WHITE PAPER

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MOF-BASED CCUS

METAL-ORGANIC FRAMEWORKS (MOFS) AS COST EFFECTIVE, INDUSTRIAL SCALE SORBENTS FOR CARBON CAPTURE, UTILISATION AND STORAGE (CCUS) APPLICATIONS

January 2022

EXECUTIVE SUMMARY

Novel approaches to carbon capture are a necessity to tackle the accelerating negative impacts of man-made climate change. Metal-organic frameworks (MOFs) are a promising, cost-effective candidate to help solve this problem.

It is widely accepted that anthropogenic climate change is having a detrimental effect on the planet. Exceeding a 1.5°C rise in global average surface temperatures from pre-industrial levels could risk the earth's stability and life support system.[1] Primary targets in the fight to limit temperature rise are greenhouse gases, particularly carbon dioxide (CO_2). In 2020, global CO_2 emissions from fossil fuels exceeded 31 billion tonnes, down 5.8% from 2019 levels. However, as an exemplar of the need for acceleration in our approach to tackling climate change, the vast majority of this decline was attributed to the COVID-19 pandemic, which impacted almost every aspect of how energy was produced, supplied, and consumed. In order to limit temperature rise to 1.5°C, Carbon Law[2] states that global greenhouse gas emissions need to be halved every decade, until we reach carbon neutrality by 2050. In addition, some of the carbon already in the atmosphere needs to be removed to prevent even more dramatic action.

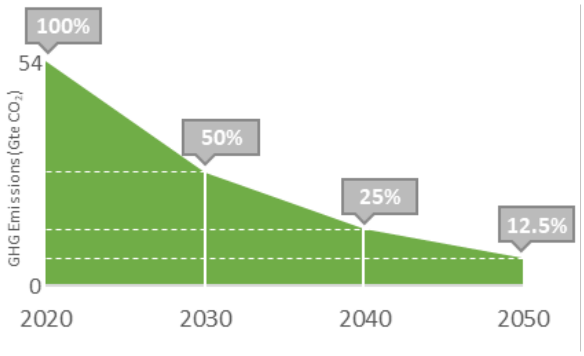

Figure 1: The Carbon Law - halving greenhouse gas emissions every decade. The estimated yearly emission level for 2020 is 54 billion tonnes of CO_2 equivalents[3]*

Accordingly, there are accelerating demands for the broader deployment and adoption of a range of decarbonisation technologies, including energy efficiency increases, fuel switching and carbon capture, utilisation, and storage (CCUS). No single approach or technology will be able to unilaterally solve the climate change challenge, so an approach akin to 'death by a thousand cuts' will be required. This opens the door to a variety of technological and policy-based solutions that will yield incredible innovation in the coming years.

This rapidly growing application space is seeing many approaches to tackling decarbonisation, including direct air capture, pre-combustion approaches, and post-combustion capture methodologies. All require advancements in materials technology and there are several promising candidates at various stages of development.

> *Promethean believes that MOFs represent a viable carbon capture technology based on their CO_2 uptake performance, selectivity, cost, versatility, and energy efficiency.*

Amine scrubbers, the predominant incumbent technology, absorb CO_2 from the flue gas of power plants. However, whilst initial costs are relatively low, they are challenged in other operational aspects, particularly their environmental profile and that the energy burden to regenerate the CO_2-saturated amine is as high as 20-30% of a power station's total output.[4]

An emerging alternative is a class of relatively new materials called metal-organic frameworks (MOFs). Some have high CO_2 uptake capacities and lower energy burdens. Until now, MOFs have been the purview of academia, developed more for novelty than a real chance of commercial success. Progress has been hampered by a perceived lack of industrial scale and prohibitive economics.

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* *This estimate represents the expected situation pre COVID-19*

CLIMATE CHANGE AND TACKLING CO_2 EMISSIONS

The issues and consequences surrounding global warming, namely from greenhouse gases such as CO_2, have been well studied. The leading cause of global warming is the trapping of infra-red radiation due to increasing concentrations of CO_2 in the atmosphere. Since the early 1800's, the volume of CO_2 in the atmosphere has increased by 40%, largely driven by human activity. It has been estimated that 2,100 gigatons (Gt) of CO_2 have been emitted anthropogenically since 1850, increasing atmospheric CO_2 levels from 280ppm to 419ppm and accounting for a global average temperature increase of 1.1°C.[5] This culminated in 33 Gt of global CO_2 emissions from fossil fuels alone in 2019. Of these emissions, 41% results from the power generation sector,[6] including coal-fired power plants.[7] However, this is not just a coal problem. Other 'cleaner' fossil fuels, like natural gas (methane), produce CO_2 when burned during gas-turbine power generation, albeit at lower levels.

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

Figure 2: Natural gas (methane) produces carbon dioxide and water as the products of combustion

This increase in CO_2 has contributed to a rise in the average global temperature, which has had major consequences for the world's climate conditions, including a rise in sea levels, ocean acidification, droughts, destruction of ecological habitats and an increased frequency of extreme weather events.[8] International efforts by governments, countries and companies continue to be made to reduce greenhouse gas emissions. One of the most prominent efforts, the Paris Agreement, is an international treaty signed in 2015 by 196 countries to reduce greenhouse gas emissions. Its goal was to maintain the global mean temperature rise for this century below two degrees Celsius.[9] As can be seen above, this already ambitious goal has been superseded with an increasing realisation that we cannot let global temperatures rise by more than 1.5°C – a number widely brought to increased prominence during the COP26 Conference held in Glasgow, 2021.

It is becoming increasingly clear that to even make a dent in a problem of this scale, a combination of approaches will be required. The IPCC's 2018 special report estimated that we have a 'Carbon Budget' of 580 Gt of CO_2 if we are to give ourselves a 50:50 chance of keeping global warming below the 1.5°C. At current rates, this limit will be exceeded within 15 years. Decreasing carbon emissions prolongs this timeline but does nothing to reverse the effects of the CO_2 already in the atmosphere. In effect, there are two challenges: slowing the problem and reversing the problem.

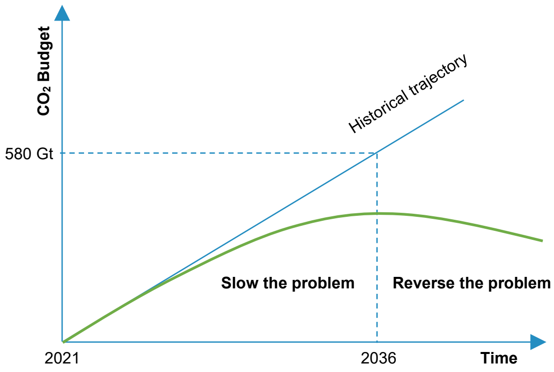
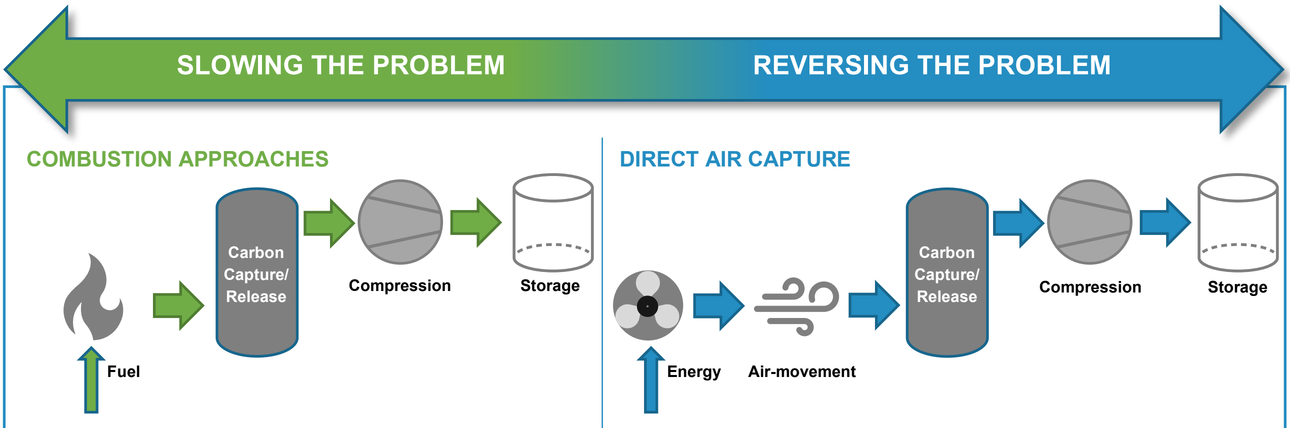


Figure 3: Schematic representation of the Carbon Budget

Slowing the Problem

Reducing the rate of emissions, whilst critical to both short and long-term progress, can only ever deliver the world to a carbon neutral point. The increase in use of renewable technologies like solar, wind, and hydroelectric, will go some way to reducing the reliance on fossil fuels in meeting our energy needs. However, certain industries that create products on which we are now so reliant, require so much electricity, at such an intensity, that electrification (and subsequent costs of a transition) remain an incredible challenge. Renewable sources are not foreseen to be effective alternatives to traditional power generation methods any time soon. The so-called 'hard to abate' sectors of heavy industry (cement, steel, chemicals) and heavy-duty transport (road trucking, container shipping, and aviation), will continue to rely on combustion-based power generation for some time.



Traditionally carbon-containing fuels are burnt to generate power. The resultant CO_2-containing gas-streams are then passed through a carbon capturing technology, and the gas eventually released, compressed, and stored.

Renewable energy is spent to flow air over a carbon-capturing technology. This lower CO_2 concentrated gas-stream is then similarly compressed and stored ready for further use or sequestration.

Figure 4: Simplified schematic representations of combustion and direct air approaches to carbon capture as they relate to slowing and reversing carbon emissions

It is fair to say that if an industry continues to burn fossil fuels, a post-combustion carbon capture (PCCC) system is the only carbon abatement option. The majority of this whitepaper will be spent covering the issues and potential solutions involved in post-combustion carbon capture in the pursuit of slowing and reducing our emissions to a sustainable level.

Reversing the Problem

Direct air capture (DAC) is an emerging technology targeting the removal of the CO_2 already present in the atmosphere. The process relies on flowing air over a carbon capturing material. The CO_2 is later compressed and stored for further use or sequestration. As atmospheric levels of CO_2 are in the low parts per million (ppm) range, the process relies upon moving vast quantities of air across a contactor. Energy is still required to power air-moving fans and to regenerate the CO_2 saturated material. Proponents of DAC are quick to point out that the energy used will be generated from renewable sources, but some critics remain unconvinced, believing that the renewable energy could serve a higher and better purpose. Another argument is that post-combustion gas streams offer a higher concentration of CO_2 and therefore represent a more inherently energy efficient opportunity for CO_2 removal in the immediate term.

There are several alternative and innovative approaches. The metal-organic framework materials described later are equally adept at capturing CO_2 from a direct air source as they are a post-combustion source and Promethean is engaged with customers pursuing both direct air as well as post-combustion approaches to carbon capture.

> *When it comes to climate change and carbon capture, the sheer scale of the challenge means that a combination of approaches will be required to make a significant impact.*

Pre-combustion Approaches

Another area of focus in trying to tackle climate change and decarbonisation are technologies being deployed ‘pre-combustion.’ These processes can offer appealing efficiency benefits over post combustion designs but often require entirely new system designs and can be difficult to retrofit onto existing infrastructure. Today, a heavy focus is on the replacement of carbon-containing fuel. In industrial settings, significant activity is focused on several approaches to replacing natural gas (methane, CH_4) with hydrogen (H_2). One method is the oxidation of fossil fuels to form synthesis gas (Syngas) – a mixture of H_2, carbon monoxide (CO) and water (H_2O). This Syngas is then further converted to generate an H_2 and CO_2 rich gas mixture. As the CO_2 concentration in this mixture is high (up to 50%), efficient capture can be undertaken prior to using the remaining hydrogen as a fuel. Hydrogen has the advantage of not containing any carbon and therefore does not produce CO_2 when burnt. However, hydrogen is 200 times more potent than CO_2 as a greenhouse gas and any leakage could result in hydrogen escaping to the atmosphere.[10] The transformation of methane into hydrogen requires energy. This is being addressed by making more efficient catalysts for processes that can be run using renewable energy sources, termed 'green hydrogen.' This fuel substitution approach to pre-combustion also applies to the electrification of motor vehicles, where the power generated from the combustion of carbon-containing petrol or diesel is being replaced by electrical energy delivered from batteries.

One area that is currently attracting a lot of attention relates the replacement of coal with biomass. The biomass (trees reduced to wood pellets) is burnt to generate steam that drives turbines and generates power. Claims of carbon neutrality are supported by the planting of trees to replace those cut down to produce the fuel pellets. Critics have been vocal about the disparity between the amount of biomass being burned and the time required for new trees to grow to sufficient size to adequately consume the appropriate offset of CO_2 from the atmosphere. Increased tree planting has also been described as a potential solution and, like many approaches, has both advantages and disadvantages. The average annual CO_2 emissions (equivalent) per person are estimated to be 4.8 tonnes[11] and an average tree can take up around 25kg of CO_2 per year. This would mean that 192 trees would need to be planted for each human, requiring more than 6 million km^2 of woodland to decarbonise the entire population. This is equivalent to 1.8x the area of India. This would directly conflict with the increasing need for agricultural land and therefore accentuates the low feasibility of tree planting alone as a primary solution to carbon capture. However, this doesn't mean that more tree planting shouldn't be undertaken, but it should not be seen as the panacea for climate change.

Global cumulative capture CO_2 by sector and source in the Sustainable Development Scenario, 2020-2070[12]

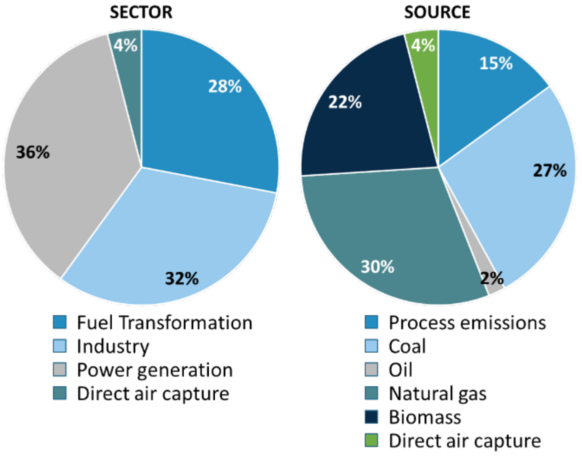


Figure 5: Transportation, industrial and power generation sectors are expected to play a major role in capturing CO_2

The following section discusses various technologies employed for carbon capture. Focus is given to applications in power generation and industry since improvements here are expected to play a leading role in meeting targets (see Figure 5 above). The CO_2 produced in these processes has historically been released into the atmosphere, and so the challenge is to capture, use, or store the CO_2, in order to mitigate against global warming.

> Whilst tree planting alone cannot abate climate change, it should still be considered as part of a suite of mitigating practices

CARBON CAPTURE TECHNOLOGIES

Given the accelerating attention and focus on carbon capture, there are an increasing number of technologies being developed to address the challenge. Technologies are at varying technology readiness levels (TRL) and both industry and academia are investing heavily in pursuing their commercialisation. A summary of technologies currently deployed and in development for carbon capture applications is summarised in Figure 6 below.

Where currently deployed, industry has focused on more mature technologies, particularly chemical absorption using amine-based solvents. Due to the maturity of this technology. a more in-depth review is provided below. In addition, there has been significant progress made on the use of solid sorbent technologies, particularly in direct air capture applications. Companies such as Climeworks (climeworks.com) and Svante (svante.com) are leading proponents of capture technology that use solid sorbents.

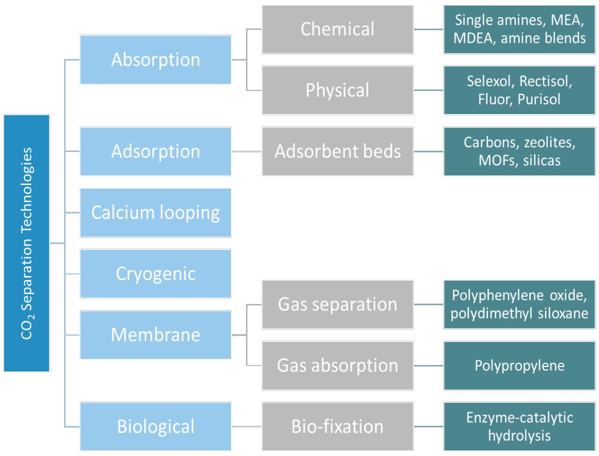


Figure 6: CO_2 separation technologies. Adaptation from Babar, Bustam, Ali, Shah Maulud, Shafiq, Mukhtar, Shah, Maqsood, Mellon and Shariff[13], Ben-Mansour, Habib, Bamidele, Basha, Qasem, Peedikakkal, Laoui and Ali[14]

Solid sorbent systems rely on a process called adsorption which can be physical, chemical, or a combination of both. Activated carbons, silicas, zeolites, and metal-organic frameworks (MOFs) are all examples of materials being used for adsorption of CO_2 and are discussed in more detail below. There are other technologies such as cryogenic distillation, membrane absorption and separation, calcium looping and biological approaches. These are not discussed in this white paper.

Amine Solvent Scrubbing

Currently, the most widely used carbon capture technology is amine scrubbing. The first amine scrubbers were reported to be in use as early as the 1930s.[4] The typical configuration for a CO_2 scrubbing-stripping system is shown in Figure 7. The main configuration (shown) has two main operations, absorbing and stripping. As the flue gas enters the bottom of the absorber, rising upwards, the CO_2 is absorbed by the downward flowing amine. The CO_2 rich amine then flows out of the bottom of the absorber, then into the stripper where CO_2 is desorbed and separated from the amine. The overhead vapour then goes into a condenser where it condenses leaving CO_2 to rise through the top as vapour. The reboiler at the bottom of the stripper provides the necessary heating for the desorption of the CO_2, with the reboiler bottoms being recycled back into the absorber, which provides the amine used for the absorption part of the process.

However, whilst amine scrubbers have a high CO_2 uptake capacity and relatively low initial capital investment, they also have several drawbacks. Firstly, and most importantly, the operational cost of amine scrubbers is expensive, mainly related to the regeneration of the amine once it is saturated with captured CO_2. This is largely because amines absorb CO_2 through a chemical reaction. This strong chemical bonding of the CO_2 to the amine structure requires significant energy to break the bonds during regeneration.

The most well-known and well-used amine is monoethanolamine (MEA). This is mainly due to its biodegradability once it has been used for carbon capture.[15] There are, however, other options for amine materials available, such as 2-amino-2-methylpropanol (AMP), methyldiethanolamine (MDEA) and piperazine (PIPA). However, these tend to be toxic to the environment and have a poor ability to biodegrade.[15]

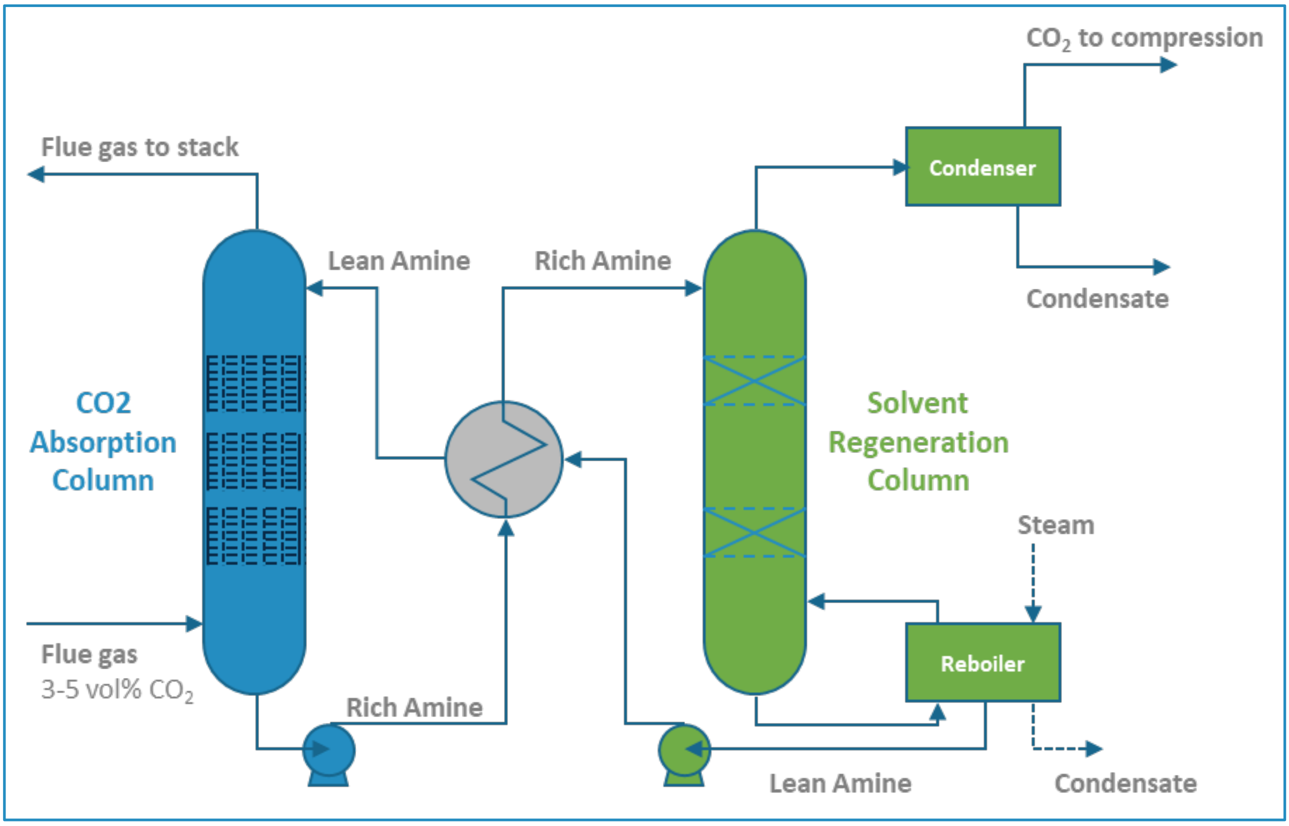


Figure 7: Typical setup for an MEA based CO2 capture system

The most prominent reason that amines are currently used for CCUS is their high CO_2 uptake capacity of ~45 wt% at 30% w/w MEA in water.[16] Not only does MEA have a high CO_2 uptake capacity, but it also removes other well-known contaminants such as NO_x, SO_2 and particulates.[15]

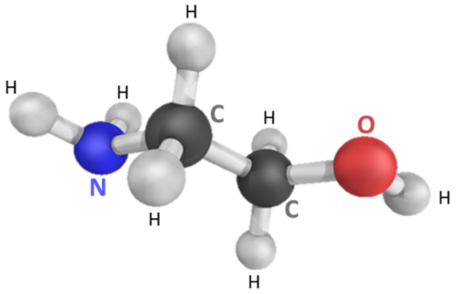


Figure 8: Chemical structure of monoethanolamine (C_2H_7NO)

Not only does MEA have a high CO_2 binding energy, leading to a high cost of regeneration and CO_2 removal, but MEA also undergoes oxidative degradation in the presence of oxygen in flue gas and thermally degrades at solvent regeneration temperatures above 120°C. It has been found that MEA undergoes an oxidative degradation at 55°C under the presence of 98% O_2 flue gas of 3.8 mM/h.[17] It is estimated that this degradation leads to an average monthly replacement requirement of 5% of the MEA.[18] Additionally, amine systems exhibit other operational issues. The amines tend to corrode the process equipment and pipework, leading to higher CAPEX and maintenance-driven downtime.

Solid Sorbents

Interest in solid sorbent materials has steadily increased over the decades for many reasons:

- Concern over emissions of volatile solvent components
- High elevation temperatures required to desorb CO_2 in chemisorption-based solvent systems
- Larger on-site capture unit footprint due to the need for a reboiler and additional solvent circulation steps when using solvent-based systems
- Concerns over solid waste and effluent production, as a portion of the chosen solvent are irreversibly converted to salt by-products
- Increased maintenance costs required for systems containing corrosive aqueous solvents

As can be seen in Table 1, there are already several different solid sorbent technologies, each with their own relative advantages and disadvantages. However, as stated at the beginning of this paper, this doesn't mean that these technologies shouldn't be deployed for carbon capture. The challenge to help solve climate change remains enormous and multiple approaches will be required. The remainder of this paper will focus on metal-organic frameworks that have been historically limited in their industrial scale adoption for a variety of reasons. These reasons will be discussed, as well as what is being done to finally overcome them.

Solid Sorbent	**Activated Carbons**	**Zeolites**	**Silica**	**Metal Oxides**	**Covalent Organic Frameworks**
Advantages	High stability Low cost	Fast adsorption / desorption kinetics	Fast adsorption / desorption kinetics	High adsorption capacities	High adsorption capacity and selectivity
Disadvantages	Low selectivity Low adsorption capacity	High moisture sensitivity	High moisture sensitivity	Require high temperature regeneration processes	Complex and expensive synthesis

Table 1: Relative advantages and disadvantages of various solid sorbents for carbon capture applications

METAL ORGANIC FRAMEWORKS

A New Class of Materials

One of the leading emerging alternative materials for carbon capture applications are a class of materials known as metal-organic frameworks, or MOFs. Metal-organic frameworks are a relatively new family of compounds which were first discovered by Tomic in 1965 and were discovered as waste material from other chemical processes. They first came to prominence in mid-1990s, with academic interest ramping in the mid-2000s. The first permanently porous metal-organic framework was discovered by Yaghi et al in 1999 where the term metal-organic framework was also coined.[19]

Metal-organic frameworks are highly porous, crystalline frameworks comprised of multivalent metals bonded to multitopic organic linkers.[20] This 'cage' structure is what creates one of their primary advantageous properties - incredibly high surface areas. Since MOFs are either two-dimensional or three-dimensional lattices, their surface area continues throughout the material. Surface areas of up to 7,000 m^2/gram have been measured. This yields surface areas of 10-100 times that of other 'high surface area' materials like activated carbons and zeolites.

The choice of metal ion and organic linker molecules is almost limitless, allowing for the tuning of the size and shape of the pores. It is estimated that more than 90,000 MOFs have been synthesised, although how many of these have been made at any industrially significant scale is unknown but believed to be very few. Unfortunately, this has also been their 'Achilles heel' from a commercial perspective.

Suitability of MOFs for Carbon Capture

Along with their high porosities and incredibly high surface areas, certain MOFs also have other advantageous properties for carbon capture applications These include:

- High thermal and chemical stabilities
- Tuneable selectivity
- Low energy of desorption
- Recyclability

High Thermal and Chemical Stabilities

High chemical stability is desirable for CCUS adsorbents due to the variability in many flue gas streams, which may contain fluctuating levels of reactive impurities such as SO_x and NO_x. These impurities can “poison” less stable adsorbents resulting in reduced performance over time. Such a loss in performance would necessitate the replacement of the material more frequently, ultimately resulting in greater cost per ton of CO_2 captured. Thermal stability is desirable for similar reasons. In many applications, thermal cycling of the adsorbent is required to regenerate it once saturated. Less thermally stable materials may lose performance over repeated heating/cooling cycles. MOFs can be engineered to excel in both regards. Careful metal/ligand selection leads to high chemical robustness and minimal thermal degradation.

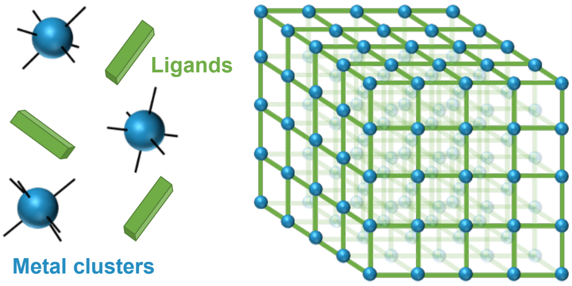


Figure 9: 3D representation of a MOF structure comprising metal clusters and ligands (linkers)

Tuneable Selectivity

Selectivity for CO_2 is key to maximising uptake performance per cycle (minimising “wasted volume” of adsorbent) as well as in generating a high purity desorption stream which could be sold on for further use, for example in the food industry. Since industrial sources of CO_2 are many and varied, it is important to be able to select the correct material for a given gas mixture, maximising CO_2 uptake whilst minimising capture of undesirable species. The huge variety of metal/ligand combinations in MOFs allows extreme tuneability when compared to similar adsorbents such as Zeolites.[21]

Low Energy of Desorption

No adsorbent material has infinite capacity. At some stage it is necessary to regenerate a saturated material to capture the adsorbed gas and free up the material to capture fresh CO_2. The energy used to perform this regeneration is typically the primary cost for any CCUS process and so minimising this value is desirable in any system. MOFs can be engineered to tune this energy of desorption into the desired range; too low and the material will have low affinity for CO_2 and poor selectivity. Too high, and the regeneration costs become uneconomical. A huge amount of academic work has gone into this optimisation resulting in MOFs with regeneration energies in the ~30 KJ/mol range[22] (compared to ~70 KJ/mol for amine-based adsorbents). Combined with the additional engineering options available to heat a solid sorbent (compared to solution-based systems), and the resulting increase in heating efficiency, ease of regeneration represents a key advantage of MOFs for CCUS applications.

Recyclability

MOF materials are inherently recyclable. What little degradation occurs during repeated capture/ regeneration cycles tends to take the form of damage to the MOF crystal structure rather than chemical changes to the metals or organic linkers that make up the structure. If the crystal can be dissolved it is thus possible to recover the “building blocks” and generate fresh MOFs using the recycled precursors.[23] This is a major advantage for any material envisioned as part of a circular economy and helps to offset the carbon footprint of synthesising these materials in the first place.

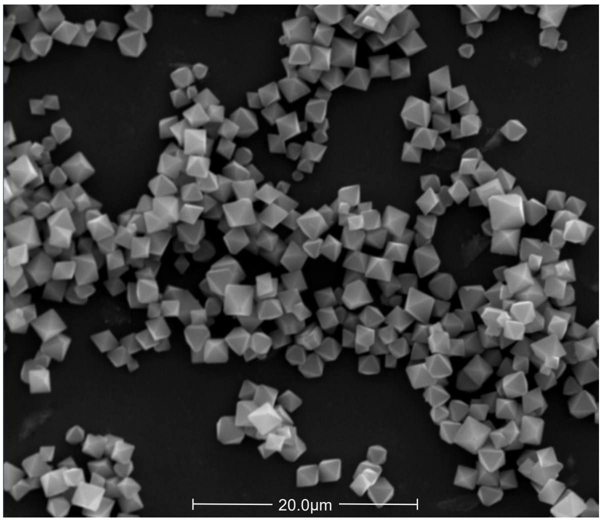


Figure 10: Scanning electron microscope image of HKUST-1 produced on Promethean’s proprietary continuous flow hydrothermal synthesis (CFHS) reactor system

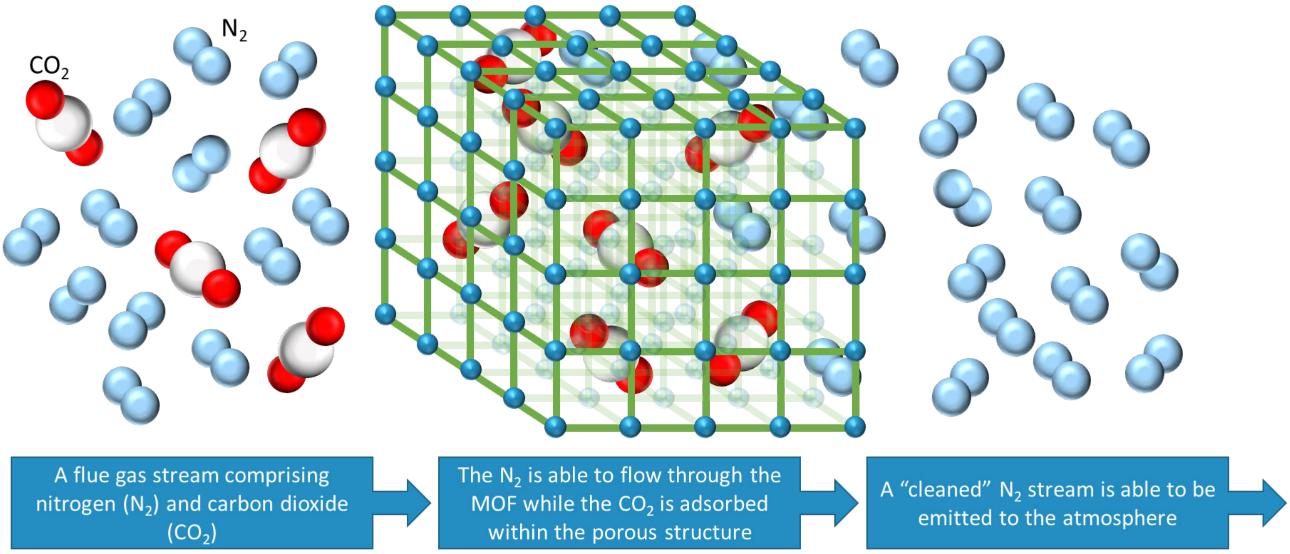


Figure 11: Schematic representation of CO_2 being selectively trapped within the MOF 'cage' structure

Historical Barriers to Industrial Use of MOFs

The amount of research activity focused on new MOFs has accelerated since the first MOF was identified. The almost limitless combination of metal clusters and ligands have made them a prime target of academic research. For a long time, MOFs have been the sole purview of academia, developed more for novelty than any real industrial commercial application. Accordingly, many MOFs have been synthesised from materials that are either prohibitively expensive and/or in short supply. In addition, they have historically been manufactured using inefficient batch hydrothermal synthesis techniques, yielding only grams of materials, and requiring hours or days to produce.

Like many nanomaterials, MOFs have already started to develop a reputation of being prohibitively expensive and simply not available at the scale necessary even for developmental research, let alone industrial scale commercial applications.

Scale

Like many manufacturing processes, scale and costs of production are inextricably linked. However, with MOFs, there is a genuine barrier with respect to scale alone. The vast majority of MOFs have been developed using batch hydrothermal synthesis methods. This involves initiating the nucleation of a MOF and then letting the crystal structure slowly grow over a period of hours, or even days. This process, at lab scale, yields materials in the grams (or even micrograms) scale which in some ways has contributed to the cost issue described below. However, regardless of cost, this is a simple barrier to industrial consideration. When pilot scale trials are not even feasible, industrial scale utility is almost impossible to imagine.

Continuous Flow Hydrothermal Synthesis

With many processes, scale can be achieved by making it bigger and/or doing more of it. However, batch synthesis of MOFs will not yield the volumes or economics of production required for industrial application. A different process is required – continuous production.

> *Promethean Particles is a world leader in continuous flow hydrothermal synthesis of nanomaterials, enabling MOFs to be a viable industrial scale carbon capture sorbent*

Continuous methods of nanomaterial production had been tried for many years, quite often ending in failure as the nucleating nanomaterials blocked the reactors during synthesis. In 2004, Prof. Edward Lester at the University of Nottingham designed and patented a method that allowed the continuous manufacture of these materials without blocking, leading to the formation of Promethean Particles in 2007.

As can be seen in Figure 12 below, in continuous flow hydrothermal synthesis, a hot pressurised water-based downflow containing the ligand precursors is collided with a cold upflow containing metal salts and the nucleation process is initiated in milliseconds. The formed products are then carried away for further processing.

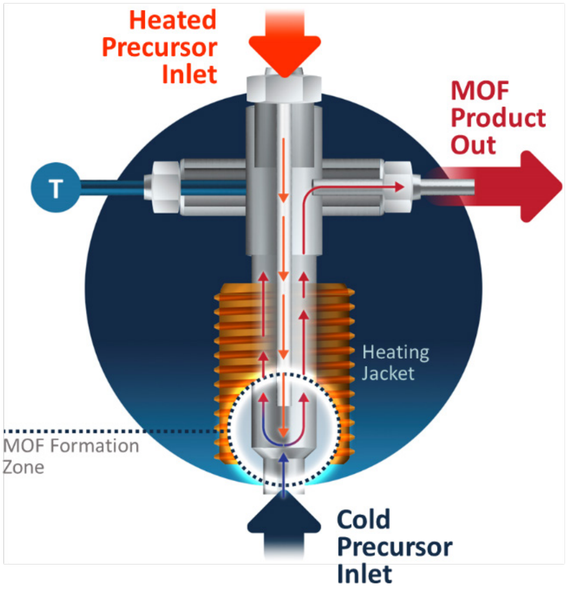


Figure 12: An overview of how continuous flow hydrothermal synthesis is used to manufacture MOFs

Not only does this process yield significantly higher volumes and lower costs, but the control of key process variables such as flow rates, temperature and pressures, allows controlled manipulation of certain MOF features, for example their particle size.

Economics

The lack of innovation in creating routes to manufacture have stifled industrial uptake of this incredible class of materials. When companies only have the capability to produce grams of material, it is easy to be seduced by the prospect of charging extremely high prices. Promethean has reports of companies receiving quotes of $60,000/kg for some materials. Whilst this may make a supplier a very profitable one-time transaction, the potential damage of this practice to the future industrial use of MOFs is being overlooked. Prospective users of MOFs won't be able to see past these exorbitant prices. Even if these numbers are halved, quartered, or reduced by 90%, it still makes it difficult for product managers to imagine the use of these materials in the millions of tonnes scale that will be necessary for some applications like carbon capture. It is critical that industry understands that these materials can, and must, be made at costs several orders of magnitude lower. Those in the industry with a significant capability to produce these materials at scale, need to be responsible in their pricing practices to avoid the prospect of killing off these materials before they have been able to demonstrate at scale the value they can bring.

Promethean's state of the art, continuous flow hydrothermal synthesis manufacturing facility is the largest of its kind in the world, helping deliver cost effective, industrial scale nanomaterials for use in carbon capture applications

CARBON CAPTURE, USE, AND STORAGE (CCUS)

With a significant amount of attention and focus on carbon capture (CC), it is also critical that we understand the issues, implications, and potential solutions with respect to the utilisation/use (U) and storage (S) of CO_2.

Uses of Carbon Dioxide

Carbon dioxide is not known as the most utilitarian of chemicals although it does play a significant role in several industrial, chemical, pharmaceutical, electronics, and oil and gas applications.

It is perhaps most well-known for adding the “fizz” to carbonated beverages but there are several industrial uses of CO_2. These include chemical and biological processes where CO_2 is a raw material, for example in the manufacture of methanol and urea. There are also various applications that utilise CO_2 directly, such as food packaging, refrigeration, welding, and fire extinguishers. The production of urea is currently the single largest use of CO_2 accounting for 57% of global demand.[24]

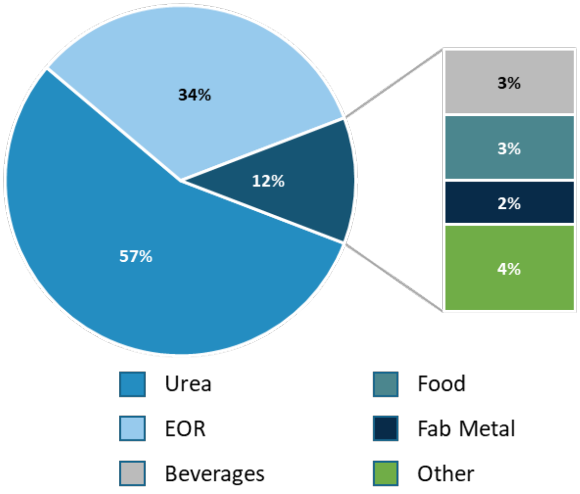


Figure 13: CO_2 breakdown of demand, 2015[24]

Current estimated demand is approximately 230 million tonnes per year (Mt CO_2/yr) and this is expected to grow steadily over the coming years.[24] Excluding enhanced oil recovery (EOR), annual industrial consumption is therefore only 150 Mt CO_2/yr. Theoretically, the industrial use of CO_2 should be possible to prevent CO_2 from playing a role in climate change however there are two main challenges.

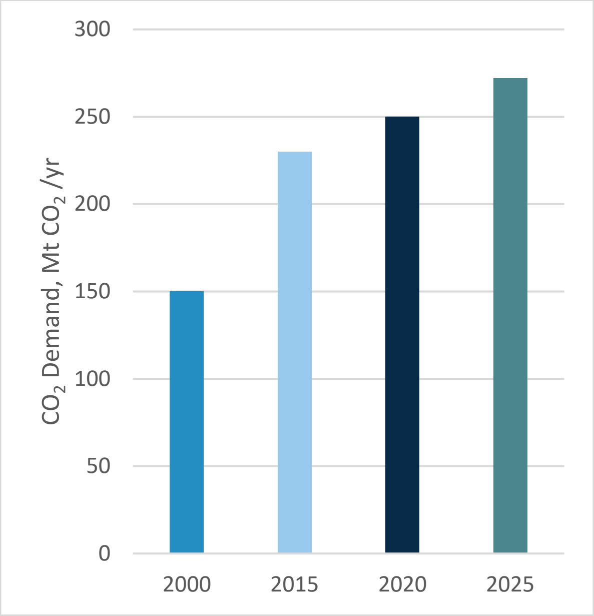


Figure 14: Growth in global demand of CO_2 over the years[24]

The first is the relative scale of CO_2 emissions versus their use. Current anthropogenic CO_2 emissions are estimated at 36 Gt CO_2/yr versus an annual consumption demand of just 150 Mt CO_2/yr. Man-made emissions are therefore 240 times greater than our potential uses for it. The second challenge is that any captured CO_2 needs to be utilised in applications where the CO_2 is bound for a long period of time and not quickly re-released into the atmosphere. Unfortunately, at present, most of the significant uses of CO_2 only fix the compound for a period of days to weeks before it degrades and is re-emitted to the atmosphere. Therefore, any future significant reliance on utilisation as a strategy is going to require significant advancement in innovation with respect to CO_2 chemistry.

Carbon Storage

As new chemistries are researched and new applications developed, there will still be a gap between the amount of carbon being captured and that being utilised. Some form of long term or permanent storage will therefore be necessary. The most commonly discussed method of carbon storage is where the captured CO_2 is transported to a storage site and then injected into naturally occurring porous rock formations such as a deep rock reservoir below the sea, or a depleted gas or oil field. Captured CO_2 is pressurised and turned into a 'fluid' called supercritical CO_2. It is then injected into the ground in what is referred to as 'geological sequestration.' There are two main concerns with this process: leakage and storage capacity.

Leakage

Whilst it is widely accepted that leakage can occur, especially if not managed properly, we only need to consider the same methods that have kept gas and oil reserves trapped underground for millennia – impermeable rock formations. When CO_2 is injected into the ground, it will rise until it meets these rock formations through which the CO_2 will not be able to pass through. We know that if these structures didn't exist, and the earth was made purely of porous rock, then the whole industry of oil and gas exploration would be unnecessary. All the oil and gas we are so familiar with today, produced from decaying vegetation and animals, would be pooled on the surface of the earth.

Storage Capacity

One of the biggest misconceptions in CCUS is that insufficient storage capacity exists in the earth and therefore the process of geological sequestration is unsustainable. A study by the Global Carbon Capture and Storage Institute found that there is significant storage capacity available and that geologic resources are sufficient to store centuries worth of CO_2 emissions.[25] With the increased focus on climate change and increasing global policy to address it, we are envisioning anthropogenic emissions to 'peak' in 2020 at 36 Gt CO_2/yr. Conservative estimates of storage reserves in the USA alone suggest there is capacity for 2,000 Gt of CO_2, with upper end estimates as high as 21,000 Gt. Current global estimates are in the 6,900 – 30,000 Gt range.[25] Therefore, with emissions only expected to decrease, there is still currently believed to be anywhere from 200-800 years of storage capacity.

> *Global geological storage capacity for CO_2 is many times larger than what is required for CCS to play its full role in supporting the achievement of net-zero emissions under any scenario.*

In addition to this, a possible further exciting use of MOF technology is their use to increase the available one-time underground storage capacity. This use of MOFs involves an adsorption step followed by a deliberately initiated temperature or pressure induced desorption. By omitting this second step, the high surface areas and high carbon dioxide selectivity could be employed to only adsorb CO_2, increasing the available storage capacity. This is still early work, although the concept has been demonstrated on a small scale.[26]

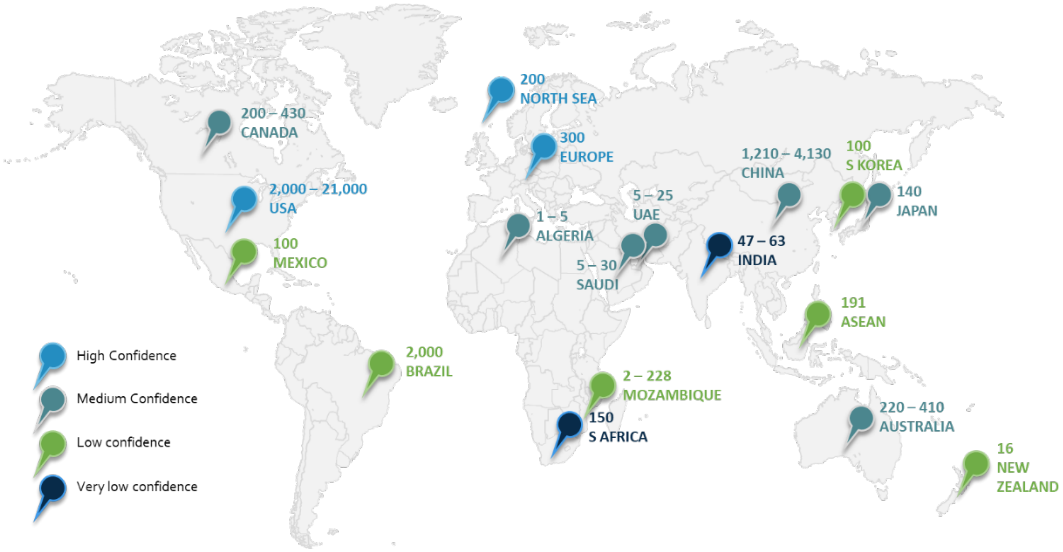


Figure 15: Estimated geologic storage reserves adapted from the Global Carbon Capture and Storage Institute

CONCLUSION

The scale of climate change is so vast that to make a meaningful impact will require many different policy and technology solutions all working side-by side.

There are numerous approaches to address climate change and greenhouse gas emissions. These include energy efficiency measures, the switching of fossil fuels for non-carbon alternatives, and a range of deep decarbonisation technologies, including carbon capture, utilisation, and storage.

No single technological solution in isolation will be able to solve the problem, but this does not mean that any solution should be excluded. Solving this problem will depend on both existing and future technologies and the rethinking of ingrained competitive beliefs.

Metal-organic frameworks represent an exciting new frontier of materials chemistry that have shown initial promise in their ability to selectively capture carbon from a gas stream and then efficiently desorb that carbon. However, to this point, they have suffered from a perception of prohibitive costs and a lack of industrial scale.

> *Promethean Particles is uniquely positioned to provide industrial scale, cost effective MOFs that can be used for carbon capture applications in addition to translating new MOFs from inefficient batch processes to continuous flow manufacturing. We have the capacity and cost structure today to help accelerate technology demonstrations through the provision of meaningful quantities of MOFs*

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