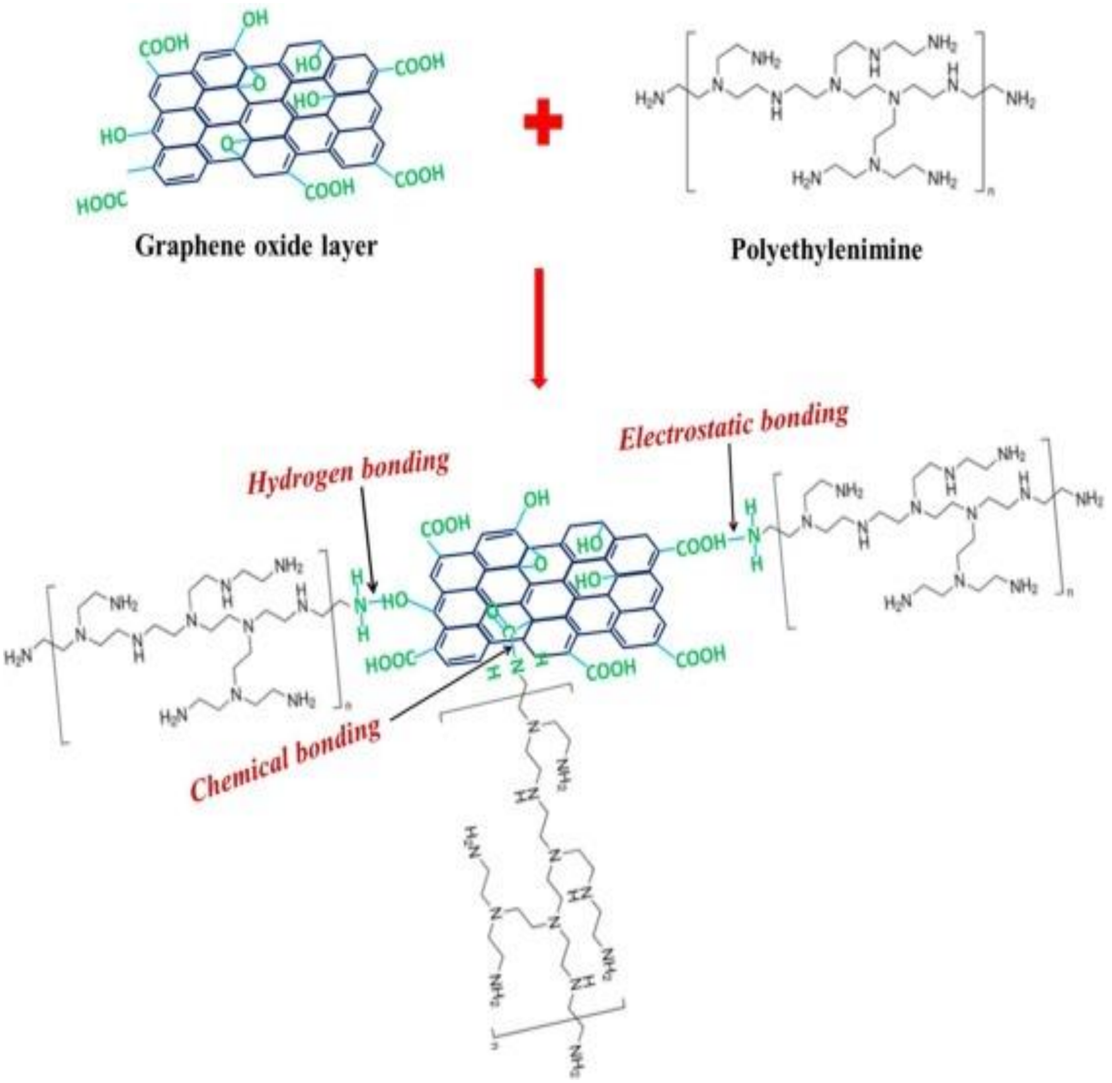


Fig. 5. Schematic representation of PEI functionalization of graphene oxide.

High CO_2 uptake for an adsorbent developed through grafting of PEI into hydroxylated version of 3-dimensional graphene. Adsorption analysis conducted at 25 °C and 1 atm showed a CO_2 uptake of ca. 4.13 mmol g^{-1} for such adsorbent with aziridine to graphene mass ratio of 1.98. This system also displayed good regenerability due to the PEI - based interaction on the hydroxylated graphene surface.

A CO_2 sorbent resulted by impregnation of PEI into graphene-silica hybrid sheets has large number of CO_2-philic amine groups, thin layered morphology, and good thermal conductivity, the resultant CO_2 sorbent exhibited more efficient thermal transfer and beneficial CO_2 adsorption and regeneration characteristics. Accordingly, the composite adsorbent composed of 12 wt.% graphene and 60 wt.% PEI showed an adsorption capacity of ca. 3.89 mmol g^{-1} at 75 °C and 100 kPa. In addition, the adsorption capacity of this adsorbent remained almost unaltered after 20 repeated CO_2 adsorption-desorption cycles.

A hybrid CO_2 adsorbent comprising PEI - functionalized graphene/γ-alumina nanorods hybrid was reported by Bhowmik et al. The influence of graphene in the formulation of such adsorbent was found to enhance the surface area and thermal conductivity. To this end, the resultant adsorbent system showed faster thermal transfer capability and reduced PEI degradation tendency. A CO_2 adsorption capacity of ca. 1.14 mmol g^{-1} was noted at 75 °C and 1 atm, for the 25 wt.% PEI - impregnated γ-alumina nanorods/graphene hybrid. In addition, efficient adsorption-desorption cyclic operation was established at 75 °C and 100 °C, respectively.

2.3.2. Carbon nanotube – supported PEI

carbon nanotubes (CNTs), roll-up analogues of graphene with nanoscale diameter in single- as well as multiple walled forms, have received considerable attention for separation applications owing to their high surface area, large aspect ratio, availability of multiple adsorption sites, light weight, flexibility, superior mechanical characteristics, chemical stability, and modification capability . For CO_2 capture, CNT - supported amine systems have attracted interest because of their thermomechanical properties, unique physicochemical features, chemical stability, and more . However, high production cost and sorbent fabrication difficulties need to be overcome for such systems to deploy their full potential for practical CO_2 capture applications .

CO_2 adsorption capacity at ambient pressure and 30 °C, namely 2.12 mmol g^{-1} for 15 % CO_2. After 10 successive adsorption-desorption cycles, a reduction of about 10 % in adsorption capacity was observed. In another work, CO_2 adsorption capacity of 2.1 mmol g^{-1} at 25 °C and 1 atm for BPEI - loaded single-walled carbon nanotubes (SWCNTs), which was higher compared to that of BPEI - loaded MWCNTs.

pre-treatment of MWCNTs using a combination of HNO_3 and H_2SO_4 before PEI impregnation to obtain more carboxyl groups and to release metal-based surface contaminants. The adsorption capacity of MWCNTs was observed to increase after the impregnation of PEI resulting in a capacity of ca. 2.14 mmol g^{-1} at 1 bar and 298 K for simulated flue gas containing 15 % CO_2. In addition, repeated cyclic operations had no significant impact on the adsorption capacity of this adsorbent.

2.3.3. Fullerene – supported PEI

Fullerenes, 0-dimensional wraps of carbon atoms in the form of hollow spheres, have also been reported for CO_2 capture applications due to unique features such as surface area, spherical shape, monodispersity, thermomechanical properties, tailorable physicochemical characteristics, and functionalization flexibility . Based on our investigation, we review available works related to fullerene-PEI based CO_2 sorbent systems in this section.

Accordingly, at 90 °C and 0.1 bar, a CO_2 uptake capacity of 3.19 mmol g^{-1} was obtained. The developed CO_2 adsorbents showed also high selectivity against methane, indicating potential in natural gas sweetening applications. In another attempt, the authors examined the effect of pyrolysis in inert atmosphere (argon) on the CO_2 performance of C_{60} - supported PEI. A higher CO_2 capture capacity of 2.73 mmol g^{-1} was discerned at 25 °C as compared to one observed at 90 °C. A reduction trend in capture capacity at 90 °C after pyrolysis at differing temperatures is related to the molecular scission of C-N backbone associated to PEI in the composite system.

2.3.4. Activated carbon – supported PEI

Activated carbon, or activated charcoal, is one of the widely reported carbonaceous materials for CO_2 capture applications by account of its large specific surface area with typically small sized pores, low regeneration energy, hydrophobicity, wide availability of sources to grow these materials, and cost effective. In order to enhance CO_2 performance, various attempts on surface functionalization have been reported. In this section, we discuss the studies related to PEI - functionalized activated carbon-based CO_2 sorbent systems.

PEI functionalization of activated carbon was found to yield enhanced CO_2 adsorption performance as temperature increase. Indicatively, an adsorption capacity of ca. 1.31 mmol g^{-1} was observed at 100 °C for 10 wt.% PEI loading. PEI - loaded activated carbon adsorbents and reported a dynamic capacity of ca. 2.55 mmol g^{-1} at 28 °C and atmospheric pressure in 15 % CO_2 for 70 wt.% PEI loading. Various compositions

studied, the 65 wt.% PEI system displayed optimum CO_2 capacity of ca. 4.82 mmol g^{-1} at 75 °C and 1 atm in a CO_2 concentration of 15 %, which is attributed to the high amine content and internal mass-transfer effects. In addition, the influence of moisture was found to be positive in the adsorption capacity of this material, which also exhibited appreciable stability and regenerability. In another study, the authors examined the effectiveness of such sorbent material in low CO_2 concentrations. Accordingly, in 5000 and 400 ppm CO_2, adsorption capacities of ca. 3.34 and 2.25 mmol g^{-1} at 25 °C, respectively, were obtained for mesoporous carbon - modified with 55 wt.% PEI and 5 wt.% of the nonionic surfactant, Span 80 .
3.6 mmol g^{-1} at 60 °C using a mixture of 8 % CO_2/10 % H_2O, compared to PEI or K_2CO_3 individually loaded systems. The combinatorial effect of PEI and K_2CO_3 was also shown to offer good regenerability upon repeated adsorption-desorption cycles.

2.3.5. Carbon spheres – supported PEI

Carbon spheres, another technologically versatile and promising class of carbonaceous materials, are also reported for CO_2 capture applications owing to features such as high specific surface area, small sized pores, large porosity, shape and curvature. The reported studies related to CO_2 sorbent systems based on carbon sphere - supported PEI are summarized below.
Among the different molecular weights used, PEI with M_n of 1200 displayed the highest CO_2 uptake (ca. 3.39 mmol g^{-1} at 75 °C and 1 atm), whereas PEI with M_n of 10,000 displayed better cyclability, with the adsorbent maintaining its adsorption capacity to an approximately 94 % level over 10 adsorption-desorption cycles. In addition, infusion of PEG into such sorbent system had a positive effect to increasing the capacity by 25.7 %.
It has been noted from above studies that carbonaceous materials are promising for the development of effective supported PEI CO_2 sorbents. In the case of graphene materials, in situ polymerized ethylenimine over hydroxylated graphene support presents enhanced performance (indicative capacity of 4.13 mmol $g^{-1.}$At the same time, graphene/silica hybrid supported PEI sorbent has demonstrated good adsorption, and kinetics .More studies are also needed to investigate the role of surface modification as well as various hybrid combinations of CNTs on the CO_2 capture performance. Among the various carbon materials, the high capture capacity of mesoporous carbon - supported

PEI can be noted (4.82 mmol g^{-1} indicatively. Furthermore, in situ polymerized ethylenimine functionalized mesoporous carbon, combined PEI/K_2CO_3 impregnated activated carbon, and carbon sphere supported PEI CO_2 sorbents have demonstrated good performance in terms of capture capacity. However, the properties other than capture capacity of carbon material supported PEI sorbents, along with the role of in situ retaining of capacity (3.89 mmol g^{-1}) over cyclic operations . A great prospect lies in proper pre-modification of various graphene forms, for example, employing advanced techniques such as UV treatment. For CNTs, it could be noted that the influence of spacer molecules is advantageous to enhance the performance of supported PEI sorbents, and, indicatively, a capacity of 3.875 mmol g^{-1} has been recorded, together with acceptable cyclic stability, heat of synthesis method and modifier/dopant addition, need to be further investigated.

2.4. Alumina supported PEI

Alumina, or aluminum oxide, has been reported for CO_2 capture due to its ability to contribute *via* both physical and chemical interaction. The associated distinctive features such as high surface area, widely distributed pore structure and morphologies, acid-base nature, and superior hydrothermal stability are driving forces behind such application for alumina . Works on alumina - supported PEI CO_2 sorbents have been reported and are discussed here.

The fabrication of CO_2 solid adsorbents based on PEI observed adsorption properties were superior for such system as compared to silica-based systems. Specifically, for mesoporous γ-alumina with 31 wt.% of BPEI, an uptake capacity of ca. 1.41 mmol g^{-1} was obtained in 10 % CO_2, which was reduced by ∼16.3 % after the application of 24 h steam exposure at 105 °C, while the observed reduction was ∼67.1 % for PEI - loaded mesoporous silica performance was also compared with that of alumina powder - supported PEI. According to gravimetric data at 30 °C in 400 ppm CO_2/N_2 mixture, 43−44 wt.% BPEI ($M_w = 800$) - loaded alumina monolith sorbent demonstrated an adsorption capacity of ca. 0.75 mmol g^{-1}, whereas the respective observed capacity for alumina powder was 0.7 mmol g^{-1}. After 5 successive adsorption - steam desorption cycles, the observed reduction in CO_2 capacity was lower for the alumina monolith - supported BPEI compared to the alumina powder analogue.

2.5. Metal organic framework (MOF) – supported PEI

MOFs are a new class of versatile crystalline materials comprising organic ligand - attached metallic ions or clusters arranged in an open network of extended porosity. CO_2 adsorption performance in terms of capacity, selectivity, and kinetics in MOFs can be tuned on demand by controlling the surface chemical potential as well as pore size and shape through simple organic ligand variations.
Enhancement of the dynamic CO_2 capacity and selectivity of UiO-66 after PEI functionalization . For 30 wt.% PEI - loaded UiO-66, uptakes of 1.65 and 2.41 mmol g^{-1} were acquired in dry and 55 % relative humidity conditions, respectively, at 65 °C, combined with high selectivity values of 111 and 251 in dry and humid conditions, respectively. Upon cyclic adsorption-desorption operation, the capability of the developed adsorbents was maintained to a good extent. An improved CO_2/N_2 selectivity of 48 and an uptake of 3.2 mmol g^{-1} were reported at 298 K and 41 wt.% BPEI ($M_w = 600$) - functionalized UiO-66-NH_2 developed by Schiff base reaction in the presence of glutaraldehyde. For comparison, UiO-66-NH_2 exhibited a selectivity of 25 and a capacity of 2.7 mmol g^{-1}. In addition, the functionalized adsorbent exhibited moisture resistance, cyclic stability, and a moderate heat of adsorption (68 kJ mol^{-1} CO_2).

Zeolitic imidazolate frameworks (ZIFs) is a subcategory of MOFs consisting of metal cluster - linked imidazole ligands that are topologically analogous to zeolites. the positive impact of PEI loading on the CO_2 adsorption of ZIF-8. Indeed, the adsorption capacity of ZIF-8 was increased from 0.126 to 1.61 mmol g^{-1} at 65 °C and 1 atm after PEI functionalization (45 wt.% of PEI), which was further increased in the influence of moisture. Also, the CO_2/N_2 selectivity of this adsorbent was increased to 62 from 1.6. This system was thermally stable up to 177 °C. studied hybrid adsorbents comprising ZIF-8 and PEI - loaded GO for CO_2 capture. Adsorption studies conducted at 273 K and 1 atm revealed a 6-fold enhancement in capacity (181.04 cm^3/g) as compared to neat GO (26.04 cm^3/g) and ZIF-8 (30.79 cm^3/g), which was attributed to the combinatorial effect of PEI functionality and the effective ZIF-8 proliferation in the GO interlayers. A CO_2/N_2 selectivity value of 184 was reported for this hybrid adsorbent due to the occupancy of amine moieties.

The above studies reveal the potential of PEI functionalization to enhance the performance of MOF CO_2 sorbents, specifically, the capture capacity and selectivity of MIL-101, UiO-66-NH_2, and ZIF-8.

2.6. Zeolite – supported PEI

Zeolites, aluminosilicate microporous materials, comprise stable, highly porous network, thus are promising for CO_2 capture applications. To overcome performance limitations originating from moisture influence and increased temperature affects, amine functionalization of zeolites has received particular attention.
CO_2 adsorption behavior of rice husk ash sourced ZSM-5 functionalized with PEI. An optimal capacity of 1.96 mmol g^{-1} was attained for 30 wt.% PEI - modified system at a temperature of 120 °C, with appreciable selectivity and regenerability values. An increase in CO_2 adsorption capacity for ZSM-5 with BPEI loading, with optimum performance obtained for the adsorbents holding 33.3 wt.% of BPEI ($M_w = 600$).
A hybrid adsorbent comprising PEI - functionalized-, mesoporous silica - coated-, zeolite Adsorption experiments performed at 25 °C revealed a high CO_2 uptake of carbon. 5.05 mmol g^{-1} in 15 % CO_2 for 30 wt.% PEI - impregnated adsorbent under the influence of a 70 % relative humidity. Interestingly, the aforesaid adsorption capacity was almost unaffected after 10 successive adsorption-desorption cycles.

2.7. Polymer – supported PEI

Porous polymeric materials having large surface area and superior physicochemical characteristics have been explored as support materials for amine-based CO_2 adsorbent systems in order to realize effective capture, including in enclosed conditions such as in aircrafts, space shuttles, and submarine, when CO_2 concentration is lower than 1 %.To this end, PEI has been widely employed for the modification of different porous polymer supports.

Moreover, this system possessed good stability as well as enhanced adsorption kinetics. The influence of moisture had also an enhancing effect on the adsorption performance of the material, which is advantageous for CO_2 capture from flue gas under humidity conditions.

Adsorption studies at 1 bar and 273 K revealed an adsorption capacity of 2.1 mmol g^{-1}, along with high CO_2 selectivity. Concerning the regenerability, the capacity of this material was observed to remain almost unaffected up to 4 consecutive adsorption/desorption cycles. Functionalization of poly(methyl methacrylate) mesoporous pellets by PEI infusion .Among the various conditions studied, a CO_2 adsorption capacity of 4.26 mmol g^{-1} was achieved at 75 °C.

Adsorption studies performed in a fixed-bed column at 0.1 MPa and 25 °C revealed capture capacities of 1.96 and 2.13 mmol g^{-1} in 400 and 5000 ppm CO_2, respectively, for a CO_2 sorbent with 50 wt.% of PEI. These values were found to increase under the influence of moisture, whereas the presence of oxygen had a negative effect. Good cyclic stability over 5 consecutive adsorption/desorption cycles was also reported for the sorbent system. Nonpolar resin (HP20) was modified by means of PEI impregnation . Among various studied compositions, 50 wt.% PEI loading yielded enhanced adsorption capacity, faster kinetics, and good recyclability. Specifically, less than 6 min was sufficient to achieve equilibrium at 70 °C, and 4.122 and 2.26 mmol g^{-1} loading were obtained at 25 °C and 1 bar for pure CO_2 and a mixture consisting of 400 ppm CO_2, respectively. Nonlocal density functional theory was also applied to find out the pore size range responsible for CO_2 sorption and it was concluded that the range of 43−68 nm granted most of the contribution to the observed sorption capacity.

A capacity of 1.48 mmol g^{-1} for 20 % PEI ($M_w = 1800$) - filled ADS-17 (a commercial nonpolar macroporous polystyrene resin) at 25 °C and 2 bar in 35.6 % CO_2/CH_4 mixture, together with appreciable regenerability. a highly CO_2/CH_4 selective adsorbent for biogas upgrading applications by BPEI ($M_w = 1200$) loading into NKA-9, a commercial polar macroporous polystyrene resin. A CO_2 uptake of 3.44 mmol g^{-1} was observed for the 50 wt.% BPEI - loaded adsorbent at 35 °C and 0.45 bar, along with good cyclic and chemical stability.

Adsorption studies at 75 °C and ambient pressure revealed an optimal capacity of 3.83 mmol g^{-1} for 70 wt.% of PEI - loaded nanoporous poly(divinylbenzene). The adsorption capacity was observed to maintain over repeated cyclic operations, while good selectivity’s were obtained under either dry or humid conditions. PEI functionalization of porous polymer prepared using ethylene glycol dimethacrylate and divinylbenzene. The resulting adsorbent system consisting of 30 wt.% of PEI was found to exhibit an uptake of 3.28 mmol g^{-1} in dry CO_2 at 25 °C. The capacity was maintained almost unaltered after 8 repeated cycles of adsorption and desorption. PEI was developed by employing freeze-drying at 25 °C, ambient pressure, and 80 % relative humidity, such composite foam holding 44 wt.% of BPEI ($M_r > 600,000$) showed a capture capacity of 2.22 mmol g^{-1}, which was maintained over cyclic operation. A considerably reduced CO_2 adsorption half-time was also reported for the aforesaid sorbent system. For direct CO_2 adsorption from air, showed the applicability of a PEI - impregnated cellulose acetate/mesoporous silica composite fiber adsorbent, with breakthrough and pseudo-equilibrium capacities of 0.44 and 0.62 mmol g^{-1}, respectively, at 35 °C and 90 scum in dry conditions, whereas these values were increased to 0.7 and 1.7 mmol g^{-1}, respectively, under humid conditions. As seen from the above literature analysis, a series of porous polymer supported PEI sorbents has been investigated for CO_2 capture. Distinctively, polymethacrylates (glycidyl and methyl versions), polydivinylbenzene, and polystyrene (polar version) - based porous materials have presented promising performance among the available materials.

2.8. Additional materials with PEI

Additional PEI based adsorbents using materials that are not included in the categories are discussed in this section. PEI - functionalized titanate nanotubes (TNTs) were developed by first preparing protonated TNTs, followed by wet impregnation with BPEI ($M_w = 600$). The resulting nanostructured adsorbent consisting of 50 wt.% BPEI exhibited a good CO_2 uptake capacity of 3.06 mmol g^{-1} at 75 °C using a 10 % CO_2 mixture. A 20 wt.% PEI - loaded $MgCO_3$ adsorbent with an uptake of 1.07 mmol g^{-1} at 75 °C , along with appreciable regenerability. The adsorption performance was enhanced by 19 % in the presence of 10 % water vapor.

The potential of PEI - functionalized magnetic nanoparticles for CO_2 capture applications. The results obtained underlined the effectiveness of PEI loading to enhancing capture capacity, selectivity, and regenerability of the magnetic nanoparticles. Compared to LPEI, BPEI was found to yield higher adsorption capacity. Specifically, the adsorbent with 16 % BPEI ($M_w = 25,000$) exhibited a CO_2 uptake of 0.36 mmol g^{-1} at

25 °C. The relatively low capacity is attributed to lack of extended porosity in the magnetic particle cores.

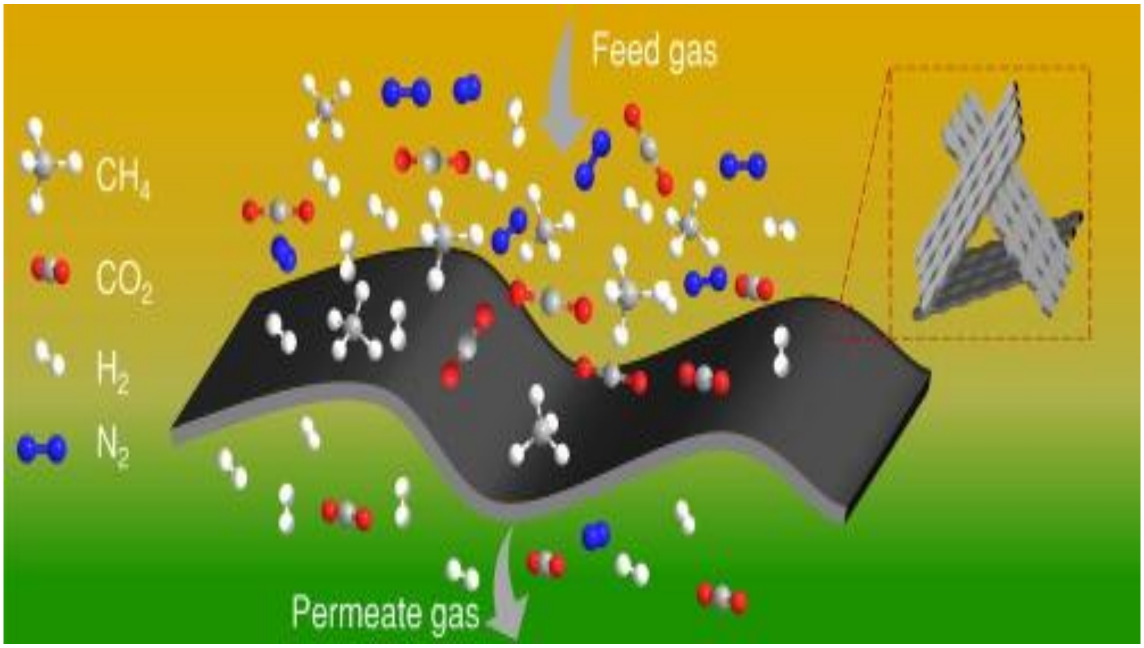
CO_2 capture performance of silane - modified-, PEI - functionalized-, Fe_3O_4 magnetic nanoparticles. The resulting adsorbent exhibited a capacity of 0.373 mol L^{-1} at 40 °C and 100 kPa, combined to fast sorption kinetics, adequate selectivity, and appreciable cyclic stability.

Chapter 6

Membrane for CO2 Separation

CO_2 removal from gas streams using energy-efficient and environmentally friendly separation technologies can contribute to achieving a low-carbon energy future. Carbon membrane systems for hydrogen purification, post-combustion CO_2 capture, and natural gas (NG) sweetening are considered as green processes because of their low energy consumption and negligible environmental impact. Much effort has been devoted to enhancing gas permeance and/or selectivity of carbon membranes by tailoring micropore structures to accomplish different CO_2 removal processes. In this review, the status of tuning microstructure and fabrication of the ultrathin selective layer of carbon membranes, as well as membrane module upscaling was analyzed. The precursors made from a clean process using the solvent of ionic liquids have a particular interest, and high-performance asymmetric carbon hollow fiber membranes (CHFMs) without complex pre-treatment were highlighted towards technology advances of carbon membrane development. Energy-efficient processes of carbon membranes for CO_2 removal in oil/gas/chemical industries and power plants were discussed for decreasing production costs, environmental impact, energy consumption, and improving process flexibility. Future perspectives on advanced carbon membrane material development based on renewable precursors and simple carbonization processes, as well as module design and process optimization, were proposed.

The outstanding separation performance coupled with excellent mechanical and chemical stabilities makes carbon membranes-based separation process as an energy-efficient and environmentally friendly technology for CO_2 removal.



Greenhouse gas emission

The rapid growth in greenhouse gas emissions has stimulated worldwide attention to look for green and clean energy resources alternatives to traditional fossil fuels. Hydrogen and methane, as clean and low-carbon energy sources, have shown the increased demands in the energy system and transport sector such as electricity generation, heating, and vehicle fuels . However, raw gas streams usually contain some impurities such as CO_2 and water which should be removed to reach the purity requirement for end-users. Compared to the conventional separation technologies of chemical absorption, pressure-swing adsorption (PSA), and cryogenic distillation, membrane-based separation technology as an energy-efficient and environmentally friendly process is currently attracting particular interest for selected CO_2 removal applications. Various membrane materials such as polymeric membranes , inorganic-based membranes like carbon molecular sieve (CMS) , graphene oxide (GO) , zeolite imidazolate framework (ZIF) , and metal organic frameworks (MOFs) have been developed for CO_2-related separations. Among them, carbon membranes have great advantages of providing strong mechanical and chemical stabilities and high separation performance, especially for high-temperature and -pressure demanded scenarios such as H_2/CO_2 separation in steam methane reforming process, and CO_2/CH_4 separation in natural gas (NG) sweetening .

The first carbon membranes were prepared by carbonization of cellulose hollow fibers , and since then carbon membranes have been developed from different precursors such as cellulose derivatives , polyimide derivatives , poly(vinylidene fluoride) (PVDF) , and polyacrylonitrile (PAN) . Carbon hollow fiber membranes (CHFMs) derived from polyimide-based precursors were prepared for different gas separations (NG sweetening and olefin/paraffin separation and demonstrated excellent performance. The PVDF based CHFMs with an average pore size of 6 Å were developed for organic solvent separations and a high ideal p-xylene/o- xylene selectivity of 26 was reported at lab-scale. The cellulose acetate (CA) based CHFMs have been developed for biogas upgrading, natural gas sweetening and H_2 separation , which showed high CO_2/CH_4 selectivity, but relatively low gas permeance (e.g., CO_2: <0.04 m^3(STP)/(m^2·h·bar)) due to a thick wall (ca. 20–30 µm) made in symmetric structure . Reducing the thickness of the carbon matrix can potentially enhance gas permeance, but the mechanical strength of membrane materials may decrease. Moreover, the main challenge of cellulose regeneration from CA precursors still hindered the large-scale production of cellulosic-based CHFMs . Recently, the preparation of carbon membranes directly from cellulose hollow fibers , which partly addressed the challenge of CA-based carbon membranes. However, the gas permeances of the reported carbon membranes are still relatively low, which should be further improved by making either asymmetric or supported carbon membranes.

Moreover, by carefully controlling carbonization conditions (e.g., final carbonization temperature, heating rate, and environment) and proper post-treatment such as post-oxidation and chemical vapor deposition (CVD), the pore structure and porosity of carbon membranes based on the specific precursors can be tailored to efficiently separate gas molecules which are much alike in both size and physical properties (e.g., H_2-CO_2 and olefin-paraffin) . The improvement of carbon membrane performances may offset the relatively high fabrication cost compared to polymeric membranes. However, the up scaling of carbon membrane modules is still challenging especially related to membrane mounting, potting, and sealing for high-pressure and high-temperature applications. Therefore, this is a need to make flexible carbon membranes and identify a suitable potting material to make modules with high packing density and high-pressure tolerance. Ceramic supported carbon membranes present much stronger mechanical strength and are easier for module construction, which has been widely studied for high-temperature H_2 purification. However, the challenges of making defect-free, thin selective carbon layer on top of support still hinder its up-scaling for large-scale commercial applications . In this work, a review of the status and challenges of both self-supported and supported carbon membranes from materials to applications was conducted. Moreover, carbon membrane development with respect to renewable precursors and low-cost carbonization procedures as well as the applications for CO_2 removals with respect to energy efficiency were clearly highlighted. Finally, future perspectives on material, module, and process development for CO_2 removal with advanced carbon membranes were also proposed.

2. Carbon membrane development

2.1. Precursor selection and preparation

In the past decades, different polymeric precursors have been employed for fabrication of high-performance carbon membranes, including cellulose and derivatives , polyimide (PI) and derivatives , polyacrylonitrile (PAN) , poly(p-phenylene oxide) (PPO) and phenolic resin . Besides the optimization of carbonization conditions and the implementation of post-treatment, the selection of suitable precursors is also a crucial factor to determine membrane separation performance. Moreover, the polymer precursor-determined properties such as chemical structures, glass transition temperature, decomposition temperature, and fractional free volume (FFV) should be well considered for making high-performance carbon membranes . The effect of the microstructure of polyimide precursors on the gas permeation properties of the derived carbon membranes was investigated by comparing three block-copolyimides with a different number of methyl substituent groups as reported by Park et al. . Gas permeability of carbon membranes can be improved by introducing the methyl substituent groups into polymer backbone to increase FFV. The current researches on carbon membrane preparation are mainly based on two representative precursors: cellulose and polyimide, and the comparison of the two materials are given in Table 1. Carbon membranes made from cellulose precursors usually present a relatively low cost with moderate separation performance. While polyimide-derived carbon membranes in general show higher performance, but production cost might be relatively higher.

Table 1. Comparison of cellulose and polyimide precursors for making carbon membranes.

Property	**Cellulose**	**Polyimide**
Availability	High (abundant)	Limited
Sustainability	Renewable biopolymer	Synthetic material
Processability	Moderate (difficult to dissolve)	High (can be dissolved in conventional solvents)
Free volume	Low to Moderate	Moderate to high
Fusing risk during carbonization	Moderate	Very high
Mechanical strength	High	High
Material cost ratio	1	10

To date, N-methyl-2-pyrrolidone (NMP) remains the dominant solvent for making carbon membrane precursors. However, it has now been faced with restriction for industrial use in some EU countries due to the risks to the health of workers exposed to NMP . Thus, alternative green solvents are required to achieve a cleaner precursor preparation process. Recently, ionic liquids (ILs), which are suggested as a green solvent because of the advanced properties of negligible volatility, high thermal and chemical stability, easy recyclability , has been successfully used for fabrication of cellulose precursors . Besides, several ILs recycling methods have been investigated involving freeze crystallization , membrane separation , and evaporation . This shows great potential on the fabrication of CMS membranes at a low environmental impact. A conceived illustration on the preparation of CMS membranes from sustainable polymer materials and the solvent of ionic liquids (ILs) is depicted in Fig. 1. The membrane precursors with tunable structures, such as symmetric, asymmetric, and composite, can be prepared from renewable materials (e.g., cellulose) that are dissolved in ILs. The diluted ILs in the waste coagulation solution can be recycled by evaporation or membrane separation processes. Then, the carbon membranes are constructed into various types of modules for energy-efficiency CO_2 removals.

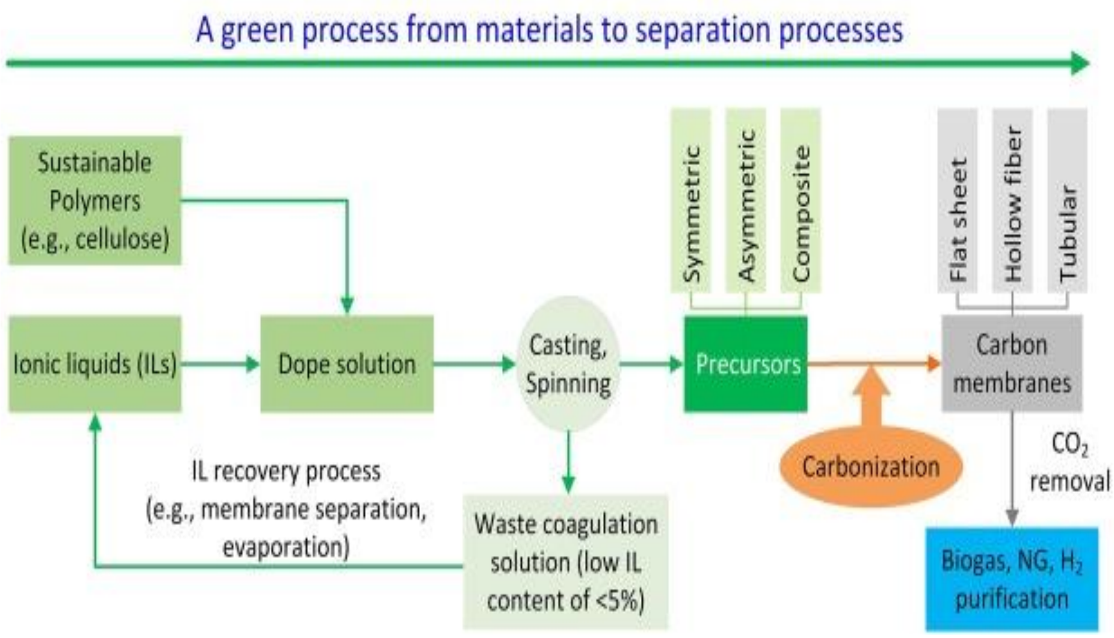
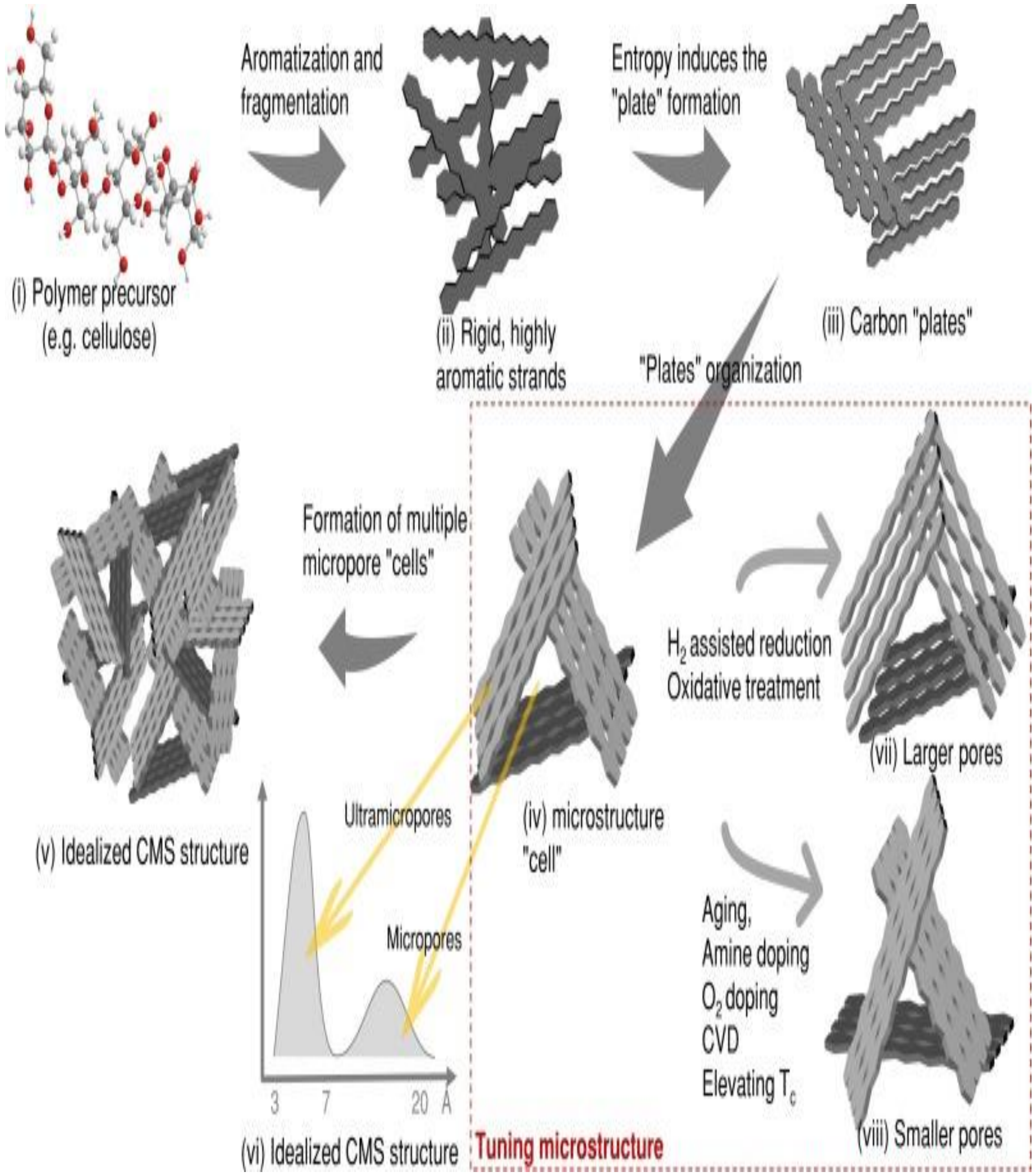


Fig. 1. Schematic illustration of a green process for preparation of carbon membrane precursors using ionic liquids. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Carbon membrane preparation

Carbon membranes are typically formed with a rigid structure via a controlled carbonization procedure applied to polymer precursors at a high temperature (e.g., 500–900 °C). During carbonization, the entangled precursors are transformed to rigidly carbonized aromatic strands, and afterward forming organized plates to approach a higher system entropy, which results in a bimodal structure of ultra-micropores and micropores .

Although carbon membranes can be prepared from diverse precursors and present different structures and separation performance, the general carbonization mechanism from polymeric precursors to carbon membranes is very similar. Mechanism for the preparation of CMS membranes by carbonization of the coil polymer precursors as illustrated in Fig. 2. The entangled precursor is initially activated to start aromatization and fragmentation at the



temperature ramping process and afterward generates periodic scissions along the polymer backbone due to enough localized stresses (Fig. 2(i) & (ii)) . By removing most of oxygen and hydrogen atoms, the backbone scissions are transformed to rigidly aromatic carbon strands . Besides, the rigid carbon strands align and form carbon “plates” to yield higher entropy to the system and reduce the excluded volume effects that existed with the random packing of the strands (Fig. 2(iii)) . During the final thermal soaking phase, it is difficult to form long- range perfect stacking of plates due to the kinetic restrictions (limited time at high temperature). Thus, the final carbon membranes usually present a microstructure with imperfectly packed plates that are formed by organized strands (ultra-micropores) as depicted in Fig. 2(iv). During the end cooling stage, the micropore “cells” are stacked to form a cellular structure (Fig. 2(v)) in which the ultra-micropores share the “walls” between micropores . The pore size distribution of CMS membranes is depicted in Fig. 2(vi), which can be adjusted by different methods listed in Fig. 2 (Red dashed square) to get larger pores (Fig. 2 (Vii)) or smaller pores (Fig. 2 (Viii)). The ultra-micropores of ca. 3–7 Å are suggested to govern gas selectivity, while the micropores (7–20 Å) contribute to a high gas permeability with larger sorption sites .

Carbon membranes are composed of sp^2- and sp^3- hybridized carbon structure . The sp^2-hybridized carbon (i.e., a two-dimensional (2D) layered graphitic carbon) is beneficial for plate packing to form a more compact ultra-micropore structure. While the three-dimensional (3D) sp^3-hybridized carbon will prevent the plate packing, which enhances gas permeability due to the widening of micropores. However, the sp^3-hybridized carbon structure is thermodynamically unstable, which can be partly transformed to sp^2-hybridized carbon at higher temperatures . Moreover, adjusting of carbon structure can be implemented either during carbonization or in an extra post-treatment process, which makes carbon membranes flexible for different applications. Tuning carbonization conditions (e.g., carbonization temperature, atmosphere, doping) and applying post-treatment steps can provide some facile ways to modify the microstructures of carbon membranes, and thus improve separation performance (especially membrane selectivity). It should be noted that the pore size controlling approach applies to all carbon membrane configurations (e.g., flat-sheet, hollow fiber and tubular). Various methods by tailoring micropores/ultra-micropores of carbon membranes during carbonization or post-treatment step (illustrated in Fig. 2 and listed in Table 2 for details) were reported to tune carbon membrane structures, which can either improve gas permeability and/or enhance selectivity.

Table 2. Representative methods for tuning carbon membrane structures and performances.

Tune carbon structure	**Methods**	**Membrane performance**	
Pore widening	H_2-assisted environment(introduce H_2 into purge gas)	Dramatic increase permeability with little loss selectivity	
	Oxidative treatment (in air at different temperatures of below 400 °C)	Improve gas permeability but may scarify gas selectivity	
Pore reducing	Chemical doping (Ozone, O_2, amine, etc.)	Increase selectivity, but may reduce gas permeability	
	Hyperaging (at a specific temperature, e.g., below 250 °C)	Enhance gas selectivity, enhance stability of gas permeability	
Increase porosity, but narrow pore size distribution	Integrating of post-treatments (post-oxidation, reduction and chemical vapor deposition (CVD))	Simultaneously enhance gas permeability and selectivity	

H_2-assisted tailoring of ultramicropores can dramatically improve gas permeability with a low selectivity loss . The H_2-contained carbonization environment can modulate the carbon hybridized structures (sp^2 and sp^3), and the ratio of sp^3/sp^2 hybridization carbon increases when the carbonization environment contains a higher H_2 concentration, which results in a more permeable but less selective membrane . That method provides a facial way for tuning micropore size and distribution.

Oxidative treatment of fresh-made carbon membranes has been successfully employed to obtain wider pores . Carbon membranes exposed in the air at an oxidation treatment of 350 °C increased H_2 permeance from 5 to 18 m^3(STP) $m^{-2}h^{-1}$ bar^{-1}) due to the increase of the sp^3 hybridized carbon atoms in carbon matrix . Moreover, the increase of pore size via oxidation treatment was verified by N_2 adsorption. Compared with the fresh-made carbon membranes, the average pore size of the post-oxidation processed membranes increases from 0.53 to 0.68 nm which significantly decreases membrane selectivity. However, introducing a trace amount of O_2 at high temperature (i.e., O_2 doping) can tighten the pore structure of carbon membranes to make more selective CMS membranes . The oxygen molecules can bind to active sites for narrowing ultra-micropore size, and thus improve membrane selectivity . Moreover, introducing other doping species such as ozone and amine can also adjust pore size. Implementation of an ozone-based post-synthetic method to enhance H_2/CH_4 selectivity from 13.3 to 50.7. Similar doping concept by applying a dopant of paraphenylenediamine (PPDA) (fit to the pore size of carbon membranes) to react with the adjacent CMS sheets to form new covalent bonds, and thus decreasing ultra micropore size.

A physical aging process, named hyperaged was introduced to improve H_2/C_2H_4 selectivity. The distance of adjacent carbon strands can be compressed when the fresh-made CHFMs were hyperaged at a hot flow of air atmosphere at a certain temperature range (e.g., 90 to 250 °C), and thereby resulting in smaller ultramicropores with a 10-fold increase of H_2/C_2H_4 selectivity. Therefore, proper aging methods can be introduced to adjust separation performance and enhance the stability of carbon membranes.

Elevating carbonization temperature was reported to reduce pore size. A CO_2/CH_4 selectivity of > 3000 was obtained by increasing the carbonization temperature to 900 °C . When carbonization temperature raises, the micropores surrounded by refined ultramicropores can be formed to provide the sorption sites for CO_2, O_2 and N_2, but rejects the CH_4 molecules. Because of the narrowed pathways, both sorption and diffusion selectivity's can be improved.

Post-treatment by the integration of post-oxidation, post-reduction and CVD was applied to improve separation performance . The post-oxidized membranes exhibited a rapid clogging when contaminated with water vapor or any other hydrogen bonding molecules. Thus, the following post-reduction step should be employed to deactivate the membrane surface but extend the micropores further. The optimized CHFM presents 50,000 times higher in terms of CO_2 permeance and 41 times higher of CO_2/CH_4 selectivity compared to the original carbon membranes by the employment of a proper post-treatment, which is considered as a promising way to enhance carbon membrane separation performance. However, the production cost increases due to the extra treatments included.

2.3. Structural characterization of carbon membranes

As mentioned previously, the microstructure of CMS membranes is a typical bimodal pore model, which consists of micropores (~7-20 Å) and ultramicropores (<7 Å). Different techniques have been employed to characterize the structures and properties of carbon membranes. Membrane morphology is widely characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Moreover, different hybridized carbons (sp^2 and sp^3) existed in the carbon matrix can be revealed by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and electron energy loss spectroscopy (EELS).

Fig. 3a-c shows the SEM and TEM images of CMS membranes prepared from different precursors, which are usually used for determining the thickness of the selective layer of a CMS membrane. For example, Fig. 3a shows a typical cross-sectional SEM image of CHFM with a symmetrical morphology where the selective layer for gas separation is the whole wall of the hollow fiber. For a supported carbon membrane, the CMS layer is commonly fabricated on a porous inorganic material (e.g., ceramic or alumina support), as shown in Fig. 3b. The fine microstructure of carbon membranes can be determined using high-resolution TEM as shown in Fig. 3c, where a typical turbotrain carbon is presented in CMS membranes. If electron microscopy equipped with energy-dispersive X-ray spectroscopy (EDX), then the elemental composition of CMS membranes can be obtained. This could provide interfacial adhesion information between CMS membrane and support when applied to a supported CMS membrane. For example, SEM-EDX line scanning method to detect mechanical interlocking between the CMS layer and the TiO_2/Al_2O_3 composite support. The superimposed carbon signal that existed in the composite support indicated that carbon has penetrated the support, which can be used as the index of the depth of mechanical interlocking .

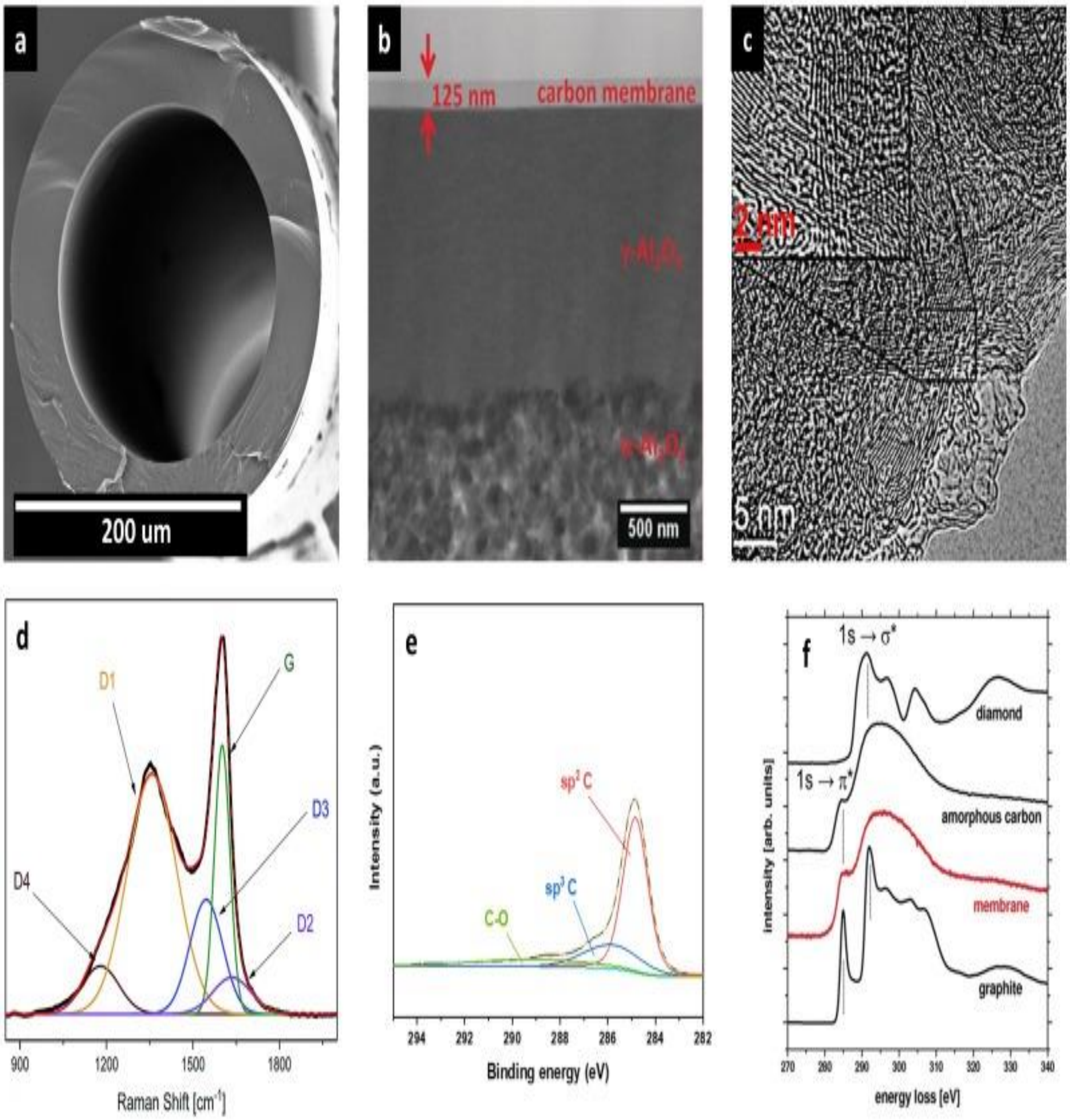


Fig. 3. Typical characterization methods for the analysis of CMS membranes.
a) SEM image of a self-supported hollow fiber CMS membrane
b) SEM image of a support carbon membrane
c) High-resolution TEM image of a CMS membrane d, e, and
f) Raman spectrum, C1s XPS spectrum, and EELS of carbon membranes

Raman spectroscopy can provide the ordered or disordered information within CMS membrane structures. In general, as shown in Fig. 3d, a G band (located at ~ 1600 cm^{-1}), and a D band (located at ~ 1380 cm^{-1}) can be observed for CMS membranes. The spectrum can be further deconvoluted into five bands: G, D1, D2, D3, and D4. The G band is assigned to the characteristic peak of the ideal graphitic vibration mode (E_{2g}-symmetry). The D1 band is the disordered graphite peak (graphene layer edges, A_{1g}-symmetry), while the D2 band corresponds to graphitic lattice vibrations mode with E_{2g}-symmetry but involving isolated graphene layers . When the D3 and D4 bands exist, the carbonaceous materials normally are highly disordered . Besides, hybridized carbon in the CMS membranes can be distinguished by the intensity ratio of D1 to D2. It was suggested that the sp^3 hybridization carbon defect occurs when the ratio is ~ 13, while vacancy like-defects dominated when ratio closes to 7 .

XPS can provide the surface elemental composition and chemical state of the elements for carbon membranes. By deconvolving the C1s XPS spectrum, it can provide the information of the chemical state of different carbons, like sp^2-hybridized carbon, sp^3-hybridized carbon, and C-N, C-O, and C = O bonds. The calculated ratio of sp^2/sp^3 can then be used as an indicator of the graphitization degree of the carbon . Fig. 3e shows a deconvolved C1s XPS spectrum of CMS membrane prepared from a PIM-1 precursor where sp^2-hybridized are mainly observed in the prepared membrane . The sp^2 and sp^3 carbons can be discerned by EELs . For carbon materials, the EELS of K-edge represent the electron transition from 1 s electronic core state to antibonding π* states (π * band) or to the antibonding σ* states (σ* band) . Specifically, the hybrid orbitals of sp^3 carbon do not possess π states, indicating that only one major feature edge at about 293 eV (σ* band) will be observed, whereas the EELS spectrum of sp^2 hybrid carbon exhibits two major features located at about 285 eV (π * band) and 295 eV (σ* band). Fig. 3f shows an EEL'S spectra of different carbon materials .

It is important to obtain the pore size distribution of CMS membranes as it directly determines the separation performances of CMS membranes. This is because the gas transport through CMS membranes relies on the combination of the selective surface flow mechanism happening in micropores (7–20 Å) and the molecular sieving mechanism happening in ultramicropores (<7 Å) . The micropores usually provide sorption sites for gas molecules, which results in a significant sorption selectivity for gas separations. Thus, the more condensable gas molecules, like CO_2, having a higher sorption capacity, which presents enhanced gas permeability and higher selectivity over less condensable gases. The ultramicropores, on the other hand, provide precise discrimination between similarly sized gas molecules (such as C_2H_4/C_2H_6), leading to an effective diffusion selectivity. As a result, the unique bimodal distribution of pores, combining micropores and ultramicropores, offers CMS membranes to achieve both high gas permeability and selectivity.

N_2 and CO_2 physisorption, and CO_2 high-pressure sorption are the common methods for determining the pore size distribution of CMS membranes. N_2 physisorption at 77 K can provide a pore size distribution of micropores, the limitation to using N_2 physisorption is that N_2 molecules (3.64 Å) are difficult to diffuse into the ultramicropores. For example, when a CMS membrane is prepared at a carbonization temperature of above 1000 °C, pore size distribution is not detectable by N_2 physisorption . To overcome this problem, the smaller molecule of CO_2 (3.3 Å) used as probe molecules conducted at 273 K is normally employed to analyze the ultramicropores and micropores. The bimodal pore size distribution was observed from CO_2 physisorption . The structure properties, such as micropore volume and average micropore width, can be also obtained by high-pressure CO_2 adsorption at 298 K .

2.4. Flat-sheet and tubular carbon membranes

Unsupported flat-sheet carbon membranes are widely prepared to investigate material properties such as sorption–diffusion properties and membrane morphology. Table 3 summaries the representative unsupported flat-sheet carbon membranes made from the respective precursors at specific carbonization conditions (CC) as well as the reported separation performances obtained at given testing conditions (TC).The sorption and diffusion coefficients of dense CMS films and found that membrane selectivity can be enhanced by increasing carbonization temperature while gas permeability reduces concomitantly. High CO_2 permeability of > 4000 barrier was obtained from a carbon-rich intrinsically microporous polyimide precursor (SBFDA-DMN) by making an ultra-selective CMS dense film . Moreover, dense CMS films with the surpass of the O_2/N_2 and H_2/N_2 Robeson upper bounds were prepared from the regenerated cellulose precursors , and the prepared CMS membranes exhibited good stability in the presence of 75 – 77% relative humidity at 25 °C. Although unsupported flat-sheet CMS membranes exhibit promising performance for gas separations, the brittleness and fragility have limited their wide potential applications where modules with large membrane surface areas are required, especially compared with supported carbon membranes or CHFMs.

Table 3. Representative unsupported flat-sheet carbon membranes for gas separation.

Precursors	**CC(Temp. (°C)/Purge gas)**	**TC(Temp. (°C)/feed pressure (bar))**	**Separation performance**						
			Permeability (barrer)				**Gas pair selectivity**		
			H_2(He)	**CO_2**	**O_2**	**CH_4**	**CO_2/CH_4**	**O_2/N_2**	**Others**
Cellulose	650/ vacuum	30/2	1300	480	130	4.4	109	8.7	H_2/CO_2 = 2.7
Cellulose	550/N_2	25/1	206	13.4	5.16	–	–	32.3	CO_2/N_2 = 83.8
Cellophane paper	550/N_2	29.5/2	168.1	17.0	4.87	0.17	100	11.3	H_2/CO_2 = 9.9
Matrimid®	550/Ar (1 ppm O_2)	30/3.4	(6 0 5)	1049	301	17	80.7	4.8	CO_2/He = 1.7
Polyimide	550/ N_2	35/--	–	428.2	377.6	23.9	17.9	4.2	–
6FDA/BPDA-DAM	550/Ar (1 ppm O_2)	30/3.4	(5 3 0)	7170	1530	247	29	7.5	CO_2/He = 13.5
6FDA/DETDA:DABA (3:2)	550/Ar	30/2	–	21,740	4293	723	30.1	4.9	–
6FDA/1,5-ND:ODA (1:1)	550/Ar	30/2	–	9791	2038	217	45.1	6.0	–
TB-PI	650/N_2	35/1	6552	4200	1092	68	62	9.3	H_2/CH_4 = 96
SBFDA-DMN	1000/N_2	35/2	(96)	30	7.5	0.02	1475	11	He/CO_2 = 3.3
PIM-6FDA-OH	800/N_2	35/10	–	512	–	–	88	–	–
PIM-6FDA-OH	800/N_2	35/2	2177	556	149	6	93	8.9	H_2/CO_2 = 3.9
PBI	900/N_2	150/11	54	–	–	0.68	–	–	H_2/CO_2 = 80

Supported CMS membranes manufactured on porous support (e.g., ceramic, stainless steel) exhibit strong mechanical strength. Different technologies such as dip coating , spin coating , spray coating and chemical vapor deposition (CVD) have been employed to coat polymeric precursor on top of support and followed by carbonization. These methods can reduce the thickness of the carbon membrane selective layer to provide higher gas permeance compared to unsupported dense carbon membranes.

2.5. Carbon hollow fiber membranes

The polymer precursors and prepared CHFMs displayed symmetric structure with a well-defined separation layer. The membrane carbonized at 900 °C presented the highest ideal selectivity for different gas pairs reported so far (e.g., $\alpha[CO_2/CH_4] = 3650$, $\alpha[H_2/CH_4] = 40350$). The enhanced CO_2/CH_4 selectivity at higher carbonization temperatures was caused by the simultaneously enhanced diffusion and sorption selectivity's . However, most of the reported symmetric carbon membranes presented relatively low gas permeability/permeance as shown in Table 5. Thus, recent research activities are focusing on the development of asymmetric CHFMs to improve gas permeance while maintaining a relatively good selectivity. Moreover, polyimide derived carbon membranes may provide a better potential for high-pressure natural gas sweetening with relatively high CO_2 permeance and comparable CO_2/CH_4 selectivity compared to cellulose-based carbon membranes.

Table 5. Representative symmetric CHFMs for gas separation.

Precursors	**CC(Temp. (°C)/Purge gas)**	**TC(Temp. (°C)/feed pressure (bar))**	**Separation performance**						
			Permeability(barrer)				**Selectivity**		
			H_2	**CO_2**	**O_2**	**CH_4**	**CO_2/CH_4**	**O_2/N_2**	**Others**
Cellulose	600/CO_2	25/2	–	239	68	1.3	186	10.9	–
Cellulose acetate	550/CO_2	30/2	–	346	87	–	–	7.9	CO_2/N_2= 31.5
Cellulose acetate	550/CO_2	30/2	–	410	63	4.0	102	6.9	CO_2/N_2= 44.6
Cellulose acetate	550/CO_2	30/2	637	268	71.5	4.1	65.5	7.4	H_2/CH_4=156
Matrimid®	900/Ar	35/6.9	266	24.1	0.14	0.0066	3650	21	H_2/CO_2=11
Matrimid®	750/Ar	35/6.9	1671	370	105	2.43	152	10	H_2/CO_2=4.5

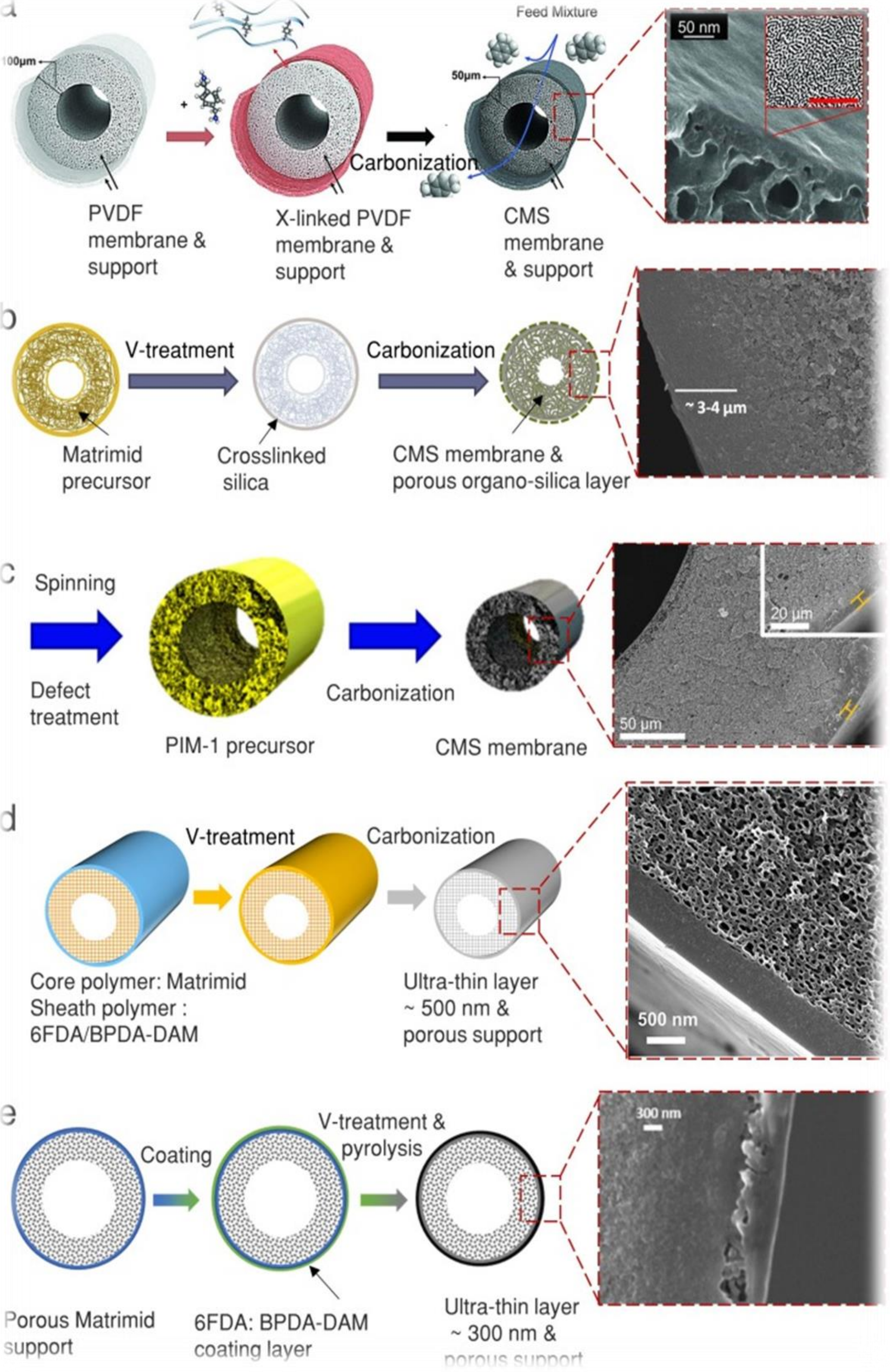
Precursors	**CC(Temp. (°C)/Purge gas)**	**TC(Temp. (°C)/feed pressure (bar))**	**Separation performance**						
			Permeability(barrer)				**Selectivity**		
			H_2	**CO_2**	**O_2**	**CH_4**	**CO_2/CH_4**	**O_2/N_2**	**Others**
PPO	650/vacuum	25/1	1900	544	126	5.36	101	9.8	H_2/CH_4=350
TMSPPO	650/vacuum	25/1	1314	216	56	1.82	118	11.6	H_2/CH_4=719
SPPO	700/N_2	90/1	2260	900	277	22	40	5.6	H_2/CH_4=101

Table 6 summaries the representative asymmetric CHFMs developed from different precursors and their performances for gas separations.

It can be seen that CO_2/CH_4 separation performance varies from 20 to 60 for the carbon membranes prepared from similar polyimide-based polymers, which is mainly due to the different precursor structure, carbonization condition as well as the testing condition reported in the literature. It is difficult to directly predict carbon membrane performance from polymer structure based on quantitative structure–property relationship (QSPR) modeling. However, increasing carbonization temperature can in general enhance both sorption and diffusion selectivity's because of the narrowed pathways. Moreover, the precursor with a relatively thinner selective layer will usually lead to the derived carbon membranes with higher CO_2 permeance. Therefore, the methodology based on the DPCOI platform may provide a guideline for systematic optimization of carbon membrane development and can be applied to different polymer precursors. Moreover, the asymmetric structures of precursors can be obtained by adjusting spinning conditions, but an extra pre-treatment step (often refers to cross-linking) is required to maintain asymmetric structure during carbonization. Preparation of asymmetric CHFMs from PVDF hollow fibers. To avoid pore collapse inside the membrane caused by the loss of storage modulus of PVDF precursor, a cross-linking method with a base treatment (NaOH + MeOH) and following a nucleophilic attack with *para*-xylylenediamine (see Fig. 4a) was used to form covalent bonds between PVDF chains. Compared to the neat PVDF hollow fibers, the cross-linked PVDF precursors maintained a high storage modulus at above 300 °C, and the asymmetric porous structure was well-kept after carbonization.

Table 6. Representative asymmetric CHFMs for gas separation.

Precursor	Thickness of skin layer (μm)	CC(Temp. (°C)/Purge gas)	TC(Temp. (°C)/feed pressure (bar))	Separation performance			
				Permeance(GPU)		Selectivity	
				CO_2	others	CO_2/CH_4	Others
Matrimid®	4–5	550/Ar	35/6.9	216		~30	–
Matrimid®	–	675/Ar	35/6.9	–	C_2H_4: 1.1	–	C_2H_4/C_2H_6=11.1
Matrimid®	3–4	550/Ar	35/3.4	164	–	55	–
6FDA: BPDA-DAM (1:1)	3–4	550/Ar	35/6.9	394		~26	–
6FDA: BPDA-DAM (1:1)	~10	675/Ar	-/3.4	–	H_2: 96.1	–	H_2/C_2H_4 = 249
6FDA/BPDA (1:1)-DAM	3	550/Ar	35/124	~100	–	~60	–
BTDA-TDI/MDI	–	900/Ar	60/-	0.42	O_2: 0.119 H_2: 6	49.4	O_2/N_2 = 11.9 H_2/CO_2 = 14.3
BTDA-TDI/MDI	2.4	800/N_2	25/2.1	1108	C_2H_4: 210	21	C_2H_4/C_2H_6=8.7
6FDA-DAM: DABA (3:2)	2.7	575/Ar	35/1	956	–	50.2	–
6FDA-DETDA: DABE	0.5	550/Ar	35/2	1000	–	25	–
6FDA: BPDA-DAM	0.3	675/Ar	35/3.4	310	–	58.8	–
6FDA/BPDA-DAM	0.5	550/Ar	35/6.9	2546	–	24	–
PIM-1	5	575/Ar	35/2	13.8	O_2: 2.9	96.8	O_2/N_2 = 9.8 C_2H_4/C_2H_6 = 7
PEI/PVP	–	650/N_2	RT/7	1.66	N_2: 0.04	55.3	CO_2/N_2 = 41.5


a
100µm
PVDF membrane & support
X-linked PVDF membrane & support
Carbonization
Feed Mixture
50µm
CMS membrane & support
50 nm
b
V-treatment
Carbonization
Matrimid precursor
Crosslinked silica
CMS membrane & porous organo-silica layer
~ 3-4 µm
c
Spinning
Defect treatment
PIM-1 precursor
Carbonization
CMS membrane
20 µm
50 µm
d
V-treatment
Carbonization
Core polymer: Matrimid
Sheath polymer : 6FDA/BPDA-DAM
Ultra-thin layer ~ 500 nm & porous support
500 nm
e
Coating
V-treatment & pyrolysis
Porous Matrimid support
6FDA: BPDA-DAM coating layer
Ultra-thin layer ~ 300 nm & porous support
300 nm

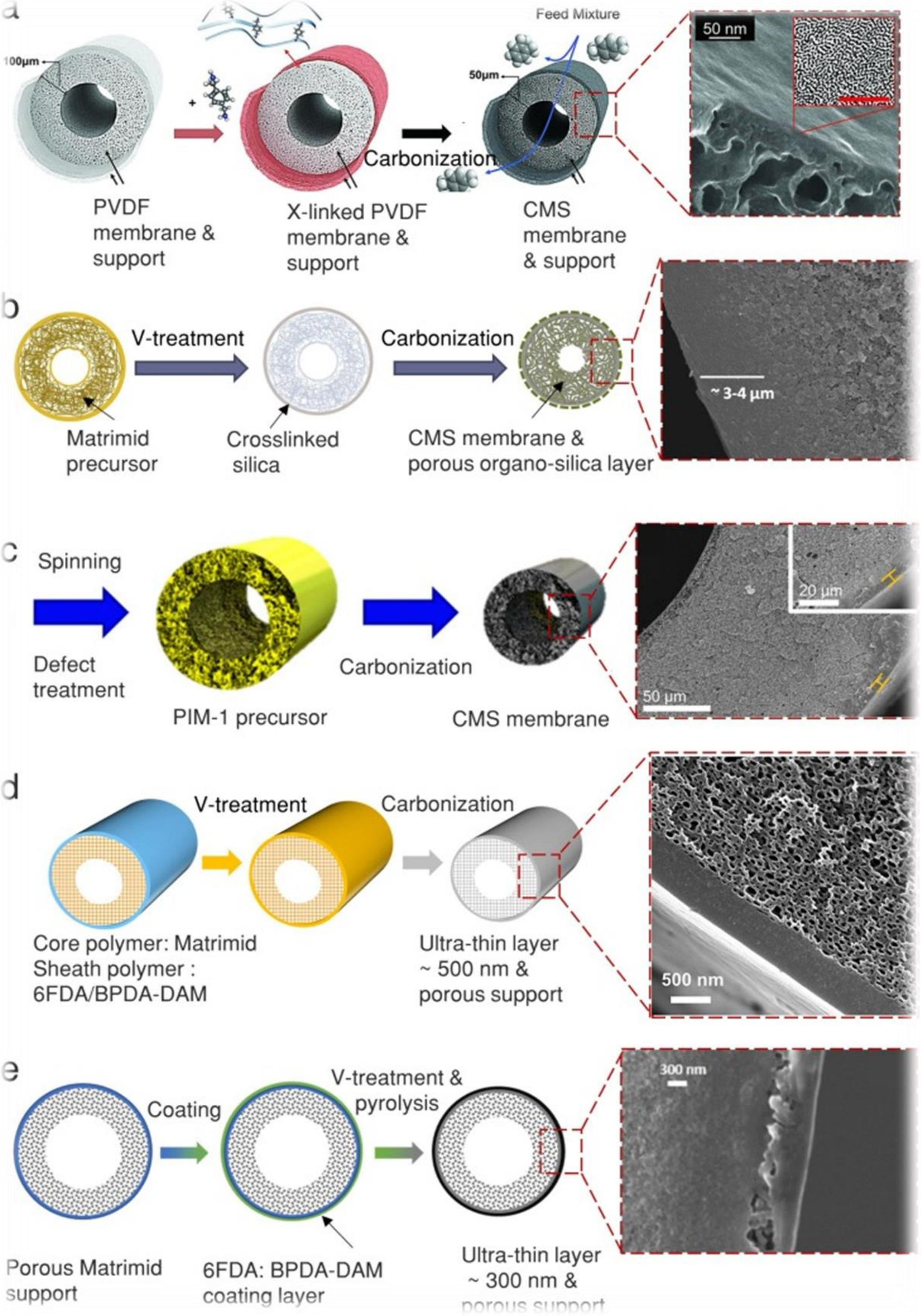

a
100µm
PVDF membrane & support
X-linked PVDF membrane & support
Feed Mixture
50µm
Carbonization
CMS membrane & support
50 nm
b
V-treatment
Carbonization
Matrimid precursor
Crosslinked silica
CMS membrane & porous organo-silica layer
~ 3-4 µm
c
Spinning
Defect treatment
PIM-1 precursor
Carbonization
CMS membrane
20 µm
50 µm
d
V-treatment
Carbonization
Core polymer: Matrimid
Sheath polymer : 6FDA/BPDA-DAM
Ultra-thin layer ~ 500 nm & porous support
500 nm
e
Coating
V-treatment & pyrolysis
Porous Matrimid support
6FDA: BPDA-DAM coating layer
Ultra-thin layer ~ 300 nm & porous support
300 nm

Fig. 4. Formation of asymmetrical CHFMs. a) base-treated crosslinking method to fabricate asymmetric CHFMs
b) schematic representation of V-treatment process in the overall asymmetric polyimide-based CHFM formation
c) asymmetric CHFMs were formed directly without cross-linking or other pretreatments
d) Formation of ultra-thin CHFMs by dual-layer spinning , and
e) dip-coating to create multi-layer asymmetric CHFMs .

A V-treatment method was used to restrict morphology shrinking of asymmetric hollow fiber membranes carbonization which can avoid a chemical reaction between polymer precursors and agents as the cross-linking reaction happens between organic-alkoxy silane (vinyltrimethoxysilane, VTMS) and moisture at room temperature. As shown in Fig. 4b, the cross-linked layer provides the reinforced sheaths on the "struts" and thus restricting substructure collapse during carbonization. Benefiting from the reduced skin layer, the gas permeance of asymmetric CHFMs was improved 4 times comparing to non-treated membranes while CO_2/CH_4 selectivity only slightly decreased . However, the associated crosslinking steps may account for ~40% cost increment of the overall membrane fabrication process . Thus, the development of CHFMs without extra treatments can reduce the production cost towards a more sustainable process for carbon membrane fabrication. Recently, asymmetric CHFMs were directly prepared from PIM-1 precursors without cross-linking or other pretreatments (see Fig. 4c) . The colocation of polymer glass transition and decomposition temperature can maintain asymmetric structure without significant changes in storage modulus during carbonization .

It should be noted that most of CHFMs reported so far still present a relatively thick selective layer (e.g., >3 μm), which restricts to reach very high gas permeance. Further reducing carbon membrane thickness can provide significantly enhanced gas permeance, and thus reduce the required membrane area for a specific application. A dual-layer precursor spinning process by co-extruding a sheath polymer dope and a core polymer dope from a multichannel spinneret , as illustrated in Fig. 4d. The dual-layer structure of precursor was well maintained after V-treatment and carbonization to obtain CHFMs with ultra-thin skin layers (~500 nm). The dual-layer precursors comprise different sheath and core layer polymers can also reduce the cost of polymer materials. Moreover, a composite precursor made by spin coating of an expensive dense skin layer on top of cheap porous support can reduce the material cost of a 25-fold compared to monolithic precursors , and the asymmetric carbon membranes with 300 nm thin layer prepared from the composite precursors (see Fig. 4e) provide excellent performance.

Although different methods have been reported to make asymmetric CHFMs, most of them need complex pre-treatment (e.g., cross-linking) to prevent pore collapse, which increases the carbon membrane production cost. Besides, fabrication of ultra-thin selective layer CHFMs normally requires more complicated precursor preparation, such as co-spinning of sheath and core polymer dopes, a combination of spinning and dip-coating. This may limit the production of carbon membranes in large-scale applications. Thus, making asymmetric CHFMs without costly pre-treatment should be pursued towards the green advances of carbon membrane development. Moreover, carbon membranes preparation in a continuous process needs to be addressed to further reduce production costs.

2.6. Carbon membrane upscaling

When membrane materials are going to be produced at a large scale, using renewable materials (e.g., cellulose) as precursors have an important advantage to secure a steady and reliable supply chain of raw materials. The general challenge for batch-wise production is to obtain equal conditions for each precursor inside a chamber or container. Hollow fibers were in contact with each other during carbonization and fused together at higher temperatures. While cellulose hollow fibers are less prone to fusing, and a large quantity of cellulose precursors can be carbonized in the same batch. 1600–4000 regenerated cellulose hollow fibers were carbonized simultaneously by using 2 m-long perforated plates with square openings. However, they also reported that it is crucial to drain the tars and vapors by setting an angle (e.g., 6°) between support and furnace during the carbonization of a large bundle of fibers. It should be noted that continuous fabrication may be pursued for the commercialization of carbon membranes in the future. Another challenge on carbon membranes up-scaling is related to module design and construction, typically CHFMs mounting, potting and sealing for high temperature/pressure applications. A suitable potting material (e.g., epoxy resin) that easily penetrates a bundle of fibers at a high module packing density should be identified. Module upscaling of cellulose-based carbon membrane to m^2 surface area with thousands of CHFMs bonding together to move towards a higher technology readiness level (TRL). However, there are still challenges related to further development and upscaling of CA-based carbon membranes due to

1) the high production cost with the extra cellulose regeneration step involved.
2) the difficulty of keeping fibers straight during fiber drying after CA deacetylation.

Recently, development of CHFMs directly from cellulose precursors may address some of these challenges . For supported carbon membranes demonstrated a membrane module consisting of tubular carbon membranes with a surface area of 0.76 m^2 and a packing density of 222 m^2/m^3. A bundle of supports was fabricated beforehand the application of carbon layers via dip-coating and carbonization. It is expected that large-scale production of supported carbon membranes will be challenging, and production cost is still quite high, which may limit the applications only in small-volume gas separation processes.

2. Carbon membrane applications for CO_2 removal

Membrane technology for gas separation is considered a green process with respect to decreasing production costs, footprint, energy consumption, and improving process flexibility . Carbon membranes with high separation performance under high-pressure and/or high-temperature conditions provide a significant green advance when applied to the integration of CO_2 capture with low-carbon or renewable energies (e.g., H_2 purification from syngas, biogas upgrading, and natural gas sweetening). Permeability and selectivity (separation factor) are commonly used to describe the membrane separation performances, which influences the productivity and separation efficiency of a membrane separation process. Generally, gas permeability (P_i) is described as the product of diffusion coefficient (D_i) and solubility coefficient (S_i): Pi=Di×Si. Accordingly, the gas pair selectivity is expressed by. αi/j=Di/DjSi/Sj The diffusion coefficient is a kinetic factor that characterizes the ability of gas molecules to penetrate through the membrane. It depends on the size and shape of the penetrated gas molecules and the critical ultramicropores dimensions . For highly adsorbing gases like CO_2, a thermodynamically corrected concentration-independent diffusion coefficient is used, refers to Maxwell-Stefan diffusivity. On the other hand, the solubility coefficient is a thermodynamic factor that determining the amount of absorbed gas by a membrane at a given temperature and pressure. Thus, for a CMS membrane-based separation process, gas permeability is significantly dependent on operating temperature. The kinetic diffusion coefficient is enhanced by rising operating temperature following the Arrhenius relationship, while the thermodynamic sorption coefficient is inhibited concomitantly. It should be noted that module design and process operating parameters will also significantly influence the process performance of carbon membrane systems besides the material property itself (i.e., ideal selectivity and gas permeability) which is usually characterized by single gas permeation testing.

3.1. Carbon membranes for hydrogen purification from syngas

Hydrogen production from natural gas through combined steam methane reforming and water–gas shift (WGS) process is considered as one of the most promising technologies for the implementation of a hydrogen economy for a low-carbon energy future, the reduction of greenhouse gas emissions and the increased demand of sustainable energy. However, the produced hydrogen stream usually contains a significant amount of CO_2 that needs to be removed to obtain high purity hydrogen (for fuels or feedstocks in the petrochemical industry). Purification of hydrogen from this gas stream requires novel separation technologies to improve energy efficiency as it consumes ca. 60% of the total energy required in the whole hydrogen production process. The state-of-the-art pre-combustion CO_2 capture technologies of pressure swing adsorption (PSA) and cryogenic distillation are energy-intensive, while membrane gas separation technology exhibits a great potential for this application. Different types of membranes such as palladium, polymeric, mixed matrix and carbon membranes have been investigated for H_2/CO_2 separation. Among them, great effort has been devoted to developing palladium-based membranes for H_2 purification . However, the cost of palladium membranes is still high, which cannot yet compete with PSA. The polymeric and mixed matrix membranes have the challenges to achieve a high H_2 purity (e.g., >99%) due to the low H_2/CO_2 selectivity (usually < 10) .

Carbon membranes have great advantages of high mechanical and chemical stabilities, and high separation performance that can exceed the Robeson upper bound 2008 for H_2/CO_2 separation , which can reach the industrially attractive region for this application . The technology feasibility of carbon membranes (with H_2/CO_2 selectivity of 40) for purification of hydrogen from a gas stream containing 35 mol.% CO_2/65 mol.% H_2 has been documented by He , and the cost was theoretically evaluated to $1/kg H_2 produced at a feed pressure of 20 bar. Developing higher performance carbon membranes can further bring down the purification cost. Recently, CMS membranes for H_2/CO_2 separation at high temperatures and the membrane performances were found to be enhanced compared to the state-of-the-art organic and inorganic membranes for H_2/CO_2 separation (seeTable 6). The CMS membranes exhibit present competitive performance with relatively good H_2/CO_2 selectivity and H_2 permeance compared to other high-performance inorganic membranes. In general, the higher operating temperatures will be favorable to enhance H_2/CO_2 separation performance especially H_2 permeance, which is typically suitable for hydrogen purification in the steam methane reforming process.

Table 6. Comparison of carbon membranes with polymeric and other inorganic membranes for H_2/CO_2 separation. The membrane thickness was assumed to be 3 µm when converting the permeability (barrer) to permeance (GPU).

Membrane materials	**Performance**		**Test conditions**		
	H_2 permeance (GPU)	αH2/CO2	**Type of analysis**	**Temperature(°C)**	**Feed pressure (bar)**
PBI	0.53	132.8	Single gas	150	14
POF	24.2	39.5	Mixed gas	150	2
MOF JUC-150	452.4	30.2	Mixed gas	200	1

Membrane materials	**Performance**		**Test conditions**		
	H_2 permeance (GPU)	αH2/CO2	**Type of analysis**	**Temperature(°C)**	**Feed pressure (bar)**
Al_2O_3/SAPO-34	214.7	23.0	Mixed gas	200	3.5
ZIF-8/ZIF-9@P84	250	9.6	Mixed gas	150	–
ZIF-90	739.2	7.3	Single gas	200	1
GO	30	30	Single gas	140	1
MoS_2	240	8.5	Mixed gas	160	1
CMS	118.4	14.5	Single gas	150	–
CMS	3250	24	Single gas	200	2
CMS	1827.5	8	Single gas	150	1

Moreover, one membrane module consisting of tubular carbon membranes with a surface area of 0.76 m^2 and a packing density of 222 m^2 m^{-3} was field-tested for hydrogen recovering from raw coal-delivered and biomass-delivered syngas with stable performance over 500 h. The integration of carbon membranes to water–gas shifting (WGS) reaction (a membrane reactor) was reported to improve CO conversion . Those carbon membranes showed high stability against H_2S, NH_3 and other contaminants in syngas compared to palladium membranes . Moreover, by combining both H_2-selective and CO_2 selective carbon membranes, a two-stage membrane system (the first stage H_2-selective CMSMs and the second stage selective surface flow carbon membranes (SSFCMs)) can be designed for integration of CO_2 capture and H_2 purification as shown in Fig. 5. This process is expected to achieve at least 20% of cost reduction compared to the state-of-the-art technologies for hydrogen purification in a steam methane reforming plant. The produced high purity H_2 (>99%) from the 2nd-stage retentate is particularly interested as H_2 resource for downstream petrochemical industries and/or catalytic conversion to chemicals or fuels (not for fuel cells where ultrapure H_2 (99.999 mol.%) is usually required). However, experimental validation at a pilot-scale should be conducted in the future work to prove the technology advance and potentially expand hydrogen economy.

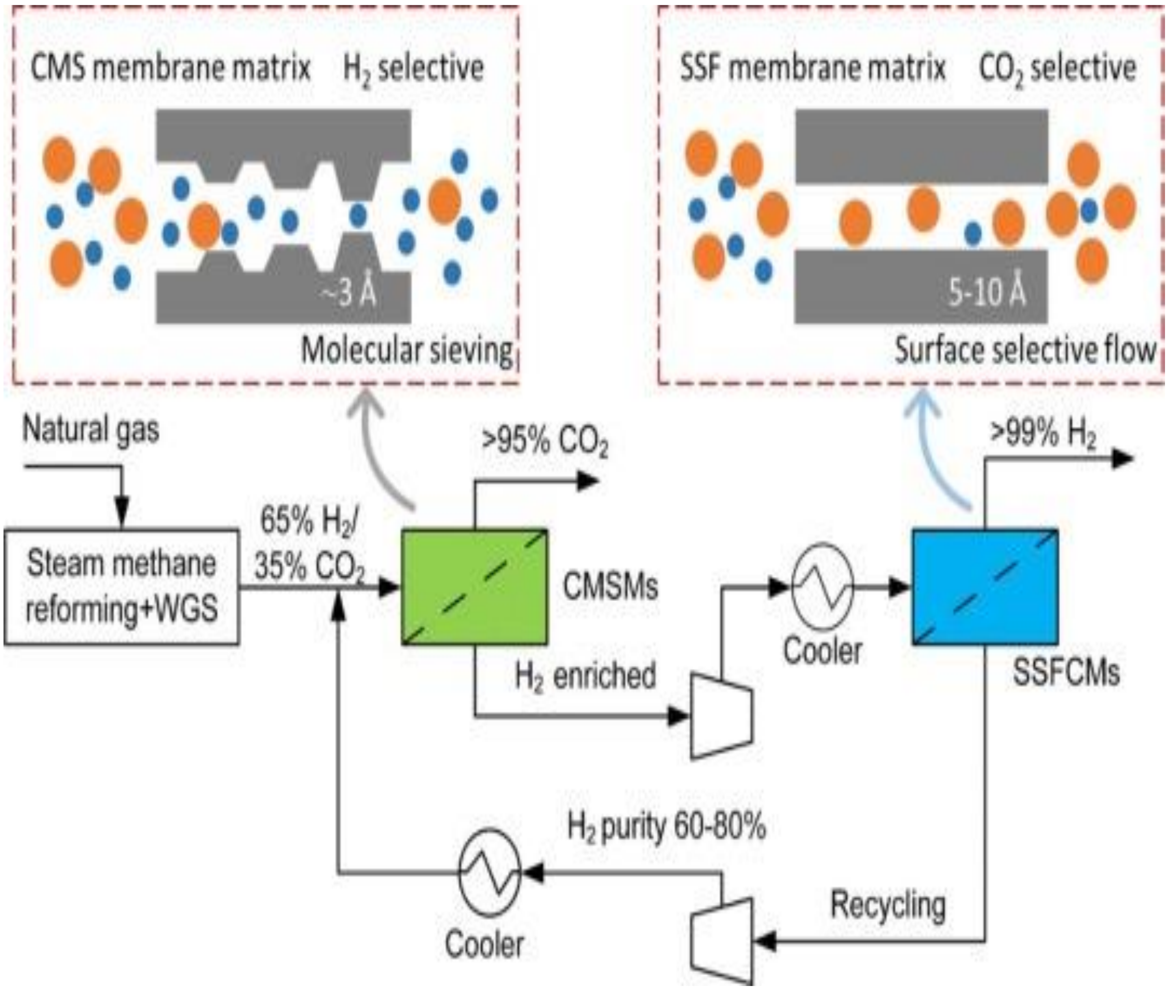


Fig. 5. The concept of a two-stage carbon membrane system for integrated CO_2 removal and H_2 purification. CMSMs (H_2-selective membranes) used in the first stage will capture CO_2, and the SSFCMs (CO_2-selective membranes) in the second stage can produce high purity H_2 (>99 mol.%) at a high H_2 recovery (>90%) with permeate recycling back to the first stage.

3.2. Carbon membranes for CO_2 capture from flue gas

In addition to H_2 purification and pre-combustion CO_2 capture as discussed in section 3.1, post-combustion CO_2 capture, which can be retrofitted to existing power plants, presents the closest marketable technology for contributing to the reduction of CO_2 emissions . The major challenges for CO_2 capture from flue gas are the low feed pressure (~1 bar), the low CO_2 concentration (usually < 20%), and the requirement of large gas volume to be processed . Besides, the discrimination of gas molecules with similar sizes like CO_2, O_2, and N_2, is another obstacle for archiving a high-efficient separation. The state-of-the-art technology for post-combustion carbon capture is amine-based absorption that occupies>90% of the market . However, the high energy demands for absorbent regeneration directs to seek for alternative technologies. Membranes-based separation processes have shown promising advantages beyond amine absorption due to their low energy consumption, small footprint, and easy scale-up , Various membrane materials have been developed for the application in post-combustion carbon capture, such as fixed-site-carrier membranes , and mixed matrix membranes . Some commercial membranes have been tested in power plants for the post-combustion CO_2 capture, such as PRISM™ from Air Products and Polaris™ from MTR Inc.

CMS membranes have been considered for post-combustion CO_2 capture due to their high separation performance of CO_2/N_2 that can surpass the Robeson upper limit. A fluorinated CMS membrane with high CO_2 permeability of 2140 barrer and CO_2/N_2 selectivity of 36 in pure gas test . When tested in a mixture of 15 mol.% CO_2-85 mol. % N_2, the membranes showed a slightly increased CO_2 permeability of 3712 barrer and CO_2/N_2 selectivity of 27, Besides, a retained CO_2 permeability and slightly reduced CO_2/N_2 selectivity under high relative humidity (~90%) testing within a CO_2/N_2 50/50 mol.% mixed gas indicated that the membrane can endure the situation of water vapor that normally presented in flue gas streams, which presents a great potential for CO_2 removal from flue gas . However, the reported CMS membrane is such thick with a symmetric structure of 75 µm selective layer that the low CO_2 permeance (e.g., ~ 50 GPU) was recorded.

Another major obstacle of CMS membranes used for CO_2 capture from flue gas is the performance deterioration caused by species sorption on the carbon matrix. CMS membranes prepared from deacetylated cellulose acetate have been systematically investigated for CO_2 capture from flue gas . A long-term aging test over ~ 7 months where the membrane module was exposed to the laboratory air without any protection showed the gas permeabilities of the fabricated CHFMs dropped by ~ 55% within the first 2 months, and afterward slightly reduced . When a membrane module was exposed to a real flue gas containing 12.4% CO_2/4.5% O_2/70.1% N_2 /13% H_2O (also impurities of 89 mg Nm^{-3} SO_2, and 246 mg m^{-3} NO_x) for 3 weeks, it was found that the permeance of the CMS membranes decreased about 40%, which was caused by pore blocking with physisorption and/or chemisorption of water vapor and oxygen .

Capturing CO_2 from flue gas using a hybrid process of membrane /cryogenic distillation under sub-ambient operating temperature (e.g., below − 20 °C) has documented a cost-effective process as reported by Air Liquide . This strategy provides a highly effective CMS membranes-based separation process for post-combustion carbon capture because reducing operating temperature can dramatically improve CO_2/N_2 selectivity. Recently, Joglekar et al. reported that a CHFM presented 4.5 times higher CO_2/N_2 selectivity at − 20 °C than tested at 35 °C (increasing from 29 to 109), whereas only ~ 33% loss in CO_2 permeance was observed (dropped from 160 to 108 GPU) . The significant improved CO_2/N_2 selectivity can thus reduce the module productivity, and therefore may offset the increased membrane area due to the reduction on gas permeance and the cooling loading.

Although good CO_2/N_2 selectivity has been reported, the application of CMS membranes for post-combustion carbon capture is however still challenging:

(1) the CO_2 permeance is relatively lower compared to many polymeric materials, which requires larger membrane area to achieve a given CO_2 capture ratio.

(2) most of CMS membranes are sensitive to water vapor that normally exists in flue gas stream.

(3) the frangibility of CMS membranes.

To address this challenge, the development of ultra-thin supported CMS membranes with highly hydrophobic membranes may be considered. For example, cellulose-based CMS membranes and fluorinated CMS membranes have shown good stabilities under > 85% RH conditions.

3.3. Carbon membranes for biogas upgrading

Biogas is a renewable energy source that can be produced in a controlled manner by microbial digestion of biomass (agricultural waste, manure, municipal waste, sewage, food waste, etc.) in the absence of O_2 . The major components are CH_4, CO_2, H_2O together with traces of H_2S and some other gases. The state-of-the-art technology for separation of CO_2 from biogas in European region is water scrubbing, pressure swing adsorption (PSA), chemical absorption (e.g., amines) . Although gas separation membranes have only 4% of the market today , the advantages of green, energy-saving, space-saving, easy to scale-up stimulate its further development on new membrane materials and processes for CO_2-CH_4 separation. The choice of suitable separation technology is mainly dependent on the specific condition at a plant, such as the availability of low-price thermal energy, electricity, and water, as well as the amount of gas to be handled. Fig. 6 shows the comparison of the key performance indicators (KPIs) such as power consumption, footprint, CH_4 purity, CH_4 loss, and process flexibility of different technologies for biogas upgrading with respect to green and sustainable solutions.

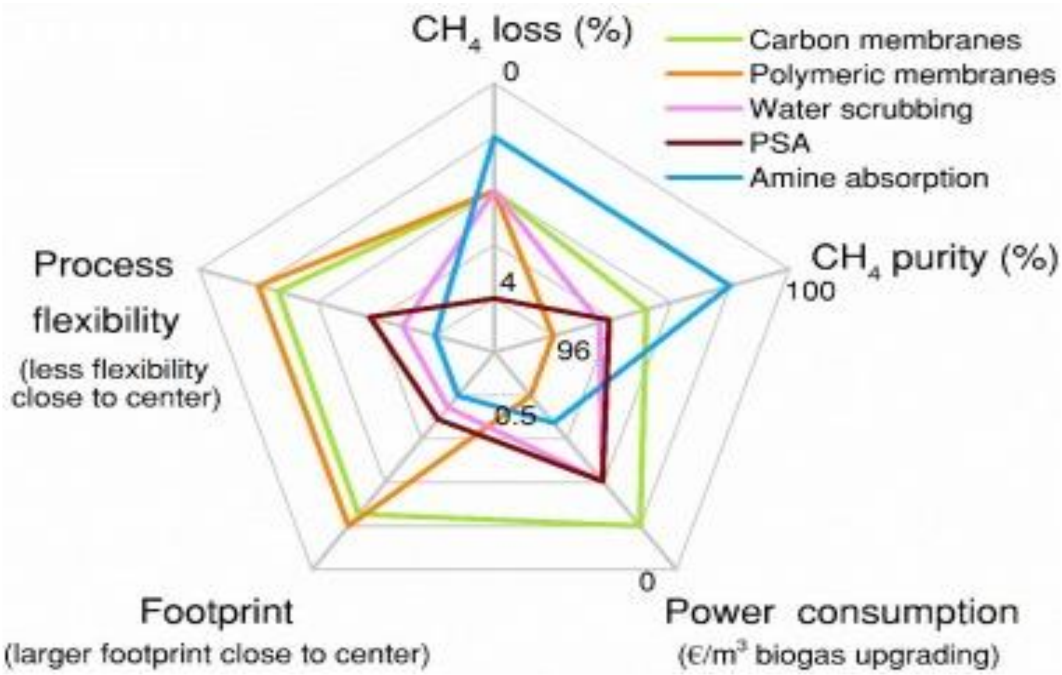


Fig. 6. Comparison of the KPIs of carbon membranes with other technologies for biogas upgrading. A larger area implies a better performance. Part of data are taken from references .

Membranes show good process flexibility and smaller footprint compared to other separation methods, but the main challenge of a polymeric membrane system for biogas upgrading is to simultaneously obtain a high CH_4 purity and a low CH_4 loss (also power consumption). It should be noted that a high CH_4 loss is negatively related to the economy and greenhouse gas performance. By using a multi-stage membrane system can reach high purity methane, but energy consumption will then be higher. Thus, the development of highly CO_2/CH_4 selective membranes is crucial to expand the applications of membranes for biogas upgrading. The trade-off between permeability and selectivity of commercially polymeric membranes (e.g., SEPURAN®, Carborex®, Prism®) directs to the development of alternative CMS membranes for biogas upgrading. Since CMS membrane separation is based on the molecular size difference, and pore structure can be tailored to achieve a high selectivity of specific gas pairs, it provides an overall technology advance (especially low power consumption as a high membrane selectivity can significantly reduce the operating cost to achieve specific separation requirement). However, the challenge up to now has been the sufficiently high CO_2 permeance to bring down capital cost and upscaling of modules.

In general, the composition and quality of biogas vary a lot, and are highly dependent on the source or substrate on which the bacteria are fed. Customizations/adaptations are usually required for each individual plant. On top of that, the intended use of upgraded biomethane may also put constraints on an upgrading process. Similarly, local or global legislations on methane emissions in the slip (rejected stream or permeate) may add to the complexity of the biogas plant. A small-scale carbon membrane system for biomethane production in the Southern part of Norway was conducted by MemfoACT (the company closed in 2014), and the intended use of biomethane is vehicle fuels complying to the Swedish biomethane standard that requires the methane content of 96–98 mol.% and specifies the allowable water content (<32 mg Nm^{-3}) and H_2S content (23 ppm) in the gas product. Several tests of stability and durability have previously been conducted with modules containing up to 2000 fibers at varying feeds reported , and no change after 16 days (10 bar feed, 1 bar on permeate side) was found regarding the testing of one module with a 5.5% CO_2 and balance CH_4 at a rate of 1 Ndm^3/h. However, by adding 1000 ppm n-heptane, the CO_2 permeance reduced 23% at the same operating condition. The effect of relative humidity and sulfur loading was also tested in a large 30-fiber module (30 cm long) exposed (dynamically) to biogas over 6 months. This was done on-site using the very same biogas source and only with limited pretreatment consisting of water knockout using a heat exchanger (dewpoint ca 10 °C), H_2S adsorption in activated carbon granulates (two 4 L tanks in parallel but no warning system for H_2S breakthrough) and particle removal (2 µm nominal size). The results of this pre-study showed a 60% drop in CO_2 permeance and a quadrupling of the CO_2/CH_4 selectivity. Thus, proper pre-treatments such as the removal of water vapor or H_2S from the gas stream might be necessary to keep high performance and a longer lifetime of carbon membranes in the real applications. Moreover, several modules of the same type as above were exposed to real biogas (63 mol.% CH_4, 1 ppm H_2S, balance CO_2), and tested with a 10 $Nm^3\ h^{-1}$ of biogas at 15–20 °C and 20 bar feed pressure . After 200 days in operation, the CO_2 permeance was reduced by 30%. They reported that the single-stage pilot system can reach a methane purity of 96 mol.% at a high methane recovery of > 98% . It was worth noting that a significant performance increase (10 to 15%) by letting the gravity pull the CO_2 out of the bore (i.e., permeate outlet pointing downwards was significantly better).

However, the challenges of getting a high mass transfer coefficient and increasing effective membrane area should be addressed due to the manually sorted and randomly packed CHFMs. Moreover, they also pointed out bore-side feeding configuration may provide a better overall module performance .

In order to evaluate the techno-economic feasibility of carbon membrane for biogas upgrading, a two-stage carbon membrane system was designed to achieve high methane purity of > 96 mol.% from biogas containing 35 mol.% CO_2/65 mol.% CH_4 . Moreover, Haider et al. conducted the comparison of carbon membranes with polyimide-based membranes for biogas upgrading based on their pilot testing results , and they found that two-stage polyimide membrane system is not commercially viable for biogas upgrading due to high recycle ratio, and carbon membrane system presented a 22% energy reduction compared to a three-stage polyimide membrane system, which is very promising for this application. The membrane production cost at a semi-industrial production plant based on CMS membranes from regenerated cellulose was estimated at about \$100 m^{-2}. The MemfoACT cost estimations of a large-scale production facility (24–7 operation) the cost of \$100 per m^2 was reasonable (the production would easily be profitable for the company if the selling prize was in the range of \$100 per m^2). The current preparation of CMS membranes directly from cellulose contains the majority of the same procedures part from the two steps: 1) direct spinning from cellulose requires more costly solvent (ionic liquid), that would need to be recovered and reused in large-scale production; 2) there would be no need to deacetylate the cellulose acetate used by the previous company so those chemicals and handling efforts would be saved.

It is then estimated that these added costs and saved costs would cancel out and hence an estimation of \$100 per m^2 cost would still be acceptable. However, due to the decrease of membrane effective area, the membrane cost doubled for a biogas pilot plant, which ultimately increased the total capital cost of further upscaling of the plant. Thus, the site owner chose to build their full-scale plant based on water scrubbing technology, and the pilot carbon membrane system developed by the previous company MemfoACT was sadly obsolete . However, a biogas processing cost of 0.078 \$/m^3 at the feed pressure of

8.5 bar in a 1000 m^3(STP) h^{-1} biogas plant was evaluated by He, which is lower compared to 0.15 € m^{-3} of amine absorption if carbon membrane cost of 50 \$ m^{-2} can be achieved. Therefore, carbon membranes show great potential for biogas upgrading if the membrane material cost at a large-scale production can be reduced.

3.4. Carbon membranes for natural gas sweetening

Though raw natural gas varies in composition from different sources, the major impurity of CO_2 should be removed before natural gas is transported to the pipeline network . Amine absorption is the most used technology for CO_2 removal from natural gas, but it faces high capital and operating cost, complex operation process, and environmental pollutions . A membrane system is a potential alternative for CO_2 removal in offshore or remote regions where small footprint, flexibility, low capital and operating costs are highly desirable. A comprehensive review on the comparison of membrane technology with conventional methods for CO_2 removal from natural gas. It was suggested that membrane technology was economically superior . The commercial polymeric membranes such as cellulose acetate, polyimide, and perfluoro membranes have been used for natural gas sweetening . However, polymeric membranes suffer the loss of selectivity induced by membrane compaction and plasticization when exposed to high-pressure of 60–90 bar. CMS membranes with rigid structure can provide a good compact- and plasticization-resistance, and thus are good candidates for CO_2 removal from high-pressure natural gas. Fig. 7 summaries the performances of carbon membranes for CO_2/CH_4 separation, which clearly exhibits better performances in both selectivity and permeability compared to typical commercial membranes.

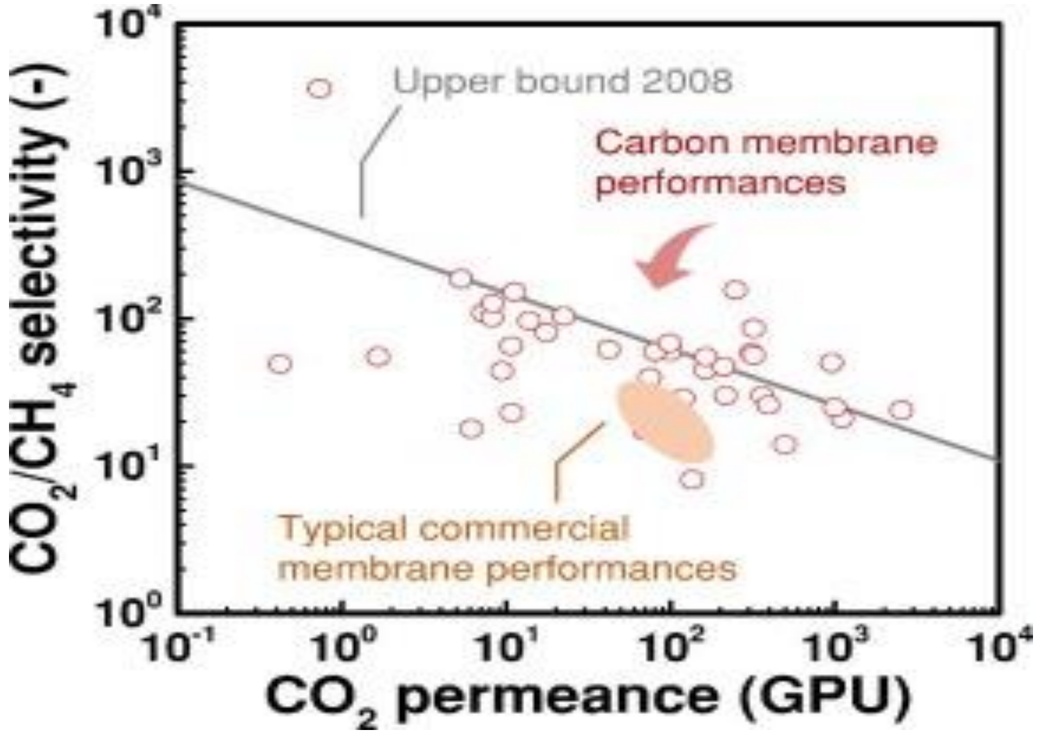


Fig. 7. The CO_2/CH_4 separation performances of different carbon membranes (Data are taken from Table 3, Table 4, Table 5, Table 6). The excellent separation performance is converted to permeance (GPU) based on the reported thickness. Gray line represents the 2008 Robeson upper bound based on 1 μm selective layer

The CO_2/CH_4 separation performance of CMS membranes derived from PIM precursors (PIM-6FDA-OH) under the testing pressure up to 30 bar . They found that CO_2/CH_4 selectivity and CO_2 permeability deteriorated in the mixed gas measurement, while CH_4 permeability increased with feed pressure. Recently, the developed polyimide-derived CHFMs were tested with supercritical natural gas (1800 psia [124 bar]) at different feed compositions (including the impurities of high hydrocarbons such as toluene and n-heptane). The separation factors for each scenario were almost the same as 50–60 within the tested feed pressure range . The CHFMs also presented stable separation factors when exposed to hydrocarbon impurities while CO_2 permeance reduced with the increase of impurity concentration. The decreased CO_2 permeances were caused by the competitive sorption behavior happening inside of the micropores of carbon membranes where heavy hydrocarbons reduce sorption sites for CO_2 and CH_4.

With attractive and stable separation performance at aggressive feed conditions, the developed CHFMs showed great potential for CO_2 removal from natural gas.

In order to develop an energy-efficient and cost-effective carbon membrane process for CO_2 removal from natural gas, process design and operating parameter optimization are also crucial besides the development of advanced membrane materials. A two-stage CMS membrane system with different CO_2 concentrations in feed gas was investigated to achieve the separation requirements . Based on HYSYS simulation, they found that the cost for a specific natural gas sweetening process was significantly affected by membrane performance, especially CO_2/CH_4 selectivity. Moreover, the 2nd-stage permeate pressure will have a great influence on the cost when the feed CO_2 content is higher. Membrane model to simulate CO_2 removal from natural gas by hollow fiber membranes, which enables to predict the flow rate, concentration and pressure profiles along hollow fiber length in both feed and permeate sides. The modeling results indicated that total pressure drop along module length can be ignored if the inner diameter of CHFMs (with total 0.6 m) is>200 μm, and extremely high packing density can lead to a significant pressure drop in shell side. Moreover, it was also found that the required membrane area and methane loss increased with the increase of CO_2 content in the feed gas, while feed pressure showed an opposite effect.

It should be noted that achieving high purity products is still challenging using commercial membranes in the real natural gas sweetening since those polymeric membranes suffer low selectivity at high-pressure operation. While the higher purity gas obtained in an amine process is paid by high capital investment and a potentially harmful environmental process. Thus, the development of advanced CMS membranes with excellent separation performance (high CO_2/CH_4 selectivity) not only provides an environmentally friendly process but also offers a membrane process to reach the high purity requirement. Haider et al. reported the pilot-scale testing of carbon membrane modules at high pressures (50 bar) for the potential application of natural gas sweetening . The separation performance was basically maintained at higher pressures, which shows an extraordinary advantage of carbon membranes for high-pressure CO_2/CH_4 separation. Moreover, the reported carbon membranes showed no signs of CO_2 plasticization which has been a drawback for most polymeric membranes.

Therefore, carbon membranes with rigid structures are promising for CO_2 removal from high-pressure natural gas.

4. Future perspectives

This review highlights the status of carbon membrane development with respect to precursor selection and preparation, tuning carbon membrane structure, membrane up-scaling and their potential applications as a green and environmentally friendly technology for CO_2 removal. Both self-supported and ceramic-supported carbon membranes in flat-sheet and hollow fiber configurations show the potentials for selected gas separations. The most promising precursors of polyimide and cellulose are identified to balance production cost and separation performance. Even though the current carbon membranes present good performances for CO_2/CH_4, CO_2/N_2, and H_2/CO_2 separations, none of them have been successfully brought to the market at an industrial scale. A sustainable process from precursors to carbon membranes should be pursued and making asymmetric CHFMs without costly pre-treatment needs to be focused on the technology advances of carbon membrane development. A potential commercialization CMS membrane for separation process basically requires that

1) the membrane retains high separation performance, robust endurability under harsh conditions, and good mechanical strength.
2) the membrane production process is easily scaled up with acceptable cost.
3) constructed membrane module adapts to different scenarios.

Although the fabrication of carbon membranes is more complicated compared to polymeric membranes as a separate process of carbonization is implemented, however, the more means that can be applied during carbonization provide more ways to enhance performances further. On the one hand, modification on the precursors, such as the FFV adjustment by grafting functional groups and element doping, has been documented as effective ways to improve the performances of resulted CMS membranes. On the other hand, diverse methods to tune microstructure/properties during the carbonization and post-treatment steps provide CMS membranes with more competitive separation performances. In the future work, applying such facile methods, like widening micropores by post-reduction and -oxidation, and narrowing micropores by chemical species doping and hype raging, to adjust microstructure and then to meet required separation performances. Furthermore, the stability under the existence of water vapor in the feed stream must be considered as the water vapor is normally presented in flue gas and raw natural gas. Thus, the design of highly hydrophobic CMS membranes to allow a fast transport of water molecules in the micropores is crucial.

The CMS membranes prepared from cellulose membranes and fluorinated triazine-based membranes have illustrated a high endurability under > 85% RH, which can be further investigated. The functionalization of CMS membranes by heteroatom-doped active sites to modify their surface properties should be promoted. Besides, to enhance the mechanical strength of CMS membranes, the carbonization process could be optimized. For example, HCl is considered as carbonization catalysts, which can make carbon hollow fibers mechanically stronger. For safety issues, ammonium chloride (NH_4Cl) can put inside the quartz tube and using a sweep gas to slowly release HCl when carbonization temperature reaches 340 ℃ (i.e., the NH_4Cl decomposition temperature). It is necessary to optimize the membrane production process, which can be scaled up in an industrial capacity. Polyimide derived hollow fiber precursors have been developed into different configurations and have shown promising performances for required separations. Nevertheless, the challenges, such as using NMP as a solvent, involving complex procedures to maintain micropores during carbonization, easily in contact with each other hollow fibers and fused together during carbonization, are needed to be addressed if a large production capacity considered. On the other hand, cellulose hollow fibers are less prone to fusing, and many cellulose fibers can be carbonized in the same batch, which can significantly bring down the production cost for commercialization. Renewable polymers of cellulose show a particular interest by using ionic liquids (ILs) as a solvent to achieve green advances on carbon membrane production.

A novel methodology by the combination of experiment, chemometrics, and molecular modeling can be introduced to spin defect-free, asymmetric cellulose hollow fiber precursors with desired structure and property by screening ILs and cellulose feedstocks will have a great potential to flexibly tune precursor structure and property (e.g., porosity, degree of polymerization, crystallinity, and hydrophilicity, etc.). Moreover, the carbonization process must be very fine-tuned to get a high yield of perfect carbon membranes. The conventional carbonization process using horizontally placed furnace suffers the

Problems of low gas permeance and defect-formation due to the accumulation/sintering of residual carbon ashes on carbon surface/matrix. Thus, a novel carbonization process might be applied to prepare straight and mechanically strong carbon hollow fibers with high porosity and less dead-end pores by setting an angle of furnace or using a vertically placed furnace during the carbonization to drain the tars and vapors can be a solution. Moreover, the challenge of high production cost due to the difficulty on fabrication of carbon membranes in a continuous process needs to be addressed. However, the excellent separation performance reported in the latest literature indicates that the research for more robust membranes will be solved. With the possibility of tailoring membrane pore size and distribution which these membranes have, there are a huge number of potential gas separation applications for carbon membranes.

Membrane module design and construction for high temperature/pressure applications is another challenge on up-scaling of carbon membranes, which is related to membrane mounting, potting and sealing. It is worth noting that the shell-side feeding configuration may not be very efficient as CHFMs can be damaged or broken at a high-pressure feed flow. Thus, future module design should be focused on bore side feeding. Moreover, due to the fragility and brittleness characteristics, CMS membranes should be fabricated in a free-stand hollow fiber configuration if considering large-scale. It is also expected that large-scale production of supported carbon membranes will be challenging, and the production cost is still quite high, which may limit the applications only in small-volume gas separation processes. One should bear in mind even though most of the reported modules are potted in both ends the individual arrangement of the carbon hollow fibers inside a module cover would probably vary slightly depending on orientation. In case of vacuum permeate operation, the feed from bottom and retentate on the top may provide a better membrane performance due to the gravity helping in keeping the heavy CO_2 from flowing to the retentate- this should be further tested in the future work.

Carbon membrane technology is considered as energy-efficient processes for CO_2 removals in different scenarios. Hydrogen purification from syngas may become a major application, but also CO_2 removal from natural gas or biogas (CO_2/CH_4 separation) has a very promising potential. However, in order to compete with the currently commercialized polymeric membranes for selected gas separation applications, the above-mentioned challenges for carbon membranes must be overcome. Moreover, collaboration with industry to test out the green advances (especially high energy efficiency and low greenhouse gas emissions) of carbon membranes technology is also essential to bring the technology to future commercialization. For some gas streams containing water vapor or higher hydrocarbons, regeneration of carbon membranes will have to be put up to recover membrane performance over time. Moreover, process design with proper pre-treatment steps (water and particle removals) should be well considered to protect carbon membranes for longer lifetime, which can reduce the capital cost of carbon membrane systems.

Chapter 7

Biological Processes for CO2 Capture

Atmospheric carbon dioxide is one of the primary greenhouse gases on earth and its continuous emission by manmade activities is leading to a rise in atmospheric temperature. On the other hand, various natural phenomena exist that contribute to the sequestration of atmospheric carbon dioxide, i.e., its capture and long-term storage. These phenomena include oceanic, geological and chemical processes happening on earth. In addition to the above-mentioned nonbiological methods, various biological methods *viz.* soil carbon sequestration and phytosequestration have also been contributing to fixation of atmospheric carbon. Phytosequestration is mainly performed by several photosynthetic mechanisms such as C_3, C_4 and crassulacean acid metabolism (CAM) pathways of plants, carboxysomes of cyanobacteria and pyrenoids of microalgae. For an effective mitigation of global climate change, it is required to stabilize the CO_2 concentration to viable levels. It requires various permutations and combinations of naturally existing and engineering strategies. Although numerous strategies are in commodious use in the present times, the issues of sustainability and long-term stability still exist. We present an overview of the natural and manmade biological and nonbiological processes used today to reduce atmospheric CO_2 levels and discuss the scope and limitations of each of them.

Rise in global surface temperature is the cumulative effect of successively increasing concentration of greenhouse gases over several decades . Greenhouse gas emission results from the continuous use of fossil fuels which are fulfilling ~85% of world's energy requirement . Most of the greenhouse gases like methane (CH_4), nitrous oxide (N_2O), chlorofluorocarbons (CFC) and carbon dioxide (CO_2) are contributing to overall climate change, wherein carbon dioxide is playing a major role. For a while, environmentalists who have been intensely involved in studying the adverse effects caused by greenhouse gases have been advocating the removal of excess CO_2 as the only way by which one can undo the harm that has already disturbed the natural balance .

In context of crop productivity, theoretically it seems that increasing atmospheric CO_2 level would enhance plant photosynthesis and ultimately crop productivity, but the long-term effects are uncertain and might involve several side issues such as negative effects on plant food web, decreased plant nutritional values, reduced N content of plant etc. Hence, there must be a balance in atmospheric carbon level.

Other part of the story says that carbon fixation by photosynthesis can also be considered as a natural method of capturing atmospheric carbon. In order to overcome negative effects of global warming and climate change that is being caused by increased carbon level, people are trying to make improvements in the naturally occurring photosynthetic reactions by transferring few mechanisms or several genes from an efficient system like cyanobacteria, microalgae and C_4 plants to inefficient photosynthetic systems such as higher C_3 plants . Success rate is, however, doubtful and, therefore, we need to develop several strategies to minimize the ever-increasing carbon levels so that side issues associated with it could also be avoided.

'Carbon sequestration' is the term given to capturing atmospheric carbon and converting it into forms unable to contribute to global warming. It is anticipated that in the coming centuries CO_2 emissions might double, so there is a serious need to overcome this problem. Carbon fixation by photosynthesis is mainly under consideration for sequestering atmospheric CO_2 for long-term period

There are three major strategies that could be used for reducing the carbon concentration in atmosphere: (a) reductions in CO_2 emissions in the global atmosphere; (b) carbon capture and long-term storage; (c) developing alternatives for carbon-based fuel.

The second strategy, i.e., carbon capture and long-term storage implicates carbon sequestration which involves capture and storage of CO_2 using various methods . In the global atmosphere, CO_2 is present in concentration lower than nitrogen (N_2) and oxygen (O_2), and this has created a thermodynamic barrier in CO_2 capture, hence making it a limiting step in sequestration process. Once captured, the second step is to store the captured carbon in long-lived pools. There could be several methods to achieve this objective which include oceanic, geological, chemical and terrestrial sequestration methods.

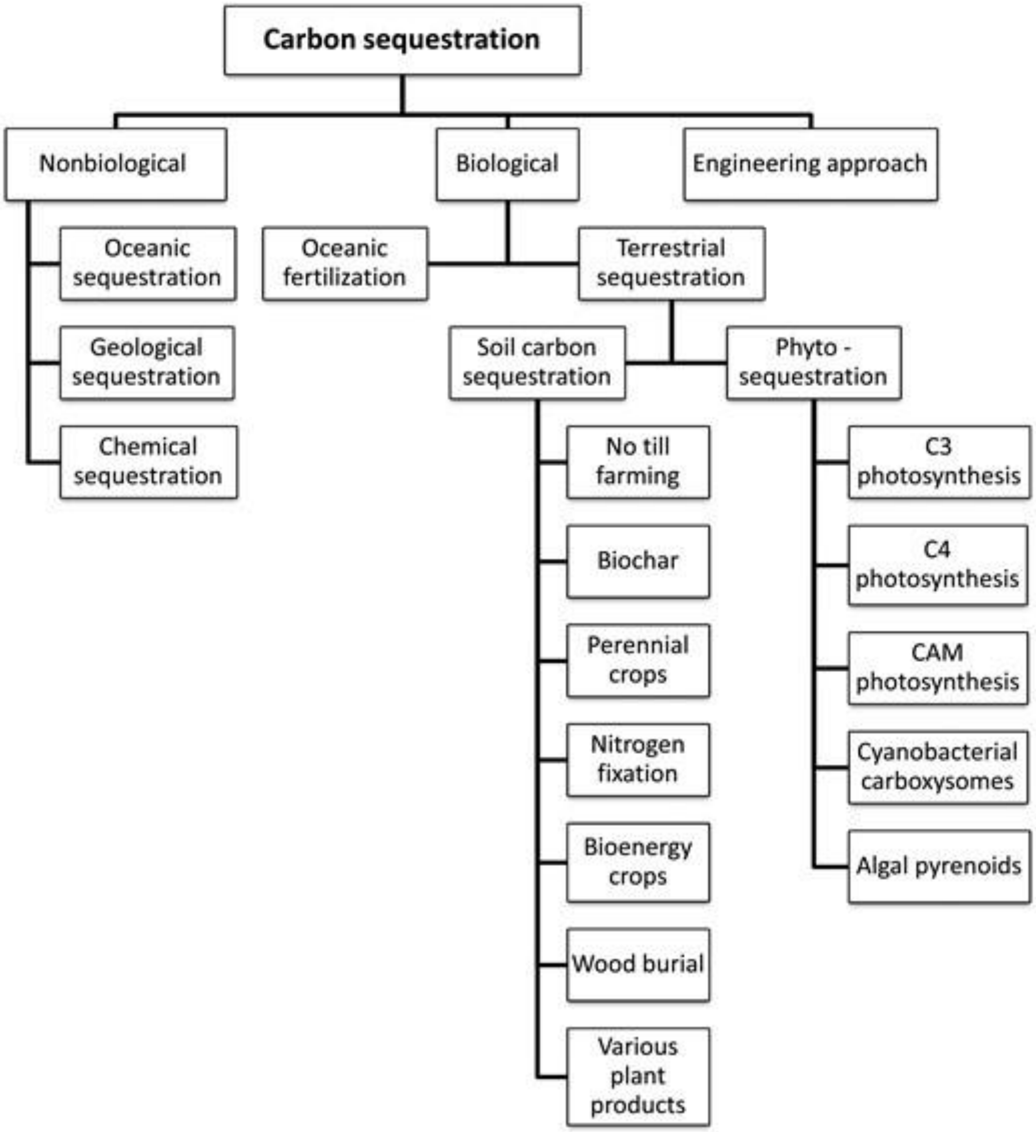
The main objective of carbon sequestration is to balance the atmospheric carbon pool to keep the CO_2 concentration below a threshold level . Carbon sequestration needs to be analyzed in terms of efficiency, cost, environmental impacts, stability of sequestered carbon and timescale of sequestration because the limiting factors must be known for analyzing the overall efficiency of any of the sequestration techniques .

2.Sequestration Strategies

There are various sequestration strategies (Figure 1) which have been classified differently by different people because a unique classification is not possible for such a huge number of categories. There could be several possible criteria for categorization such as methods of sequestration, types of organisms involved in sequestration, based on possible carbon sinks and many more. The major classification system is based on biological and nonbiological sequestration strategies. Moreover, all these different strategies may also show few overlapping features. The following text involves discussion of the strategies developed followed by a comparison of these strategies in context to the advantages and disadvantages/limitations linked to each of them.

CS, carbon sequestration; GHG, greenhouse gas.

Figure 1.



Various modes of carbon sequestration.

2.1 Nonbiological sequestration

Nonbiological sequestration methods involve capture of atmospheric carbon by nonbiological means which is accomplished by different kinds of chemical and physical reactions and many other approaches which do not consider the role of living organisms. This strategy includes oceanic, geological and chemical sequestration methods. All these methods can also be further subdivided as discussed below.

2.1.1 Oceanic sequestration

Oceanic sequestration provides a way to store atmospheric carbon into deep oceans. At the global level, ocean contains 50 times more inorganic carbon than the atmosphere, thus providing a significant proof that oceans could also serve as a sink for storage of atmospheric carbon . Oceanic carbon sequestration further can be categorized in abiotic and biotic types, which involve direct injection of CO_2 into the ocean and ocean fertilization methods, respectively . Distribution of CO_2 between the ocean and atmosphere is affected by many factors including temperature, pH and salt concentration in water for example higher concentration of salt and high temperature negatively regulate CO_2 solubility in oceanic water .

2.1.1.1 Direct injection of CO_2 into the ocean

Direct CO_2 injection into the ocean is considered as the nonbiological mode of oceanic sequestration. Engineers have been continuously trying toward generating the viable options for CO_2 injection into deep oceanic areas. Essentially, the process needs to be stabilized with minimum leakage of CO_2, for which CO_2 must be injected at the maximum possible depth of ocean . Although the strategy seems promising but is hurdled by the fact that this concept may affect the marine biota present in the vicinity of injected CO_2. The location where CO_2 is injected becomes acidic in nature because of the reduction in pH by CO_2, which is toxic to marine microorganisms in long run; hence, adversely affects deep sea biota . In order to minimize the leakage of stored CO_2, this method provides a usable approach because being lighter in weight than water and the greater depths that are under consideration for sequestration are providing stability in the ocean, hence preventing the CO_2 from releasing back into the environment. It is believed that ∼3000 m depth is enough for stable injection of CO_2 . Sequestration efficiency in terms of time of storage depends on depth of CO_2 injection ; hence, the duration for which it would be residing in the ocean can be anticipated from the depth of injection.

2.1.2 Geological sequestration

Geological sequestration method provides an attractive opportunity for carbon storage using various underground geological formations. Various petroleum industries have been using this method for a long time because of two major advantages; first that it reduces greenhouse gas emission and secondly because it contributes to oil recovery process. It is difficult, however, to predict the storage volume and there is no guarantee of long-term storage .

CO_2 can be stored in various geological structures including oil and gas reservoirs, unmendable coal seams and deep saline aquifers, and it is believed that geological sequestration would be effective in terms of carbon storage for longer time duration. Petroleum industries have been using geological sequestration for enhanced oil recovery since 1970's because injected CO_2 displaces oil or gas, providing an economically beneficial scenario for oil recovery. In order to minimize the chances of leakage, these geological structures are quite favorable; hence, CO_2 storage needs to be promoted in depleted oil and gas reservoirs. So far, research is going on but still safety, stability and public acceptance are the main issues which need to be addressed. Moreover, practical trials are the only successful and viable options for large scale sequestration projects.

Unmineable coal seams are inaccessible due to their depth of occurrence and uneconomical due to poor quality and land use restrictions though for CO_2 sequestration this could be a positively responding approach . Using unmineable coal seams for CO_2 sequestration offers advantages in the sense that these formations can adsorb CO_2 with high efficiency and have the capability to displace adsorbed methane. The appropriate mechanism reported is that one molecule of methane which is absorbed at the coal surface gets replaced by two molecules of CO_2. This technique offers 2-fold benefit in the sense that this methane, also known as coal bed methane, gets recovered and the CO_2 gets adsorbed .

Saline aquifers are defined as underground geological formations made up of water permeable rocks saturated with salt water (brine). Supercritical CO_2 can be injected into saline aquifers, which gets dissolved in brine or reacts with dissolved mineral or surrounding rock, hence gets trapped in the porous sediments with a comparatively enhanced efficiency when compared with other sequestration methods .

As described in oceanic sequestration method, here also various limiting factors are affecting the overall efficiency of sequestration. Cost associated with the global use of this method and leakage probabilities are the main limiting factors which need to be analyzed and overcome.

2.1.3 Chemical sequestration by mineral carbonation

Chemical sequestration methods involve several specific chemical reactions and are hence known as nonbiological methods. These chemical reactions convert atmospheric CO_2 into a modified and stable compound, one of which is chemical weathering of rocks by mineral carbonation. In this process, rocks are sources of minerals . In the process of mineral carbonation CO_2 reacts with various mineral metal oxides which are present in the form of rocks, leading to formation of mineral carbonates. These carbonates remain stable in solid rocks and so CO_2 (in carbonate form) could be stored for a longer period of time . Mineral carbonation reactions occur naturally as well as using industrial processes, although efficiency of the process is too less at industrial level.

(a) Oceanic injection of bicarbonate salts

(b) Underground or surface storage of solid carbonates

(c) Storage of carbonate brines into underground reservoirs.

Rock weathering naturally results into mineral carbonation. In this process, CO_2 present in rainwater reacts with minerals. This is an acid–base reaction in which an acid (CO_2) is neutralized by a base (mineral) to form stable carbonates. Some of the chemical reactions are as mentioned below :

$$\mathrm{(1)2Mg2SiO4+CO2(g)+2H2O\rightarrow Mg3Si2O5(OH)4+MgCO3,2Mg2SiO4+CO2(g)+2H2O\rightarrow Mg3Si2O5(OH)4+MgCO3,}$$

$$\mathrm{(2)Mg2SiO4+2CO2(g)\rightarrow 2MgCO3+SiO2,Mg2SiO4+2CO2(g)\rightarrow 2MgCO3+SiO2,}$$

$$\mathrm{(3)CaSiO3+CO2(g)\rightarrow CaCO3+SiO2.CaSiO3+CO2(g)\rightarrow CaCO3+SiO2.}$$

These chemical equations explain the mineral carbonation process. In Equations (1) and (2), formation of magnesium carbonate, while in Equation (3) formation of calcium carbonate have been shown.

Industrial usefulness of naturally occurring mineral carbonation reactions but they have also mentioned that being a slow process mineral carbonation has limitations. To obtain the maximal advantage of this strategy, several engineering parameters such as temperature and pressure of reaction, sample preparation, solution chemistry and post-treatment separation for enhancement of reaction rate need to be optimized.

Preparation of minerals for carbonation is one of the most energy demanding steps due to requirement of extremely high temperature treatments which reach up to 650°C for activation of minerals . The reaction rates could be enhanced substantially by various approaches such as decreasing the particle size, raising the reaction temperature, increasing the pressure, changing the solution chemistry and using a catalyst . Enhancement of reaction rate involves input of extra energy for several processes such as generating high temperature (650°C) and high partial pressure (150 atm) for

CO_2 injection and therefore incur huge cost at industrial level. However, probabilities of long-term storage and less possibility of CO_2 leakage favor the use of this strategy.

2.2 Biological sequestration

Biological sequestration is basically performed by living organisms including plants and many microorganisms which lead to carbon capture and storage via various biological processes. Biological sequestration is majorly the result of natural processes, although now a days, few artificial strategies are also considered to be a part of this. This mainly includes ocean sequestration through fertilization and terrestrial sequestration. Terrestrial sequestration can be further subdivided into soil carbon sequestration and Phyto sequestration.

2.2.1 Ocean fertilization

As mentioned previously, ocean sequestration includes both biotic and abiotic modes of sequestration. We have earlier discussed about the abiotic mode of oceanic sequestration and now we will be discussing biotic mode. Ocean fertilization is basically a biological method which helps in carbon sequestration by the phytoplanktonic photosynthesis process. In terms of definition this process simply means that by carrying out an increment in fertilization of the oceans, i.e., enhancing the concentration of limiting nutrients that would stimulate growth and production of phytoplankton will ultimately enhance carbon fixation. effect of iron in high nutrient, low chlorophyll oceanic water and found that iron addition enhances the primary production by stimulating the growth of phytoplankton. Other nutrients including ammonium, nitrate and so on could also be used along with iron for enhancement of primary productivity in the ocean. But this method faces the same disadvantages as faced by the direct injection method, i.e., it may lead to such changes that affect the ecology of the ocean in several ways. One outcome could be that the stored organic matter could decompose and produce some other detrimental greenhouse gases such as methane and nitrogen monoxide. The ultimate benefit from this method, therefore, may or may not be up to a significant level . So far, this method has been still a questionable topic of discussion because ocean fertilization needs to be done at a huge level which is practically very challenging and less feasible.

2.2.2 Terrestrial sequestration

Terrestrial carbon sequestration deals with storage of CO_2 in vegetation and in soils, in the above ground and below ground biomass , processes termed as Phyto sequestration and soil carbon sequestration, respectively . This process has been widely accepted because of advantage of long-term storage. In terrestrial ecosystems, carbon storage mainly occurs by photosynthesis as well as in the form of live and dead organic matter, hence acting as major carbon sinks, several scenarios for terrestrial sequestration which include sequestration by soils, vegetation, forests and wetlands . So far, it is known that the carbon storage capacity of soil is more than the storage capacity of both vegetation and the atmosphere and hence a small increase in soil carbon surely provides significant effects on overall carbon balance of the environment .

2.2.2.1 Soil carbon sequestration

Atmospheric CO_2 captured by plants is majorly converted into organic material by photosynthesis while a small proportion of it is translocated through plant roots into the soil, where it is stored in organic as well as inorganic forms . Soil carbon sequestration and Phyto sequestration both are co-related terms. The efficiency of soil carbon sequestration mainly depends on climate, temperature, rainfall, clay content, mineralogy, moisture content and soil texture . For enhanced carbon sequestration, proper management of ecosystems using various advanced management practices such as restoration of degraded soils for increment in biomass production as well as decrement in net CO_2 emissions are considered essential .

There are various ways for increasing soil organic carbon pool such as:

No-till farming

Farmers usually prefer tillage practices which includes physical disturbances in soil for enhancement of soil respiration as well as decomposition of soil organic pool. This practice increases turnover of soil aggregates and results in reduction in carbon content of soil . For sequestering/retaining atmospheric carbon into soil system, ‘no-till’ farming practices are now a days in use by growing crops year after year without disturbing the soil by tillage.

No-till farming practices promote minimum soil loss because soil is not mixed properly and remains more fertile due to the retention of residue from previous crops which improves carbon content of the soil. This conservation technique reduces soil erosion, enhances infiltration as well as water holding capacity of the soil and it also favors the formation of soil aggregates the fact that no tillage favors the formation of stable soil organic matter has been experimentally proven using ^{13}C-labeling comparison between no-till and tillage product/practice situation .Hence, no-till practices contribute directly or indirectly in retention of soil carbon which helps in sequestration process.

Biochar

Biochar also called as black carbon, acts as a very poor substrate for microorganisms and is therefore more resistant to microbial decomposition. Black carbon is generally assumed to be chemically inert and highly resistant towards degradation . Aspects of biochar decay kinetics, in which they had described Biochar as, ‘Biochar is a mixture of heterogenous substances including both labile (easy to decompose) and recalcitrant (difficult to decompose) aromatic compounds, hence half-life depends on the percentage of both components. So, increase in the number of recalcitrant compounds lead to increase in the half-life of biochar. Since long half-life of biochar has been measured across a very high and variable range of several hundred to several thousand years . Therefore, long-term storage of carbon can be achieved by converting it into biochar form. It has already been discussed that biochar is relatively stable in soil because of its chemical nature since it contains polycyclic aromatic rings and forms solid structures which lead to the formation of stable structure.

Biochar has an appearance like charcoal. Difference between the two lies in the fact that former is a product of incomplete combustion process of wood and other organic material in limited oxygen condition while latter is the product of complete combustion process ,biochar and charcoal are more or less similar in terms of their properties and both may be applied to the soil for carbon sequestration and increment in soil fertility .

Perennial crops

Besides the use of no-till farming method and biochar application, another technique available for management of soil organic carbon is introduction of perennial crop species This practice increases soil organic pool and assists in long-term carbon storage. Because of their expanded root system, larger amount of carbon can be stored in root biomass of perennial crops . Moreover, perennial species respond positively toward agricultural activities with minimum soil disturbances for example expanding the duration of growing season is considered as high-yielding better cultivation option than growing annual crops .

Nitrogen fixation

Nitrogen fixing plants having larger tendency of soil carbon accumulation than non-nitrogen fixing plants , hence have greater effect on soil organic biomass . Fixed nitrogen becomes a part of the ecosystem nutrient cycle further decreasing soil carbon decomposition and increasing its storage. Nitrogen fixation process favors litter fall and mycorrhizal production thereby increasing the carbon input of soil.

Bioenergy crops

A plant species which can be used as a renewable energy source for future prospective is called as bio-energy crop. These crops upon complete characterization can be intentionally designed for enhancing biomass and energy potential and hence increased production of bioenergy . These crops have been categorized as the fourth largest energy source in developing countries. At-present sugarcane, oil crops and some of the cereals such as maize and wheat are being utilized as bio-energy crops.

Bio-energy crops have the potential to replace conventional fossil fuel energy sources since they can reduce atmospheric CO_2 concentration due to their potential of high biomass accumulation , and hence contribute to carbon sequestration. Bio-energy crops also sequester carbon via roots and soil the efficiency and effectiveness of bio-energy crops largely depends on the type of species with the factors under consideration including high productivity, fertilization and harvest management .

Wood burial

For producing wood burial, dead or live trees are collected and buried in above ground areas in largely anaerobic conditions. This will not allow decomposition, but CO_2 will remain sequestrated, that wood burial strategy can be used to mitigate global climate change by reducing atmospheric CO_2 concentrations.

Theoretically sequestration of the whole CO_2 emission from the present-day environment using tree planting and burial would require approximately one billion hectares area. In a nutshell wood, burial appears to be a time taking but a sustainable strategy for balancing atmospheric carbon level.

Various plant products

Various plant products including wood material used as raw material for construction of buildings, houses and furniture , provide the way for long-term carbon sequestration.

Phytoliths are also a sort of plant products which are released after burning, digestion and decaying of plant parts. These can be silicates and calcareous deposits, phytoliths could serve as sustainable soil carbon pool because these are very stable and insensitive toward various land use changes and hence carbon remains sequestered for millennia.

Phyto sequestration

Capturing atmospheric CO_2 by photosynthesis *viz.* Phyto sequestration is a more beneficial way of carbon sequestration in several ways,~99.9% carbon biota is being contributed by vegetation and microbial biomass. Phyto sequestration could serve as the most suitable carbon sink for several centuries provided the plantation remains undisturbed and properly maintained. In fact, depletion of forests is one of the main reasons for the increase in atmospheric $CO_{2,}$ hence removing the cause could reverse the process. Photosynthesis is a natural process through which plants convert inorganic carbon into organic carbon, i.e., CO_2 into sugar in the presence of solar energy. This way atmospheric carbon is allocated to various plant parts such as seeds, stems, roots and various other organs. Hence, CO_2 fixation processes enhance sequestration of global atmospheric carbon. It was postulated that by enhancing photosynthetic efficiencies either by employing natural or engineering approaches, atmospheric carbon capture and storage would increase .

The various photosynthetic organisms such as C_3 plants, C_4 plants, crassulacean acid metabolism (CAM) plants, cyanobacteria, microalgae and many others possess different kinds of carbon fixation pathways. Apart from C_3 plants, all others mentioned above contain some or the other kind of carbon concentrating mechanisms (CCMs).

C_3 photosynthesis

C_3 photosynthesis is the most ancient pathway for CO_2 fixation, found in a large group of plants. In this pathway, first product of photosynthesis is a three-carbon molecule, i.e., phosphoglyceric acid (PGA), so-termed as C_3 photosynthesis. This pathway involves carboxylation of ribulose bis-phosphate (RuBP) in the presence of enzyme ribulose 1,5-bisphosphate carboxylase oxygenase (RuBisCO), leads to the formation of PGA. RuBisCO can use two different substrates, i.e., CO_2 or O_2 which leads to both carboxylation as well as oxygenation of RuBP, thereby decreasing its specificity toward

CO_2. In high O_2 and the low CO_2 environment, RuBisCO acts as an oxygenase and further catalyzes the wasteful photorespiration reaction resulting in less carbon fixation because 2-carbon molecule phosphoglycerates is produced. Because of this fickle specificity of RuBisCO for two different substrates, there was a need for enhancement of the RuBisCOs carboxylation activity and henceforth various other photosynthetic pathways evolved *viz.* C_4 and CAM pathways .

C_4 photosynthesis

C_4 photosynthesis is common among monocot plants. These plants have different leaf anatomy than C_3 plants, which facilitates reduction of RuBisCO oxygenase activity. Further, in this pathway, first product is a 4-carbon molecule and hence, the pathway is termed as C_4 photosynthesis. Under the conditions of low CO_2 and high temperature, C_4 plants are more efficient than C_3 plants because photorespiration rates are reduced in C_4 plants. While studying cross sections of leaves, it was observed that C_3 plants contain only mesophyll cells while C_4 plants have two different chloroplast containing cells: mesophyll cells and bundle sheath cells, arranged in a distinct way . The peculiar leaf structure of C_4 plant species is called as Kranz anatomy in which undifferentiated mesophyll cells are present in the form of concentric layer around bundle sheath cells, although both are connected by plasmodesmata. The initial carboxylation reaction occurs in outer mesophyll cells by the enzyme phosphoenol pyruvate (PEP) carboxylase and the 4-carbon compound malate or aspartate is formed that is further translocated to the interior of bundle sheath cells, where CO_2 released from 4-carbon compound is again fixed by RuBisCO enzyme to form two molecules of 3-phosphoglycerate. In this way, RuBisCO remains separated from atmospheric O_2 in the bundle sheath cells and CO_2 is continuously concentrated around RuBisCO, leading to increase in efficiency of photosynthesis . Hence, C_4 pathway is the way of spatial separation of atmospheric O_2 from RuBisCO.

CAM photosynthesis

In CAM plants, various adaptations are found to cope up with the hot arid conditions. CAM pathway is found in many epiphytes and succulent plants of arid region . These plants close their stomata during the hot day time, to reduce water loss through transpiration and open during the cool nighttime to collect CO_2. Thus, they temporally regulate the efficiency of CO_2 fixation pathway . At the same time, in CAM plants also, spatial regulation like that of C_4 plants is found. During the night CO_2 is taken up by PEP carboxylase present in cytosol to form malate and then stored in vacuoles that further transport it to chloroplast during the day and where the CO_2 fixation of RuBP occurs. This way CAM plants can work efficiently in water and CO_2 stressed conditions .

Cyanobacterial carboxysomes

Cyanobacteria possess a unique kind of CCMs to enhance photosynthetic efficiency of RuBisCO. In cyanobacteria carboxysome, structures and various inorganic carbon transporters are present for concentrating CO_2 nearby RuBisCO. Carboxysomes are proteinaceous polyhedral bodies covered by a protein shell. Most of the RuBisCO content of the cell is present in carboxysomes .

In cyanobacteria, bicarbonate (HCO_3^-) and carbon dioxide (CO_2) are taken up into the cell cytosol via transporters. CO_2 is converted into HCO_3^- by carbonic anhydrase activity and ultimately whole HCO_3^- pool is further transported to carboxysomes through protein shell, where HCO_3^- is converted into CO_2 by the carbonic anhydrase enzyme in the carboxysomes. In this manner, CO_2 is concentrated around RuBisCO . Thus, carboxysomes are sites in a cyanobacterial cell where CO_2 levels remain high for further capture by RubisCO for CO_2 fixation process.

Algal pyrenoids

Algae also contain CCMs. The carbon concentrating structures of algae are called pyrenoids. These structures are analogous to cyanobacterial carboxysomes . Although structural features of pyrenoids vary with species of algae but in all cases, pyrenoids are present within the chloroplast stroma, where RuBisCO molecules are found and help in concentrating CO_2 around RuBisCO. These pyrenoids also deal with the inhibition of photorespiration process thus aiding in increasing carboxylase activity of RuBisCO .

The C_4 pathway, CAM pathway, carboxysomes of cyanobacteria and pyrenoids of microalgae are some of the naturally occurring mechanisms for enhancing efficiency of an inefficient RuBisCO enzyme. In all these mechanisms, CO_2 is concentrated around RuBisCO and, therefore, photosynthetic efficiency is increased. As already discussed, enhancing photosynthetic efficiency by incorporation or the capture of atmospheric CO_2 aids in fulfilling the objective of carbon bio sequestration .

Engineering approaches

There are various genetic engineering approaches that can be employed for enhancement of photosynthetic efficiency especially in case of C_3 plants. So, these engineering approaches would provide combined effects of both biological and nonbiological approaches in terms of carbon capture and storage.

Some of these approaches are mentioned in the text below.

In C3 photosynthesis, RuBisCO catalyzes the rate limiting step of CO_2 fixation, and there is no mechanism present in C3 plants for CO_2 concentration . So, for enhancing photosynthesis, there is a need to improve performance of RuBisCO. RuBisCO needs to be modified in such a way that its specificity decreases towards O_2 so that photorespiration is reduced, and the other aspect is to increase the catalytic rate so that CO_2 fixation is enhanced. Studies reveal that the RuBisCOs of red algae and a few C4 plants are more efficient than those of C_3 plants and hence in order to enhance efficiency of C_3 photosynthesis, such a RuBisCO could be incorporated into C_3 plants .

Another approach could be introduction of various cyanobacterial bicarbonate transporters to the chloroplast envelope of C_3 plants . Cyanobacterial cells contain various transporters for uptake of CO_2 and HCO_3^- while C_3 plants lack any kind of active uptake system except stomata, which are available for exchange of gases. Providing the

C_3 plants with efficient transporter system could lead to increase in the photosynthetic yield with the additional benefit of greater CO_2 sequestration.

Although there are various strategies already present, and many others are continually being developed for sequestration of atmospheric carbon but still sustainability and long-term effects are not guaranteed. In the present day, environmental rise in atmospheric carbon level is the most debatable issue to be discussed, analyzed and most importantly resolved.

Increased carbon levels are affecting at the global level, so it is not possible to overcome this problem by using any of the single approach due to various drawbacks associated with each strategy. So, it can be concluded that for efficient carbon sequestration more than one strategy needs to be used in combination to achieve sustainability. Genetic engineering is emerging out to be the most promising approach in this direction and hence should be given a thrust.

Along with the main strategies discussed several carbon level management practices could aid in the maintenance of atmospheric carbon level. There are various management practices that could be coupled with biological sequestration methods such as forest and soil management that would lead to enhancement of the sink capacity of forest and soil system respectively and ultimately improve carbon sequestration. The examples of such practices include no-till farming, bio energy crops, perennial crops etc., which play role in conservation of soil organic pool. It is suggested that along with carbon sequestration strategies, management practices as mentioned above would be beneficial for balancing atmospheric carbon level. Although extensive research is going on in this area but still more research is the need of the hour.

Chapter 8

Carbon Capture and Climate Change

The widespread deployment of carbon capture and storage (CCS) to address climate change will require the construction and operation of a large network of pipeline systems to transport the CO2 from the capture facility to storage sites. Because of the expected scale of these systems and the properties of the CO2 being transported, CCS pipeline systems may require different approaches for risk assessment and regulation compared to other, more common gasses, such as natural gas. There is also a general lack of knowledge amongst stakeholders around the safety issues of CCS, which must be addressed to achieve acceptance. This paper outlines the results of a study undertaken by Environmental Resources Management (ERM) for the CO2 Capture Project (CCP) to better understand these considerations. This includes: . A comparative overview on the risks posed by natural gas, sour gas and CO2 pipelines . A review of the safety regulatory requirements for pipelines in general, with a special focus on CO2 pipelines where these exist (for Canada, US, UK and Europe). .

Characterizing the current state of acceptance of CO2 pipelines from NGOs and other stakeholders that could have an influence on the implementation of regulations and oversight for CO2 pipeline systems an assessment of the risks associated with pipelines transporting CO2, along with stakeholder acceptance of their operation, will be a key element in securing a ‘license to operate’ for CCS facilities.

The primary objective of the CO2 Capture Project (CCP) is to develop new, breakthrough technologies to reduce the cost of CO2 separation, capture, and geologic storage from fuel combustion sources such as turbines, heaters, and boilers. CCP has a parallel work stream exploring ‘softer’ issues around policies and incentives for CCS activities. Phase 3 of CCP is planned to be an industrial-scale demonstration of some CCS technologies, which would represent a major step towards wider commercial deployment (Ref 1). A common requirement for all these technologies is a safe pipeline

system for the transportation of CO2 from capturing facilities to storage sites. This chapter presents an overview of key risks associated with the operation of natural and sour gas and CO2 pipelines, an evaluation of how the current regulations associated with pipeline operations address these risks and highlights relevant stakeholder views and perceptions of the risks of CCS and/or CO2 pipeline operation.

Pipeline Comparative Risk

The overall level of risk to humans and the environment associated with pipeline operation is a combination of the above two factors. This combination of the likelihood of failure and the severity of the impact is illustrated in Figure 1, which also highlights some of the failure causes and the different categories of impact (or consequences). The safety related issues that could potentially differentiate CO2 from natural gas, sour gas or CO2 transportation for Enhanced Oil Recovery (EOR) operations can be summarized as follows: . Additional risks associated with higher population densities where CO2 is transported via pipeline as part of SYMPOSIUM SERIES NO. 155 Hazards XXI # 2009 Chem E 411 CCS activities compared to CO2 for EOR pipeline and other pipelines. . Purity requirements and impurities in the transported stream. . Higher operating pressures and the volume associated with transporting CO2 in the dense/supercritical phase for CCS than other gas pipelines. Research, modelling and interviews undertaken by ERM suggest that the overall level of risk posed by CO2 pipelines may be difficult to assess with a high degree of confidence at the current time. This is due to knowledge gaps currently surrounding the behavior of supercritical CO2 releases and limitations in existing models for simulating a 3-phase release associated with supercritical CO2. When the level of uncertainty concerning the risk increases, regulators' decisions related to the management of risk tend to be more cautious in order to provide higher levels of protection. However, the European Commission's preliminary analysis of available empirical and modelled evidence indicates that the risks from CO2 pipeline transport are "no higher than for pipeline transport of natural gas" (Ref 2). Furthermore, when risks posed by CO2 pipelines are viewed in the context of risks imposed by existing hydrocarbon pipelines it appears that CO2 pipelines should not pose higher risks than those already tolerated by wider society if standards, controls and design factors for supercritical CO2 transportation are taken into consideration (Ref 3). Standard controls and design factors have been in place for some time for supercritical CO2 transportation in North America (for enhanced oil recovery). The experience so far with CO2 transport in the US suggests that the existing pipeline technology would be suitable for transportation of CO2 from the perspective of providing adequate protection to the public

It is likely that the already established design, construction and operating requirements that apply to existing gas pipelines operating in densely populated areas would be applicable for CO2 pipelines sited in sub-urban and urban areas and would be able to deal with the population density issues. The US Office of Pipeline Safety statistics indicate that the frequency of incidents for CO2 pipelines is like that of natural gas pipelines. This finding is also supported by IPCC Special Report on Carbon Capture and Storage . In relation to impurities, even though work has been undertaken in this area, there is currently no uniform definition of the required quality of CCS streams in order to transport CO2 safely; standards may therefore need to be developed to expedite permitting. As transportation of CO2 cannot be seen in isolation from the rest of the CCS chain, all relevant parties (i.e., capture, transport and storage site operators) would need to be involved to understand the practical implications that pipeline safety requirements (especially in relation to impurities) could have at each CCS stage. Prospective CO2 pipeline developers should anticipate that filling the current knowledge gaps in relation to CO2 modelling, risk assessment and the effect of impurities in the overall level of risk could help support potential risk-based planning, safety and permitting issues and thereby inform the regulatory development process.

Pipeline Regulatory Review CO2

Can be treated by regulators as a fluid or gas, hazardous or non-hazardous. CO2 has been categorized in the US and Canada as Class 2.2 non-flammable hazardous material and Class 2.2 Non-Flammable, Non-Toxic Gas respectively; however, in the UK there is currently no categorization for CO2. Based on an extensive regulatory review and interviews with regulators in the UK it is likely that CO2 will be regulated under the existing Pipeline Safety Regulations. CO2 pipelines are built to defined standards and are subject to regulatory approval in the US and Canada Corrosion Construction/ Material Defect External Interference Ground Movement Hot-tap by error Other/ Unknown Likelihood of loss of containment Fire and explosion Toxic Effects Blast Effects Cryogenic Effects Asphyxiation Other Severity of impact Corrosion Construction/

Material Defect External Interference Ground Movement Hot-tap by error Other/ Unknown Likelihood of loss of containment Corrosion Construction/ Material Defect External Interference Ground Movement Hot-tap by error Other/ Unknown Likelihood of loss of containment Fire and explosion Toxic Effects Blast Effects Cryogenic Effects Asphyxiation Other Severity of impact Fire and explosion Toxic Effects Blast Effects Cryogenic Effects Asphyxiation Other Severity of impact

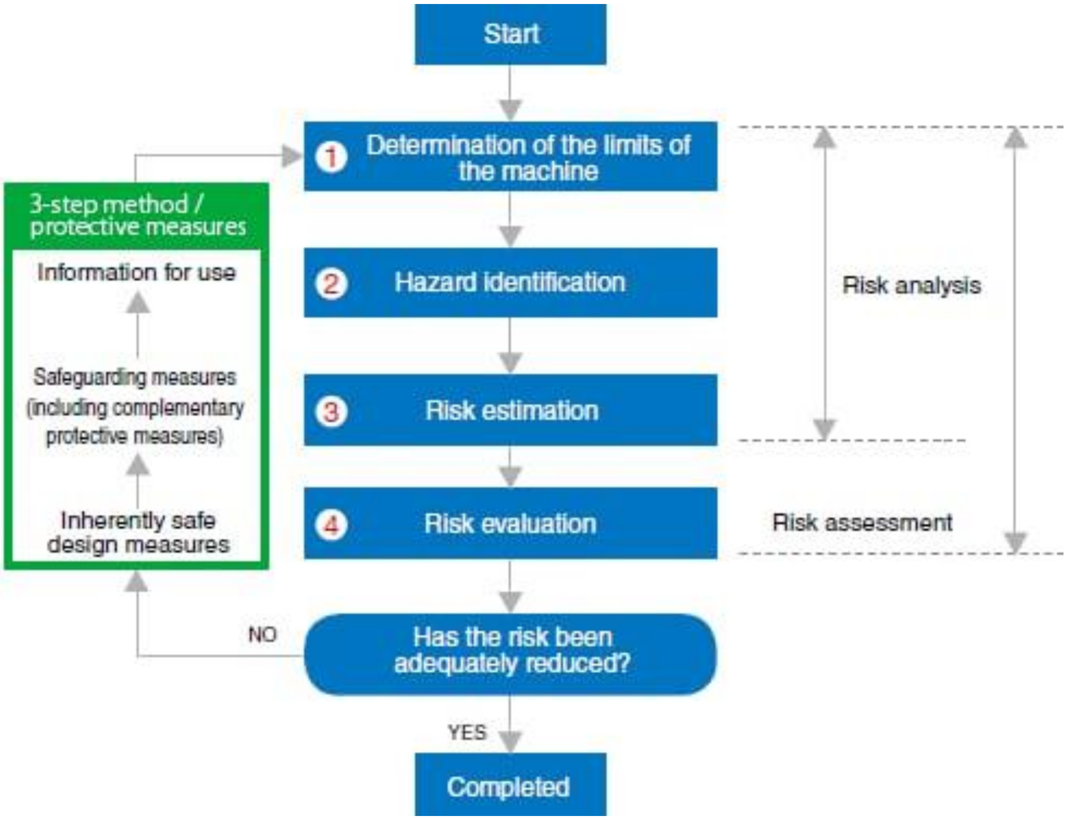


Figure 1. Overview of risk for a pipeline system SYMPOSIUM SERIES NO. 155 Hazards XXI # 2009 IChemE 412 where experience in CO2 transportation exists

In the UK there is currently a knowledge gap in transporting supercritical CO2. A regulatory framework is currently being developed but in the meantime UK regulators consider that there may be technical benefit in applying the US Federal Code for CO2 transportation in the supercritical phase in the UK. Higher population densities are likely to be encountered in CO2 pipeline deployment for CCS and hence the overall risk would be higher compared to equivalent CO2 pipelines for EOR. The existing regulatory approach for dealing with risk, along with the uncertainty that surrounds modelling of supercritical CO2 releases, indicate that CO2 pipelines might be routed to avoid centers of population and individual dwellings where possible. In cases where this is not possible additional design, construction and operating requirements established for existing pipelines operating in densely populated areas could be applicable for CO2 pipelines sited in sub-urban and urban areas; however, the process of planning, licensing and building new pipelines may be difficult and time-consuming. No regulatory amendments are anticipated in the countries and regions examined in this study in relation to population density issues.

Purity requirements are not currently addressed by UK legislation; at a European level the Commission has no intention of mandating specific purity requirements at this stage and it would be dealt with on a case-by-case basis at a member state level through a risk assessment approach. In Canada, there are no specific purity requirements for CO2 pipelines as the regulator assesses the pipelines risk on a case-by-case basis. However, pipeline regulations refer to the Z662 Standard which only covers high-purity onshore CO2 for EOR; therefore, some generic minimum purity requirements are indirectly in place. In a wide-scale CCS deployment scenario this case-by-case approach could present difficulties and some minimum explicit purity specifications that address safety issues could be required in the future.

In the US D.O.T regulations specify 90% purity levels in their definition of CO2 and most CO2 currently transported ranges in purity between 90% and 96%. Neither the States of Colorado nor Texas regulates the purity for transport; purity requirements is a concern expressed by industry as CCS moves forward especially for purities ,90% CO2. Table 1 provides a snapshot of the regulatory gaps in relation to the above CO2 transportation issues discussed in this section for each jurisdiction. The color coding used in Table 1 is as follows: green – no issue; orange – minor issue; and red – major issue.

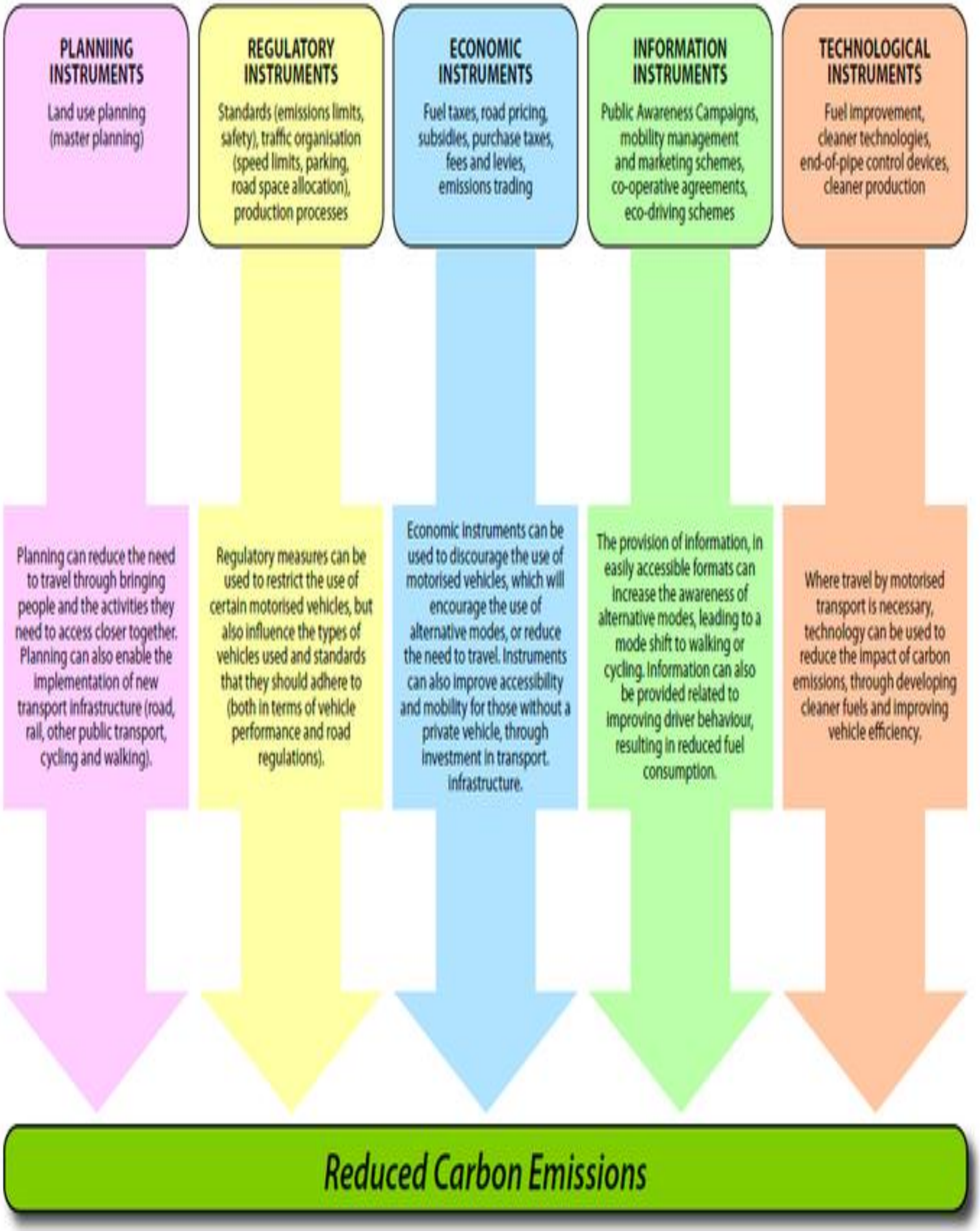
Risk Perception

Pipeline routes are frequently the subject of public inquiries, and the public perception of risk could be an important factor for CCS acceptance in a wide-spread deployment scenario. When risks are perceived by the public as being too high then societal concerns can arise. Such concerns could potentially result in socio-political responses, loss of confidence by society in the provisions and arrangements in place for protecting people and a loss of trust in the regulator and duty-holders.

Eventually such developments could have an impact on CCS deployment and related implementation costs. Key messages from the surveys and interviews undertaken by ERM suggest that: . CO2 pipelines are perceived as safe by most of the stakeholders . There is a lack of awareness of CCS among the participants of the surveys, which is likely to be even greater amongst the general public. . The perception of CO2 pipeline risk demonstrates variation between different countries and regions with some being less risk averse (Germany, UK, Italy and Norway, State of Texas) than others (Sweden, Denmark, State of Illinois) based on the surveys that ERM reviewed or interviews with stakeholders. . Some of the positive aspects associated with hydrocarbon pipelines (such as economic growth or enhanced energy security) which are sometimes used to influence the acceptance of projects by affected communities are typically absent for CO2 pipeline projects. Nonetheless, given the higher relative population densities between countries and regions it is likely that some public opposition to CO2 pipelines could develop in the UK and in certain states or regions in other countries (e.g., Illinois). Problems can be exacerbated when affected communities are not well informed about the CCS pipeline project, as suggested by the experience of past hydrocarbon pipeline projects.

The current lack of awareness concerning CCS suggests that individual stakeholders as well as the general public would like more information in relation to risks of CO2 leakage and the associated risks to human health and the environment. This can present an opportunity to establish communication channels that will enable a wider distribution of the relevant information on CCS technologies and serve to influence the risk perception of CCS and its related infrastructure in order to ease the CCS deployment process. CO2 pipeline developers are aware of the wider societal benefits, whilst acknowledging that the risks are borne by the local communities affected by pipeline projects. Pipeline developers and government should engage early on to educate local communities on the wider societal benefits to support project acceptance. It can be reasonably expected that communities would be more positive to CCS projects when they feel that by supporting a CCS project, they form an integral part of the solution to climate change.

Sustainable Transport Instruments



PLANNIING INSTRUMENTS

Land use planning (master planning)

Planning can reduce the need to travel through bringing people and the activities they need to access closer together. Planning can also enable the implementation of new transport infrastructure (road, rail, other public transport, cycling and walking).

REGULATORY INSTRUMENTS

Standards (emissions limits, safety), traffic organisation (speed limits, parking, road space allocation), production processes

Regulatory measures can be used to restrict the use of certain motorised vehicles, but also influence the types of vehicles used and standards that they should adhere to (both in terms of vehicle performance and road regulations).

ECONOMIC INSTRUMENTS

Fuel taxes, road pricing, subsidies, purchase taxes, fees and levies, emissions trading

Economic instruments can be used to discourage the use of motorised vehicles, which will encourage the use of alternative modes, or reduce the need to travel. Instruments can also improve accessibility and mobility for those without a private vehicle, through investment in transport. infrastructure.

INFORMATION INSTRUMENTS

Public Awareness Campaigns, mobility management and marketing schemes, co-operative agreements, eco-driving schemes

The provision of information, in easily accessible formats can increase the awareness of alternative modes, leading to a mode shift to walking or cycling. Information can also be provided related to improving driver behaviour, resulting in reduced fuel consumption.

TECHNOLOGICAL INSTRUMENTS

Fuel improvement, cleaner technologies, end-of-pipe control devices, cleaner production

Where travel by motorised transport is necessary, technology can be used to reduce the impact of carbon emissions, through developing cleaner fuels and improving vehicle efficiency.

Reduced Carbon Emissions

Planning Instruments

Land use planning: Smart infrastructure design will influence both the demand for and the efficiency of transport. “Mixed land use” mixes the various forms of land use like housing, working, shopping, or public services within one city quarter. A smart mixture can significantly reduce the need to travel, or distances travelled and thus decrease energy consumption and emissions. Good access to public transport can also be a major contributor to cutting emissions. Parking management can affect the relative price and convenience of driving.

Planning for public transport modes: Public transport includes buses, rail, light rail, metro, and underground systems. Attractive, accessible and reliable public transport systems can provide the basis for alternative mode use in cities. Expansion of the systems and services or improving the operation of systems helps to improve public transport. A sufficient ridership is required to avoid transit vehicles running at half occupancy.

Planning for non-motorized modes: Cycling and walking do not produce direct emissions. Creating continuous cycle networks, separating cycle lanes, or integrating with other transport modes encourage cycling and walking. Support instruments are awareness campaigns and information, which may also include cycling and walking routes and maps.

Regulatory Instruments

Physical restraint measures:

These measures include physical restriction to access certain motorized vehicles reducing traffic volumes and associated GHG emissions. One such measure is the restriction of vehicles on certain days depending on their registration plate number. To avoid second car purchases such schemes should be well-designed and limited to restrictions during peak periods.

Low emissions zones:

Low emissions zones are areas into which access is allowed only to vehicles meeting a prescribed standard of emission. Such restrictions have benefits for local air quality improvements and for GHG emission reductions, if the area is big enough. However, this instrument requires a high level of administration and technology to set up and enforce the restrictions.

Traffic management measures:

Traffic management measures smooth traffic flows and thus helps to ease congestion and improve fuel efficiency. Area traffic control systems, where signals are linked across a whole network, are most efficient. In developed countries, traffic management has been estimated to reduce emissions by 2% to 5%. There is potential for similar benefits in developing cities due to the poor initial traffic considerations.

Regulation of parking supply:

Parking supply restrictions can make car use unattractive and thus contribute to mode shift. In addition, illegal parking must be avoided, e.g., by providing bollards on pavements. Transport authorities should also work in partnership with employers and other commercial business, which have a role to play in reducing private parking allocations reserved for employees.

Speed restrictions:

At higher speeds (generally above 55 km/h) fuel consumption is often an increasing function of speed for cars and trucks. In order to reduce emissions, the implementation of lower speed limits should be considered.

Economic Instruments

Road priding: In general, road pricing increases the cost of running a vehicle thus encouraging the use of alternative modes. Key factors that affect the effectiveness of road pricing include: the level of fee charged, the current cost of driving per kilometer, responsiveness of travelers to the price of travel, and the nature and extent of pricing. The two main road pricing options are: national pricing schemes, where charges are applied to long-distance highway use, and local road pricing schemes, which typically cover city center areas.

Fuel taxation:

Fuel taxes are a way of charging the users of transport infrastructure relative to individual use. Fuel taxation raises the price of travel per kilometer and fuel taxation is directly proportional to fuel consumption. Both effects can contribute to reducing GHG emissions.

Vehicle taxation: 0.85em;">:

The main principle behind vehicle taxation is to charge vehicle ownership. There are two key forms of vehicle taxation: Sales taxes are charged when the vehicle is purchased, sometimes contributing significantly to the overall cost of the vehicle. Annual vehicle taxes/registration fees are a continuous financial burden rather than a one-off tax. They also apply to all vehicles rather than just new ones. Vehicle taxes can be differentiated according to vehicle type, vehicle size or emissions, and noise levels.

Parking pricing:

Parking pricing increases the cost of using a vehicle by raising the cost of parking. To increase the effectiveness of parking pricing, it should be coupled with limits to the physical availability of parking spaces, and it is recommended to introduce it on a region-wide basis.

Information Instruments

Public awareness campaigns and mobility management: Public awareness campaigns can take many forms. Most often they are used to inform the public about the travel alternatives available to them or about the environmental, economic and social impacts of transport. Marketing of sustainable transport solutions is essential when attempting to secure public acceptance.

Driver behavior training and education/eco-driving: Through the provision of Eco-Driving education and training, driver behavior may be altered to achieve greater fuel efficiencies. Key methods of improving fuel efficiency can relate to driving style/behavior (speed, braking and acceleration, engine idling, carrying capacity and cold starts) and vehicle condition (maintenance-engine, tires, oil and air filter, and vehicle age). Driver training is particularly effective when commercial vehicles, such as bus, taxi or freight fleets, are included.

Technology improvements and Instruments

The key aims in order to achieve reduced GHG emissions from transport are to change travel behavior and/or the technology used. Technology improvements often focus on fuels, propulsion technology, other vehicle attributes, and use of communication and information technologies. They may sometimes seem to be easier to implement than policies that may restrain vehicle demand and use, primarily as they require less behavioral and lifestyle change. However, technology improvements are most effective when implemented in conjunction with other instruments within a larger strategy.

Strategies to Reduce Emissions of Greenhouse Gas Emissions

A Comprehensive Approach

Evidence suggests that a comprehensive sustainable urban transport approach that takes advantage of a variety of instruments will have a larger impact on emission reductions and will result in a more co-benefits through the improvement of local transport systems. Taking a comprehensive approach will typically include, e.g., the provision of cycling and walking facilities, attractive and reliable alternatives to the private vehicle, it will make use of measures that restrict the use of the car, it will help establish good land use planning practices; and it will promote technological improvements such as cleaner fuels; it will set (monetary) incentives by applying appropriate economic instruments.

Potential Strategy Outcomes- Greenhouse Gas Emission Reduction and Co-benefits

The level of greenhouse gas reduction that could be achieved as a result of individual instruments is difficult to predict. Reductions are most likely to be achieved where a higher share of public transport or non-motorized modes is attained.

The largest CO_2 reduction can be achieved by the implementation of a package of measures, including **Bus Rapid Transit (BRT)**, pedestrian upgrades and cycle ways. This is estimated to result in a reduction of more than 12 million tons of CO_2 from the baseline at mitigation costs of US$30 per ton of CO_2.

A range of co-benefits can be achieved through the implementation of sustainable transport instruments. Co-benefits include health and safety, the economy, accessibility to key services and activities and air pollution.

Financial Mechanisms to Tackle Climate Change

Clean Development Mechanism(CDM)

Global Environment Facility(GEF)

The GEF was set up to fund projects and programs aimed to protect the global environment. It only proved co-funding; a significant contribution to financing of the project needs to come from other sources. Projects can include biodiversity, climate change, international waters, land degradation, the ozone layer and persistent organic pollutants. By using the GEF developing countries and cities can mobilize additional funding to implement projects that are their core interest. In the transport sector, co-funding from the GEF can be used to improve public transport or promote non-motorized transport. To be eligible for GEF funding, projects must have a benefit for the global environment and fulfill specific formal criteria.

Transport is one of the key sources of GHG emissions. In order to effectively reduce global GHG emissions, developing cities with dramatically increasing populations and emissions will have to address climate change issues and contribute to its mitigation. The comprehensive approach that sustainable urban transport policies offer is a way forward to meet the needs for transport and mobility in an environmentally, socially and economically sustainable way.

Decision-makers and city administrations may have concerns regarding the impact of reducing the level of motorized transport on the economy. But there is evidence to suggest that by encouraging travel by sustainable transport modes GDP can continue to grow and economies can continue to develop. Sustainable urban transport can improve the local environment, reduce local air pollution and congestion levels – and thus make cities more desirable places to live, work, and visit