

CATALOGUE OF MOST IMPORTANT SCIENTIFIC ADVANCES IN CCUS OVER THE PAST 3 YEARS

A techno-economic investigation commissioned by the members of the
Carbon Dioxide Capture and Conversion (CO₂CC) Program

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1



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Introduction

Carbon Capture Utilization and Storage (CCUS) technologies are essential to help achieve global climate targets.

- ▶ The main objective of this report is to give an update of the recent progress made in CCUS technologies.
- ▶ CCUS is considered a critical part of climate change mitigation plans and reaching net zero.
- ▶ Carbon dioxide (CO₂) accounts for 65% of global greenhouse gas emissions.
- ▶ CO₂ emissions can be reduced via several mitigation options such as energy efficiency improvements, replacement of fossil fuel with renewable energy, implementation of nuclear power, and CCS.

Recent advances in CO₂ capture technologies can be divided into three categories: post-combustion capture, pre-combustion capture and oxyfuel-combustion.

- ✓ Post-combustion capture offers a mature technology which can be easily retrofitted to existing plants.
- ✓ **Capture technologies** include absorption, adsorption, membrane separation, calcium looping, chemical looping, and direct air capture (DAC).
- ✓ Recent developments in **Carbon Capture and Utilization (CCU)** technologies include utilisation of CO₂ to produce fuels, chemicals and construction materials.
- ✓ A careful assessment of the lifecycle emissions of each product and process is required to ensure the lifetime CO₂ emissions of the product do not exceed the amount of CO₂ utilized.
- ✓ Recent progress in **Carbon Capture and Storage (CCS)** methods include enhanced oil recovery (EOR), geological storage and natural sequestration.
- ✓ For industrial applications, carbon capture via absorption is the most commercially mature technology to date, and in recent years a steady increase of CCS projects using this technology has been observed.
- ✓ Growing interest in new technologies for **CO₂ utilization**, such as the production of synthetic fuels, chemicals and construction materials has been reflected in the increasing support from governments, industry, and investors
- ✓ **Geological sequestration** is relatively well understood and recent developments have focused on the effect of location, monitoring methods and site characterization. However, due to low economic value and liability concerns, governments' intervention is needed

An overview of each technology is presented at the beginning of each section, followed by the recent advances. Current projects and future hurdles of each technology are outlined, and the most important findings and the challenges related to each technology are addressed in this report.

SCOPE OF REPORT:

- CCUS** technologies involve the capture of CO₂ from the power sector or industrial processes, the transport of the CO₂ via ship or pipeline, and either its conversion into valuable products or its permanent storage.
- Recent research regarding geological sequestration and enhanced oil recovery **EOR** has mainly focused on estimating capacity of CO₂ storage sites and evaluating health, safety and environmental concerns related to CO₂ leakage.
- Research of natural based methods has focused on understanding the complexity of ecosystems and long-term project monitoring.
- Many studies are focusing on the implementation of **CCS** to the top-emitting industries including iron and steel, cement, petroleum refining, and petrochemical. Unlike fossil fuel power plants, many industries have few or no CO₂-free alternatives to manufacture products.

Carbon capture and utilisation (CCU) involves the capture of CO₂ from a point source (power plant, steelmaking, etc.), transport, and subsequent use as a feedstock.

There is growing interest in **CCU** as a climate change mitigation tool where the captured CO₂ is converted into valuable products rather than sequestered underground.

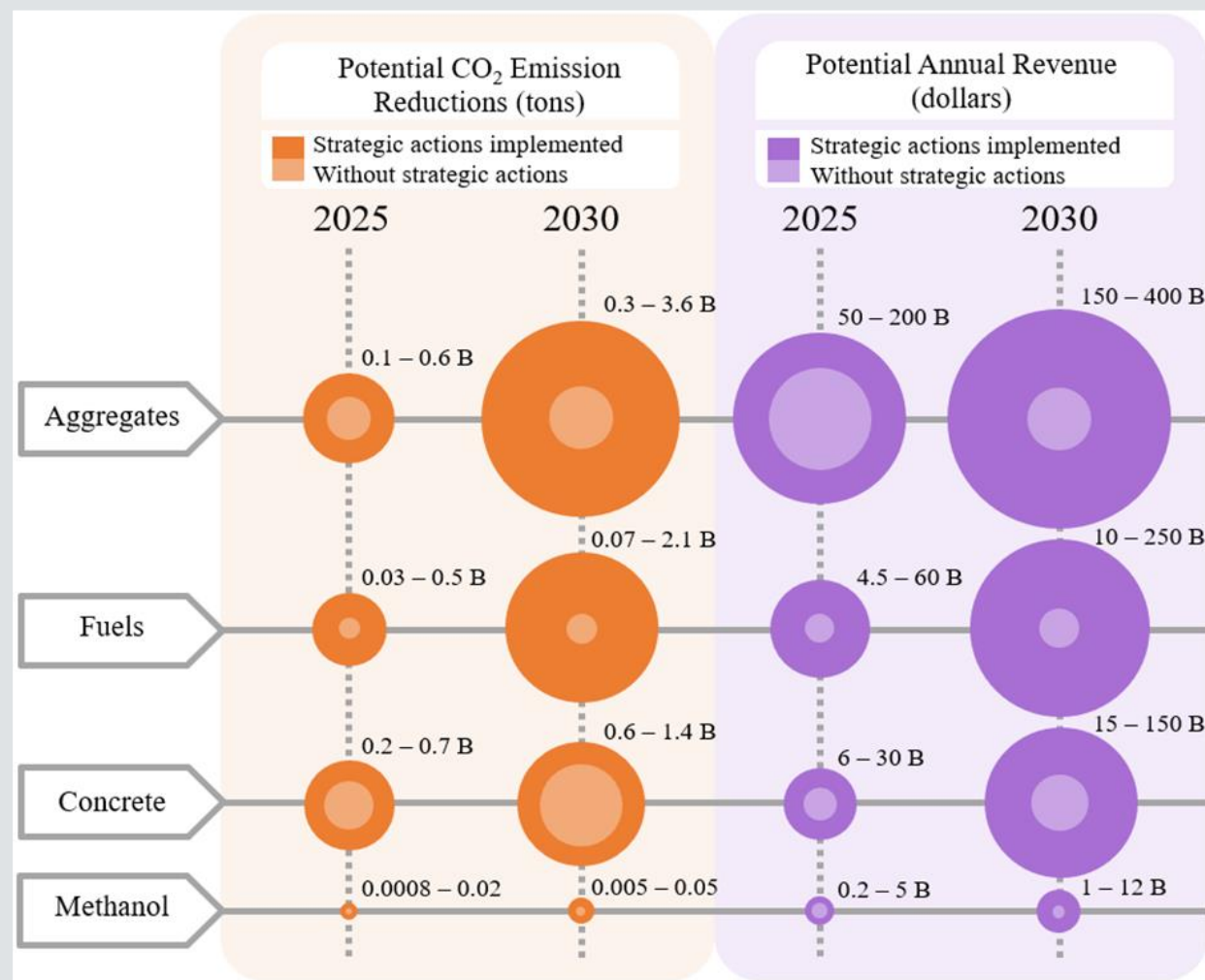


Figure 1: Emissions reduction and market potential of CO₂ utilization products. Source: Global CO₂ Initiative, 2016

ADVANCES IN CAPTURE TECHNOLOGY

Ionic liquids are salts with melting points less than 100 °C. Ionic liquids comprise of organic cations and anions with a potential number in the order of 10^{18} , due to the substantial possibilities of ions studied (Krishnan et al., 2020). The characteristic of ionic liquids can be altered via different ions and functional groups involved in the solvent.

- ✓ The development of new solvents with fast kinetics, low regeneration energy, low toxicity, high thermal stability, and high capacity have been the primary focus of research. Many screening experiments have been performed for different promoters and novel solvents including but not limited to water lean solvents, biphasic solvents, ionic liquids, and amino acid salts.
- ✓ In post combustion capture based on **amine solvents**, CO_2 is removed via a chemical absorption process, which involves passing a flue gas stream to an aqueous amine solution. The CO_2 can subsequently be released by heating the solution in a desorber. In the absorption process CO_2 is captured from the flue gas in an absorber and released in the stripper (desorber) by changing the temperature and/or pressure. Ionic liquids exhibit high viscosity, occasional toxicity, and combustible character.
- ✓ They can be functionalised by adding solvents such as amines and amino acids. Ionic liquids based on amino acids negate drawbacks seen in other ionic liquids such as toxicity and non-biodegradability whilst having relatively high CO_2 absorption capacity.
- ✓ Amino-acid-based ILs (aa-ILs) encounter kinetic limitations due to their high viscosity showed some dual amino group functionalised imidazolium AAILs presented more than quadruple the cyclic capacity of 30 wt.% MEA, with comparable viscosities. Imidazolium-based ionic liquids, Butyl-3-methylimidazolium Acetate [bmim][Ac]-impregnated into silica sorbents showed up to 600% higher CO_2 capacity when compared to silica sorbents alone. [bmim][Ac]-impregnated silica sorbents also showed significantly higher CO_2 absorption rate than pure [bmim][Ac]. Alumina had higher CO_2 uptake and selectivity capacity (CO_2/N_2). The highest selectivity and CO_2 uptake were exhibited by alumina-mbmim [Tf2N] and silica-[mbmim][Br] respectively. The materials also showed faster kinetics than pure ILs.

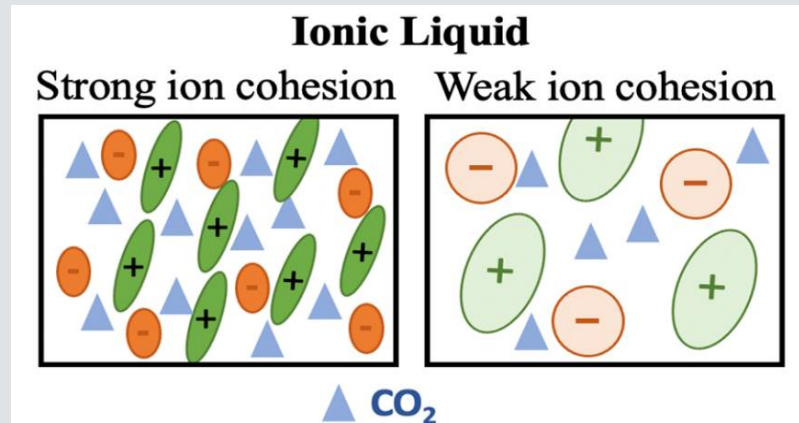


Figure 2: A schematic to show the mechanism of CO_2 absorption in ionic liquids. Adapted from Ochedi et al., 2021

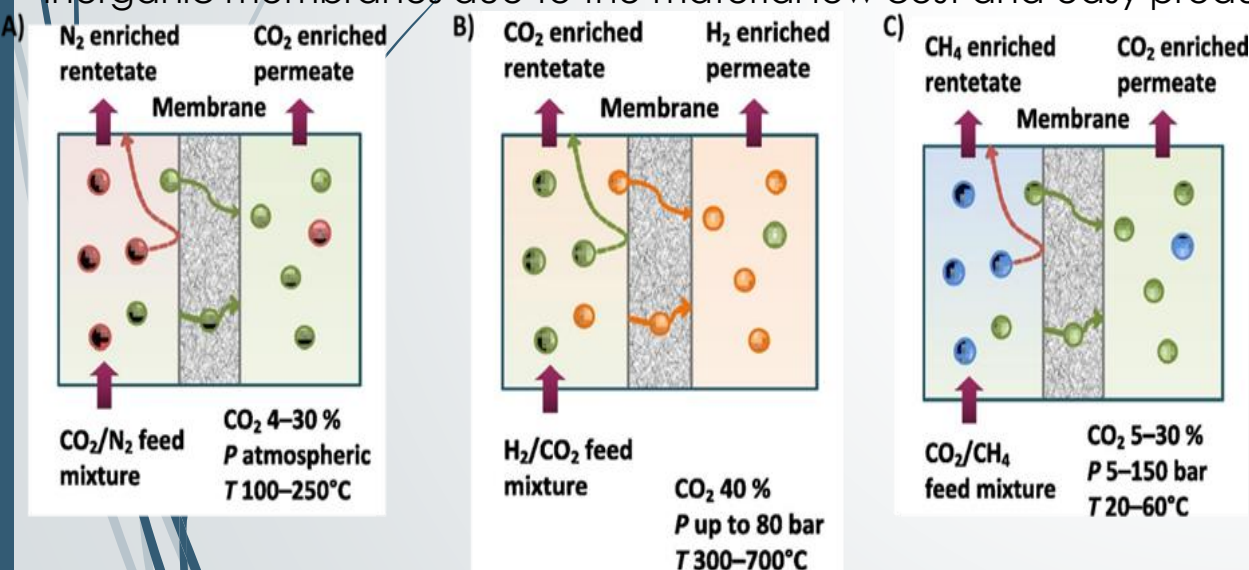
ADVANCES IN CAPTURE TECHNOLOGY

Membrane Materials - separation technologies can be applied to pre-combustion, oxy-combustion, and post-combustion carbon capture processes. During membrane gas separation, polymeric or inorganic membranes separate gases by means of selective permeation. One or more gaseous components are transported from one side to another due to a concentration gradient, since the difference in partial pressure is the main driving force, membrane separation is more favourable when the gas stream is at high pressure. For natural gas processing the CO_2 membrane permeance is targeted at more than 100 Barrer (non SI units for gas permeability) with 1 μm membrane thickness and a CO_2/CH_4 selectivity in the range of 20–30, whereas for pre-combustion CO_2 capture, the H_2 membrane permeance has been stated to be more than 200 Barrer with at least 10 H_2/CO_2 selectivity. For CO_2 capture from flue gas, the membrane is expected to have CO_2 permeance of more than 1000–5000 Barrer with CO_2/N_2 selectivity in the range of 50–200, which is significantly higher than both natural gas processing and pre-combustion CO_2 capture. **Organic polymer membranes** are preferred over inorganic membranes due to the material low cost and easy production. The most common polymers used are polyimide (PI) which is

used in the Medal Air Liquide/GTL membrane and polysulfone (PSf) which is used in the PRISM™ membrane from Air Products.

Polyimides are the most widely used and investigated materials for CO_2 separation due to their good physical properties and suitable mechanical strength. They are commercially manufactured under the trade name of Matrimid®, they exhibit a permeability of 4–30 Barrer and a selectivity of CO_2/N_2 between 23–36. Research-scale polyimides such as the hexafluoro-substituted aromatic polyimide (6-FDA) have shown a superior CO_2 permeability (400 Barrer) than the commercially available ones, with a CO_2/N_2 selectivity of 17.

Figure 3: Potential applications for membranes in CO_2 separation: (A) post-combustion, (B) pre-combustion, and (C) natural gas processing. Adapted from Prasetya et al., 2020



Strong collaborations between the National Carbon Capture Centre and various partners including the Gas Technology Institute, the Department of Energy's National Energy Technology Laboratory Membrane Technology and Research, and France's Air Liquide have positioned membrane separation as a next-generation carbon capture technology.

ADVANCES IN CARBON CAPTURE AND UTILIZATION

Using **captured CO₂ as a feedstock to produce fuels** could provide new opportunities for diverse industries to lower their carbon footprint. The production of fuels could increase the CO₂ demand by up to 2050Mt per year. It is important to note that CO₂ based fuels will eventually end up releasing CO₂ to the atmosphere, thus conversion of CO₂ into fuels can only be a carbon-neutral technology (in the best-case scenario, where atmospheric CO₂, electrolytic hydrogen, and exclusively renewable energy are used as feedstock). The most common fuels derived from CO₂ conversion are methane (CH₄) and methanol (CH₃OH), although CO (syngas) and ethanol can also be produced via CO₂ reduction. CO₂ conversion into CH₄ or the so called “power to gas” (PtG) process, also known as CO₂ methanation can occur via various pathways. The PtG concept has been proven at pilot scale in various projects, mainly based in Germany. The most common pathways to convert CO₂ into methanol include homogeneous/ heterogeneous catalytic, electrochemical, photochemical, and photoelectrochemical reduction.

Catalysts are central to the conversion process; therefore, much of the research efforts in the past few years have focused on developing new catalysts that are more chemically stable, less corrosive, non-toxic and have lower production cost.

Catalysts used for CH₄ production are typically composed of active metal particles dispersed on a metal oxide support. Nickel based catalysts are usually the preferred catalyst for this reaction because of their high catalytic activity and CH₄ selectivity. Other active metals such as rhodium, ruthenium, cobalt, and iron present the same or higher activity and selectivity towards CH₄ compared to nickel but are not used due to their high cost. Additives such as ZrO₂ and ZrO have demonstrated to improve the stability and activity of heterogeneous based catalysts. Some of the companies that are currently commercializing Cu and Zn based high stable catalysts for methanol production include **Mitsubishi Gas Chemical**, **Sinetix**, and **Haldor Topsøe**. The use of novel structured porous catalysts in different conversion pathways to produce methane and methanol has also gained significant interest in the past few years. Structured porous catalysts with their highly containing order structure and high surface area provide several advantages over conventional catalysts aiding in metal site poisoning, sintering, and deactivation due to exposure to high temperatures.

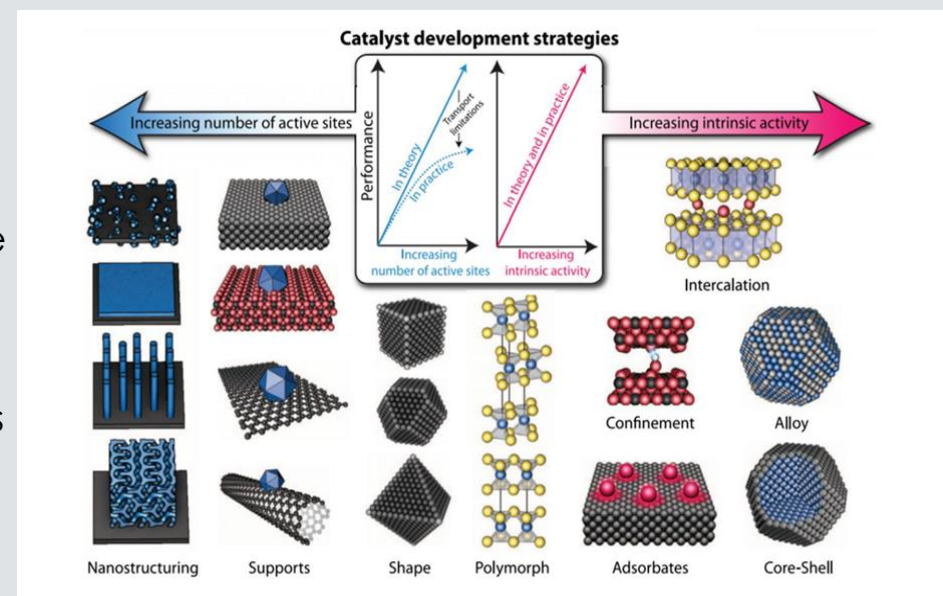


Figure 4: Strategies for catalyst development, open access. Source: Ochedi et al., 2020

ADVANCES IN CARBON CAPTURE AND UTILIZATION

Carbon conversion into chemicals represents a large CO₂ sequestration potential of approximately 500 Mt/year.

The production of various chemicals is possible through carbon capture and utilisation including urea, formic acid, salicylic acid, organic carbonates, methanol, and syngas. A researched route of CO₂ utilisation involves transforming CO₂ into hydrocarbon chains that could be used as fuels, chemicals, or plastic. Products involved in reactions undergone in mild conditions include carbamates, urea, and carbonates.

On the other hand, products that require high temperature and pressure include carbon monoxide, methanol, and ethylene

- Urea.** Urea has the largest market size amongst the other chemicals with an annual production of 150 Mt/year and CO₂ sequestration rate of approximately 112 Mt/year. It is used as an agricultural fertiliser. It is also used in other applications such as the production of pharmaceutical, polymer synthesis and inorganic chemicals.
- Acids.** Formic acid (FA) is a valuable chemical product that is used in food, agriculture, textiles, chemicals, and pharmaceuticals. The conventional process of FA involves the carbonylation of methanol and subsequent hydrolysis of the methyl formate that is produced. Challenges associated with this process include slow kinetics, low yield, high capital costs and energy requirements and a noticeable dependence on fossil fuels.
- Carbonates.** The use of CO₂ in carbonate production has potential to decrease carbon emissions. Carbonates are usually classified as inorganic (metal) and organic where organic carbonates can be further classified as cyclic, acyclic and polycarbonates. Industrially important organic carbonates include dimethyl carbonate (DMC), diphenyl carbonate (DPC) ethylene carbonate (EC) and propylene carbonate (PC).
- Polymers.** CO₂-based polymers are produced by copolymerization of hydrocarbons and around 31-50% CO₂, which in turn reduces the dependency of petrochemical products. Owing to its quadrupolar nature, in the presence of two electronegative oxygen atoms, the carbon atom depicts somewhat electrophilic behaviour which makes it susceptible to undergo nucleophilic attack. Polycarbonates, which can be prepared by using CO₂ as a comonomer, have recently gained attention due to their biodegradability which could lead to sustainable plastic and as a CO₂ utilisation option.

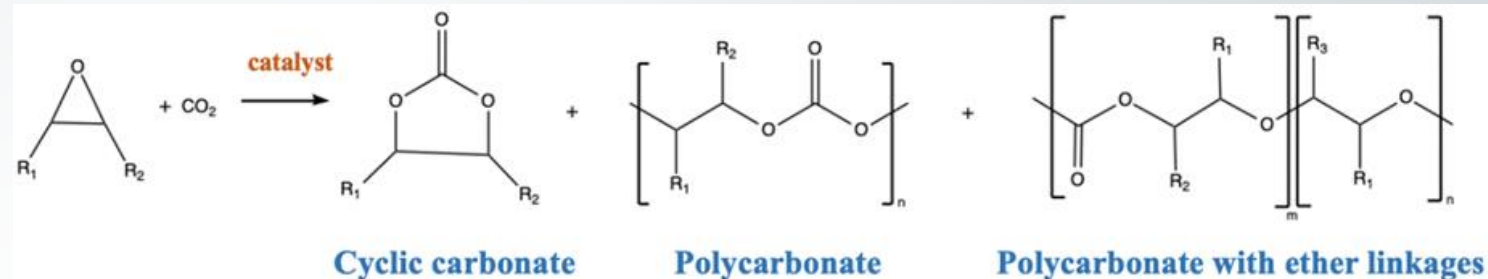


Figure 5: Different products resulting from the reaction of CO₂ with epoxides includes cyclic carbonates, polycarbonates, and, polycarbonates with ether linkages. Adapted from Zhang et al., 2020

ADVANCES IN CARBON CAPTURE AND STORAGE

Carbon sequestration in geological formations involves CO₂ being injected deep underground at depths of significantly more than 1 km. The CO₂ is injected into sedimentary rock which comprises of sand, crushed seashells, or precipitated carbonates. These rocks are permeable with around 10-30% total pore space volume. The void space is full of water unless it also contains oil and gas. More generally, there are four principal mechanisms that prevent CO₂ from reaching the surface

- 1) **Cap rock:** Structural trapping is related to low-permeability layers of rock (cap rock) that prevent CO₂ from moving upwards. The traps are made up of salt, shale or clays with small pore volumes which means that CO₂ has insufficient pressure to enter and migrate upwards. In **Sleipner**, the use period seismic surveys, which involves sound waves to image the subsurface, showed that injected CO₂ migrates to the top of the aquifer and then spreads out under cap rock layers at the top. Comprehensive store characterisation is crucial to evaluate and certify a given formation for use as a CO₂ store.
- 2) **Dissolution:** The CO₂ will dissolve in the brine and carbonate minerals precipitate immobilizing the injected CO₂ in chemically stable forms,
- 3) **Reaction:** The dissolved CO₂ in brine forms an acidic solution which will react with alkaline rocks to form carbonates. The opposite can also occur where the acidic brine dissolves part of the rocks and hence increases pore volume and permeability.
- 4) **Capillary trapping:** This process is the fastest and occurs when water displaces CO₂ in the pore space. Water tends to wet the surface which leaves CO₂ surrounded in water in a pore space bubble. The thermophysical properties of CO₂, reservoir brines and their mixtures influence the injection and subsequent storage of CO₂. The thermophysical properties of CO₂ including interfacial tension, density and viscosity and density and viscosity of synthetic brines, have all been very well studied.

Carbon mineralization is a long-term and non-toxic method of storing CO₂ in solid form. It also has the potential to mitigate health and environmental hazards in specific contexts. Carbonation of alkaline industrial wastes reduces chemical contamination and hence environmental hazards.

- Natural minerals most investigated are silicates including serpentine, olivine, pyroxene, and Wollaston. The use of industrial solid residues is attractive due to its higher chemical reactivity, low energy intensity since no mining activities are required and can support waste management strategies.
- It has been estimated that there is a mineralization potential of 7.5 MtCO₂ per year from alkaline waste in the USA. Whereas natural minerals and alkaline residues were estimated to have a combined maximum potential of 1500 MtCO₂ per year

ADVANCES IN CARBON CAPTURE AND STORAGE

Enhanced Oil Recovery (EOR)

Initial research in the field was focused on improving recovery through the development of chemical foaming agents to decrease CO_2 mobility, simple models to predict EOR performance using reservoir characteristics, and evaluations of EOR potential across the world.

- ▶ In recent years there has been renewed interest in EOR from unconventional reservoirs like the Bakken shale, the use of computer aided techniques for co-optimisation of oil recovery and CO_2 sequestration, and the recovery of methane from methane hydrates by the exchange of CO_2 .
 - ▶ The initial production of an oil field uses primary recovery techniques whereby the natural reservoir pressure is the main mechanism for oil recovery.
 - ▶ Operations were historically abandoned after secondary recovery, with subsequent extraction of oil requiring more advanced tertiary recovery techniques, also called enhanced oil recovery (EOR). There are three main types of EOR, chemical flooding, thermal recovery, and gas injection.
- Typically, 30 – 70 % of the injected CO_2 is extracted with the residual oil, with the remaining CO_2 remains trapped in the oil pore space. There has been renewed interest in EOR from unconventional reservoirs like the Bakken shale, the use of computer aided techniques for co-optimisation of oil recovery and CO_2 sequestration, and the recovery of methane from methane hydrates by the exchange of CO_2 .
- ▶ Bakken, Eagle Ford, Wolfcamp, and Barnett shale reservoirs have become primary targets for oil recovery from unconventional reservoirs, with estimated reserves of 15 – 24 billion bbl from the Bakken reservoirs alone.
 - ▶ Recent research into oil recovery from unconventional reservoirs have focused on the addition of surfactants to act as wettability agents and/or foaming agents, and the use of novel gas blends for EOR.
 - ▶ Two commercially available non-ionic surfactants were tested, Indorama SURFONIC® N-100 and Indorama SURFONIC® TDA-9. Early results showed oil recoveries of 79 %, 85 % and 75 % for pure CO_2 , TDA-9, and N-100, respectively.
 - ▶ Non-ionic surfactants have also been used to stabilize foams for in-situ CO_2 mobility control during EOR.

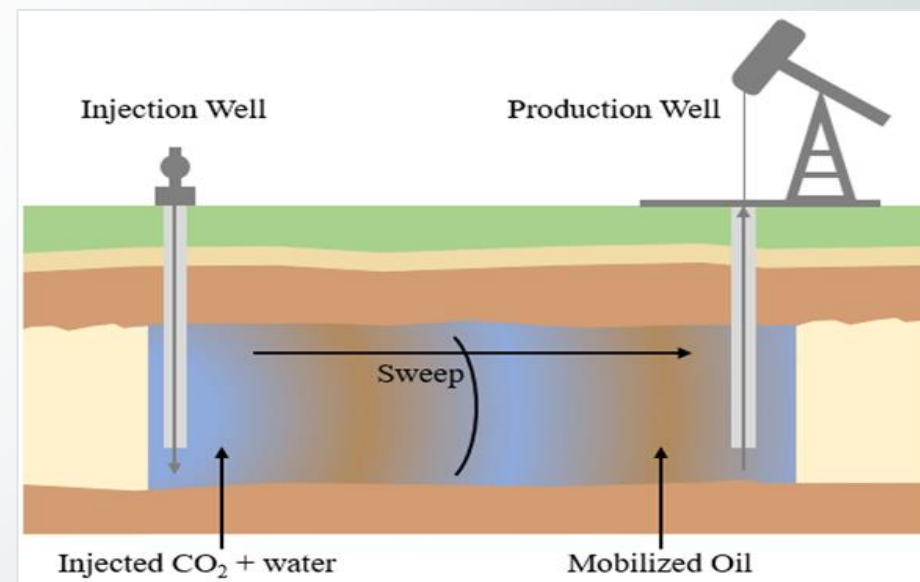


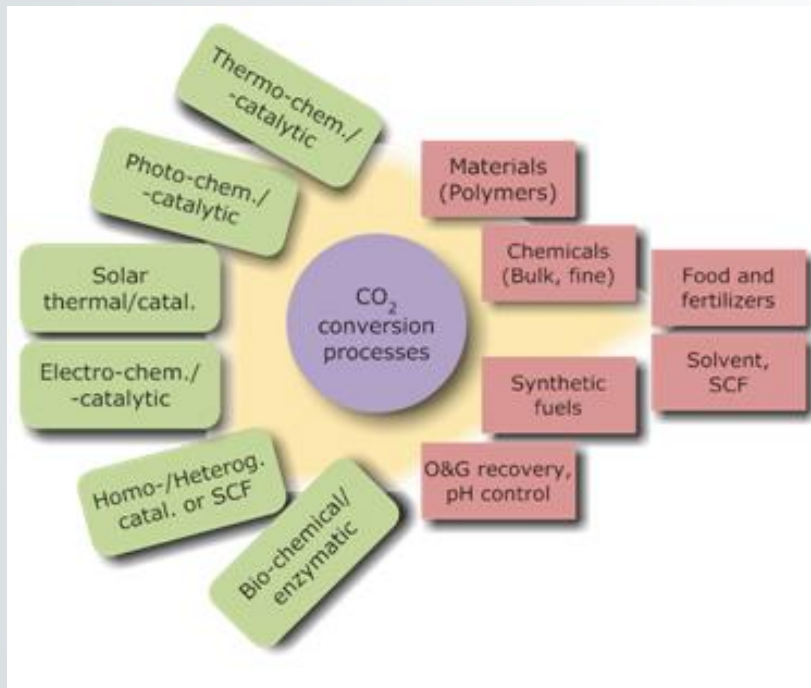
Figure 6: CO_2 -EOR using WAG. Source: Created originally by authors.

OUTLOOK

- ▶ Despite the efforts made in membrane materials development and their fabrication, what is vital for large scale post-combustion capture (PCC) are effective techno-economic analysis of process flowsheets and pilot scale assessment of different system configurations using real flue gas streams
- ▶ Converting CO₂ to useful chemicals and or plastics could, under certain circumstances, have an impact on decreasing CO₂ emissions.
- ▶ Currently various conversion pathways for CO₂ conversion to fuels are being explored. Electrocatalysis, photocatalysis and a combination of thereof are the most well studied pathways with the former being the most suitable for large scale deployment.
- ▶ In the United States, more than 70% of CO₂ used for EOR is sourced from natural underground reservoirs due to the absence of infrastructure for capture from industrial emitters close to oil fields.
- ▶ Incentives to store CO₂ through tax credits or a carbon market could shift CO₂-EOR projects from producing more oil with less purchased CO₂ to achieving a secondary goal of storing more CO₂.
- ▶ Despite EOR being a long-established technology, CO₂ monitoring, quantifying and reporting standards must be improved to validate the potential emissions benefit to meet climate change targets.
- ▶ There are a small number of active (Sleipner, North Sea, Norway; Snohvit, Barents Sea Norway) and completed (K12-B, North Sea Netherlands) offshore CO₂ injection projects in Europe that provide confidence in the performance of offshore injection and storage.

Unlike fossil fuel power plants, many industries have few or no CO₂-free alternatives to manufacture products. While some investigate novel production pathways for some industries, it is highly unlikely that they will be commercially ready to meet climate mitigation goals.

Carbon Dioxide Capture and Conversion (CO₂CC) Program



The **Carbon Dioxide Capture and Conversion (CO₂CC) Program** is a membership-directed consortium, launched in January 2010, whose members are involved in developing, monitoring and utilizing the "state-of-the-art" in technological progress and commercial implementation of carbon dioxide capture and conversion.

The program's objective is to document and assess technically and commercially viable options for the capture/clean-up/utilization of CO₂ and its mitigation via energy efficiency gains which meaningfully address the challenges posed by CO₂ life-cycle and overall sustainability issues. Included in the program's scope are:

- Global decarbonization efforts towards net zero or negative carbon emissions
- Industrial process technology shifts towards renewable, circular and sustainable practices
- CO₂ capture and/or separation
- CO₂ concentration, purification and/or other post-treatment
- CO₂ utilization/conversion (e.g., CO₂ as a feedstock) for use as a fuel or intermediate, including enhanced oil recovery (EOR)
- Energy requirements (and other costs), including energy efficiency
- Industrial process improvements and energy saving initiatives which mitigate CO₂ production
- Bottom-line financial (income) impacts resulting from CO₂ reduction programs
- Life-cycle considerations and sustainability of CO₂ applications
- GHG/CO₂ regulation and "cap and trade" developments

By the direction of the member companies (through balloting and other interactive means) and operated by TCGR, the program delivers weekly monitoring communications via email (**CO₂CC Communiqués**), three techno-economic reports (highly referenced and peer reviewed) and scheduled meetings of members (either in-person or via webinar). **Access to deliverables is exclusive to members.**

Contact & More Information

More information about this and other services of the **CO₂CC Program** can be seen at http://www.catalystgrp.com/php/tcgr_co2cc.php.

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