Beneficial Utilisation of Carbon Dioxide

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Introduction

Carbon dioxide (CO_2) is the major cause of climate change, because of its greenhouse properties and continuous accumulation in the atmosphere. The atmospheric concentration of CO_2 has risen from 278 ppm during the pre-industrial era to a current level of 416 ppm (Global Monitoring Laboratory, 2021). The Intergovernmental Panel on Climate Change (IPCC, 2014) has estimated that to limit global warming to 1,5°C above pre-industrial levels will mean holding concentrations of atmospheric CO_2 to below 430 ppm.

It is necessary to drastically reduce emissions of CO_2 and other greenhouse gases to counter further climate change. Making use of CO_2 as a chemical feedstock can make a significant contribution to reducing CO_2 emissions in several industrial sectors provided that certain conditions are met, particularly the use of renewable sources of energy to drive the processes involved. It must be emphasised that CO_2 utilisation represents only a small portion of the total quantities of CO_2 currently being emitted into the atmosphere and that using CO_2 as a chemical feedstock cannot be the sole solution to the greenhouse gas emissions problem. A concerted effort is required to reduce CO_2 generation and emissions, as well as to increase CO_2 sequestration through capture and storage, biochar, and forestation.

One possibility is the use of CO_2 as a material resource to produce chemicals and fuels. Crude oil and coal are currently the primary sources of carbon for almost all the world's plastics, organic chemicals, and fuels, of which carbon is an essential element. CO_2 is present in almost endless quantities and using it as a chemical feedstock will lessen the chemical industry's dependence on oil and coal as the main sources of the carbon that the chemical sector requires. CO_2 should be used as a source of carbon in combination with renewable energy sources to reverse the rapid build-up of CO_2 in the environment.

In this article, we take a brief look at the thermodynamics of CO_2 and present an overview of some of the more interesting and promising applications for CO_2, based on public domain information.

Thermodynamics of CO_2

Chemical thermodynamics covers the interrelation of heat and work with chemical reactions or with physical changes of state within the confines of the laws of thermodynamics.

Thermodynamics provides a quantitative measure of what is possible and realistic in chemical conversion of CO_2. As an example, we consider the combustion of methane (CH_4) in air (oxygen (O_2)) to produce CO_2 and water (H_2O). We know that much heat is generated by this reaction. We can see from Figure 1 that the heat generated by the combustion of CH_4 is equal to 803 KJ/mol CH_4. Both the products from this reaction, namely CO_2 and H_2O, are extremely stable molecules.

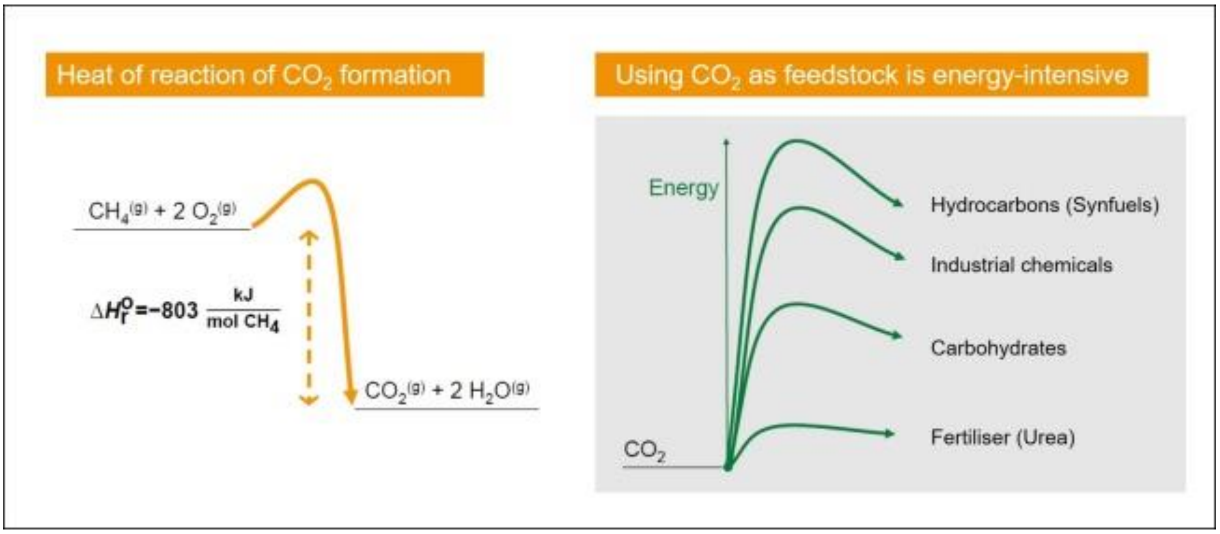

Figure 1: The thermodynamics of CO_2 (Adapted from Brudermüller, 2019)

Because of the inherent stability of CO_2, large-scale conversion of CO_2 to more reduced carbon products (such as fuels, acids, aldehydes, carbohydrates, alcohols, or alkanes) will require a large source of energy. The relative energy required for converting CO_2 to other chemical and hydrocarbon products is shown in the grey box in Figure 1. Using fossil fuels to provide this energy will be counter-productive, since this will generate more CO_2 in turn.

The only workable option is to use renewable energy and green hydrogen as the energy sources for using CO_2 as feedstock to produce fuels, chemicals, and other products. An overview of technologies to produce hydrogen can be found in the article by Steyn and Render (2020).

Overview of CO_2 utilisation

According to the International Energy Agency (IEA, 2019), approximately 230 million tons of CO_2 are currently used every year. The fertiliser industry is the largest consumer, where 130 million tons CO_2 is used in urea manufacturing. The second largest consumer is the oil and gas industry, which uses between 70 and 80 million tons of CO_2 for enhanced oil recovery. Other commercial applications include food and beverage production, metal fabrication, cooling, fire suppression and stimulating plant growth in greenhouses.

The range of potential CO_2 use applications is large and includes direct applications, where CO_2 is not chemically altered, and conversion applications, where CO_2 is transformed via chemical and biological processes to fuels, chemicals and building materials. Figure 2 summarises the CO_2 applications and CO_2-derived products. Note that carbon capture and storage (CCS) is not shown as an application, because this only deals with the storage of CO_2 in suitable geological formations. Hopefully, the CO_2 can in future be mined from these formations for conversion applications.

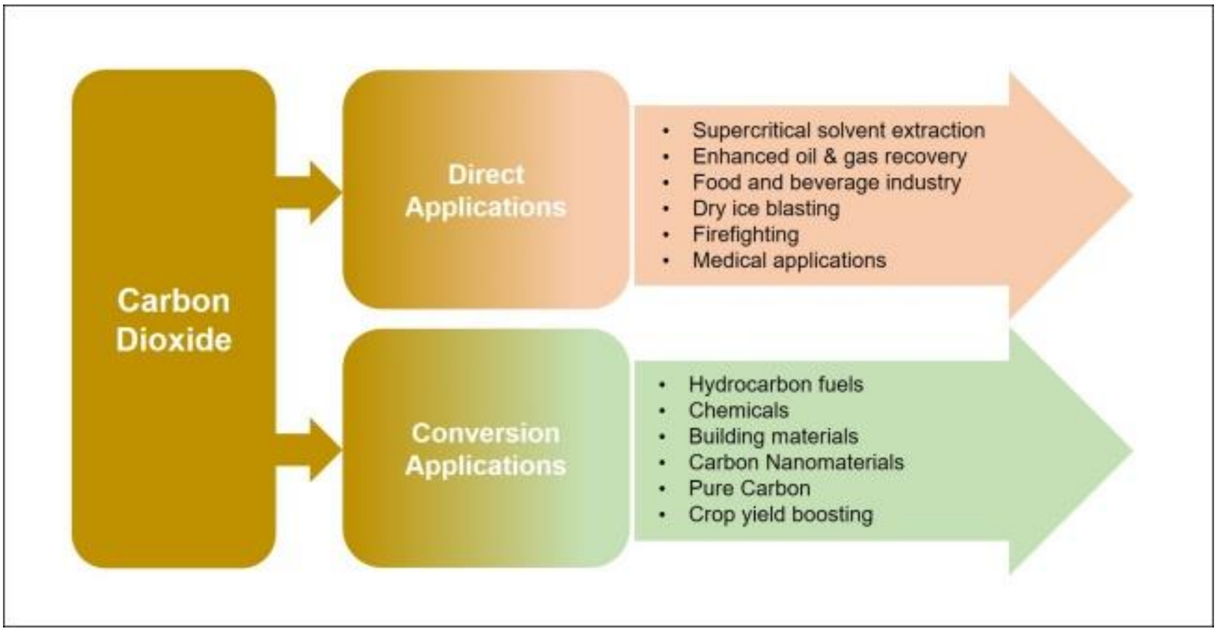

Figure 2: CO_2 applications and CO_2-derived products

The International Energy Agency (IEA, 2019) warns that the use of CO_2 is not the same as avoiding the generation thereof, especially in direct applications. The carbon retention time for CO_2 use applications is extremely important and can vary greatly per application. For instance, CO_2 used for firefighting can have a carbon retention time of several weeks, whilst the carbon retention time for polymers can be hundreds of years. CO_2 applications do not necessarily reduce emissions and quantifying the impact of CO_2 utilisation requires a comprehensive life-cycle assessment. CO_2 utilisation can provide climate benefits where the application is scalable, uses low-carbon energy, and displaces a product or technology with higher life-cycle emissions.

Figure 2 also provides the structure for the remainder of this article. Each of the applications is described in more detail in the sections that follow.

Direct applications of CO_2

Opening comments

Direct CO_2 applications imply that CO_2 is not chemically or biochemically altered during the use thereof. Instead, the direct applications are based on the unique physical properties of CO_2. Unfortunately, this also means that in most cases, CO_2 is only temporarily stored before release to the atmosphere.

Supercritical solvent extraction

The density of a liquid decreases when the temperature of the liquid is increased. Similarly, the density of a gas increases when its pressure is increased. At the critical point, the liquid and gas phases have the same density, and only a single phase exists. This single phase is called a supercritical fluid and it occurs at temperatures over 31,04°C and pressures over 73,85 bar. The supercritical CO_2 has properties of both gas and liquid including low viscosity and easy diffusibility of gas and high density and solubility of liquid.

Supercritical fluid extraction is an environmentally safe and cost-effective alternative to traditional organic solvents. Supercritical CO_2 is widely used as the solvent of choice for applications such as caffeine extraction for decaffeinated coffee, hops extraction for beer making, vanilla and maple extraction for cooking, and extraction of essential oils due to its mild critical temperature, nontoxicity, nonflammability, and low cost.

Once the plant oils have been stripped from the source plant material, the CO_2 is evaporated off and collected for re-use.

Enhanced oil & gas recovery

In the first phase of the oil field's productive life, called primary production, oil is produced due to the natural pressure from the earth which causes the oil to flow to the wellbore. Primary production can result in the recovery of up to 20% of the oil originally in the rock. This means that at least 80% of the oil may remain in the rock unless additional technology is used to increase the recovery.

The next step in the oil field life-cycle is the injection of water into the oil-bearing formation to maintain reservoir pressure and recover more oil. This is called secondary recovery or water flooding. The addition of secondary recovery has the potential to recover a further 15% to 20% of the original oil in place.

Even after primary and secondary recovery, up to 65% of the original oil still exists in the rock formation. Enhanced oil recovery using CO_2 (CO_2 EOR) is a type of tertiary oil recovery that can recover an additional 15% to 20% of the original oil in place. CO_2 from industrial or natural sources is pumped directly into the oil-bearing rock formation.

CO_2 at its supercritical pressure and temperature is completely miscible with oil. In CO_2 EOR, the CO_2 combines with the oil and helps move it through the rock pore spaces.

The technology used for CO_2-enhanced gas recovery (CO_2 EGR) is like that for CO_2 EOR. The main difference between CO_2 EGR and CO_2 EOR is that the EGR relies on physical displacement (upwards) of the lighter natural gas by the heavier CO_2, with minimal mixing.

The U.S. Department of Energy (DOE) projects potential additional oil resources recoverable with CO_2 EOR of up to 137 billion barrels (Institute for 21st Century Energy, 2012). Captured CO_2 has the added environmental benefit of not being released into the atmosphere. After the completion of EOR activities, the CO_2 used in oil recovery is permanently sequestered in the old oil formation.

Food & beverage industry

A wide range of direct applications exist for CO_2 in the food and beverage industry, which account for approximately 39% of all CO_2 used directly. CO_2 is used in its gaseous, liquid, and solid forms.

In the beverage industry, CO_2 is used for the carbonation of drinks. Carbonation occurs when CO_2 gas dissolves completely in beverage. This provides the “fizz”, adds a sour taste, and has antibacterial properties.

CO_2 is used in the food industry to stun animals for slaughter, for controlled atmosphere storage for the preservation of food and produce, displacement of air during canning, freezing of poultry and food products, refrigerated transport of foods, and pH control. Changing lifestyle preferences have increased the demand for ready-to-make and frozen foods, thereby increasing demand for CO_2.

Dry ice blasting

The solid form of CO_2 is known as dry ice, as shown in Figure 3. Fine dry ice particles have proven to be an excellent blasting medium for cleaning production equipment. Tyre manufacturers became one of the early adopters of dry ice blasting technology. Not only was it a non-abrasive cleaning method that did not damage the moulds, presses, vents, and other machinery they were cleaning, but it was also significantly more cost effective than previously employed methods.

Dry ice blasting removes built-up residue and rubber from the surface of the equipment being cleaned. Over time, the vents in the tyre moulds get clogged and prevent them from functioning properly. This causes faults and irregularities in the tyres, which then must be scrapped. These vents used to be cleaned by using small drill bits to remove the extruded rubber. However, the problem with this method was the drill bits broke off in the vents and permanently clogged them. As more drill bits broke off, vents had to be replaced. Dry ice blasting eliminated this issue while making the cleaning process faster than ever.

Figure 3: Solid CO_2 or dry ice

Approximately 7% of the total direct application of CO_2 is used for blasting. Dry ice blasting results in the immediate release of CO_2 to the atmosphere as dry ice particles evaporate to the gaseous state upon use.

Firefighting

CO_2 fire extinguishers are ideal for fires involving delicate electrical equipment and Class B liquid fires. They do not work by cooling the fire and is therefore not recommended for controlling Class A fires involving solids. CO_2 fire extinguishers discharge CO_2 gas under pressure and suffocate fires by displacing the oxygen the fire needs to burn.

Approximately 8% of the total direct application of CO_2 is used for firefighting. CO_2 fire extinguishers have a short carbon retention time and its use results in the immediate release of CO_2 to the atmosphere.

Medical uses

The medical segment is also among the fastest-growing application segments of CO_2. CO_2 is used in surgeries, such as arthroscopy, laparoscopy, and endoscopy, to stabilize body cavities and to enlarge the surgical surface area. It is also used for maintaining cryotherapy temperatures of approximately -76°C.

Medical applications of CO_2 currently account for approximately 18% of the total mass used for direct application. Medical applications also have a short carbon retention time and its use results in the immediate release of CO_2 to the atmosphere.

Conversion applications of CO_2

Opening comments

The chemical and biochemical utilisation of CO_2 means using it as a reactant in chemical and biochemical reactions. The use of CO_2 as a resource in chemical reactions is not new and several long-established processes based on this concept already exist. CO_2 can be used as a reactant or feedstock in products ranging from basic chemicals to polymers, specialty chemicals, and synthetic fuels (IEA, 2019). Figure 4 shows a few of the many products that can be produced via CO_2-based syntheses.

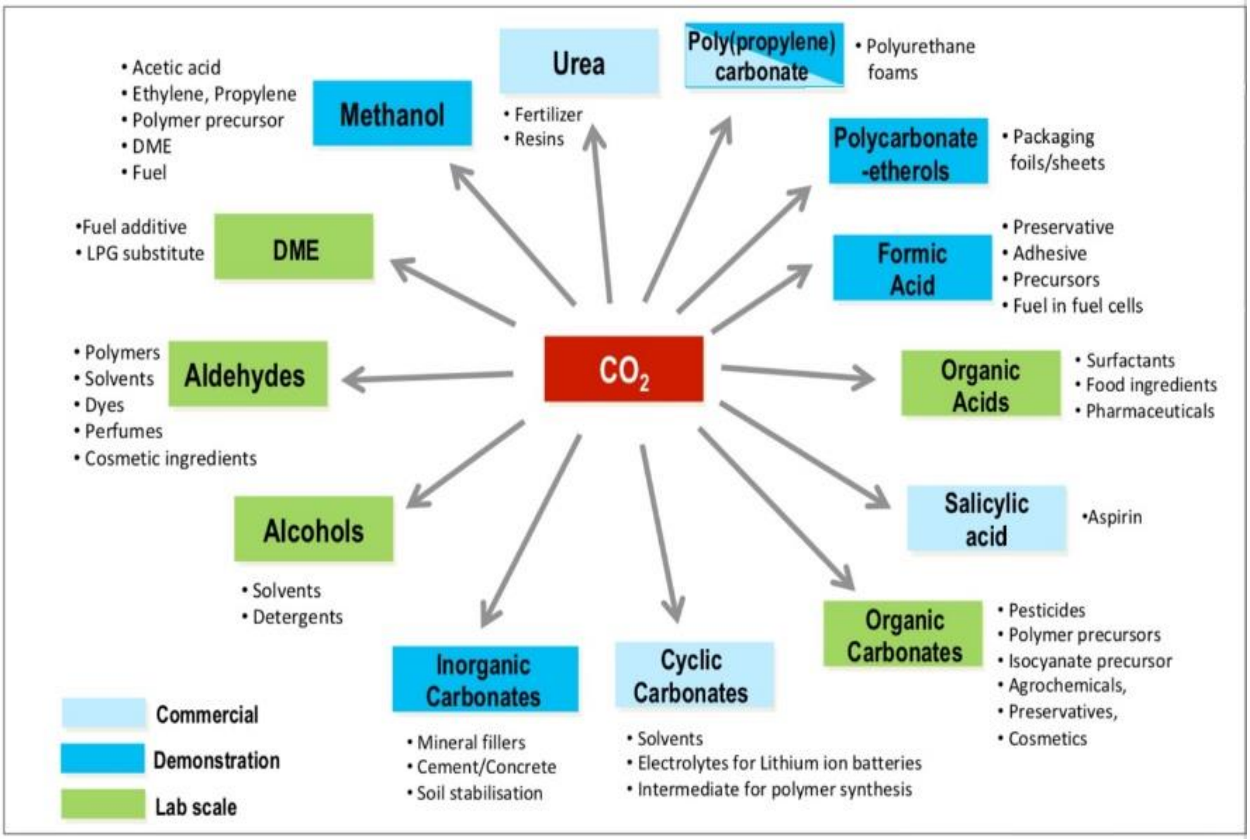

Figure 4: Products from CO_2-based synthesis (IEA, 2019)

It is important to note from Figure 4 that, although most of these technologies are in the development phase, at least four of them already find commercial application, as illustrated by the light blue boxes.

Hydrocarbon fuels from CO_2

Low-carbon hydrogen

The carbon in CO_2 can be used to produce hydrocarbon fuels that are in use today, including methane, methanol, petrol, diesel, and aviation fuels. The process involves using the CO_2 in combination with hydrogen, which is energy-intensive to produce. Low-carbon hydrogen can be produced from fossil fuels when combined with carbon capture and storage (blue hydrogen), or through electrolysis of water using renewable energy (green hydrogen).

Synthetic fuels

The production of synthetic fuels is a promising area for the chemical utilisation of CO_2. In addition to using CO_2 as a feedstock, an added benefit of CO_2-based fuels is that they can be introduced into an existing market infrastructure.

This processing route to produce synthetic fuels from CO_2, as proposed by several companies, entails three different steps:

- The production of hydrogen from water by electrolysis and renewable power.
- The use of the reverse water-gas shift reaction to convert CO_2 and hydrogen to CO and water.
- The use of CO and hydrogen (syngas) to produce synthetic fuels via the normal Fischer-Tropsch synthesis route.

Greyrock Energy developed standardised plant designs for their industry leading Direct Fuel Production™ systems to produce premium, clean burning liquid fuels from alternative and waste resources including flare gas, natural gas, CO_2, and other materials.

Denmark's Sunfire is a global leader for industrial electrolysers. Sunfire's technology is based on high-temperature co-electrolysis of steam (H_2O) and captured CO_2 using solid oxide electrolysis cells to produce syngas which is then converted into synthetic fuels.

Methanol

We list methanol under hydrocarbon fuels, but it also falls under chemicals. While methanol is typically synthesised from syngas, it can also be produced from the hydrogenation reaction of CO_2 and hydrogen.

Commercial production of CO_2-derived methanol could be possible in markets where both low-cost renewable energy and CO_2 are available. One such example is Carbon Recycling International's George Olah CO_2-to-methanol plant in Iceland that converts around 5 500 tpa of CO_2 into methanol using hydrogen produced from renewable electricity. The production unit captures CO_2 released by an adjacent geothermal power plant. The plant has been in operation since 2011 and is powered using electricity from hydrothermal and geothermal sources in Iceland.

Chemicals from CO_2

Urea

Urea is an organic chemical compound that is produced in a two-step process from liquid CO_2 and liquid ammonia. The technology was developed in 1922, is well established and has been commercially proven for many decades. The most popular and most common use of urea is as a fertilizer, not only because it has the highest nitrogen content of 46% compared to other fertilizers but also because it dissolves readily in water and leaves no salt residues on the soil and crops. Although urea is produced in many countries, there is today zero urea production in southern Africa and large volumes of urea is imported.

Baking soda

Baking soda, also known as sodium bicarbonate, is a white crystalline compound with the chemical formula $NaHCO_3$. Sodium bicarbonate is synthesized through Solvay's process, which involves the reaction of sodium chloride, ammonia, and CO_2, in water. The chemical and physical properties of baking soda account for its wide range of applications, including baking, cleaning, deodorizing, pH buffering, and fire extinguishing.

Chemicals from methanol

Converting CO_2 to methanol and methane is the most technologically mature pathway for producing chemicals. The methanol can be subsequently converted into other carbon-containing high-value chemical intermediates such as olefins, which are used to manufacture plastics, and aromatics, which are used in a range of sectors including health and hygiene, food production and processing.

Polymers

The carbon in CO_2 is used to replace part of the fossil fuel-based raw material in the production of plastics, foams, and resins. This requires little energy input since carbonates are at even a lower energy state than CO_2. The Chimei Asai facility in Taiwan (joint venture between Asahi Kasai Chemicals and Chi Mei Corp) has been manufacturing around 150 000 tpa of polycarbonates using CO_2 as starting material for more than a decade.

Newlight Technologies, Inc., converts greenhouse gases into a high-performance biodegradable plastic replacement called AirCarbon®, a material that is estimated to have the ability to out-compete fossil-fuel based plastics globally on a price and sustainability basis. AirCarbon® is produced from clean energy, saltwater and CO_2 using microorganisms.

Covestro funded its own commercial CO_2 to polymer production plant in Dormagen, Germany, which went on stream in 2016. The product is a novel polyol containing about 20 % CO_2. The polyol is a central component for synthesising a polyurethane foam that will be used in the manufacture of foam mattresses. The commercial plant in Dormagen has a production capacity of 5 000 tpa of polyether carbonate polyol.

Superabsorbents

BASF is developing a process for using CO_2 as a chemical feedstock to produce sodium acrylate from ethylene and CO_2. Sodium acrylate is the most important starting material for superabsorbents, which are widely used in diapers and other hygiene products. Compared to the current propylene-based production method for superabsorbents, in the new process CO_2 could replace around 30% of the fossil fuels.

Building materials from CO_2

Concrete curing using CO_2

CO_2 curing of concrete is an emerging technology developed by CarbonCure and Solidia Technologies (Zhu, 2018). Ready-mixed concrete can set and harden through a carbonation process instead of hydration. The CO_2 curing of concrete involves reactions between calcium silicate in cement and CO_2 in the presence of water to form both calcium carbonate and calcium silicate hydrate gel. The carbonation reactions are exothermic, which helps speed up the curing process. CO_2 cured concrete has an improved early compressive strength. A cubic meter of concrete can take up to around 3,5 kg CO_2 (Monkman et al, 2016). CO_2-cured concrete is considered one of the most mature and promising applications of CO_2 use.

Building materials from waste and CO_2

Construction aggregates (small particulates used in building materials) can be produced by reacting CO_2 with waste materials from power plants or industrial processes. Among these are iron slag and coal fly ash, which would otherwise be stockpiled or stored in landfill. Producing building materials from waste and CO_2 can be competitive as it offsets the cost associated with conventional waste disposal. Blue Planet has developed technology to produce construction aggregates by coating small waste material particles, including crushed concrete, with CO_2 derived carbonates. Each ton of CO_2-sequestered limestone traps 440 kg CO_2, preventing it from accumulating in the atmosphere. The technology is considered a cost-effective carbon capture and storage option for permanently sequestering and converting CO_2 emissions from industrial sources (Schmidt, 2020).

Carbon nanomaterials from CO_2

The C2CNT process can convert CO_2 into carbon nanomaterials with inexpensive nickel and steel electrodes and low voltage. Carbon nanomaterials have a wide variety of applications including batteries, electronics, lighter weight alternatives to metals that are used today in aircraft, high end sport cars, and athletic equipment.

The C2CNT process is applicable to the direct removal of atmospheric CO_2 or CO_2 capture from various sources such as power plants and cement production plants. Examples of carbon nanomaterials are shown in Figure 5. Nanotubes are approximately 1 000 times smaller in diameter than conventional carbon fibres. Single wall carbon nanotubes have a typical outside diameter of 1 to 2 nanometers.

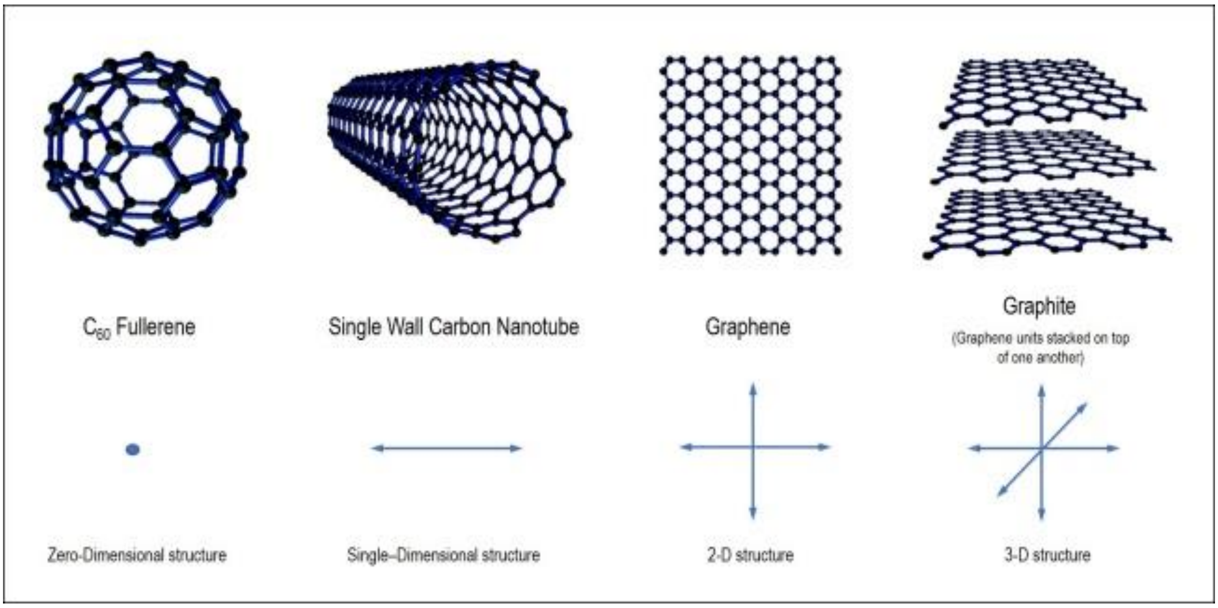

Figure 5: Examples of carbon nanomaterials

In the C2CNT process, CO_2 is bubbled into, and dissolved in a molten lithium carbonate bath. The CO_2 is split by electrolysis at electrodes immersed in the molten bath into oxygen at the anode, and into carbon as pure carbon nanotubes, at the cathode. The process relies on molten lithium carbonate and lithium oxide. The lithium oxide, which is dissolved in the lithium carbonate, combines with CO_2 to make more lithium carbonate. When voltage is applied across two electrodes immersed in the molten lithium carbonate, an electrochemical reaction produces oxygen at the anode and pure carbon nanofibers at the cathode.

C2CNT claims it can produce nanotubes 100x more cheaply than the current industry standard (XPrize, 2018). Its process can use cheap and abundant flue gas input without separating or concentrating the CO_2 and produces a highly pure and compact material whose stable molecular structure sequesters carbon over the long term. Those nanotubes are valued at over US$100 000 per ton, resulting in high revenue potential and a strong economic driver for greenhouse gas mitigation.

Pure carbon from CO_2

Carbon nanomaterials as described above are forms of pure carbon. However, Australian scientists (Esrafilzadeh et al, 2019) have created a liquid metal electrocatalyst that contains cerium nanoparticles, which facilitates the electrochemical reduction of CO_2 to solid, storable carbon at room temperature. Essentially, this means turning the CO_2 back into coal for easy storage.

The as-produced solid carbonaceous material could be used for the fabrication of electrodes. A side benefit of the process is that the carbon can hold an electrical charge and can be used to produce supercapacitors for potential use as an energy carrier in future vehicles.

Overall, this process may result in a viable negative CO_2 emission technology. However, it is still at an early stage of development and scalability and commercial application have not been demonstrated.

Crop yield boosting

CO_2 is an essential component of photosynthesis, the chemical process that uses light energy to convert CO_2 and water into sugars in green plants. These sugars are then used for growth within the plant, through respiration.

Crop yield boosting is an example of the biochemical application of CO_2. CO_2 can be used to enhance yields of biological processes, such as algae production and crop cultivation in greenhouses. An increase in the CO_2 concentration increases the rate at which carbon is incorporated into carbohydrate, and thus the rate of photosynthesis generally increases until limited by other factors.

Determining the correct dosage level of CO_2 for different plant species, or different growth phases, is as important as it is with nutrient levels. While the benefits and levels of CO_2 enrichment is crop dependent, most plants respond well to levels in the range of 500 to 1,500ppm. Below 200ppm, CO_2 begins to severely limit plant growth, but more than 2,000ppm of CO_2 becomes toxic to many plants (Morgan, 2019). Mild CO_2 toxicity can cause stunting of growth, or leaf-aging type symptoms, while excessive levels may cause leaf damage.

Unfortunately, most of the applied CO_2 will end up in the atmosphere.

Closing remarks

CO_2 utilisation can provide the chemical industry with a fresh source of essential carbon feedstock in the transition away from fossil resources. Despite its potential, CO_2 utilisation for chemicals is at an early stage of development and highly energy-intensive. Commercial viability of CO_2 for chemicals depends on the availability of cheap renewable energy and green hydrogen.

XPrize is a non-profit organisation that designs and manages public competitions intended to encourage technological development that could benefit mankind. The US$20-million NRG COSIA Carbon XPrize is a global competition to develop breakthrough technologies that will convert CO_2 emissions into valuable products like building materials, alternative fuels, and other items that we use every day. The 10 finalists of the competition are currently being assessed to see who can convert the most CO_2 into the most valuable and useful products. The contest's winners will be announced shortly. We will report on the winning teams and technologies.

BASF is focussing on 'carbon management' rather than 'decarbonisation' because the BASF product spectrum contain 50% of carbon on average. Not using carbon (i.e., to decarbonise the products) is therefore not an option. All the different approaches to CO_2 utilisation contribute to CO_2 emissions mitigation, with some more so than others.

References

Brudermüller, M. (2019) *Carbon management at BASF: R&D strategies to reduce CO_2. R&D webcast for investors and analysts on January 10, 2019*. Available from https://www.basf.com/za/en/media/publications.html. Accessed on 20 March 2021.

Esrafilzadeh, D., Zavabeti, A., Jalili, R., Atkin, P., Choi, J., Carey, B.J., Brkljaca, R., O'Mullane, A.P., Dickey, M.D., Officer D.L., MacFarlane, D.R., Daeneke, T., & Kalantar-Zadeh, K. (2019) Room temperature CO_2 reduction to solid carbon species on liquid metals featuring atomically thin ceria interfaces. *Nature Communications*, Article number: 865.

Global Monitoring Laboratory. (2021) *Trends in Atmospheric Carbon Dioxide*. Available from Global Monitoring Laboratory - Carbon Cycle Greenhouse Gases (noaa.gov). Accessed on 20 March 2021.

IEA. (2019), *Putting CO_2 to Use: Creating value from emissions*. Available from https://www.iea.org/reports/putting-co2-to-use. Accessed 24 March 2021.

Institute for 21st Century Energy (2012) CO_2 enhanced oil recovery. Available from https://www.globalenergyinstitute.org/sites/default/files/020174_EI21_EnhancedOilRecovery_final.pdf. Accessed 29 March 2021.

IPCC. (2014) *Climate Change 2014 - Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report*. Intergovernmental Panel on Climate Change, Geneva, Switzerland.

Monkman, S., MacDonald, M., Hooton, R.D. & Dandberg, P. (2016) Properties and durability of concrete produced using CO_2 as an accelerating admixture. *Cement and Concrete Composites*; 74, 2016, 218-224.

Morgan, L. (2019) *CO_2 enrichment, acclimation, and efficiency in hydroponic growing*. Available from CO2 Enrichment, Acclimation, and Efficiency in Hydroponic Growing (maximumyield.com). Accessed on 24 March 2021.

Schmidt, R. (2020) *Blue Planet economically sustainable carbon capture. Presentation to Global Carbon Capture and Storage Institute.* Available from https://www.globalccsinstitute.com/wp-content/uploads/2020/03/5-BLUE-PLANET-DC-FORUM.pdf. Accessed on 4 April 2021.

Steyn, J.W. & Render, C.L. (2020) *Hydrogen as energy carrier*. Available from https://www.ownerteamconsult.com/hydrogen-as-energy-carrier/. Accessed on 28 March 2021.

Xprize. (2018) *NRG COSIA Carbon XPrize finalists 2019. Reimagine CO_2*. Available from https://carbon.xprize.org/prizes/carbon/articles/finalist-team-profiles. Accessed on 24 March 2021.

Zhu, Q. (2018) *Developments in CO_2 utilisation technologies*. IEA Clean Coal Centre, London, UK.