WEBSITE: chem-tox-ecotox.org/Scientific Reviews …15 MAY, 2020

SCIENTIFIC REVIEWS

Removal Technologies for Atmospheric Carbon Dioxide (CO_2).

Negative emission technologies, carbon capture and catalytic conversion of CO_2 into valuable commodity chemicals

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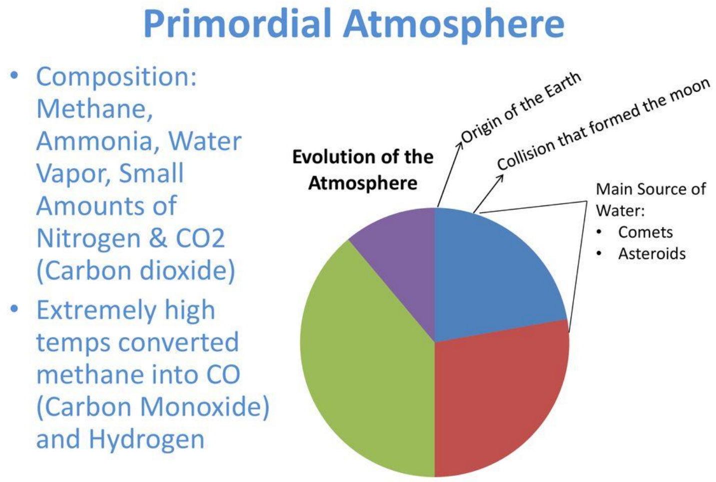
Abstract. Scientific studies of the last decades prove that to reduce the rise in global average temperature to 1.5 degrees Celsius over the preindustrial baseline, (1750) of our industrial civilization needs to stabilize the atmospheric concentration of carbon dioxide (CO_2) at around 350 parts per million (ppm). In the last decades the CO_2 atmospheric concentration was about 400-415 ppm causing a dangerous climate overheating. This year, Earth's CO_2 in atmosphere reached about 415 ppm (6.4.2020). Global CO_2 emissions continue to rise (in particular from burning fossil fuels) and hundreds of gigatons of CO_2 every year concentrate in the air. Every model used by the Intergovernmental Panel on Climate Change (IPCC) shows that to reach the desired climate change we must bury large amounts of CO_2, so-called "negative carbon emissions" by removing CO_2 directly out of the air and bury it underground in saline aquifers, a process known as carbon capture and sequestration (CCS). A number of negative emission technologies (NET) have been proposed in the last decades but all of them have some fundamental problems or are expensive. Also, scientists and synthetic organic chemists have been aware for many decades of the potential economic and environmental benefits of using CO_2 as a feedstock for the synthesis of commodity chemicals and renewable fuels. Despite the large amount of fundamental research that has been performed regarding the conversion of CO_2 into valuable chemical products there are relatively few examples of industrially viable processes. The conversion of CO_2 faces an important obstacle, its kinetic and thermodynamic stability. CO_2 cannot be converted into commodity chemicals or fuels without significant inputs of energy and catalysts since it contains strong bonds that are not particularly reactive. As a consequence, many of the available transformations of CO_2 require stoichiometric amounts of energy-intensive reagents. This can often generate significant amounts of waste and can result in large greenhouse gas footprints. This review collected some of the most interesting studies and technological applications for the sequestration of atmospheric CO_2. Also, the review contains advanced methods for converting CO_2 by catalytic hydrogenation into useful commodity products, feedstock chemicals, and hydrocarbons (urea, methanol, dimethyl ether, formic acid, ethanol, ethylene, dimethyl and diphenyl carbonates, polymers, fuels, etc).

Introduction: Carbon dioxide in the atmosphere of primordial Earth

The gas Carbon Dioxide (CO_2) is one of the most important trace gas in Earth's atmosphere. Carbon dioxide in the Earth’s atmosphere is at a very low concentration, 0,04%. The other gases are 78.09% Nitrogen, 20.95% Oxygen and 0.93% Argon. Carbon dioxide plays a fundamental role as a gaseous warming blanket that helps to trap heat in Earth’s atmosphere. The warming aspect of CO_2 is apparent for the evolution and survival of living organisms on Earth. Without atmospheric CO_2, planet Earth would be inhospitably cold (estimated at an atmospheric temperature of around -18^oC) like other colder planets in the solar system. [Mercury -170^oC, Mars -125^oC] which proved to be without any traces of living biological organisms.[1,2]

Carbon dioxide (CO_2) has been present in the primodrial atmosphere since the Earth formation 4,6 billion years ago in the solar system. Earth was condensed from a ball of hot gases, solid rocks and dust following explosions of huge stars. At that time the Earth’s atmosphere was mainly composed of nitrogen (N), CO_2 and water vapour (H_2O). As it cooled further some of the water vapour condensed out to form oceans and they dissolved a portion of the CO_2 which was still present in the Earth’s atmosphere in large amounts.[3.4]

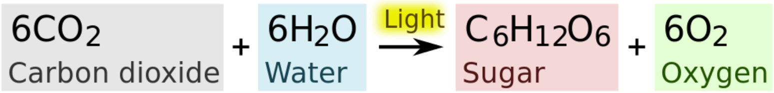


Primordial Atmosphere

- Composition: Methane, Ammonia, Water Vapor, Small Amounts of Nitrogen & CO2 (Carbon dioxide)
- Extremely high temps converted methane into CO (Carbon Monoxide) and Hydrogen

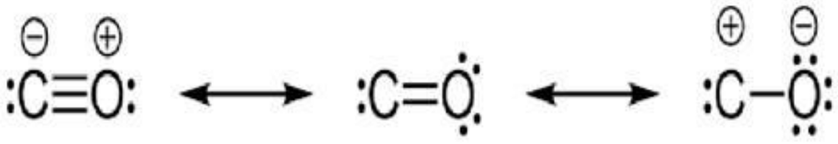
Figure1. Earth’s primordial original atmosphere was rich in methane (CH_4), CO_2, nitrogen (N_2), ammonia (NH_3), water vapour (H_2O), and the noble gas neon (Ne). Earth’s atmosphere lacked free oxygen (O_2) because it reacted earlier with metals of the melting and soil-rocks on Earth’s surface.

Carbon dioxide (CO_2) is an integral part of the carbon cycle on Earth, a biogeochemical cycle in which carbon is exchanged between the Earth's oceans, soil, rocks and the biosphere. Plants and other photoautotrophs (organisms that carry out photosynthesis) use energy from sunlight and atmospheric CO_2 and water for the synthesis of organic chemicals (sugar). Fundamental ancient mechanism on Earth to produce carbohydrates. Almost all other living organisms depend on carbohydrates derived from photosynthesis as their primary source of energy and for synthesis of other organic carbon compounds.



$$6CO_2 + 6H_2O \xrightarrow{\text{Light}} C_6H_{12}O_6 + 6O_2$$

Another important property of atmospheric CO_2 is that absorbs and emits infrared radiation (IR) at wavelengths of 4.26 μm (asymmetric stretching vibrational mode) and 14.99 μm (bending vibrational mode) and consequently behaves as a greenhouse gas (i.e. contributes to greenhouse effect) that plays a significant role in influencing Earth's surface temperature. Concentrations of CO_2 in the Earth's atmosphere were as high as 4,000 parts per million (ppm, on a molar basis) during the Cambrian period about 500 million years ago to as low as 180 ppm during the Quaternary glaciation of the last two million years. [5,6]



Resonance structure of carbon dioxide

The first Industrial Revolut**ion** lasted from the mid-18th century (1750) to about 1830 and was mostly confined to Britain, a period which was formulated mainly by the rise of industries mechanized by steam energy. The second Industrial Revolution lasted from the mid-19th century until the early 20th century and took place in Britain, continental Europe, North America, and Japan. It is well known that CO_2 concentration in the atmosphere increased in parallel with the amount of burning fossil fuels (coal, petrol, natural gas) for industrial purposes, transportation, agriculture, heating and other uses.

The International Panel on Climate Change (IPCC) uses the year 1750 as its pre-industrial baseline to show changes in atmospheric CO_2, global temperature rises and other climate indicators in the post-industrial era. Scientific studies revealed that atmospheric CO_2 has ranged between 172 and 300 part per million (ppm) for the past 1 million years. The Earth cycled through cold glacial and warm inter-glacial periods without atmospheric CO_2 exceeding 300 ppm. The first time in human history that atmospheric CO_2 exceeded 300 ppm was about the time the Titanic sank in the North Atlantic Ocean (1912) and reached average monthly levels of 400 ppm in 2013.

Increases of CO_2 in the Earth's atmosphere in the last century

Studies of long term climate change have discovered a connection between the concentration of carbon dioxide (CO_2) in the Earth's atmosphere and mean global temperature, which is at the present 15° Celsius.

In 2011 the CLIMAP project was formed in the USA (a multiuniversity research project) which reconstructed the Earth's climate for the last million years by examining proxy data from ocean sediment cores. [https://www.climaterealityproject.org/]. The Climate Reality Project (CLIMAR) came into being in July 2011 as the consolidation of two environmental groups, the Alliance for Climate Protection and the Climate Project, both of which were founded by ex vice president Al Gore, and hosts an annual event.

Researchers working for the CLIMAR project found strong evidence in deep-ocean sediments of variations in the Earth's global temperature during the past several hundred thousand years of the Earth's history. Other subsequent studies have confirmed these findings and have discovered that these temperature variations were closely correlated to the concentration of carbon dioxide (CO_2) in the atmosphere and variations in solar radiation received by the Earth. Measurements indicated that CO_2 atmospheric levels were about 30% lower during colder glacial periods and that the oceans were a major store of CO_2 controlling the movement of this gas to and from the atmosphere. The amount of carbon dioxide that can be held in oceans is a function of temperature. Carbon dioxide is released from the oceans when global temperatures become warmer and diffuses into the ocean when temperatures are cooler.

Other studies estimated that in the past 300 years the concentration of CO_2 has been increasing in the Earth's atmosphere because of human industrial activities, transport, burning of fossil fuels for electricity, conversion of natural prairie to farmland, and vast deforestation in many areas of the Earth. The concentration of CO_2 in the atmosphere from 280 ppm in the period 1700-1750 increased to 380 ppm by 2005, exceeded 400 ppm in 2013 and in April 2019 the average monthly concentration was 413 ppm. These concentrations are enhancing the greenhouse effect and making the planet warmer. Scientists formulated computer climate models that predicted with certain accuracy the globe will warm up by 1.5 - 4.5° Celsius if CO_2 reaches level of 600 ppm by the year 2050.[7,8]

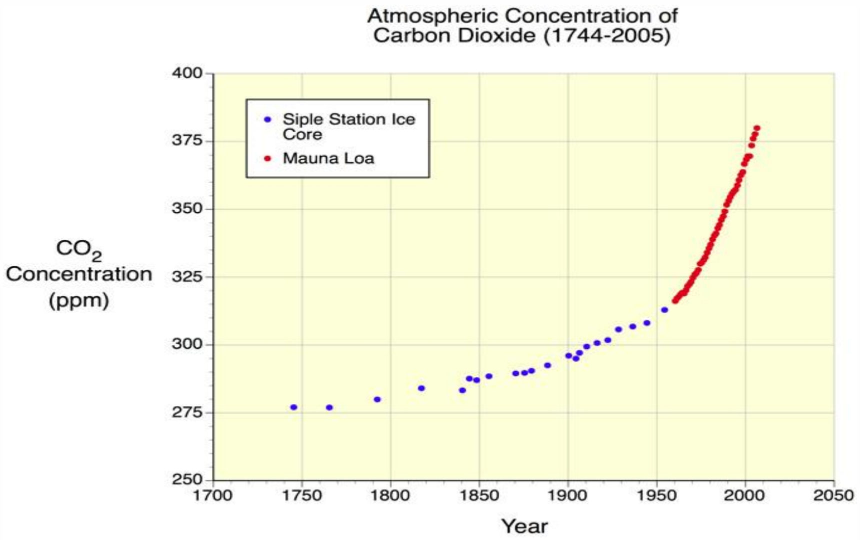


Figure 2. The graph illustrates the rise in atmospheric carbon dioxide (CO_2) from 1744 to 2005. The CO_2 concentration in the Earth's atmosphere has been exponential during this period and will continue because of the use of fossil fuels. [PhysicalGeorgaphy.Net, Causes of Climate Change, and CO_2 2019. http://www.physicalgeography.net/fundamentals/7y.html].

In the last 3000 years increase of CO_2 in the Earth's atmosphere followed a clear path with parallel increases in the emissions from burning fossil fuels (coal, petrol, natural gas). Carbon emissions (billions of tones) rose slowly from about 5 billion tons a year in the mid-20th century before skyrocketing to more than 35 billion tons per year by the end of the century. There are also major natural sources of CO_2 emissions in the atmosphere. Animals and plants breathe and exhale CO_2 into the atmosphere. Another source is the decomposition of organic matter. Natural disasters can release significant amounts of CO_2, like forest fires and volcanic eruptions. The greatest source of CO_2 are the oceans. Annually, oceans produce more CO_2 than any natural or manmade source, by far. But naturally-generated CO_2 is a part of a very natural cycle in the atmosphere. That's why the levels remained stable. The CO_2 on land and in Earth's oceans has stayed in balance. By measuring ice cores and other methods, scientists have been able to study historic CO_2 levels both directly and indirectly. The Earth has been able to generate, absorb, and cycle through CO_2 naturally for generations.[9,10]

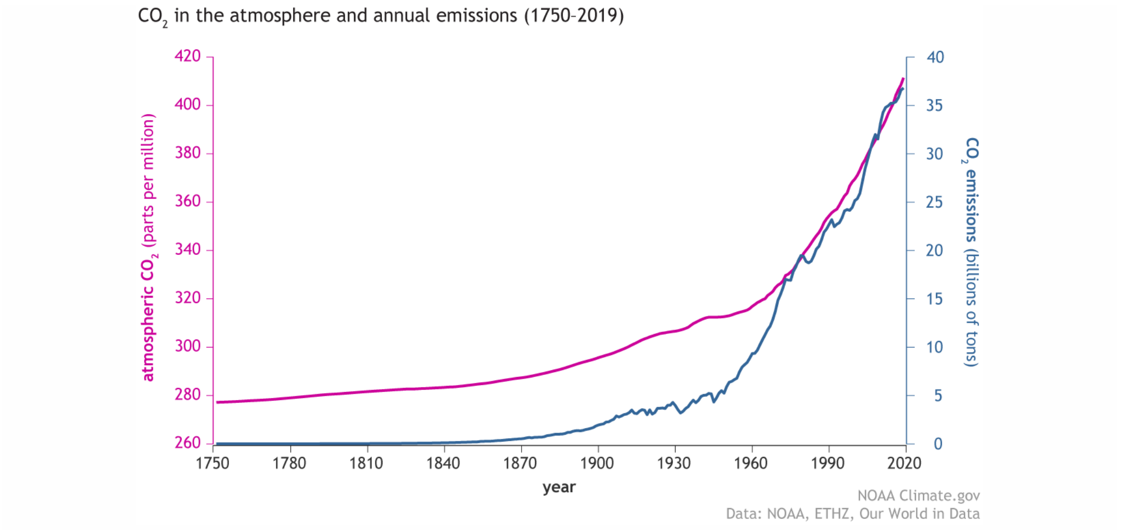


Figure 3. Concentration of CO_2 in the atmosphere (red line, ppm) has increased along with human carbon emissions (blue line, billion of tons) since the start of the Industrial Revolution in the 1750-2000 period. National Oceanic and Atmospheric Administration (NOAA, USA) Climate.gov graph, adapted, CO_2 emissions data from Our World in Data and the Global Carbon Project. [https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide].

Continuous observations of CO_2 in the Earth's atmosphere began at **Mauna Loa Volcanic Observatory** in 1958 when the levels of CO_2 were around 320 ppm and in 2015 the concentration increased to 400 ppm. The Mauna Loa Observatory is part of the USA National Oceanic and Atmospheric

Administration (NOAA) - Earth System Research Laboratory (ESRL) - Global Monitoring Division (GMD) and supported hundreds of cooperative research programs with national and international universities and government organizations. Mauna Loa Observatory (MLO) is located at an elevation of 3,397 meters. The undisturbed air, remote location, and minimal influences of vegetation and human activity at MLO are ideal for monitoring constituents in the atmosphere that can cause climate change.

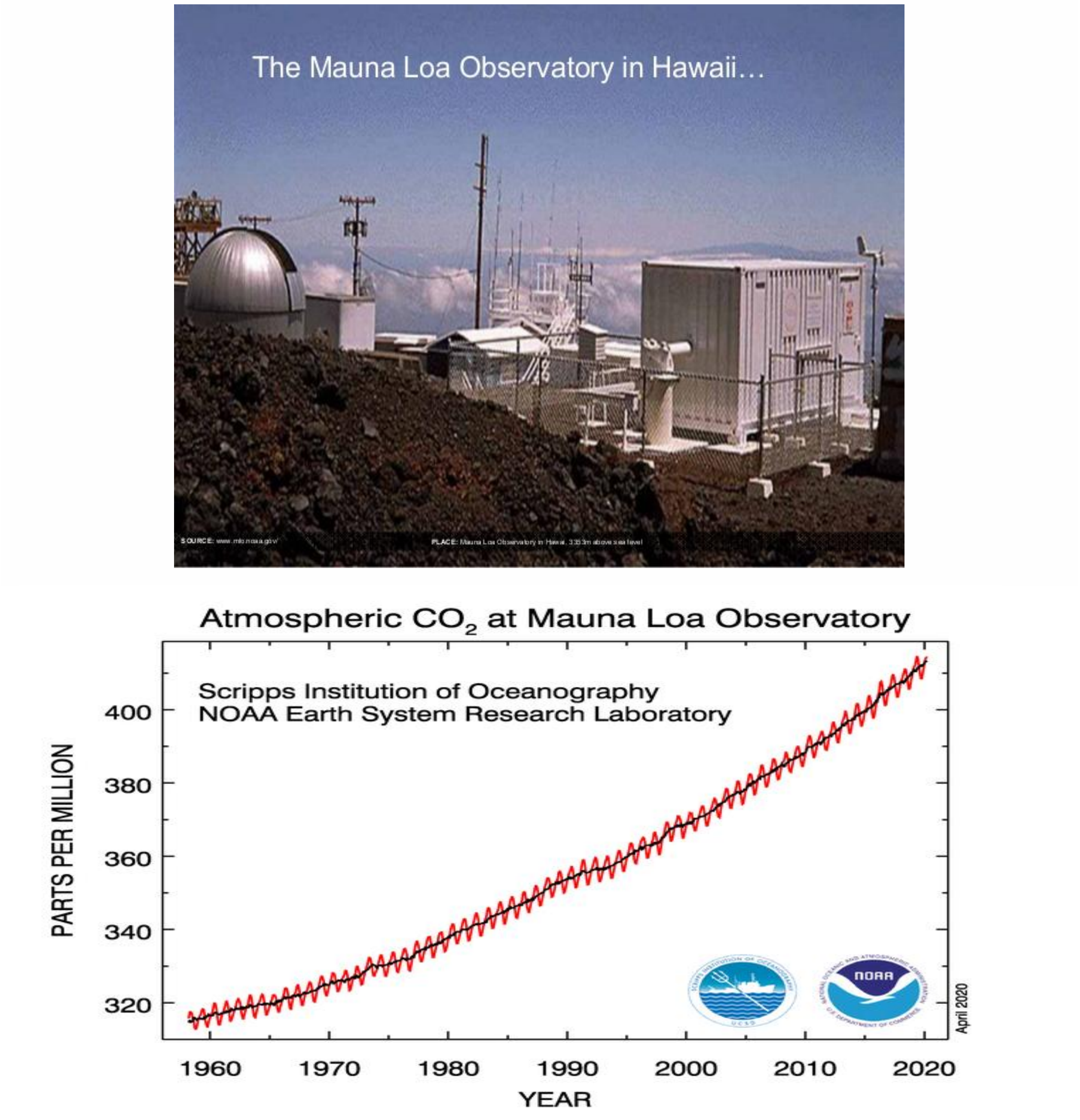


Figure 4. **Mauna Loa Observatory** (MLO) is located on the north flank of Mauna Loa Volcano, on the Big Island of Hawaii, at an elevation of 3,397 meters and originally chosen as a monitoring site because, located far from any continent, the air is a good average for the central Pacific [Earth System Research Laboratories, https://www.esrl.noaa.gov/gmd/obop/mlo/].

Negative Emission Technologies (NET) for reduction of CO_2 that could slow climate change

The Paris Agreement, adopted at the COP21 (United Nations, Framework Convention on Climate Change, Conference of Parties-Twenty first Session, Paris) climate talks in December 2015, sets out a global aim to limit average global surface temperatures to “well below 2C” above pre-industrial levels (aiming at $1.5^{o}C$). But as countries across the world move towards signing and ratifying the agreement, there remains the key question of how these ambitious targets can be met.

In the meantime a number of negative emissions technologies (NET) have been proposed by scientists and environmental institutions for the reduction of CO_2 in the Earth’s atmosphere. It is well known that no one single technology or method can solve climate change, but taking them together could contribute to reduce atmospheric CO_2 before 2050.[11]

There are various and different options called “negative emission technologies” with the most potential to achieve a substantial reduction of atmospheric CO_2.[12]

Afforestation and reforestation for climate change

Afforestation refers to planting trees on patches of land which were not previously covered in forest, while reforestation refers to planting trees on land that was previously a forest. After many decades of deforestation and soil degradation for agricultural use in various areas on the Earth, restoring areas where the trees have been cut down in the past for agricultural of other reasons is a useful solution. Trees and vegetation in general take up CO_2 from the atmosphere as they grow and produce organic material with photosynthesis. Afforestation for removing CO_2 from the atmosphere is the most feasible option, in particular if re-planting native trees to tackle specifically climate change. The UN’s Clean Development Mechanism provides a financial incentive for countries to increase their forest stocks. The **Clean Development Mechanism** (**CDM**) under the Kyoto Protocol to the UN Convention on Climate Change (UNFCCC) allows industrialized countries with a greenhouse gas reduction commitment to invest in emission reducing projects in developing countries with planting new trees on massive scale [ScienceDirect, CDM, 2019. https://www.sciencedirect.com/topics/earth-and-planetary-sciences/clean-development-mechanism]. Scientific estimates suggested that afforestation and reforestation can sequester CO_2 at a rate of 3.7 tonnes per hectare per year.[13,14]

Figure 5. Planting trees down in areas without forests is beneficial for reduction of green house gases. Trees photosynthesise and produce oxygen and at same time take carbon dioxide (CO_2) out of Earth's atmosphere.

Planting trees in general remains among the most effective strategies with great potential for climate change mitigation. Under the current climate 4.4 billion hectares of canopy could exist on Earth surface. Scientists estimated that there is extra land of 0.9 billion hectares for new trees which could store 205 gigatonnes of carbon dioxide in areas that would naturally support woodland and forests. But climate change and higher temperatures by 2050 may shrink canopy cover by ~223 million hectares with the vast majority of losses occurring in the tropics.[15]

Biochar. Charcoal added to the soil for CO_2 reduction

Biochar is the name given to charcoal that is added to soils rather than burned as a fuel. The charcoal is produced by burning biomass, such as wood, crop wastes and manure, while cutting off the supply of oxygen. (process known as pyrolysis). The carbon in the resulting biochar is very slow to break down. This means the carbon it absorbed from the atmosphere while it was mere biomass is locked up for – potentially – hundreds or even thousands of years.[16]

Figure 6. Biochar, is considered as another strategy for atmospheric carbon sequestration. This is a 2000-year-old practice that indigenous people of the Amazonian basin used to create rich, fertile soils called terra preta (meaning "dark earth."). It is a valuable material used in farming that has been lost in our modern day farming.

Soils on Earth store three times more carbon than exists in the atmosphere. Plants absorb atmospheric carbon during photosynthesis, so the return of plant residues into the soil contributing to soil carbon. Biochar has the potential (according to some studies) to sequester up to 4.8bn tonnes of CO_2 per year. While biochar does contain high levels of carbon, there remains uncertainty as to how long that carbon will persist in the soil following application. Soil scientists think that charcoal might not stay in soils for long and instead much of it might dissolve and is washed into rivers, wetlands, and eventually the oceans. The UK has its own Biochar Research Centre based at the University of Edinburgh, which was launched in 2009.[17,18]

Bioenergy, carbon capture and storage (BECCS)

Bioenergy with carbon capture and storage (BECCS) is widely viewed as another interesting negative emissions technology offering the most promise of drawing significant quantities of CO_2 out of the atmosphere at the lowest cost. BECCS achieves net negative emissions through sequestering underground the emissions resulting from the burning of biomass for power. Negative emissions are achieved because of a "double gain" with the biomass, as it grows, having already drawn CO_2 out of the atmosphere before the CCS process begins at the power plant. The IPCC Fifth Assessment Report by the Intergovernmental Panel on Climate Change (IPCC), suggested a potential range of negative emissions from BECCS of 0 to 22 gigatonnes per year.[18] As of 2019, five facilities around the world were actively using BECCS technologies and were capturing approximately 1.5 million tonnes per year of CO_2. Wide deployment of BECCS is constrained by cost and availability of biomass.[20,21]

Figure 7. The Drax power station in North Yorkshire (UK) is in the final stages of commissioning Europe's first trial of negative emissions technology. The demonstrator captures CO_2 generated by burning biomass using a novel solvent developed by C-Capture, a spin-out from Leeds University. It follows successful laboratory tests, and the pilot project aims to trap one tonne of CO_2 a day, with capture rate of 90%.[Chemistry World, 2019,https://www.chemistryworld.com/news/biomass-carbon-capture-pilot-points-to-a-new-sector-whose-time-has-come/3010037.article].

'Blue carbon' habitat restoration and CO_2 capture

Salt marshes, mangroves, and seagrass beds act as natural defences against climate change, capturing atmospheric CO_2 even faster than terrestrial forests, and storing it in their leaves, stems and in the soil. Carbon stored in coastal or marine ecosystems is known as 'blue carbon'. Globally, the destruction of a third of coastal and marine wetlands to make way for houses, ports and other commercial activity is shrinking the size of the 'blue carbon' sink. Exposed soils also release CO_2, turning coastal ecosystems from net absorbers of greenhouse gases to net sources. Carbon emissions from degraded mangroves, tidal marshes and seagrasses are thought to be equivalent to 3–19% of those produced annually from deforestation, though some large uncertainties still remain. Mangrove forests are one of the most productive and efficient long-term natural carbon sinks and as such have been identified alongside seagrasses and saltmarshes as key 'blue carbon' ecosystems.[22,23]

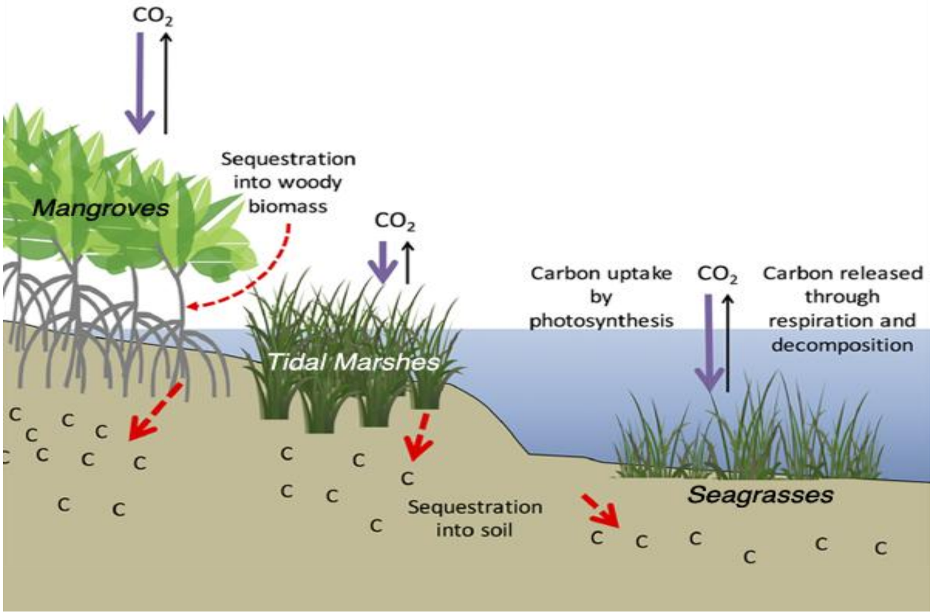


Figure 8. "Blue Carbon" is the carbon absorbed and stored by marine and coastal ecosystems like wetlands marshes, mangroves and seagrass meadows. The capacity of these natural ecosystems, makes them large natural carbon sinks. Coastal wetlands (mangroves, tidal marshes, and seagrasses) effectively sequester carbon long-term and up to 10x more carbon stored per unit area than terrestrial forests with 50-90% of the stored carbon residing in the soil. [U.S. Ocean Carbon & Biogeochemistry, 2019 https://www.us-ocb.org/quantifying-coastal-and-marine-ecosystem-carbon-storage-potential-for-climate-mitigation-policy-and-management/].

Building and construction materials from biomass

Biomass is natural matter based on carbon, hydrogen and oxygen. Chemical compositions and structure of biomass are very variable and components of biomass are forming a chemical complex of cellulose, lignin, hemicelluloses, inorganic substances, extractives (pectins, waxes) and other water-soluble substances. Polymeric cellulose, hemicelluloses and lignin are the three principle main constituents with regard to the physical properties of the biomass. These plant-based materials can be used in construction, storing carbon and preserving it for as long as the building remains standing. For example, timber and bamboo can be used for structural elements, hemp and wool for insulation, and hemp-lime for walling. These materials provide an alternative to standard construction materials, including steel and concrete, which are typically carbon-intensive to produce. Natural materials have additional benefits, such as the ability to regulate moisture and absorb pollution.[24,25]

The use of plant biomass for developing energy efficient and low cost construction materials is an emerging field in building construction and civil engineering. Although the biomass-based cement and concrete composites have several advantages, such as low densities, low amount of CO_2 gas emission, good thermal and acoustic insulation, there are also disadvantages like the durability of biomass in alkaline cement matrix, the high absorption of water and the cement-biomass compatibility, all deteriorating concrete mechanical properties, which are already intrinsically low due to the low mechanical properties of biomass-based fillers.[26]

Figure 9. Lignocellulosic biomass materials are receiving increased attention as a renewable, economical, and abundant alternative to sossil resources for the production of various value-added products. Biomass feedstocks utilized for these productions include energy crops, agricultural biomass residues, forest biomass and food-based biomass wastes. Conversion technologies are used to transform them into valuable building material products

Increasing ocean alkalinity for carbon sequestration

The oceans contain more CO_2 than soils, plants, animals and the Earth's atmosphere combined. Seawater contains about 120 grams of negatively charged bicarbonate ions [HCO_3^-] per square meter, which are balanced with positive ions such as calcium (Ca+) and magnesium (Mg+). This carbon pool was created naturally over millions of years by mineral weathering. A recent paper (2017) explored the possibility of accelerating weathering processes to increase bicarbonate ions in the ocean, and thus prevent climate change and potentially ameliorate ocean acidification.[27]

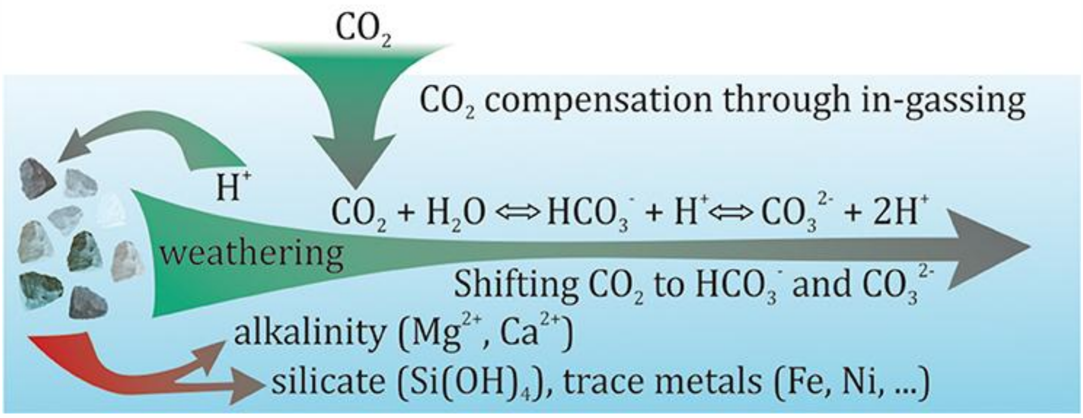


Figure 10. A widely recognized idea for atmospheric CO_2 reduction is to accelerate weathering reactions of minerals that consume CO_2 when they dissolve in the oceans. Acceleration could be realized by pulverizing and distributing gigatons of these minerals onto land (termed "enhanced weathering") or sea (termed "ocean alkalinity enhancement") thereby largely increasing their reactive surfaces. [Bach LT, Gill SJ, Rickaby REM, et al. https://www.frontiersin.org/articles/ 10.3389/fclim.2019.00007/full].

Scientific studies estimated that about 25% of the current Earth's CO_2 emissions in the atmosphere are absorbed by the oceans. This has caused a slight decrease in pH levels (below 7), a process known as "ocean acidification". If the CO_2 emission will decrease substantially in the future the oceans would eventually absorb most of the emitted CO_2 but the acidification would be neutralized by the dissolution of carbonate sediments. This would take thousands of years. Small perturbations in the chemistry of the global oceans is thought to be responsible for some of the climate variability of the past million years. An increase in ocean alkalinity could be achieved by dissolving rocks and minerals either directly in the open ocean or through engineered systems. This would lead to a build-up of calcium, magnesium, or sodium ions in seawater and thus an uptake of CO_2 to form bicarbonate ions. [$Ca(HCO_3)_2$, $Mg(HCO_3)_2$]. This long-term storage of carbon in order to mitigate climate change is known as “carbon sequestration.”. [28]

An additional benefit of artificial ocean alkalinization (AOA) is that it could alleviate regions from ocean acidification. Ocean acidification has already influenced the marine environment by making it more difficult for some marine calcifiers to produce their calcium carbonate ($CaCO_3$) shells. Artificially increasing ocean total alkalinity and the resulting increase in calcium carbonate saturation state, Ω_{CaCO3} , would have the opposite effect, making it easier to calcify. Therefore, AOA could potentially allow ecosystems previously affected by reduced calcification (due to ocean acidification) to return to pre-industrial calcification values.[29,30]

Direct air capture of CO_2 from the air

Direct air capture (DAC) of CO_2 from the Earth’s atmosphere is considered as a straitforward method to reduce it. The captured CO_2 can be buried underground or used in chemical processes to make useful commodity chemicals and plastic materials. In the last century various methods of atmospheric CO_2 capture were developed and many chemical sorbents have been developed which cycled through sorption and desorption cycles for CO_2 removal from the air. A recent review provided a historical overview of the field of DAC, and description of the use of chemical sorbents targeted at this application. Solvents and solid sorbents that interact strongly with CO_2 including basic solvents, supported amine and ammonium materials, and metal–organic frameworks, as the primary classes of chemical sorbents. In general the review concluded that there are many new materials that could play a role in emerging DAC technologies. Sorbents for CO_2 can be liquids or solids but most air-capture processes use solid sorbents.[31]

Direct Air Capture (DAC) of CO_2 may play important roles in stabilizing atmospheric CO_2.[32]

a. Compensating for mobile CO_2 emissions: CO_2 emissions from small sources and the transport sector account for between 1/3 to 1/2 of the total CO_2 emissions,

b. Direct air capture can operate at remote storage sites and eliminate expensive pipeline systems for CO_2 transport,

c. DAC can offer leakage insurance and could also recapture CO_2 leaking from point sources or geologic CO_2 storage sites,

d. DAC can close the carbon cycle by producing synthetic fuels The use of carbon-based fuels in the transportation sector is not sustainable unless CO_2 is eventually removed from the atmosphere,

e. DAC can provide a carbon feedstock for producing carbon-based materials. These range from CO_2 for curing cement, to feedstocks for plastics, carbon fibers, and carbon composites for a broad range of industries.[32]

Enhanced ocean productivity for absorption of CO_2

Phytoplankton, both algae and cyanobacteria, can be found in fresh water or saltwater. They are similar to terrestrial plants in that they contain chlorophyll and require sunlight in order to live and grow. Most phytoplankton are buoyant and float in the upper part of the ocean, where sunlight penetrates the water. Phytoplankton in the oceans plays fundamental roles in climate control, oxygen supply and food production. These single-celled organisms are responsible for more than 40% of Earth’s photosynthetic production and uses up vast amounts of atmospheric CO_2. In addition to providing food and oxygen for nearly all life on Earth, phytoplankton helps to regulate CO_2 in the Earth’s atmosphere.

Scientists many years ago proposed artificially to increase the rate at which phytoplankton and algae photosynthesise in the oceans, thus accelerating the removal of atmospheric CO_2 and slow the pace of climate change. One idea was to inject the nutrient iron (Fe) into parts of the ocean where it is currently lacking, triggering a “bloom” of microscopic plants - phytoplankton. As CO_2 is removed from the surface ocean, more can enter from the air above it. And when the plants die, they fall to the bottom of the ocean and lock carbon away in the sediment for hundreds or thousands of years. Iron can act as a fertilizer for the oceans phytoplankton that form the base of the marine food web, and accelerate its growth which in turn absorbs CO_2 through photosynthesis. Numerous iron dumping trials have been conducted since oceanographer John Martin suggested the idea more than 15 years ago. One trial conducted in 2004 indicated that each atom of iron added to the water could draw between 10,000 and 100,000 atoms of carbon out of the atmosphere by encouraging plankton growth. Some scientists theorize that adding iron to the Southern Ocean alone could reduce carbon dioxide levels by 15%.[33-36]

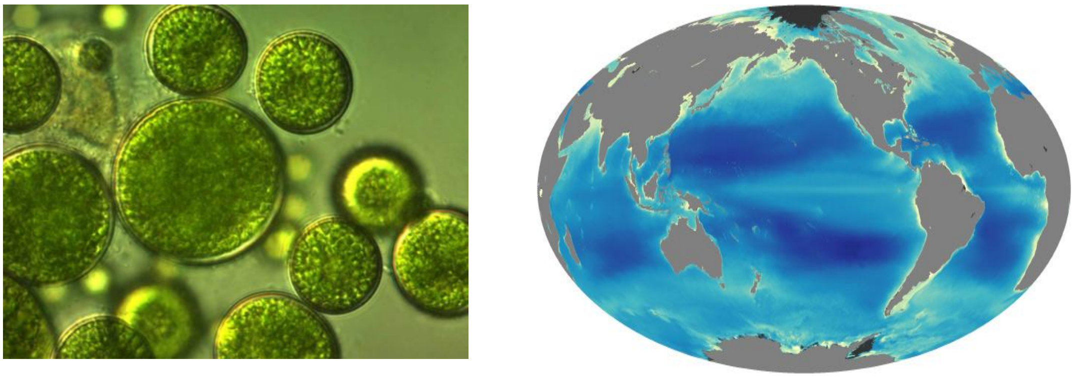


Figure 11. Microalgae and phytoplankton single-celled organisms are responsible for more than 40% of Earth’s photosynthesis. Phytoplankton can be found along coastline and areas of upwelling. Average chlorophyll concentration July 2002- May 2010, MODIS, (Photo Credit: NASA, Jesse Allen & Robert Simmon) [Fondriest Environmental, Inc. “Algae, Phytoplankton and Chlorophyll.” Fundamentals of Environmental Measurements. 2014. Web. https://www.fondriest.com/environmental-measurements/parameters/water-quality/algae-phytoplankton-chlorophyll/].

Other studies suggest fertilising the ocean with nitrogen or pumping nutrient-rich, deep water into the nutrient-depleted surface ocean could do a similar job in terms of stimulating plant growth. As well as drawing down CO_2, it’s thought ocean fertilisation could increase the amount of dimethyl sulphide $[(CH_3)_2S]$ marine organisms release, altering the reflectivity of clouds and potentially slowing temperature rise.[37]

Microalgae CO_2 fixation has the advantage of high photosynthetic efficiency, fast growth rate, good environment adaptability, high lipid productivities and the ability to sequester carbon, and thus has been regarded as a promising method for post-combustion CO_2 capture and utilization.[38-40]

Carbon capture and utilization for valuable chemicals and fuel products

Carbon dioxide as a chemical has been used, both directly and as a feedstock, by a range of industries for over a century. Using CO_2 from the air for products and services is known as **carbon capture and utilization** (CCU) and by some estimates, it has a potential to form an industrial sector valued at $1 trillion market by 2030. Carbon capture and utilization could reduce atmospheric CO_2 emissions by sequestration and at the same time produce useful chemicals and fuels. Currently, CO_2 is only used for the production of chemicals, such as urea, salicylic acid and polycarbonates. Catalytic hydrogenation of CO_2 can produce oxygenates, fuel additives usually in the form of alcohol or ether that can enhance fuel combustion and reduce exhaust emissions and also boost gasoline octane.[41]

8th Conference on

CO_2

Carbon Dioxide as Feedstock for Fuels, Chemistry and Polymers

24–25 March 2020

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In the last decade numerous methods have been advanced for the catalytic CO_2 hydrogenation into various value-added hydrocarbons, such as lower olefins, liquefied petroleum gas, gasoline, aromatics and other chemical substances which can be used as feedstock to synthesize other important chemical products.[42,43]

Also, substantial progress has been achieved by heterogeneous catalysis and plasma catalysis of CO_2 into useful chemicals. A recent (2019) review summarized the progress in CO_2 hydrogenation to value-added chemicals (e.g., CO, CH_4, CH_3OH, DME, olefins, and higher hydrocarbons) driven by both heterogeneous catalysis and plasma catalysis.[44]

There is a great variety of catalytic CO_2 conversions to high-value-added chemicals with applications in the chemical industry. The electrocatalytic pathway has mainly focused on the CO_2 reduction reaction to hydrocarbons, as well as to CO and alcohols. This process is already close to commercialization, but its economic viability depends strongly on the cost of electricity. Another alternative is photocatalysis, typically with semiconductor catalysts, which can enable direct solar to fuel conversion. Although photocatalysis is independent of an electricity source, its efficiency is still too low for industrial applications. Plasma and plasma catalytic reactions are also gaining attention, especially CO_2 splitting and dry reforming of methane. Thermocatalytic CO_2 conversion is also another method with high potential, for instance, to produce syngas ($CO+H_2$), which is then used for the production of hydrocarbons or alcohols through the Fischer–Tropsch synthesis. The thermocatalytic hydrogenation of CO_2 is interesting because of different products that can be obtained, mainly alkanes (liquefied petroleum gas and gasoline), alkenes, and aromatic chemichals.[45]

Researchers at the University of Toronto and the California Institute of Technology (MIT) reported in a paper in 2020 that they have carried a trick by improving the efficiency of a process to make the plastics precursor ethylene ($CH_2{=}{=}CH_2$) from CO_2 electrochemically. The electrocatalytic carbon dioxide reduction reaction (CO_2RR) to value-added fuels and feedstocks provides a sustainable and carbon-neutral approach to the storage of intermittent renewable electricity and economically desirable C_2 products such as ethylene. Tuning the stabilities of intermediates to favour a desired reaction pathway offers the opportunity to enhance selectivity. The scientific group presented a molecular tuning strategy—the functionalization of the surface of electrocatalysts with organic molecules—that stabilizes intermediates for enhanced CO_2RR to ethylene. Using electrochemical, operando spectroscopy (analytical methodology for spectroscopic characterization of materials undergoing reaction is coupled simultaneously with measurement of catalytic activity and selectivity) or in situ spectroscopic and computational studies, they investigated the influence of a library of molecules, derived via electro-dimerization of arylpyridiniums on Cu. They found that the adhered molecules improve the stabilization of an *atop*-bound CO intermediate, thereby favouring further reduction to ethylene. They reported stable ethylene electrosynthesis for 190 hours in a membrane-electrode-assembly-based system that provides a full-cell energy efficiency of 20%.[46]

Ethylene is the most important feedstock chemical (chemical used to support a large-scale chemical reaction) by tonnage for the chemical industry. Ethylene is the building block for a vast range of industrial chemicals from plastics to antifreeze solutions, solvents and epoxyethane. It is estimated that 60% of ethylene is used for the production of plastics (low and high density polyethylene, LDPE, HDPE) with a huge existing market demand.

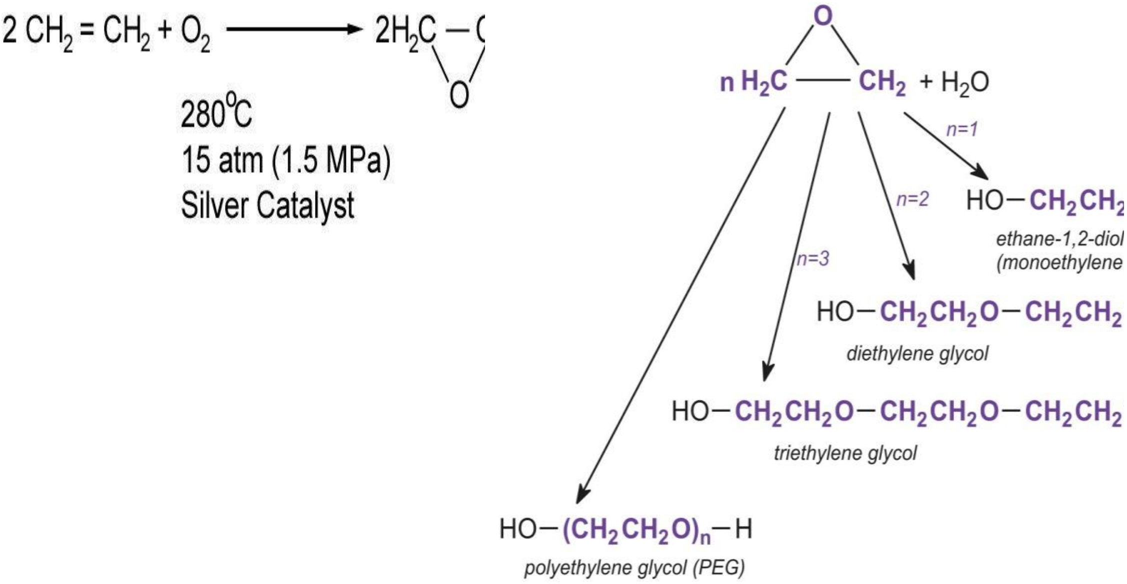


Figure 12. Epoxyethane can be synthesized from ethylene and then can be used for stepwise reactions for a range of industrial chemical products

Another industrial chemical synthesized from ethylene is dichloro-1,2-ethane, the precursor for chloroethylene and thence the important plastic PVC (polyvinyl chloride), which accounts for a further 11%. Ethylbenzene, the route to poly(phenylethene), uses another 5% and about 16% is used worldwide to make epoxyethane (ethylene oxide). The principal use of epoxyethane is in the production of ethane-1,2-diol, the basic constituent of engine coolants, and production of other diols used to make polyesters.

The manufacture of ethylene was fossil fuel based for decades. Now, scientists suggest that ethylene can be prepared by the electrochemical synthesis using captured CO_2 as a feedstock chemical that will reduce atmospheric CO_2. But there are some serious obstacles since the reduction mechanism of CO_2 has very low efficiency, low production rates and low catalyst stability. Scientists tried for many years to discover methods by improving the electrochemical system. Recently a group of scientists added a new coating to the surface of the copper electrocatalyst (at an abrupt reaction interface in an alkaline electrolyte) which helps the carbon compounds stick to its surface thereby encouraging the coupling reaction that yield ethylene. The system is efficient compared with previous attempts, converting 72% of the energy input into ethylene product. The research team also ran the electrochemical synthesis at a high enough current to appeal to industry. They propose that the reaction can be powered by renewable electricity, and the CO_2 would come from an industrial flue (emissions).[47]

Conversion of CO_2 into value-added chemicals

There are at present a number of industrial and commercial process that involve conversion of CO_2 into value-added chemicals for the chemical industry and in parallel removal of atmospheric CO_2 and therefore as a way to mitigate climate change.[48] Using CO_2 as a feedstock in the chemical industry replacing fossil fuels can result in a cheaper or cleaner production process and at the same time CO_2 utilization is often promoted as a way to reduce emissions or removing carbon dioxide from the atmosphere.[49-51]

The IPCC 2005 Special Report on Carbon Dioxide Capture and Storage and in other scientific papers the term ‘CO_2 utilization’ refers to the use of CO_2, at concentrations above atmospheric levels, directly or as a feedstock in industrial chemical processes, to produce valuable carbon-containing chemical products. The IPCC report provides an overview of the technology and expected costs of carbon capture and sequestration, and provides a key definition of CO_2 utilization.[52] Included in this conventional definition is the industrial production of fuels using, for example, amines to capture and concentrate the CO_2 from air, potentially with solar energy. However, the definition excludes cases in which an identical fuel is produced from the same essential inputs, but the CO_2 utilized is captured by plant-based photosynthetic processes.[53-56]

Production of Urea fertilizer from ammonia and CO_2

Urea is used extensively in agriculture as a nitrogenous fertilizer on crops and as a feed additive for ruminants to provide an inexpensive protein substitute in their diet. Urea is produced on an industrial scale: In the last decade worldwide production was ~200 million tons. Urea is produced from synthetic ammonia (NH_3) and CO_2 which is produced during the ammonia manufacturing process as a byproduct. Also in the past CO_2 was from fossil fuels (predominantly natural gas, or occasionally from coal).

Figure 13. Synthetic nitrogen fertilizers such as **urea** are a necessity for food production, making them invaluable toward achieving global food security. More than 90% of world industrial production of Urea is destined for use as a nitrogen-release fertilizer in crops

Urea (carbamide) is the world's most commonly used nitrogen fertilizer and indeed more urea is manufactured by mass than any other organic chemical. It is the cheapest form of nitrogen fertilizer and is favoured in developing countries.

$$2NH_3 + CO_2 \rightleftharpoons CO(NH_2)_2 + H2O$$

In recent years due to the environmental overheating due to increases of atmospheric CO_2 and the effects of greenhouse gases on the climate changes, the atmospheric CO_2 capture and storage process have been developed to reduce this pollutant from its main sources such as power stations, petrochemical plants, cement factories, oil refineries, etc. In this case the CO_2, is not considered as a waste but as a valuable raw material to be converted into valuable chemical products. Atmospheric CO_2 can be used as a feedstock material for the production of many petrochemical products and specially for urea and methanol. [57-60]

Captured atmospheric CO_2 for the synthesis of Methanol

"The Methanol Economy" (CH_3OH) is a concept that the Olah-Prakash team first began refining in the mid-1990s, right after the time Professor George Olah [University of Southern California (USC)] was awarded (1994) the Nobel Prize in Chemistry for his contributions to the discovery of carbocations via superacids. According to Olah and Prakash, the goal of a methanol-based economy would be to develop renewable sources of energy, led by Methanol, that could mitigate the problem of climate change caused by carbon emissions, as well as the U.S. dependence on other countries for energy, particularly fossil oil.[61,62]

Figure 14. The world's first commercial carbon-capture plant opened in Switzerland in 2017. Founded by Climeworks, the direct from air capture (DAC) plant is capable of removing 900 tons of CO_2 from ambient air annually. The CO_2 as feedstock material can be used to make carbonated drinks, carbon-neutral fuels, value-added chemicals, methanol and other chemicals.

It has been proposed many years ago to convert CO_2 into methanol, (CH_3OH) which may be used as a fuel or fuel additive. Methanol can be used as precursor for more complex transportation fuels, or even as an intermediate for a diverse array of industrial chemicals including plastics, paints, textiles, and other uses. Scientists suggested that synthetic methanol could be an effective alternative for disposition of greenhouse gas CO_2.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (1)$$
$$\Delta H_{298} = 11.9 \text{ kcal mol}^{-1}$$

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (2)$$
$$\Delta H_{298} = -21.7 \text{ kcal mol}^{-1}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad (3)$$
$$\Delta H_{298} = -9.8 \text{ kcal mol}^{-1}$$

Figure 15. The formation of methanol from CO_2 and syngas proceeds through the equilibria in equations 1-3 and is exothermic. Optimum reaction conditions typically require low temperatures and increased pressure.

Methanol is a simple organic molecule, liquid at room temperature, and a chemical which is easier for storage and transport than alternative fuels such as methane (CH_4) or hydrogen (H_2). If for the synthesis of Methanol can be used electricity from renewable sources and atmospheric CO_2, then this energy can be converted into chemical energy and stored in the chemical bonds of methanol which is easy to transport. In addition, given the massive global methanol demand–200,000 tons per day and growing. Global methanol demand reached 75 million metric tons in 2015 (or 91 billion liters), driven in large part for emerging energy applications (accounting for 40% of methanol consumption). Direct blending use of methanol with gasoline has seen an average annual growth rate of 25% from 2000 to 2015, resulting in gasoline blending becoming the third largest demand segment for methanol by 2015. [The changing face of the global methanol industry, HIS Chemical Bulletin, 2016 http://www.methanol.org/wp-content/uploads/2016/07/IHS-ChemicalBulletin-Issue3-Alvarado-Jun16.pdf]. In parallel, diverting CO_2 from the atmosphere into the synthesis of methanol has not only significant potential for growth as a commodity chemical or fuel, but also the potential to recycle, by catalytic processes, a large quantity of atmospheric CO_2.[63,64,65]

The scientific literature has a high number of studies on synthetic catalytic applications for the hydrogenation and conversion of CO_2 (as a feedstock chemical captured from air) into methanol on an industrial scale. In the last decade a wide variety of heterogeneous catalysts have been evaluated in the CO_2 hydrogenation to methanol. There are three catalyst categories: a. Metal-based catalysts, including modified Cu-based methanol catalysts and noble metals such as Au, Ag, Pd and Pt; b. Oxygen deficient materials; and c. Other catalytic system with novel reaction mechanism and catalytic structure.[66,67,68,69]

Decarbonize transportation sector. Dimethyl ether from CO_2

Dimethyl ether (DME), the simplest of the ethers, is a non toxic molecule with a boiling point of −25 ◦C, but it is a liquid at room temperature under a relatively low pressure.

$$2CO_2 + 6H_2 = CH_3OCH_3 + 3H_2O$$

Chemical and physical properties of DME are close to liquid petroleum gas (LPG) and published studies suggested that the technologies developed for storage and transport of LPG can be easily converted to accommodate DME with similar safety guidelines and codes. DME is also an important chemical intermediate for production of widely used chemicals, such as diethyl sulphate, methyl acetate and, as mentioned before, light olefins and gasoline.[70]

Fossil fuels have until now been the sole energy fuels used in the transportation sector. The aim to decarbonise the transportation sector has triggered the exploration of alternative cleaner fuels and renewable electricity for electric cars, that can successfully substitute fossil derived fuels. Dimethyl ether (DME) poses some advantages as a promising candidate due to excellent combustion properties and low greenhouse gas emissions. Recently, the power to liquids concept in conjunction with the atmospheric

CO_2 capture and utilisation (CCU) scenario have emerged as sustainable ways to produce carbon based material and contribute into satisfying the ever growing energy demand. A recent study determined the technical performance and economic viability of a novel dimethyl ether (DME) production route via captured CO_2 hydrogenation within a power to liquid context. The results showed that DME can be an economically viable alternative fuel for means of transportation.[71]

Methods for conversion of CO_2 into formic acid (HCOOH)

Formic acid (HCOOH) is an industrial chemical that finds applications in textiles, pharmaceuticals and food chemicals, due to its strong acidic nature and reducing properties. Traditionally, the leather and tanning industry has been the biggest consumer of formic acid. Since 2006, and due to the total European ban on non-prescribed feed antibiotics, formic acid is used mainly as a preservative and antibacterial agent in livestock feed. Global production in 2019 was more than 760 thousand tons (kt) by volume.

Recently, scientists in Europe have identified formic acid as one of the most promising materials for hydrogen storage because formic acid is a liquid that contains 4.4 wt.% of hydrogen with a volumetric capacity of 53.4 g/l at standard temperature and pressure.[72,73]

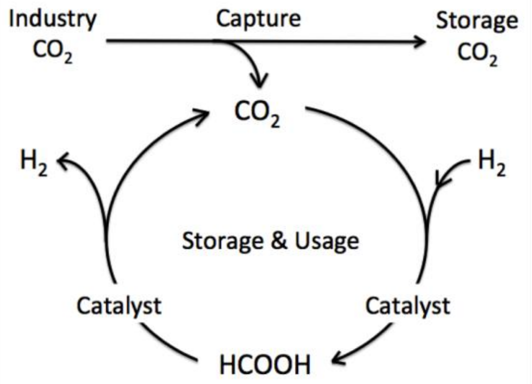


Figure 16. The CO_2 captured from industrial emissions can be transformed by hydrogenation into formic acid. Most research has been performed into developing formic acid as a hydrogen storage material. Studies focused on finding the right catalyst materials for formic acid decomposition into hydrogen again. [Boddien A, Junge H. Acidic Ideas for hydrogen storage. *Nat. Nanotechnology.* **6**: 265-, 2011].

A variety of methods have been experimentally explored for the use of CO_2 captured from air for catalytic conversion into formic acid. were There are at present three types of reactions: photocatalytic conversion, electrochemical conversion, and direct hydrogenation of CO_2 into formic acid using metallic catalysts (e.g. Ruthenium in acidic media). [74,75,76]

Methane production from atmospheric CO_2

The conversion of CO_2 to methane (CH_4) has drawn great attention among scientists for use in supporting carbon capture from the atmosphere and utilization into valuable chemicals. Methane is important fuel for electricity generation (from gas turbine or steam generators). Compared to other hydrocarbon fuels CH_4 produces less CO_2 for each unit of heat. Especially, methane can be used not only as fuel but also as a hydrogen carrier, transporting town gas to existing infrastructure.

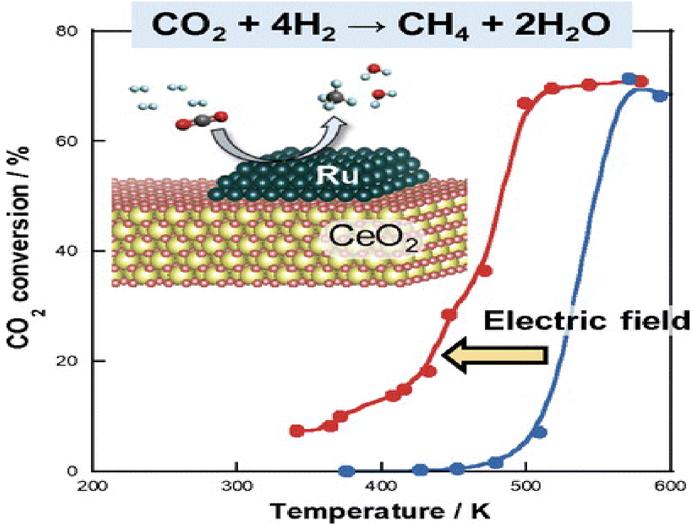


Figure 17. Hydrogenation of CO_2 to CH_4 proceeds over Ru/CeO_2 catalyst in an electric field even at low temperatures below 473 K, [Yamade K, et al. Low-temperature conversion of carbon dioxide to methane in an electric field. *Chemistry Letters* 49 (3): 303-306, 2020].

The use of CO_2 into methane (methanation), involves the reaction of hydrogen (H_2) and CO_2 using a ruthenium-based catalyst at temperatures of 300 to 400 degrees Celsius, but this method limited how much and when methane could be produced since it requires such high temperature. Additionally, operation at low temperatures was demonstrated to be favorable to improve carbon dioxide conversion and increase the amount of methane produced. A new method has been reported recently in *Chemistry Letters*, CO_2 can be converted into CH_4 more efficiently and quickly in the 100 degrees Celsius range. CO_2 methanation was conducted at low temperatures with an electric field. Results show that 5 wt %Ru/CeO_2 catalyst exhibited high and stable catalytic activity for CO_2 methanation with the electric field. The kinetic investigations and *in-situ* DRIFTS measurements revealed that Ru/CeO_2 catalyst promoted CO_2 methanation and Ru at the Ru–CeO_2 interface (low-coordinated Ru sites) contributes to the reverse water gas shift reaction at low temperatures in the electric field..[77]

Most recent studies showed that captured atmospheric CO_2 can be converted by hydrogenation to methane, by using appropriate heterogeneous catalysts. In the last 30 years, studies of CO_2 methanation have intensively focused on various supported catalysts. Catalysts for hydrogenation are based on Ni, Ru, Rh, Pd , Fe and Co . Carrier or supports are Al_2O_3, SiO_2, ZrO_2 , TiO_2, carbon materials and zeolites. Among these catalytic systems, a Ru-based catalyst seems to be a good choice when supported on the inexpensive carrier γ-Al_2O_3.[78,79]

Dimethyl- Diethyl, and Diphenyl carbonate from captured CO_2

Several organic carbonates such as dimethyl carbonate, diethyl carbonate, diphenyl carbonate, propylene carbonate, and styrene carbonate are important products of the chemical industry. They are used in the synthesis of polycarbonates and polyurethanes, which are among the most extensively used plastics. In addition, they can be employed in lithium-ion batteries and are used as aprotic polar solvents. Diethyl carbonate (DEC) is one of the most important green chemicals among carbonate esters. It is an excellent solvent and an intermediate for various pharmaceuticals, such as antibiotics and phenobarbital.

Polycarbonates are widely used polymers. Because of their remarkable properties, they are flame and heat resistant, tough and transparent. Among the uses of the polycarbonates and their blends are: medical products (e.g. dialysis machines, spectacle lenses), electro-electronic products (e.g.

sockets, lamp covers, fuse-boxes, computer and television housings), construction materials (stadium roofs, signs, skylights), optical storage items (CDs, DVD, HD-DVDs), cars (interior lighting and headlamps, sunroofs, side windows), packaging materials. [https://www.essentialchemicalindustry.org/ polymers/ polycarbonates.html].

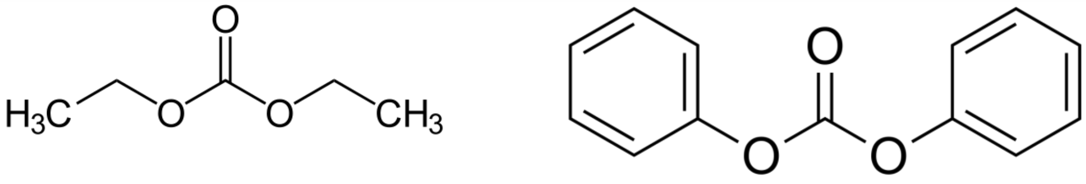


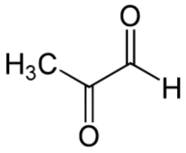
Figure 17. Diethyl carbonate (left), Diphenyl carbonate (right). The properties of polycarbonates (strength, remarkable transparency) and their biocompatibility make them ideal materials for medical plastic appliances. They are used in dialysis machines for kidney problems and for oxygenators which take over the work of the heart and lungs during serious operations.

In the last decade selective catalytic systems were developed to quantitatively capture CO_2 from industrial flue gas and other sources of atmospheric carbon and transforme with catalytic transition metals into a variety of carbonates.[80-85]

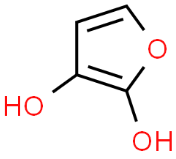
Capture and storage CO_2 for the production of polymers

In the last decade numerous research groups are experimenting with catalysts that can convert captured CO_2 into plastics, fabrics, resins, and other polymeric products. Electrocatalysts are the first materials, aside from enzymes, that can turn CO_2 and water into polymeric carbon building blocks.
Two of the products that can be produced from these catalytic methods are: methylglyoxal (C3) and 2,3-furandiol (C4) can be used as feedstock precursors for plastics, adhesives, and pharmaceuticals. [ScienceAlert, CO_2 into plastic , 2018, https://www.sciencealert.com/ scientists-have-figured-out-a-way-to-convert-carbon-dioxide-into-plastic]. The method use CO_2 emissions and renewable electricity to convert CO_2 and water into useful methylglyoxal and 2,3-furandiol for plastic production. These productions are inefficient and too costly to be commercially feasible. But using five catalysts made of nickel

and phosphorus, which are cheap and abundant researchers can electrochemically convert CO_2 and water into a wide array of carbon-based products which can be polymerized into resins, plastic containers and pharmaceutical products.[86]



Methylglyoxal



2,3-furandiol

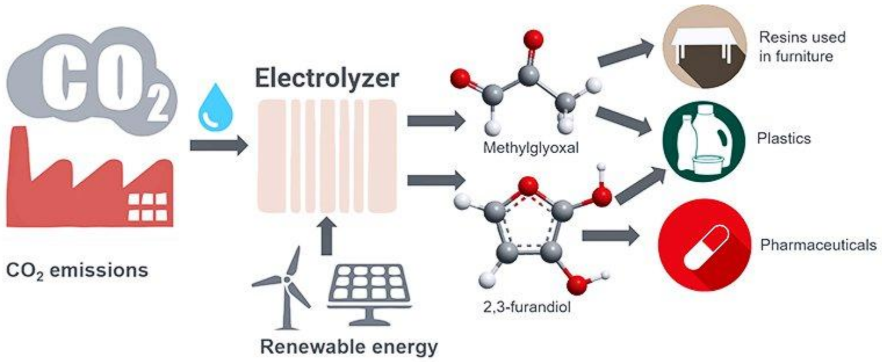


Figure 18. The choise of electrocatalysts and other conditions determine how many carbon atoms can be stitched together to make molecules or even generate longer polymers. Various research groups have applied for patents to turn their catalytic research discoveries into start-up companies that can transform captured CO_2 into polymers.

Artificial chloroplasts that convert CO_2 into organic compounds with the aid of sunlight

For many years researchers were experimenting in the laboratory with artificial version of chloroplasts, the photosynthetic structures inside plant cells, that with the use of sunlight can transform CO_2 into sugars. Researchers hope that an artificial photosynthetic pathway in chloroplasts can remove CO_2 from the atmosphere and turn it into useful chemicals by a large scale and economically feasible operation, or help genetically engineered plants absorb up to 10 times the atmospheric CO_2 of regular ones.

In 2016, Tobias Erb, a synthetic biologist at the Max Planck Institute for Terrestrial Microbiology in Marburg, Germany, and his colleagues designed and used a thermodynamic and kinetic pathway to ask for CO_2 fixation. The new pathway was the CETCH cycle — a complicated network of enzymes that is 20% more energy efficient than the pathway used in natural forms of plant photosynthesis. Erb and his colleagues sought to ramp things up by designing a new set of chemical reactions. Instead of RuBisCO, they substituted a bacterial enzyme that can catch CO_2 molecules and force them to react 10 times faster. In combination with 16 other enzymes from nine different organisms, this created **a** new CO_2-to-organic-chemical cycle they dubbed the CETCH cycle [The crotonyl-coenzyme A (CoA)/ethylmalonyl-CoA/hydroxybutyryl-CoA (CETCH) cycle is a reaction network of 17 enzymes that converts CO_2 into organic molecules].[87]

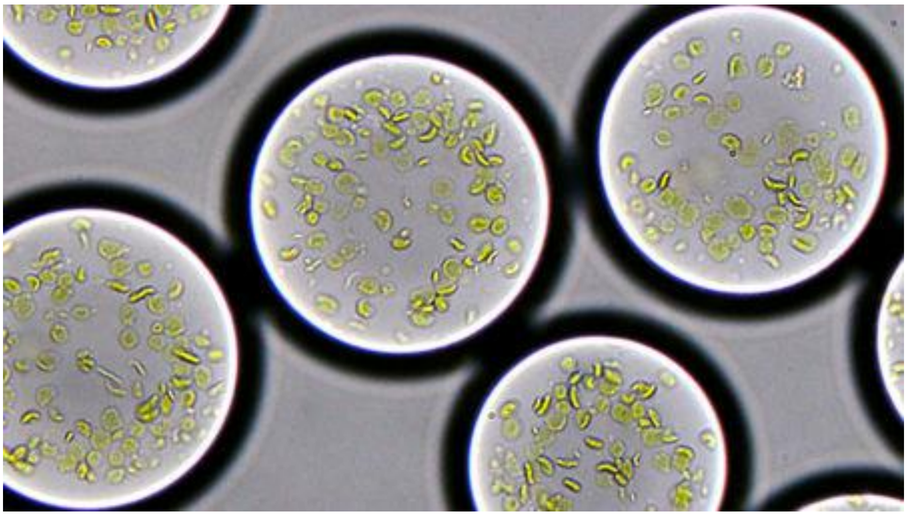
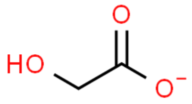


Figure 19. Chloroplast components called thylakoids in these 90-micrometer droplets use sunlight to convert carbon dioxide (CO_2) to organic compounds.

The same group of scientists with the collaboration with other scientists in 2020 published a modified version of the original idea. They change the process to run on sunlight and turned to chloroplast components called thylakoid membranes, pouchlike assemblies that hold chlorophyll and other photosynthesizing enzymes (thylakoid membranes can operate outside plant cells). They used thylakoid membranes from spinach leaf cells and showed that their assemblies, too, could absorb light and transfer its energy to ATP and NADPH molecules. Pairing the light-harvesting thylakoids with their CETCH cycle system allowed the team to use light to continually convert

CO_2 to an organic metabolite called glycolate ($C_2H_3O_3$). To optimize the full ensemble, Erb and his colleagues teamed up with Jean-Christophe Baret, a microfluidics expert at the Paul Pascal Research Center. Baret's team designed a device that generates thousands of tiny water droplets in oil and injects each one with different amounts of thylakoid membrane assemblies and CETCH cycle enzymes. That allowed the researchers to home in on the most efficient recipe for producing glycolate.[88]



The research group tried to integrate the light-harvesting apparatus with the CETCH cycle, the researchers designed a device that generates thousands of tiny water droplets in oil and injects each one with different amounts of thylakoid membrane assemblies and CETCH cycle enzymes. That allowed the researchers to home in on the most efficient recipe for producing glycolate. The research group hopes to modify their setup further to produce other organic compounds that are even more valuable than glycolate, such as drug molecules. They also hope to more efficiently convert captured CO_2 into organic compounds that plants need to grow. That would open the door to engineering the genes for this novel photosynthesis pathway into crops to create novel varieties.[89]

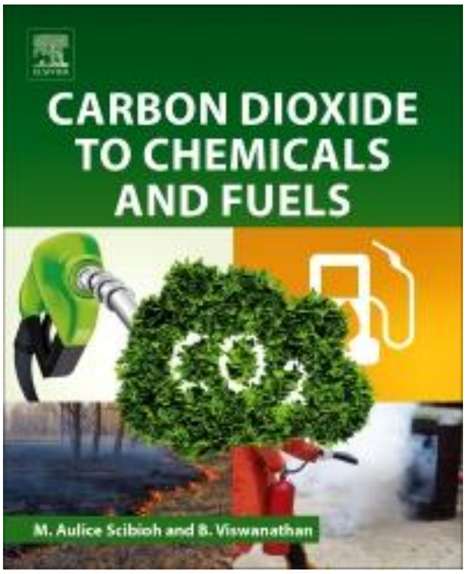
Scientists explore lately the idea of artificially replicating the photosynthetic process which can be able to lower CO_2 concentrations in the atmosphere, while also producing sugar that can be used for food and energy production. The ultimate goal though is to improve substantially photosynthesis, making it more efficient, to absorb more light at a wider range of wavelengths. Artificial photosynthesis can create fuel directly from sunlight on an economic scale, to be used for chemical synthesis, to split H_2O into hydrogen and oxygen and reduce atmospheric CO_2. [The Green Age, 2019, https://www.thegreenage.co.uk/tech/artificial-photosynthesis/].

Conclusions

The impending threat of climate change and the rise of global temperatures in the near future, has forced many researchers and policymakers to think seriously of technological strategies and innovative scientific solutions for removing CO_2 from the Earth's atmosphere as a necessary step for keeping increase of global temperatures below two degrees Celsius – as agreed to in the Paris Climate Agreement (2015).

Strategies to remove atmospheric CO_2 are mainly divided into two categories: natural CO_2 removal and technological CO_2 removal. Carbon removal by naturally occurring processes is simply the uptake and storage of carbon dioxide (CO_2) by the Earth's environmental sources and natural ecosystems. Science has to think the appropriate "carbon sinks;" specifically, land-based carbon sinks (large swaths of forests, wetlands, agricultural lands and soil) and "blue carbon" sinks. Blue carbon sinks are the coastal ecosystems of mangroves, seagrass meadows for sequestering atmospheric CO_2 and oceans (covering 71% of the Earth's surface) that can significantly absorb higher rates of CO_2, per unit area, than terrestrial forests. In the last decades, scientists have developed strategic technologies to reduce anthropogenic CO_2 emissions (energy conservation, low carbon fuels, renewable energy sources, bioenergy, etc). Also, they developed capture and storage methods of CO_2, to be used as feedstock into valuable chemical products. But all these technological approaches have advantages and limitations. Scientists propose in the first phase the deployment of Negative Emissions Technologies (NETs). Four of them are already applied on a large scale and can be very effective in reducing atmospheric CO_2: afforestation/reforestation, changes in forest management, uptake and storage by agricultural soils, and bioenergy with carbon capture and storage (BECCS). These NETs have low to medium costs (\$100/t CO_2 or less) and substantial potential. These NETs can provide co-benefits, such as forest productivity, improved agricultural productivity (increased soil retention of nitrogen and water), production of low carbon fuels and renewable electricity production from captured atmospheric CO_2. These NETS can be scaled-up to capture and store substantial amounts of CO_2 at low cost.

In the last decades scientific groups and industrial laboratories have been working on the technological front for CO_2 capture and utilization (CCU) and its catalytic use for synthetic commodity chemicals and low carbon fuel products (plastics, drugs, methanol, formic acid, diethyl ether, urea, etc). Using atmospheric CO_2 for valuable chemical products, by some estimates, has a potential to form a large industrial sector valued at $1 trillion market by 2030. Catalytic hydrogenation of CO_2 can produce oxygenates, fuel additives usually in the form of alcohol or ether that can enhance fuel combustion and reduce exhaust emissions and also boost gasoline octane.



The scientific literature has a vast number of studies on synthetic catalytic applications (mostly heterogeneous) for the hydrogenation and conversion of CO_2 into methanol on an industrial scale and on CO_2 methanation by various supported catalysts for the conversion into methane (CH_4) and other chemicals. The book by Scibioh MA, Viswanathan B. *Carbon Dioxide to Chemicals and Fuels* (Elsevier, 2018) describes the various methods, both currently available and potential, for conversion of CO_2 into fuels and valuable chemicals, with explanation of concepts and their applications and offer at the same time an interdisciplinary approach that draws on and clarifies the most recent research trends on the subject.

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