UNIVERSITÀ POLITECNICA DELLE MARCHE

FACOLTÀ DI INGEGNERIA

Corso di Laurea triennale in Ingegneria gestionale

The utilization of carbon dioxide (CO2) in industries and processes.

Gli utilizzi dell'anidride carbonica (CO2) nelle industrie e nei processi.

Relatore:

Prof. Francesco Corvaro

Tesi di Laurea di:

Pasquale Tosches

Correlatore:

Ing. Matteo Vitali

A.A. **2020 / 2021**

INDEX

INTRODUCTION

GHG emissions have reached their greatest levels in history, resulting in a multi-decadal warming influence on the climate, as evidenced by rising sea levels, hotter and acidified seas, less ice, and higher surface temperatures, among other things. Climate change has begun to alter natural ecosystems and society, forcing dramatic changes in natural resource management and allocation, as well as occupancy patterns. As a result, climate change experts recommend keeping surface temperature rises below 2°C relative to pre-industrial levels throughout the twenty-first century, but previous efforts to reduce GHG emissions are insufficient considering rapid population growth and economic development, with a mean surface temperature increase of 3.7 to 4.8°C above pre-industrial levels expected by 2100. To meet the 2°C temperature target and minimize global warming, sufficient adaptation and mitigation activities are required. As a result, the Paris Agreement was approved at COP 21 in order to re-energize the global response to climate change in areas such as GHG emissions mitigation and climate change adaptation. To accomplish the ambitious global warming goal, adaptation and mitigation techniques must reduce GHG emissions by 40%–70% by 2050 compared to 2010 levels and achieve neutral to negative emissions by the end of the century.

The present worldwide agenda is to address the issue of global warming, which is producing serious difficulties such as global temperature rise and glacier melting. The constant growth in CO2 levels in the atmosphere is one of the key causes of fast climate change. The ever-increasing population, together with ever-expanding industrialization and modernity, has resulted in an increase in CO2 levels in the atmosphere due to a variety of factors. CO2 is presently the focus of attention due to the unavoidable repercussions of its large-scale presence in the atmosphere. Controlling its emissions has been a long and arduous effort that has yet to yield results. It is the most difficult environmental policy that the world has ever seen. Power generation, which includes natural gas and coal, is the single largest source of CO2 emissions in the world. Significant reductions in carbon dioxide (CO2) emissions, as well as the development of non-fossil fuel energy sources, are critical for lowering CO2 emissions while also lowering our reliance on non-renewable energy sources. As a result, the scientific community is always proposing new ways to absorb, utilize, and transform CO2 into valuable molecules. Carbon Capture and Utilization (CCU), in addition to the well-known CCS, is one of the most successful ways to alleviate the problem by converting a waste like CO2 into a commodity.

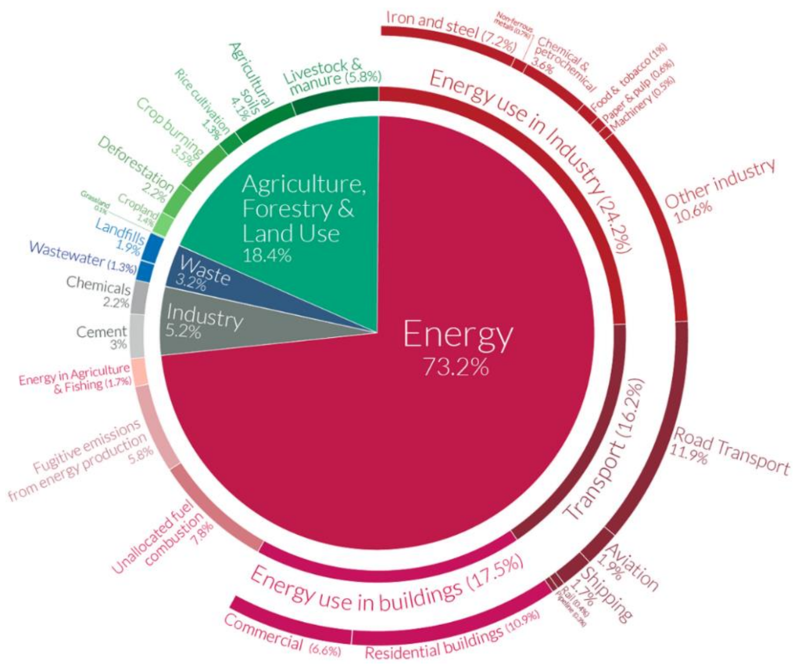
1. CO_2

Carbon dioxide is a colourless gas and microscopically it is composed of a single carbon atom and two oxygen ones held together by a double covalent bond. In nature, it can be found in volcanoes, hot springs, and geysers, being released from carbonate rocks, but also in groundwater, rivers and lakes, ice caps, glaciers and seawater, due to its property to be soluble in water. On the other hand, CO_2 is issued by aerobic organisms who use it for respiration. But mainly, it is the main greenhouse gas in our atmosphere and so represents a problem for modern society. Its concentration in atmosphere is incessantly increasing from the Industrial Revolution causing global warming and ocean acidification.

1.1 CO_2 : FROM WASTE TO COMMODITY

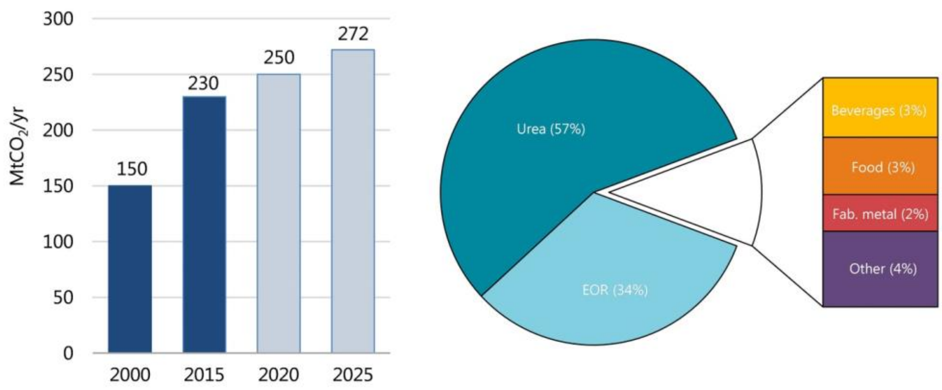
Since the first industrial revolution, CO_2 has been seen as a waste and a problem; in fact, its emissions are the primary driver of global climate change and therefore it's widely recognised that, to avoid the worst impacts of climate change, the world needs to urgently reduce emissions.

To do this, it's not enough just to reduce emissions (we are still heavily relying on fossil fuels, which for instance make up 80% of the electricity source) but it's also crucial to develop technologies to capture and use Carbon Dioxide known as CCU. In accordance with the latest data [1], 36 billion million tonnes of carbon dioxide are issued every year, especially by advanced countries which emissions are much greater than those of developing countries.



A Global Breakdown of Greenhouse Gas Emissions by Sector. [2]

On the other hand, the largest consumer is the fertiliser industry, where 130 Mt of CO2 are used in urea manufacturing, followed by oil and gas with a consumption of 70 to 80 Mt CO2. In a smaller part, also sectors like food and beverage, metal fabrication, fire suppression and greenhouses are responsible for CO2 emissions. New solutions, in addition to the more established CCS, involve using this compound to produce fuels, chemicals and building materials or to increase yield in greenhouses. The latter, although a lot is been invested lately, are still in developing phase and only few plants are in operation. This is due to many constraint; for example, fuel and chemicals production requires a lot of energy and hydrogen, making these solutions too expensive. Furthermore, it can be used to produce chemicals and polymers, replacing the commonly used fossil fuels. Another path, with a lower energy consumption, is to make CO2 react with minerals to form carbonates for building materials.



Growth in global demand of CO2 over the years (left); breakdown of demand in 2015 (right).

[3]

1.2 PARIS AGREEMENT

The Paris Agreement's goal is to slow down the rise in temperatures, trying to maintain the latter below 2 degrees above pre-industrial levels. To do so, especially advanced countries are working hard to achieve green transition within 2050 investing large amounts of money in the R&D of green technologies. The partecipating countries have decided to meet every five years to periodically assess the progress made, with the more industrialized states that - in accordance with the binding commitment taken in the negotiations - will have to support the less developed countries in the activities aimed at reducing the volume emissions.

To achieve the common goal, social and economic changes will have to be made in the coming years based on the most promising technologies. Every 5 years countries have to communicate their plans to reduce GHG emissions for the next 5 ones in the Nationally Determined Contribution as well as the actions that will be taken to adapt to the consequences of global warming. In addition to this, also long-term strategies are required from nations that are part of it and must be submitted by 2020.

The impact of the Paris Agreement has been huge during the last years. In fact, soliciting governments and firms to develop competitive green solutions able to compete with traditional counterpart, it is allowing several countries to reach carbon neutrality in the near future.

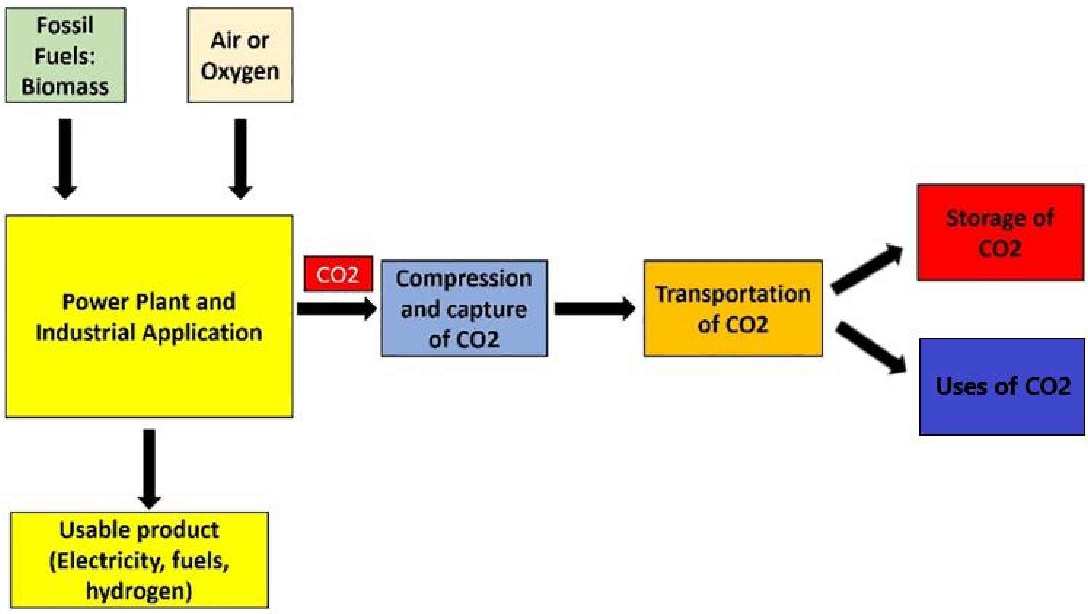
Thanks to the progress made in the management and reduction of CO_2 emissions and the ones that will be made, in an optimistic scenario carbon-neutral solutions could be cost-effective in the 70% of gas emission sectors before 2030.

[4]

2. CARBON CAPTURE

Currently, the majority of countries still heavily rely on fossil commodities for power generation although they release significant amounts of CO_2. For instance, almost 85% of electricity generated worldwide comes from fossil fuels, making green changes like automotive electrification useless for CO_2 reduction. The first idea could be to shut down power plants but, unfortunately, alternatives which produce no CO_2, will surely not be available in the near future. Therefore, the only way to reduce CO_2 emissions is to capture it with various technologies that have received increased awareness by research community. Carbon capture, hence, is expected to be one of the most cost-effective ways to minimize greenhouse gases in the coming years, but significant developments are needed to abate costs.

The first phase consists of capturing the CO_2 produced by the upstream process. After it, the CO_2 is compressed to a liquid phase in order to facilitate its transport through pipelines until geological formation (Storage) or industrial plants (Use).



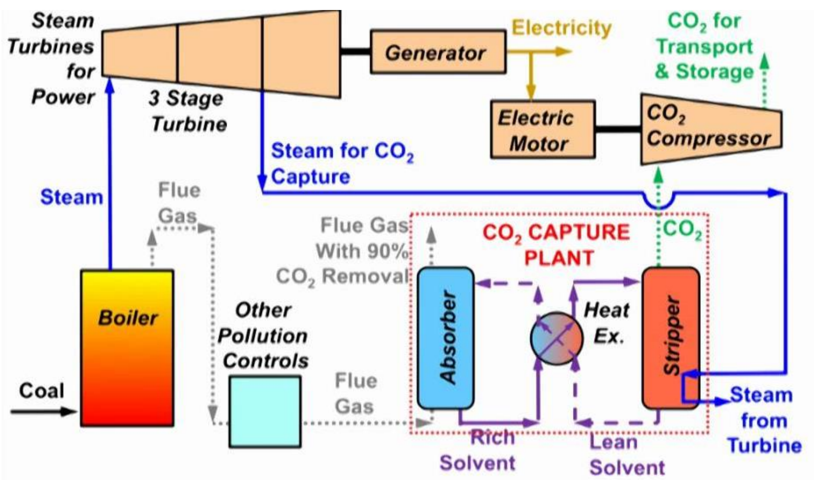
Main steps of CCSU. [5]

Unfortunately, the majority of CO_2 ends up in the atmosphere and only a small part is stored or used after being captured. However, many approaches to capture CO_2 have been developed and are being used in several sectors. The type of technology used depends on the purity and state of the gas in relation to ambient conditions. In general, CC (Carbon Capture) systems separate pollutants from the CO_2 during natural gas refining process and generate H, NH_3 and other chemicals for industrial purposes. Then, CO_2 is compressed to a liquid state to facilitate its transport through pipelines until geological formation (Storage) or industrial plants (Use). The technologies utilized can be divided in pre-combustion and post-combustion systems depending on whether the carbon is separated before or after combustion. Yet, although still under development, another technology known as oxy-combustion is considered an alternative to the other two.

2.1 CO2 separation techniques

2.1.1 Physical absorption

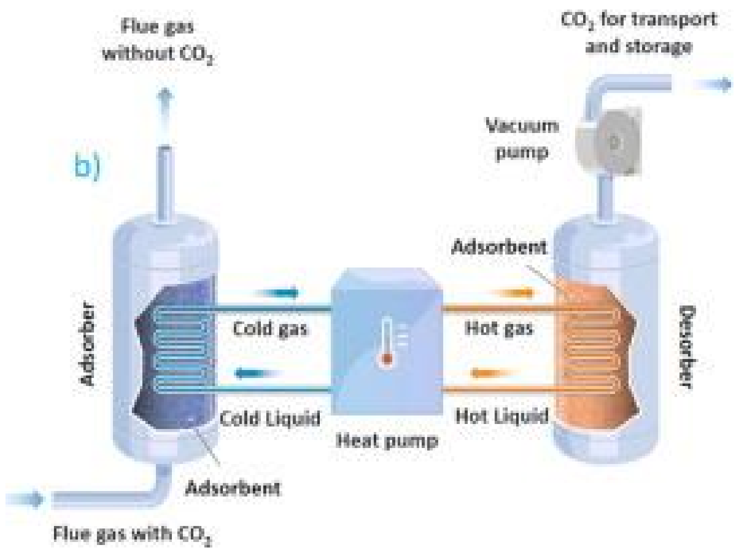
The physical absorption process consists of two main stages: the absorption and stripping process. In the adsorption, the treated gas comes into contact with the solvent stream to capture physically the CO2 from the flue gas. The stripping involves CO2 and solvent, saturated after the absorption, to which heat is supplied to enrich solvent and to release the CO2 at the apex of the stripping chamber. Electrostatic forces are essential for the dissolution of CO2. The electrostatic forces that are generated between the solvent and the CO2 are fundamental for the absorption of the latter. Furthermore, low temperature and high pressure, kept in the absorber, are the best operating conditions for physical absorption, whereas high temperature and low pressure are maintained in the stripper to allow desorption [6]. As a whole, this technology has good absorption characteristics and predominates in the pre-combustion CC technology. This is mainly due to the more convenient regeneration phase through depressurization requiring low energy in input. It must be noted that the absorption capacity of the absorbent is useful at lower temperatures physically, so it is crucial to reduce the gas stream's temperature before entering the adsorber.



CO2 capture system using physical absorption interfaced with a power plant. [7]

2.1.2 Adsorption

Adsorption is slightly different from absorption because it involves the specific creation of a physical and chemical connections between CO2 and the adsorbent's surface. Afterwards, the captured CO2 is separated from the adsorbent, which will be reused, by Pressure Swing Adsorption (PSA) or Temperature Swing Adsorption (TSA). In TSA, the saturated adsorbent is heated by a heat pump to operating conditions at which physical and chemical bond is disintegrated (from liquid to gas) leading to the detachment of adsorbed reactants. Whereas, in PSA the heat pump is replaced with a pressure variator where the pressure fluctuation generates the same effect. TSA is commonly used when the CO2 concentration in the flue gas is insignificant, while PSA when CO2 percentage is high. However, Pressure Swing Adsorption is the preferred solution because of the short time needed to regenerate the adsorbent. In both cases, as shown in the figure, CO2 is compressed by a vacuum pump to be transported in a liquid phase.

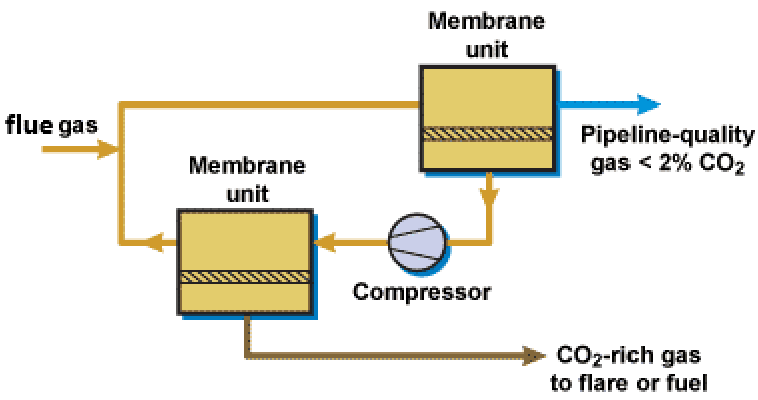


Temperature Swing Adsorption to capture CO2. [8]

2.1.3 Membrane technology

The phenomenon that leads to membrane separation in this technology is the Knudsen diffusion principle. Knudsen diffusion occurs when the mean pore diameter of the membrane is smaller than the mean free path of the gas particles. This type of diffusion occurs in low permeability porous media, which have small pore radii, and at low gas pressures, when the mean free path becomes large. [9]

Non-facilitated membrane technology, based on the Knudsen diffusion principle, is used to capture CO2 from natural gas and generally from flue gasses where its partial pressure is high. Using this technology with flue gas, where CO2 pressure is low, requires more energy to compress the fluid and so obtain the required carbon capture ratio. The improvement of its selectivity rate depends on how permeable the membrane is designed to be, making it difficult to integrate into existing and already designed power plants. Among all the possible solutions to this challenge being investigated by researchers, the facilitated transport membrane separation is one of the most promising. It consists of a liquid phase carrier that facilitates the movement of CO2 through the membrane increasing both permeability and selectivity of CO2 across the membrane.



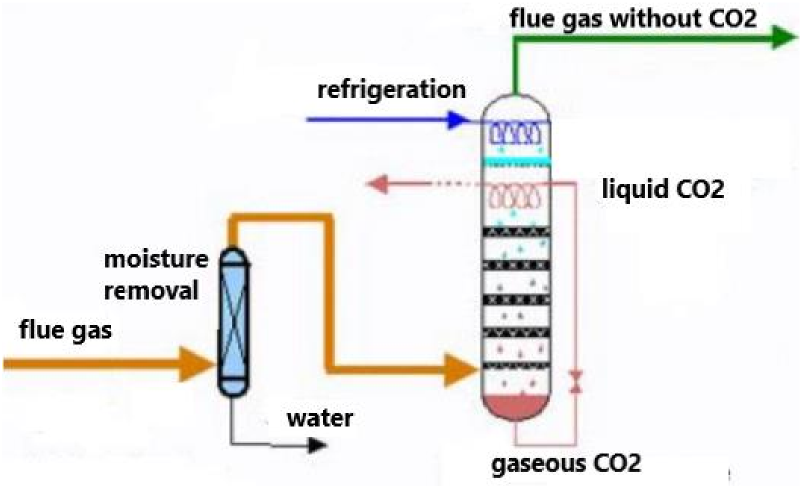
CO2 capture with membrane from flue gas. [10]

A new type of membrane named mixed matrix, made of polymer membrane fillers like zeolite, reduces the processing cost and increases permeability. Also, the strength and stability regarding heat for these membranes are very good. Another new type of membrane separation technology is the gas membrane contactor. This type of membrane is not based on the Knudsen diffusion approach but only acts as a point of application between the flue gas and the CO_2 absorption solvent. The main pros are the compactness of the membrane system and the high selectivity of the absorption process, whereas cons are limitations in terms of mass transport due to resistance on the membrane framework.

In conclusion, even if there are some design challenges, this technology has a low environmental effect and degradation which makes its LCA lower than the other techs.

2.1.4 Cryogenic separation

The cryogenic separation is a valid path for carbon capture but, unlike the other technologies, it occurs at extremely low temperatures (-100 to -135 °C) and so CO_2 is directly obtained in a liquid phase after being compressed to 100-200 atm. It is ideal for flue gasses with high CO_2 concentrations. This technology utilizes less water, uses cheap chemical agents and issues less pollutants than the other technologies. Important perks are the ambient pressure required during the process and the liquid CO_2 obtained, reducing transport costs toward storage or use place. Unfortunately, to keep cryogenic operating temperature a lot of energy is necessary, causing an increase in operating costs. In addition, at these temperatures ice formation is easy and can block the piping system; this reduces the drop pressure causing safety issues. To prevent it, moisture is removed from the fluid before the separation, further increasing total costs.



Simplified diagram showing cryogenic separation of CO2 from flue gas. [11]

2.2 CO2-capture approaches

2.2.1 Pre-combustion

This approach consists of capturing CO2 from the fuel before the combustion ends. In gasification processes, the fuel is transformed into a synthesis gas via partial oxidation at high temperature. This syngas is composed mainly of hydrogen, carbon monoxide and CO2. The latter is burned for energy purposes in the so-called IGCC plants. Subsequently, the CO issued in the first step is made to react with steam to obtain CO2 and hydrogen. At this point, a glycol solvent (Selexol) is used to trap the CO2 through physical absorption, separating the two compounds.

Although IGCC plants with Carbon capture are more expensive than the common ones, they allow obtaining high purity CO2, requiring a high-pressure environment (already present at that stage). It is also possible to use this approach in power plants that utilizes natural gas but, also these, are very expensive compared to its traditional process.

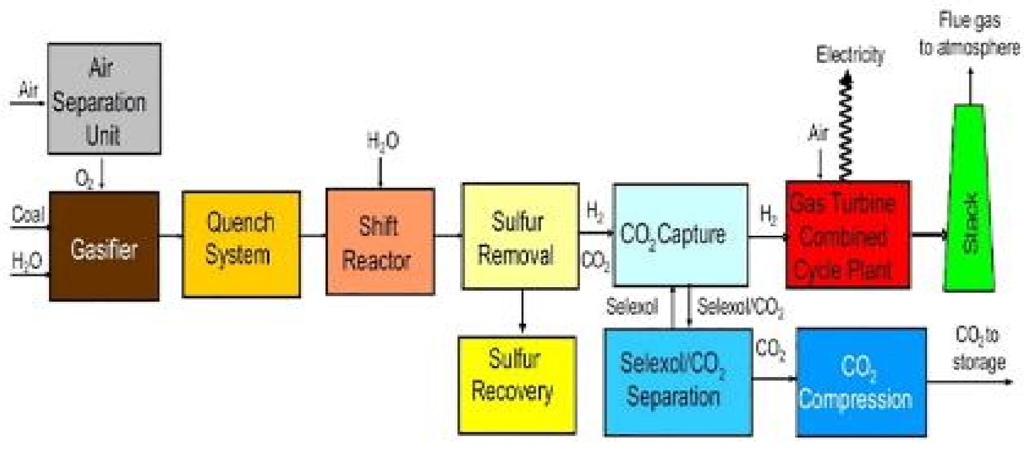
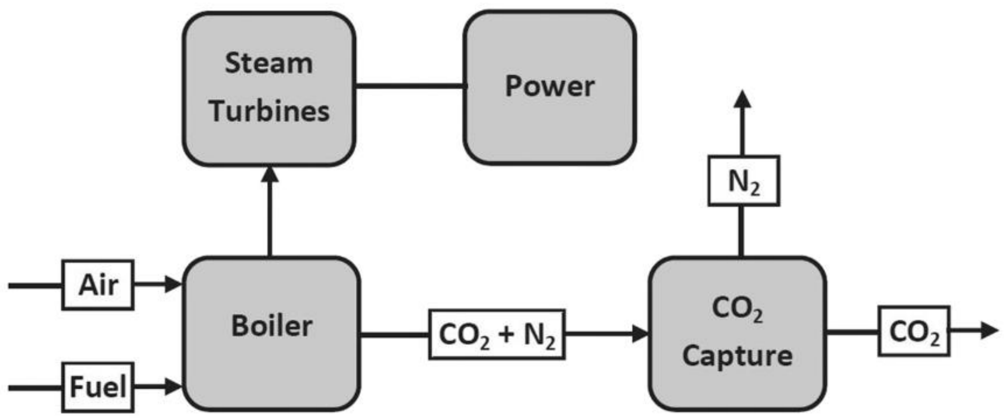


Diagram of CO2 capture using the pre combustion technology approach. [5]

2.2.2 Post-combustion approach

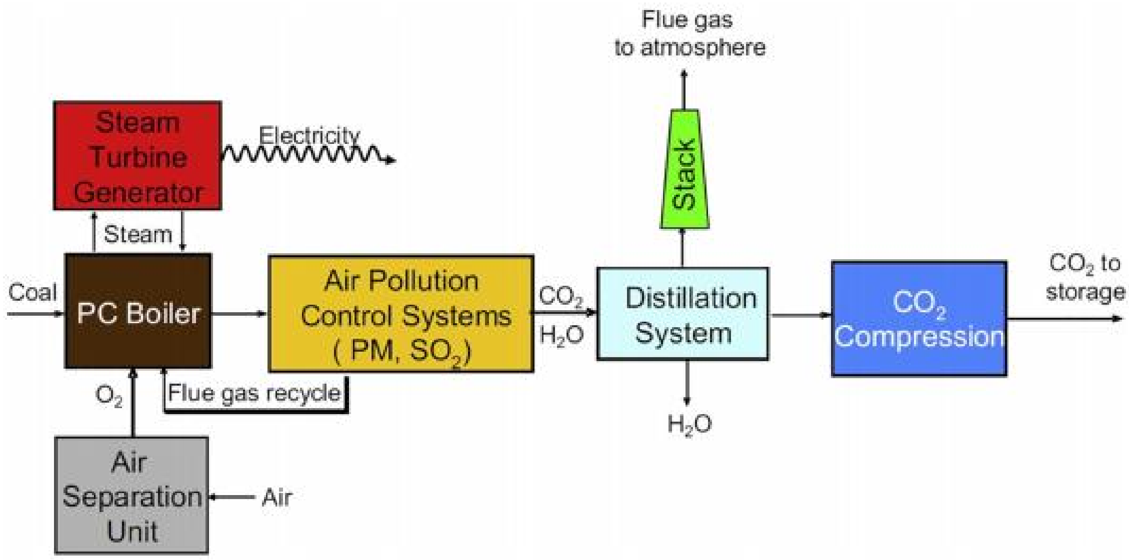
In this approach, the CO_2 is absorbed from the combustion exhaust gases. These high-temperature gases that flow out of the boiler are made up of nitrogen (N_2), CO_2 and water vapor in smaller concentrations. Some toxic gases like Sulphide dioxide (SO_2), nitrogen oxide (NO) and fly ash must be eliminated as they are considered as pollutants, going to purify the fluid further. At this point, the CO_2 is captured using physical absorption and a high-concentration gas is obtained, which is compressed and conveyed to be stored or used.



A diagram showing post combustion CO_2 capture. [5]

2.2.3 Oxy combustion

This approach has been recently developed by researchers as an alternative to the post-combustion one. The air is replaced with oxygen as a comburent, heavily reducing the nitrogen emitted. Also, fly ash is eliminated from the flue gas stream leaving only CO_2, water droplets and some impurities like sulphur dioxide. Later, to remove the water the gas is compressed and cooled. At the end of the process pure CO_2 gas is obtained which is compressed to facilitate its transport. The main advantage over the post-combustion approach is the avoidance of the CO_2 capture system, responsible for a significant part of the costs, replaced by an air separation unit (ASU) that produces pure oxygen needed for the oxy-combustion. After combustion, there are Air Pollution Control Systems to reduce the percentage of pollutants and hence meet environmental laws. It must be said that the temperature required by this type of reaction is higher so, to maintain it, a huge portion of flue gases is reused in the boiler. Moreover, a challenge is represented by the sealing of the system, necessary to maintain the needed oxygen and nitrogen found in the gas. In conclusion, there is a lot of research conducted on thermal plant that uses the oxy combustion technology but still in a developing phase.



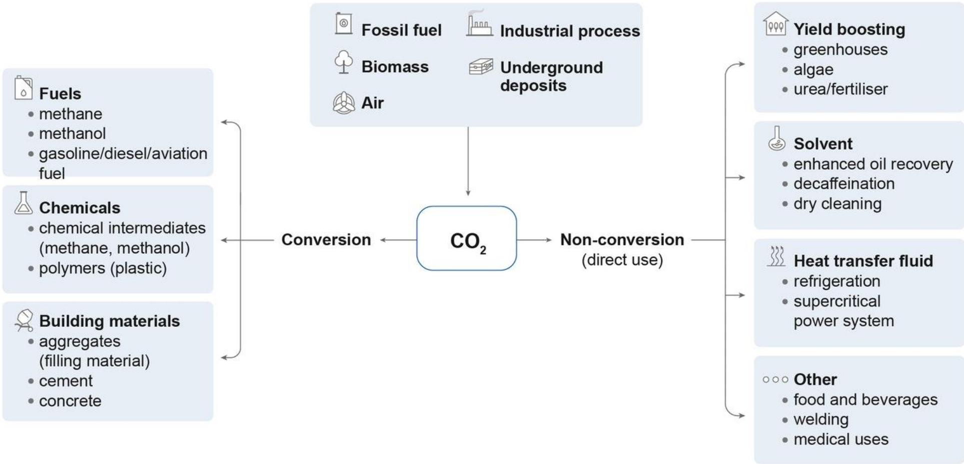
Oxy-combustion technology utilized in a coal fired power plant. [5]

3. USES (CCU)

As an additional CO2 mitigation strategy to carbon capture and storage, CO_2 capture and utilization (CCU) are attracting growing global interest. The potential applications of CCU are diverse, ranging from using CO_2 in greenhouses and farming to the conversion of CO2 into fuels, chemicals, polymers and building materials. In general, they can be classified into two categories: direct use, by which CO_2 is not chemically altered, and conversion, via multiple chemical and biological processes.

However, CO_2 has already been used for decades with mature technologies in various industrial processes such as CO_2-enhanced oil recovery, the food and beverage industry, urea production, water treatment and the production of fire retardants and coolants. There are also many new CO_2-utilization technologies at various stages of development and commercialization. These technologies have the potential to provide opportunities for emission savings for power and other industrial sectors by partially substituting fossil-fuel raw materials, increasing efficiency and using renewable energy, and generating revenues through producing marketable products.

Many funds have been allocated to incentivize CCU which has a lot of benefits but is still an expensive alternative. In North America, XPrize is supporting the development of novel CO2 use opportunities with a $20 million global competition (XPRIZE, 2019). Governments all over the world, including European ones, are also providing significant RD&D support for CO2 use. This interest is mainly due to climate changes, but also technology leadership, energy security, availability of cheap and abundant renewable energy (which could make CO2 conversion routes more economical) are crucial factors for the future development of CCU. Some uses are already competitive, for instance the production of building materials which provide better features at a lower price. It must be said that CO2 is one of the few green alternatives to fossil fuels as a source of carbon, hence it is crucial to make CCU affordable.



General classification of pathways for CO2 use. [3]

3.1 CO_2-derived fuels

Transports and energy production are the sectors that emit the majority of CO_2, and this is due to their dependence on hydrocarbons. Consequently, to limit their impact is more and more necessary to use carbon-neutral fuels, the so-called e-fuels, obtained from the reaction of CO_2 with H_2. One of the most promising e-fuels is the Fischer-Tropsch (FT) fuel for its compatibility with the existing fuel grid.

The FT fuel production consists of 6 stages: H_2 and CO_2 compression, RWGS reaction, FT synthesis, hydro-processing, power generation and utility.

In the first stage, the CO_2 and H_2 are compressed to 25 bar by three compressors: two for the CO_2 in input, one for the recycled CO_2 and one for the hydrogen. While the compression of H_2 is done in a single stage, CO_2 compression needs multiple stages, each separated by an intercooler.

In the RWGS reaction part, the RWGS reaction, syngas cooling and drying, compression, and the CO_2 separator are all simulated. Two majority modelling methods to simulate the RWGS reaction are a chemical equilibrium model and a kinetic control experimental model. The low H_2/CO_2 molar ratio of 1.0 is used to produce only enough CO while excluding the additional hydrogen used for the FT. This method avoids the H_2 separation/recycling phase in addition to CO_2 recycling, as well as energy waste (which occurs when the excess hydrogen is heated to 600°C for RWGS and then cooled to 300°C for the FT process). At 600°C and 24.5 bar, the RWGS reaction is planned to have a CO_2 conversion ratio of 36 percent. The syngas formed by the RWGS reaction is cooled to 43 degrees Celsius, then dried and compressed to 30 bar using a five-stage inter-cooling compressor.

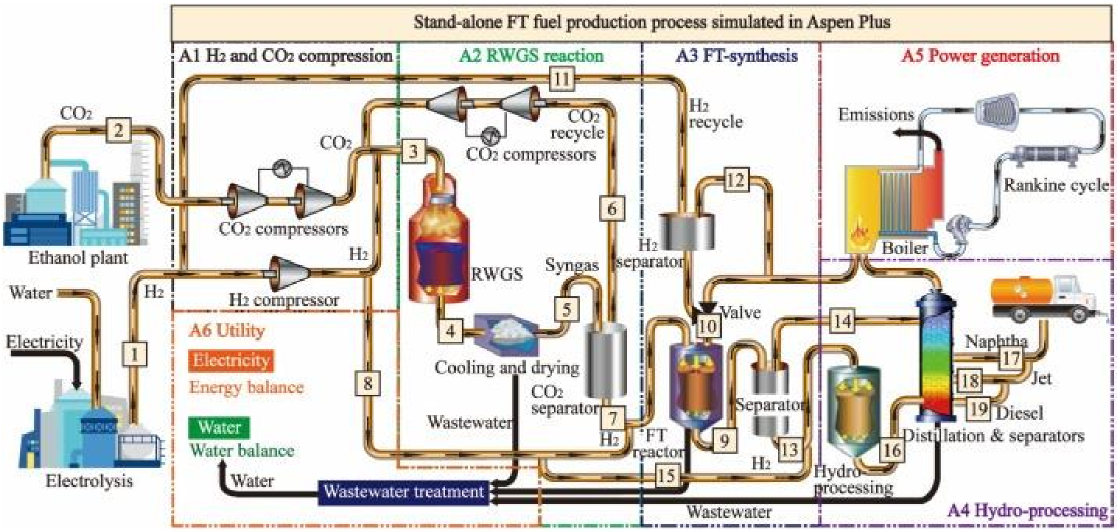
The CO_2 separation unit uses ethylene-glycol as the solvent, which absorbs CO_2 at 30 bar in the absorber and releases CO_2 at 3.4, 1.0, and 0.3 bar from flash tanks for CO_2 recycling. After cooling to 43 °C, the water generated by the RWGS reaction is isolated from the produced syngas by a flasher and separator, and then processed in the utility region by a wastewater treatment procedure.

The FT synthesis area is made up of two classes of FT fixed-bed reactors, a wax separator, a liquid/gas separator, and one PSA H2 separator to increase the yield of hydrocarbon products. For FT synthesis, cobalt- and iron-based catalysts are commonly used. Cobalt-based catalysts can only be used at low temperatures (200–240 °C), while iron-based catalysts can be used at both low and high temperatures (300–360 °C). In this analysis, cobalt-based catalysts are used in the FT reactor to transform 52.2 percent of CO into hydrocarbons at 220 °C and 24.3 bar, with an H2/CO molar ratio of 2.2. At 220 °C, the hydrocarbons formed by the FT reactor are flashed to distinguish heavier hydrocarbons (wax) from lighter hydrocarbons. The wax is cooled (to condense the water) and dried for further hydrocracking, while the lighter hydrocarbons are refined to create liquid fuels in the hydro-processing sector. PSA is used to recover 85 percent of the H2 material of flue gas with a high purity of 99.9 percent at 23.2 bar [27]. After cooling to 43 °C, the water created by the FT synthesis process is segregated by a flasher and separator and processed by the wastewater treatment process in the utility sector.

The hydro-processing area consists primarily of a hydro-processing and a fuel distillation tower. At 290 °C and 23.2 bar, the hydro-processing process converts 89 percent of wax into lighter hydrocarbons, with the hydrocarbon delivery following the work of Kang et al. (2012) over the Pt/Si–Al catalyst [28]. The distribution of hydrocarbons generated by the hydro-processing reactor is shown in Fig. 2(b). The molar ratio and mass ratio of hydrocarbons with carbon numbers ranging from 1 to 20 are shown in Fig. 2(b), while the heavier hydrocarbons are considered to be the unconverted wax returned to the hydro-processing reactor.

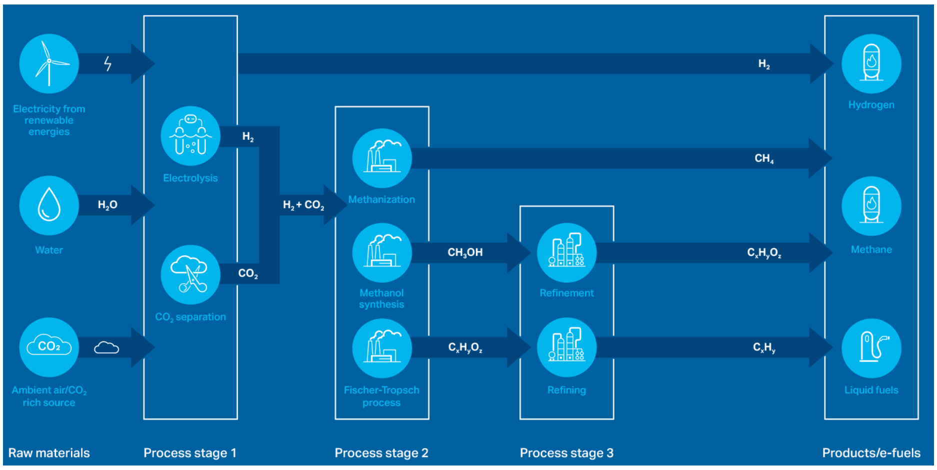
All combustible traces from the other reaction areas are burned in a boiler (900 °C) to produce power through a steam turbine. The steam turbine's initial steam temperature and pressure are 505 °C and 103 bar, respectively, with an isentropic efficiency of 88 percent [23]. Two steam flows are drawn from the steam turbine at 477 °C, 87 bar and 326 °C, 30 bar to provide heat for the hydro-processing and distillation processes.

The utility area is the last reaction area in the FT fuel production system, which evaluates the water and energy exchange/balance for the total system. This area includes wastewater treatment, cooling towers, and product storage units.



E-fuel production system from H2 and CO2 based on the FT process. [12]

Producing e-fuels from CO2 requires huge amounts of electricity, thus increasing production costs. However, this price difference can be minimized in areas where electricity prices are low. As a consequence, the scalability of this solution is limited to areas where the price of electricity is low and sufficient quantities of CO2 are available, for example, Chile, North Africa and Iceland. Right in Iceland, the George Olah facility in Iceland uses around 5 600 tonnes of CO2 and sustainable Hydrogen to produce methanol. Furthermore, it must be said that e-fuels really reduce CO2 emissions only if they use green energy.

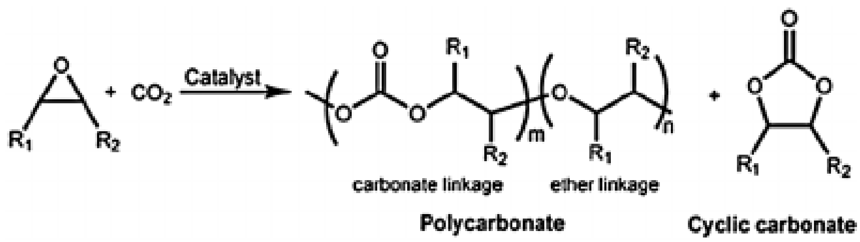


Production of e-fuels. [13]

3.2 CO2-derived chemicals

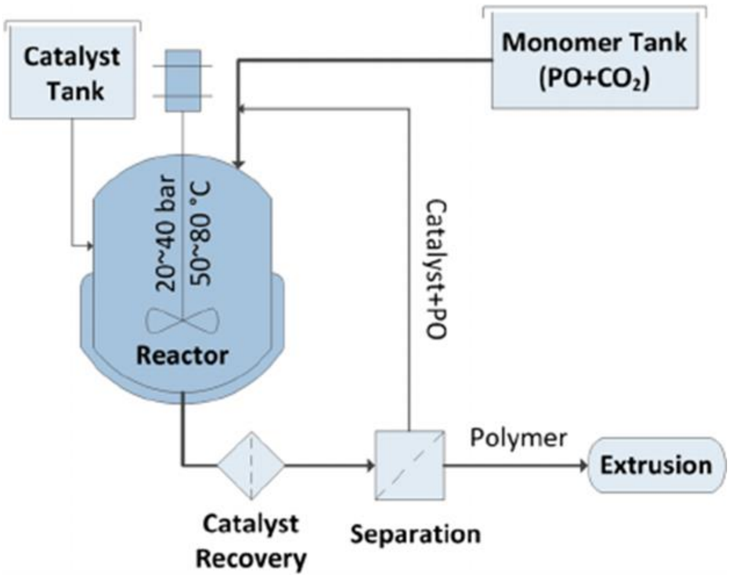
If CO2-to-fuel conversion is considered an ambitious solution for CO2 chemical sequestration, the polymerization approach is a more realistic one. There is a myriad of pathways from CO2 to useful materials, but the polymerization is the most industrially viable use of CO2 as a feedstock in large scales because polymer processing with CO2 requires little energy input, since CO2 is converted into a molecule with a lower energy state (carbonate). Moreover, plastic production plants are among the major CO2 emitters with a carbon footprint of about 6 kg of CO2 per kg of plastic (LDPE, PET and polyethylene). For these reasons, several companies are currently operating polymer plants using CO2 as a raw material.

The core idea is to develop a green catalytic process that consumes CO2 as a raw material for making more polymers, achieving net-zero carbon emission in the plastic industry. CO2 cannot be directly polymerized but can yield polymer in the presence of certain epoxides (e.g., ethylene oxide, propylene oxide (like in the following figure) and cyclohexene oxide), catalysed by the well-designed metal complexes.



CO2/PO (propylene oxide) copolymerization reaction, introducing polycarbonates as the main product and cyclic carbonates as a by-product. [14]

The first thought of CO2 copolymerization was first triggered in 1969 at the Tokyo Institute of Technology with addressing poor catalyst activity. Since this inspiring work, numerous studies performed on the various types of catalysts and processes to enhance their performance for higher copolymerization yields. The major breakthroughs were made in the 2000s using binary catalytic systems of cobalt and chromium. Around 2010, highly active catalytic systems were introduced for CO2/PO copolymerization, selectively producing high molecular weight copolymers. The designed homogenous catalyst can be readily separated by filtration through a short pad of silica gel to yield a resin containing negligible amounts of metal residue and the separated catalyst can be recovered without a significant loss of catalytic performance. Hence, all these features are positive for the commercialization of the CO2/PO copolymer production, so operating a continuous process of this kind is feasible, based on the viable studies conducted in the last few years.



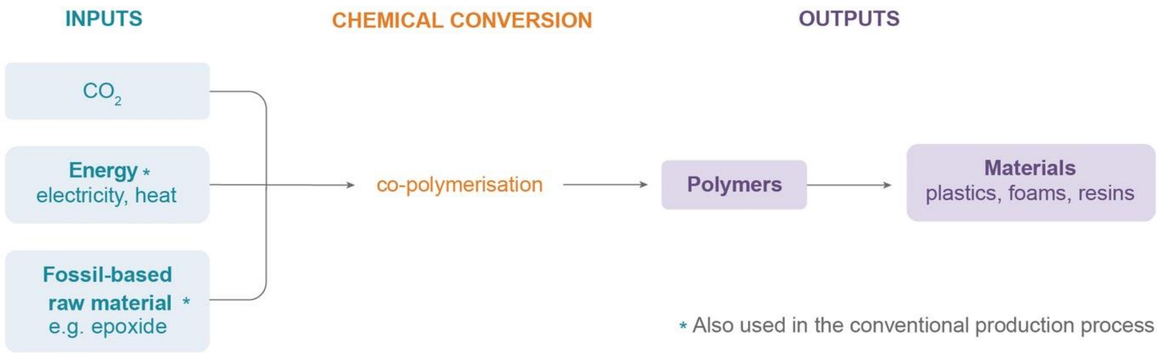
Schematic diagram of the continuous CO2 copolymerization process, employing an effective catalyst recovery system. [14]

The result of the process is a biodegradable polycarbonate with excellent optical properties, like transparency, which up to 44% of its weight is originated from CO2conversion. The produced polymer possesses impressive barrier characteristics towards O2 and H2O, comparable with Nylon, which make it proper for the food packaging industry. It can be also used in polymeric alloys with reasonable adhesive features. In addition, CO2-derived polymer burns smoothly in the air without toxic emission or ash residue, making its disposal by incineration practical and safe, whereas the main disadvantages are the weak thermal properties and low glass transition temperatures. Also, the synthesized polycarbonates typically start to decompose at 180°C which is a limiting factor. However, the drawbacks can be hindered via changing the epoxides and/or introducing the terpolymerization process (use of three monomers in the polymerization reaction), which improves the glass transition temperatures, thermal properties, and other polymer characteristics.

Overall, polymer processing with CO2 is already competitive, owing to the low input energy and higher value than its competitors. In some cases, the production of polymers is up to 30% cheaper, due to the low-cost CO2 used. A glaring example is the Chimei Asai facility in Chinese Taipei manufactures approximately 150 000 tonnes of polycarbonates per year using CO2 for several years.

Climate benefits that this solution can deliver is strictly related to the amount of CO2 that can be absorbed by the material, which can be up to 50% of the polymer's mass. In addition, the CO2 is trapped in chemicals only for a limited period, as, at the end of their life cycle, it will inevitably be released. As a result, potential climate benefits will come from the replacement of conventionally produced chemicals with the ones with a lower life-cycle emission. Nevertheless, similarly to CO2-derived fuels, further compliance testing is needed to meet industrial quality standards and regulations before polymers with high mass percentages of CO2 can enter the market.

The available literature on the more comprehensive studies about CO2 copolymerization is limited but growing year in year. This using path is one of the most scalable and economical candidates for the CO2 chemical transformation as well as offering a sustainable approach to the plastic production industry, which is crucial for the reduction of CO2 emissions. Importantly, green energy supply for the subsequent equipment design is a must to achieve carbon neutrality for the entire polymerization process to make this technology fully sustainable.



conversion pathway for CO2-derived polymers. [3]

3.3 Building materials

Concrete and cement are two of the most used materials in the world. Globally, approximately 30 billion tonnes of concrete are made per year from a supply base of approximately 4.2 billion tonnes of cement, and demand is expected to increase more in the coming decades due to increasing demographics and infrastructure needs. For this reason, is necessary to find a sustainable way to meet the demand of these products and a promising path includes the use of CO2 combined with minerals or waste which could revolutionize the construction sector of the future.

3.3.1 CO2 and minerals

Carbon dioxide can be used to produce building materials, to replace water in concrete (CO2 curing) or as a raw ingredient in its constituents (cement and construction aggregates). Concrete is made up of cement, water, and solid aggregates like sand, gravel, and crushed stone. It may be manufactured as ready-mixed concrete that is shipped in trucks and installed on-site, or as pre-cast concrete materials. CO2 can be used as a filler (aggregate), a feedstock in the manufacture of the binding medium (cement), and as an input for concrete curing.

In the carbon cure process, fresh concrete is placed in a chamber with CO_2, at fixed temperature and pressure. This causes a carbonation reaction (shown below) resulting in a solid compound (Calcium Carbonate) which gives greater strength to the concrete in less time.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

The preceding refers to a series of processes in which cement is converted into interlocking crystals that bind the components of concrete together, thus increasing its strength. During the concrete mixing process, CO2 replaces water, resulting in calcium carbonate. This process occurs in natural concrete, but at a very slow rate because CO2 from the air penetrates the concrete at a rate of just a few millimetres per year.

Incorporating CO2 into cement production by reacting it with magnesium minerals or other additives, on the other hand, is a more complex process that is still in its early stages of development than CO2-cured concrete. Novel cement may have the advantage of being able to use low-grade CO2 or even flue gas directly from manufacturing processes or power plants. The main perk for companies using CO2 is to make concrete with higher performance and a smaller CO2 footprint than conventional building materials. Other important potential benefits are shorter curing times, less water consumption, and higher strength of concrete compared to conventional products, thus reducing the demand for cement and cost per unit of concrete produced.

However, since the manufacturing of building materials is a localized operation (transportation has a significant effect on the overall cost), concrete plants are widely distributed in the developing world (in the United States alone there are over 5.500 ready-mix concrete plants, hundreds of precast concrete plants and nearly 100 cement production plants). This means that CO2 would have to be absorbed in a variety of places on a wide scale. Concrete plants, unlike cement plants, do not have significant sources of CO2. One of the logistics problems is that CO2 supplies and concrete plants are not all in the same location, necessitating long-distance transport, which can impact the profitability of the manufactured product, making it no more cost-effective. To sum up, the energy required for CO2-derived concrete products is less, provided the transport of cement and CO2 can be minimised, as said earlier.

Overall, even though cement and concrete are highly standardised materials in a low-margin and dynamic environment, CO2 curing methods can manufacture concrete with lower manufacturing costs and higher strength than traditional curing paths. The key cost advantages were due to the shorter drying period and a decreased demand for cement in the concrete mix. However, the future production of CO2-cured concrete will inevitably be determined by the prices, characteristics, and applicability in different markets, as well as market adoption. The low-carbon quality of these goods could boost their competitiveness in countries where sustainability is valued, such as Europe. As an option, this technology allows for the use of less pure sources of CO2, which may improve the economic feasibility of CO2 curing concrete. Several businesses are seeking business prospects for CO2-cured concrete or innovative cement processes, but two North American companies are leading the production and promotion of them: the Canadian CarbonCure, which has developed a commercial CO2 curing method that can be retrofitted to traditional "ready-mix" concrete plants and the US-based Solidia Technologies that is developing specialised cement-making that binds with more CO2.

Concerning sustainability, the lower cement supply used to produce concrete, and hence the lower upstream emissions associated with the latter is the main contributor to the lower life-cycle emissions of CO2-cured concrete compared to those of conventionally cured concrete. Another critical aspect is the irreversible accumulation of carbon in concrete, which makes for a greater decrease of the carbon footprint as compared to other applications. To date, the precise pollution control capacity of CO2-cured concrete vs standard concrete is unknown, but some studies suggest that the CO2 footprint of concrete can be reduced by around 80%, making this technology one of the most promising solution for CO2 use.

CO2-derived building materials from CO2 and minerals through a carbonation process. [3]

3.3.2 CO2 and waste

Alternatively, CO2 can be used to process metal-containing waste products into stable and solid carbonates that can be used as aggregates in the building industry. Meanwhile, carbonation with CO2 is an incentive to reduce the likelihood of metals causing environmental damage while still avoiding waste disposal costs. A wide range of waste sources from the electricity or manufacturing sectors, including coal fly ash, steel slag, cement-kiln mud, bauxite debris, and silicate mine tailings, may be potentially remediated with CO2. Because of their high concentration of reactive elements, such as calcium and magnesium ions, alkaline wastes make an excellent candidate for this usage. However, the reactivity and CO2 absorption potential of waste vary. Natural mineral-based construction materials use very little CO2, but the carbon is permanently deposited in the cement. CO2 consumption concentrations differ by waste content, with coal ash emitting 7 to 25 percent of CO2, cement dust emitting 8 to 25 per cent, and blast furnace slag emitting 26 to 38 per cent. However, certain alkaline waste streams need pre-treatment or harsh operating conditions, such as elevated pressure and temperature, in order to react at industrially suitable concentrations. The aim of pre-treatment is to accelerate the slow carbonation process by increasing the surface area of the sample or chemically separating the reactive metal ion from the stone. After the carbonation process, other waste materials and processes necessitate a separation stage. Inevitably, all activities are energy-consuming and costly, both in terms of resources and operations, increasing the gross output rate to unsustainable levels. Furthermore, vast quantities of mineral feedstock are needed per tonne of CO2 used, which must be shipped to the carbonation site, making its location a critical decision that will have a significant effect on transport costs. However, to boost the CO2 absorption capacity of waste materials under acceptable operational conditions (low temperature and pressure) and industrially acceptable reaction times, further technological improvements are needed in this field.

In addition, further insight is required into the effect of the purity level of CO2 on most mineral carbonation technologies. According to some research, while waste materials can tolerate CO2 at a wide range of purity levels (approximately between 10% and 90%), reaction rates tend to decline with lower purity levels. The main benefit for companies in reacting waste materials with CO2 is to abruptly reduce waste disposal costs while creating a competitive and sustainable product for the construction sector. Companies around the world are scaling up industries based on this technology, using about 75 kt of CO_2 annually and converting waste such as bauxite residue, steel slag, and air pollution residues into a productive resource. The supply of waste sources, on the other hand, could be a significant long-term limitation because of decreased coal-fired power generation and primary steel production caused by the green transition. Furthermore, technological improvements may allow the treatment of waste materials that cannot be converted at industrially acceptable rates today.

Based on the supply of CO_2 and appropriate waste of construction materials, the British company Carbon8 believes that about 15 Mt of CO_2 a year will be used for the carbonation of waste materials using existing technologies. In fact, in some areas, there may not be sufficient waste material in the short term to feed these plants, because most of the litter is already under contract with waste disposal companies.

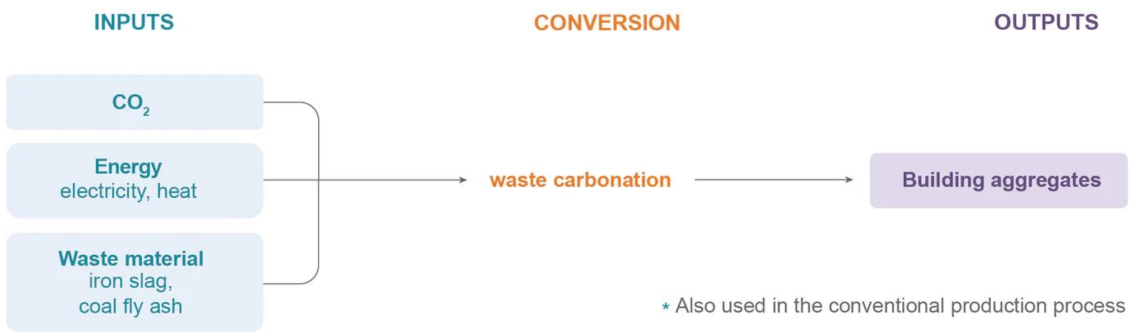
It must be said that the relatively low value of building materials makes it difficult for these products to compete with their counterparts. Carbonated waste materials are only economically feasible if the costs of transportation, pre-treatment, and carbonation, less the avoided cost of waste treatment, are less than the selling price of the commodity. Nevertheless, the main perk of this technology remains the CO_2 avoidance costs estimated between \$50 and \$300 per tCO_2 sequestered.

First applications involve materials with low processing costs and locations where enough low-cost CO_2 and waste streams coexist with a stable demand for building materials. Some research shows that the European Union, where these conditions exist and costs of waste disposal are high, will likely host the first plants, paving the way for the spread of this technology.

The permanent deposition of carbon in the construction material is a significant contributor to the lower life-cycle emissions as compared to conventionally manufactured aggregates. However, not all of the CO_2 used is trapped in the carbonate product; however, the relatively high cost of the CO_2 input facilitates recovery of the unreacted portion, resulting in a high percentage of CO_2 sequestered. The net CO_2 emission reductions, however, are highly dependent on the energy consumed for waste pre-treatment and reaction, as well as the transport of all inputs and carbonate products. Any European industrial areas with ideal waste products, CO_2, and future product customers are also good locations to import carbonate materials with the greatest total pollution reductions.

For the moment, only a few LCA studies on carbonated waste products have been conducted, even if a leading company in this field named Carbon8 reports an average absorption rate of 40 kgCO2 per tonne of aggregate, which depends on the type of waste material. In addition, the firm claims that more carbon is permanently stored during the process than emitted as CO_2 in its manufacture, resulting in a carbon-negative aggregate.

The last constraint to industrial production is the existing regulations that may prohibit the integration of waste in products; consequently, further studies are required to demonstrate the safety and environment-friendly performance of this CO_2 use.



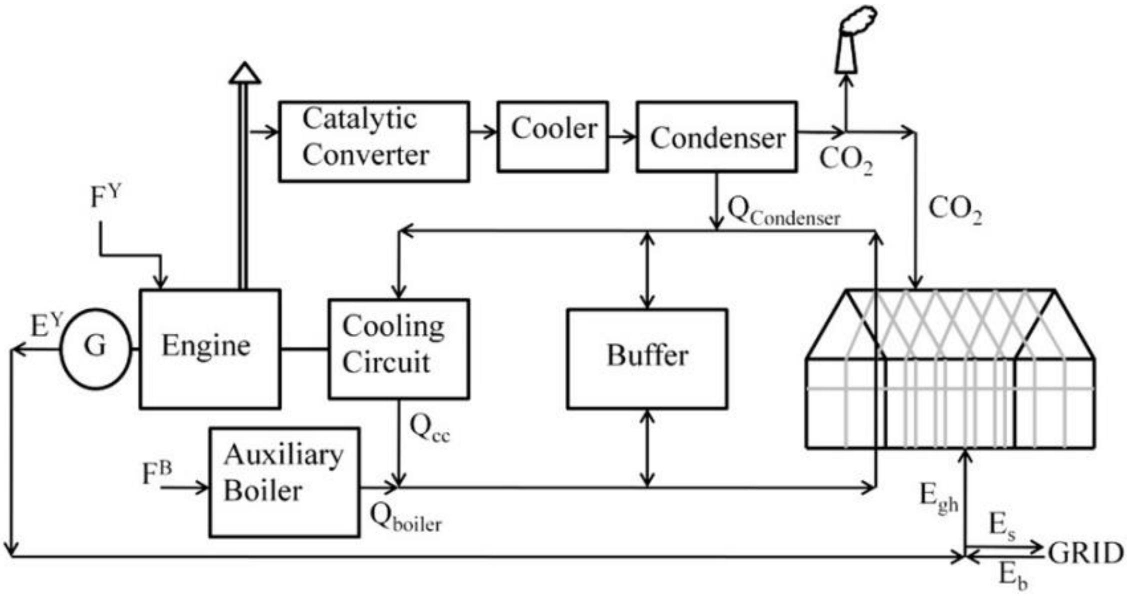
Building materials production from waste and CO_2 through a carbonation process. [3]

3.4 Crop yield boosting with CO_2

In the agricultural sector, CO_2 can be used to enhance the yield in biological and chemical processes increasing the quantity used in them. Several uses of this type are now commercial in some environments and regions around the world. This includes fertilizer and methanol production, as well as greenhouse crop cultivation.

The latter is the most common and most mature application that has proven to be valid in enriching the growing environment and so causing an increase in crop yields by up to 25% to 30%. However, to avoid damage to the crops, a high purity level of CO_2 are needed. But, to stimulate plant growth, it is also required low-temperature heat.

Nowadays, the most efficient way of meeting both CO_2 and heat demand is through cogeneration systems (CHP) powered mainly by internal combustion engines (ICE). In the CHP system, the exhaust gasses from the ICE pass through a catalytic converter and a condenser before entering the greenhouse. The catalytic converter aims to purify the flue gasses by making them suitable for CO_2 enrichment. Heat is not only recovered from the cooling circuit but, by installing a cooler and condenser, heat is retrieved from the flue gasses as well, resulting in higher thermal efficiency of the CHP system. Also, a buffer is added to store heat so that the CHP can run during the day using less electricity possible when its price is high, and releasing in the greenhouse the heat during the night to guarantee a stable temperature. Peaks in the heat demand are managed using an auxiliary boiler when the cogenerated heat is not enough, whereas excess electricity is sold to the grid. However, the CHP system is designed proportionally to the greenhouse’s demand in order to be as independent as possible from the outside.



Flow diagram of the CHP system feeding the greenhouse. [15]

Also on-site gas-fired boilers are used, although the application of externally sourced CO2 and heat is increasingly being practised.

The CO2 can also be utilized to cultivate algae, used to produce petroleum substitutes. Like in greenhouses, the CO2 is injected into a closed environment to boost algal growth. But, although algae cultivation has been studied and tested by R&D over the last years, it is still far to be used on a large scale. Though, several test plants have been edified in different parts of the world using purified CO2 from power plants or industrial facilities picking a huge quantity of data valuable to assess its economic feasibility.

Low yield rates, susceptibility to impurities, and the high energy needs for processing algal products are the key problems facing this approach. The research in this field focuses mainly on improving conversion efficiencies, enhancing production rates and reducing costs of bioreactors in order to make this technology scalable.

About its scalability, only a small part of greenhouses utilize CO2 to stimulate plant growth and the majority of these are located in the Netherlands, with an estimated annual consumption of between 5 and 6.3 Mt of CO2. Of this amount, around 500 ktCO2 per year come from external industrial plants and feed nearly 600 greenhouses scattered throughout the western part of the country.

Greenhouses using externally sourced CO_2, are the most sustainable solution with 140 million cubic metres of natural gas saved every year, causing a reduction of some 250 ktCO_2 per year. The global potential for CO_2 use esteemed in greenhouses is at least 10 MtCO_2 per year, but much still needs to be done to achieve this ambitious target. In addition, other crucial conditions to further expand the market are CO_2 and heat transport infrastructures, as well as heat sources close to the existing greenhouses, preferably cogenerative. A glaring case is the Netherlands, where the main limitation is not the demand, but the supply of high purity CO_2 at a competitive price combined with the lack of an appropriate pipeline to ease its transport.

Considering the competitive aspect, the use of CO_2 in this context is already well on the way in several places. The latter are located near industrial areas that can provide: low-cost and high-purity CO_2, low-cost waste and heat with a CO_2 pipeline infrastructure (all the features listed earlier). Only in this case, the costs for CO_2 and heat supply can be lower than potential revenues allowing a future market growth of CO_2 use. The experts suggest that the ideal distances between the greenhouse and industrial source of CO_2 and heat are respectively within 10 km and 5 km, but nevertheless at least a small cluster of greenhouses is required to allow investments in CO_2 capture and transportation infrastructures.

To summarize, climate benefits can be maximized only if cogeneration systems are embedded in plants or the CO_2 is captured directly from the air. On average, only 20% of the CO_2 fed to the greenhouses is absorbed by the crops, while the other 80% is vented with air in order to control humidity. The 20% absorbed is stored in the crops for a shorter period than other uses to be subsequently released into the atmosphere. Nevertheless, this path can substantially contribute to carbon abatement, provided that the emissions caused by capture, purification and transport are lower than CO_2 emissions from the traditional natural gas combustion.

Flow chart describing the combined use of CO2 and heat to boost plant yield. [3]

4. STORAGE

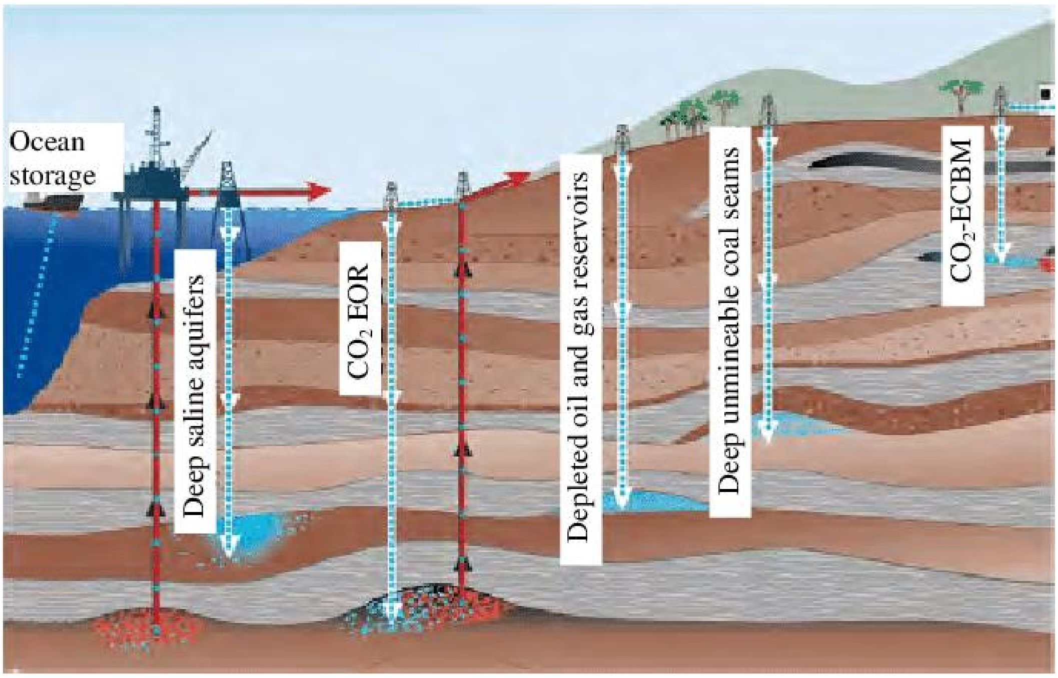
To improve oil recovery, CO_2 can be deposited in natural formations such as deep saline aquifer and oil or gas reserves (over a km in depth). At this time, geological storage is thought to be the most promising solution for storing the vast amounts of CO_2 needed to successfully offset global warming and climate change. At high temperature and pressure (around 500 kg/m3), a standard geological storage site can store many tens of millions of tonnes of CO_2.

The selection of suitable geological locations for CO_2 storage must be done with caution. A safe geological climate, sufficient porosity, thickness, and permeability of the reservoir rock, and a cap rock with good sealing capabilities are all criteria for geological CO_2 storage. In addition, infrastructure-related economics and socio-political factors can influence site selection. Furthermore, while geological storage techniques can be derived from existing processes, no commercial experience has yet been gained. Exhausted oil and gas deposits, unmineable coal fields, and saline aquifers are three natural formations widely used for CO_2 storage. While environmental issues (such as ocean acidification and eutrophication) would undoubtedly hinder its use, deep ocean storage is a viable choice for CO_2 storage.

Carbon dioxide may be pumped into exhausted (or almost depleted) oil/gas reserves to improve oil recovery (CO_2-EOR), with the injected CO_2 remaining indefinitely deposited there. After primary processing, up to 40% of the residual oil remaining in an active reservoir can be recovered using CO_2. Fluid injection is currently used in the oil and gas production industry to improve the recovery of residual oil and gas, so no development studies are needed. As a result, unlike any of the options, injecting CO_2 into exhausted oil and gas reserves has a financial opportunity to cover the high CCS’s costs. Deep coal beds can also store CO_2 while retrieving methane trapped in coal seams' porous structure. CO_2 enhanced coal bed methane (CO_2-ECBM) is a mechanism that requires CO_2 to be deposited in the empty fraction of a coal bed after it has been filled by gas. It, like the EOR, has been in use for a long time and therefore needs little further testing. While deep saline aquifers have no commercial value, they can be used to store CO_2

collected by CCS. They can be located both onshore and offshore and have immense potential for CO2 storage in theory, but further research and security measures are needed before they can be used on a wide scale.

CO2 can also be pumped into deep-sea sediments at depths greater than 3 km, resulting in long-term geological CO2 preservation. This process, however, is riskier than other geological storage systems. Injecting significant quantities of CO2 directly into our oceans, on the other hand, may alter the chemistry of seawater (for example, by lowering its pH), resulting in ocean acidification, which could have catastrophic effects on the marine environment.



CO2 storage solutions. [16]

5. PUBLIC ACCEPTANCE OF CCU

The successful rollout of the manufacturing infrastructure and market adoption of CCU goods by customers strongly depends on public approval of emerging low-carbon technologies. Previously, widespread opposition to the implementation of low-carbon technology such as wind turbines, electricity transmission lines, and biogas plants was often expressed by demonstrations. These, indeed, must be taken into account because they have led to the cancellation of programs on several previous occasions.

First research on CCU acceptance have appeared in recent years, with marginally favourable acceptance levels for CCU infrastructure and CO2-derived goods. Research has described possible advantages and drawbacks that people consider when deciding whether or not to use CCU technology. Before choosing to implement a technology, laypeople, in particular, weigh possible health hazards, implying that it is worthwhile to examine the interplay between technology-related expectations such as risks and advantages in the formulation of adoption. The public is impacted on many levels by the implementation of large-scale technologies: not only must the basic concept of the system and its derived goods be accepted, but the public must either promote, or at the very least accommodate, the requisite technological infrastructure and its implications in terms of land usage, pollution, and visibility.

Generally, public resistance to technology is often fuelled by fears of potential threats, such as CO2 leaks during storage and transportation in the case of CCS. In contrast to the well-known definition of "risk," which is defined as the product of an adverse event's probability and the magnitude of its effects; whereas "risk perceptions" refers to a person's subjective estimation of risks, and therefore the perceived probability compounded by the possible (negative) outcome of an adverse event.

Gain expectations, including risk perceptions, influence the general understanding and appraisal of a technology. When it came to forecasting the adoption of a technology, benefit judgments were much more influential than risk expectations in some research. The environmental advantages of CCU were recognized in observational research in Germany, and CCU was used as part of a climate reduction policy. Concerning risk beliefs, laypeople, in particular, shared unfavourable experiences with "CO2," such as fear of toxicity. Furthermore, the CCU infrastructure can cause health concerns as well as feelings of fear. Furthermore, qualitative interviews found that potential risks were multifaceted, including questions about sustainability, environmental and health risks, and small product quality risks.

In addition to technology-related expectations such as costs and advantages, research has established a number of human variables that influence whether a technology is accepted or rejected. Individually different psychological considerations, such as risk controllability, affect risk expectations on the acceptability of technology threats. Perceived uncontrollability is a psychological factor that has a big influence on people's feelings, motivation, and behaviour. It refers to one's belief in one's ability to bring about good consequences and prevent negative ones through one's behaviour.

The concept of controllability is often linked to risk perception. Risks that are considered to be under one's influence or managed by trusted authority, on the other hand, are more reasonable than risks that are perceived to be uncontrollable or controlled by untrustworthy others. Fear and perception of risk are the results of a sense of reduced controllability. However, a distinction must be made between personal and large-scale technical threats in terms of potential controllability.

Personal threats are often viewed as manageable and are often overlooked due to unrealistic expectations regarding their prevalence. Large-scale technologies, on the other hand, are linked to fewer controllable consequences and risks, as well as lower social approval. The impact of a technology's perceived controllability on expectations of advantages, dangers, and adoption has yet to be thoroughly investigated in the context of sustainable low-carbon technologies.

Research made in this field have obtained the following results:

CCU Benefit Perceptions:

CCU benefit evaluations are positively related to affective benefit evaluations.
CCU benefit evaluations are positively related to general and local acceptance.
Affective CCU benefit evaluations are positively related to general and local acceptance

CCU Risk Perceptions:

Cognitive CCU risk perception dimensions are positively related.
CCU risk perceptions are positively related to affective risk evaluations
CCU risk perceptions are negatively related to general and local acceptance.
Affective CCU risk perceptions are negatively related to affective benefit evaluations.
Affective CCU risk perceptions are negatively related to general and local acceptance

Perceived Uncontrollability of Risks (PUR):

PUR is negatively related to CCU benefit perceptions.
PUR is negatively related to affective benefit perceptions.
PUR is positively related to cognitive and affective risk perceptions.
PUR is negatively related to general and local acceptance.

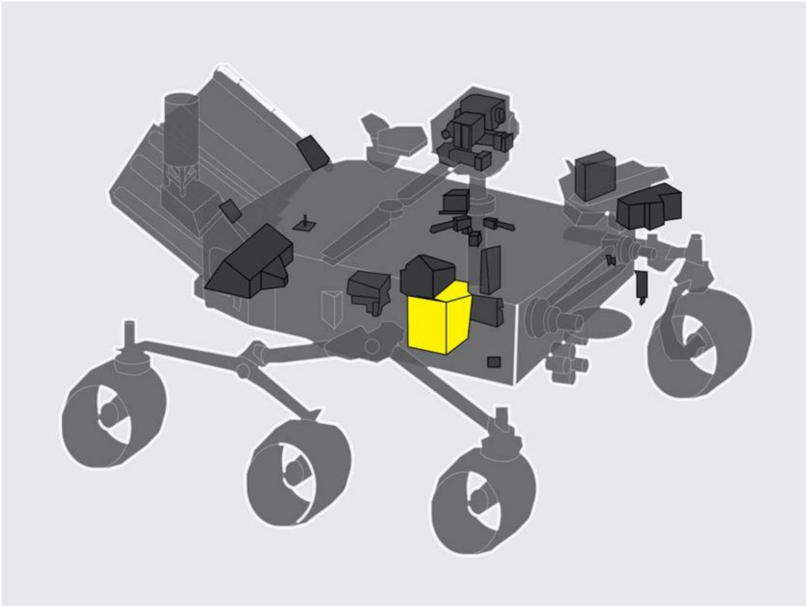
[17]

6. INNOVATIVE PROJECTS FOR CO2 UTILIZATION

6.1 The Moxie project

One of the most advanced applications of CO2 is the production of O2, which is part of the In-Situ Resource Utilisation (ISRU). Its development is crucial to reduce the mass and cost of space missions, particularly those to Mars, making the dream of becoming a multi planetary species a reality. Despite the lower launch costs achieved by SPACEX's latest generations of recycled rockets, the expense of releasing all of the propellants from Earth will still be in the billions of dollars. Furthermore, transporting massive amounts of oxygen from Earth to Mars will necessitate a zero boil-off facility, which would necessitate ventilation, refrigeration, and fuel, as well as the logistics of handling several heavy-lift launches in a manner consistent with the 26-month duration of Mars launch opportunities. By generating oxygen on-site, it is possible to refuel return rockets as well as provide artificial air to a livable closed structure (a future Martian city). Synthesize 1 kg of oxygen on Mars, for example, lowers the payload mass to be launched from Earth by approximately 10 kg, lowering costs considerably.

The MOXIE (Mars Oxygen In-Situ Resource Utilization Experiment) projected by NASA is a small-scale ISRU technology demonstrator that produces oxygen from Mars' atmospheric CO2 using solid oxide electrolysis. It is embedded in the Perseverance rover, which has been on Mars for a few months now (landing date: 18 Feb 2021), and produces up to 10 g of O2 per hour from Martian carbon-dioxide atmosphere, during intermittent one-hour experiments.



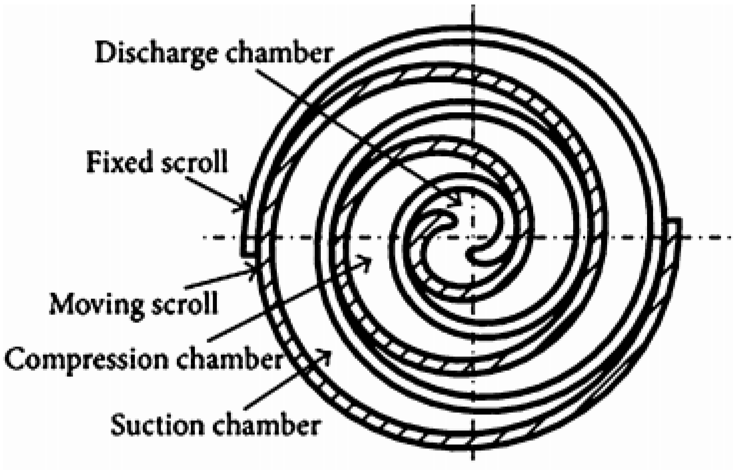
Location of the MOXIE in the Perseverance rover. [18]

The atmosphere of Mars is composed of approximately 95% CO_2, 2.6% molecular nitrogen (N_2), 1.9% argon (Ar), 0.16% molecular oxygen (O_2), and 0.06% carbon monoxide (CO). The gas is pulled into the compressor using a HEPA (High-Efficiency Particulate Air) filter. The outlet pressure of the MOXIE gas collection system is constrained by Viscous Flow Control Devices (VFCDs) at the outlets rather than gas regulators to reduce mass and volume. Since VFCDs are essentially temperature-compensated precision apertures, the outlet pressure can vary depending on the inlet gas density, motor speed, and gas collection system output. The VFCDs' throughput represents a design option that balances optimum operational pressures for the SOXE with mass and power resource minimization.

The compressor mixes two mass streams: one from Mars and one recirculated from the cathode exhaust. The compressor feeds the cumulative mass flow into the SOXE, where the second stream accounts for just a small percentage of the overall mass. The gas leaves the SOXE in two streams: one from the cathode (which contains CO, unused CO_2, and 4–5% inert gases) and one from the anode (consisting of pure O_2). The cathode exhaust is further separated into two sources, one of which is recirculated to the compressor inlet by a third VFCD and the other of which is returned to the ambient. Five pressure sensors are mounted in the flow system to track relevant parameters.

Furthermore, the dust in Mars' atmosphere can contaminate the electrodes of the solid oxide electrolysis subsystem if MOXIE consumes it. MOXIE is dust-free thanks to a High-Efficiency Particulate Air (HEPA) filter. In Earth atmospheric conditions, HEPA filters operate in the slip flow regime, where pressure reduces over a filter (ΔP) and is completely independent of atmospheric pressure P. In contrast, the MOXIE HEPA filter can operate under Mars atmospheric conditions in the free molecular flow regime, where the pressure drop through the filter is proportional to atmospheric pressure. It is only necessary to keep ΔP/P as low as possible, regardless of atmospheric pressure variations, to maintain efficient filter performance. The HEPA filter triggers a visible pressure drop when MOXIE is turned on. When dust accumulates on the sensor, the pressure drop increases, lowering the mass flow rate.

A mechanical compressor is used to acquire and pressurize Mars' atmosphere. With each revolution, the MOXIE compressor takes in a fixed volume of gas and compresses it to a much smaller fixed volume. The compressed gas is then released into the downstream plenum toward the SOXE. The MOXIE compressor is a motor-driven scroll pump. A scroll compressor works by rotating a movable scroll past a fixed scroll, sealing off a suction volume of inlet gas, compressing it, and pushing it out towards the compressor exhaust for each revolution. As a consequence, the influx of gas through the downstream plenum oscillates at rotational velocity. The scroll compressor at MOXIE is controlled by a controller, which controls the power input to the compressor to reach the desired rotational speed.



Cross section of a scroll compressor. [19]

Zirconia (ZrO2) is an unstable ceramic that is stabilized by replacing any of the Zr ions with a larger ion like Sc (Scandium). ScSZ – Scandia-Stabilized-Zirconia – is the name given to the resulting "doped" zirconia. As a result of the presence of Sc^{3+} in the ZrO_2 lattice, oxygen ions are drawn away from the Zr ions, resulting in oxygen vacancies within the lattice. These materials have a one-of-a-kind property. When an electric field is spread over a sheet of ScSZ, oxygen ions will flow from the cathode through the ScSZ lattice, moving from vacancy to vacancy until they reach the other side of the ScSZ (anode), where they give up their electrons and oxygen gas forms. Scandia stabilized zirconia (ScSZ) electrolyte is made by tape-casting a slurry of ScSZ powder with an acceptable blend of organic binder, plasticizer, and solvent. The dry tape is then laser cut to the appropriate dimensions, taking lateral shrinkage into account during sintering. The resulting sintered ceramic is non-porous, forming a gas-impermeable layer between the incoming CO/CO2 and the formed O2. On one side of the ScSZ electrolyte, a doped lanthanum cobalt ferrite oxygen evolution electrode (anode) is used, with a nickel-ceria cermet CO/CO2 electrode (cathode) on the other. As heated CO2 at 800 degrees flows over the nickel-catalyzed cathode surface under an applied electric potential, a fraction of the CO2 can be electrolyzed as follows:

$$CO_2 + 2e^- \Rightarrow CO + O^{2-}$$

The CO and any unreacted CO2 are exhausted by an outlet duct, while the oxygen ions are electrochemically guided to the anode by the solid oxide electrolyte, where the O2 ions interact to create the gaseous O2 that is emitted from the anode cavity at a rate equal to the current. Furthermore, it is critical to prevent the deposition of carbon, which can settle on the electrodes and disrupt the process. On the Moxie, the SOXE section consists of ten SOXE cells in series, sealed together to prevent leakage of hot gas.

Since an O2 molecule needs precisely four electrons to make, the mass flow of oxygen FO2 can be calculated using the following relationship:

$$F_{O2}= nI/4F$$

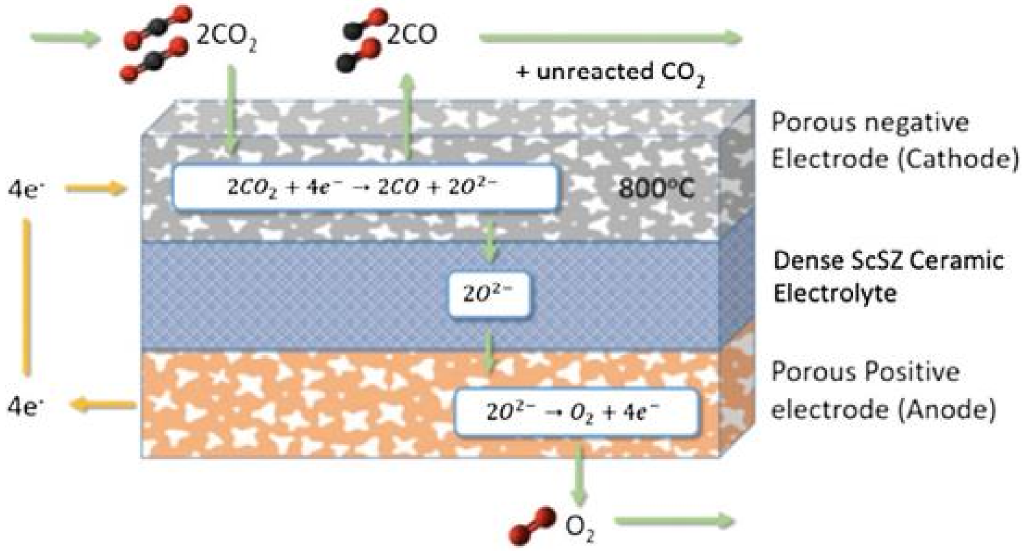
where I is the ion current through the membrane, F is Faraday's constant, and n is the number of series-connected cells (10 for MOXIE). As a result, for MOXIE:

$$F_{O2} = I/0.335 \text{ (g/h)}$$

where I = 2 A (enough to produce oxygen at a minimum rate of 6 g/h). Since each oxygen atom emitted corresponds to one molecule of CO, the mass flow rate of CO can be determined using the formula:

$$F_{CO} = F_i + (28/16)\ F_{O2}$$

where Fi denotes the sum of CO in the SOXE inlet stream and 28/16 denotes the CO/O mass ratio.

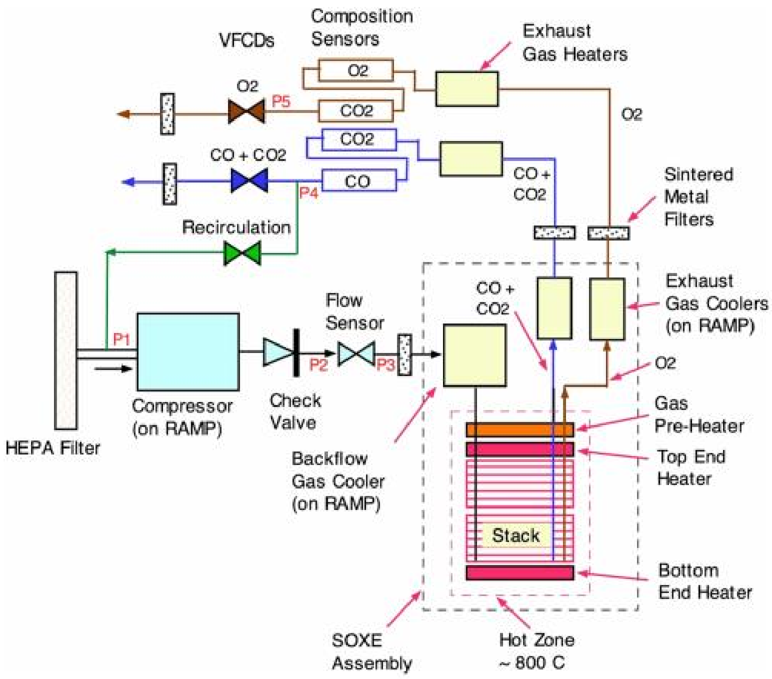


SOXE cell's section. [19]

From the perspective of total system energy, it is desirable to utilize as much of the incoming CO2 as possible without risking carbon formation, which must be avoided in the SOXE. The power needed can be calculated from the simple formula P = IV, where V = 1.46 V is the voltage for the reaction. A decrease in the power P = IV causes the reaction to become more endothermic, requiring more heat to compensate for the reduction in temperature.

The pure oxygen product is guided away from the anodes and into the oxygen plenum by the other side of the interconnects. From the standpoint of gas processing, a single inlet stream results in two outlet streams, one for waste gases and the other for the oxygen product. MOXIE's activity is controlled by a plethora of sensors and transducers, including 5 pressure transducers, 4 gas composition sensors, 16 ambient temperature sensors, 2 SOXE high-temperature sensors, 2 SOXE voltage and current meter circuits, and a sensor to calculate compressor motor rpm. Their measurements are read once a second and saved in the device's memory.

The Long-term activity of Mars inlet gas will result in oxidation of the nickel catalyst in the cathode due to CO2 being a slightly oxidizing gas. To avoid this, a VFCD taps off a small percentage of the exhaust gas in the cathode line and recirculates it back to the compressor inlet, so that the gas entering the SOXE retains a small percentage of CO, whose reducing property counteracts possible oxidation by CO2.



Schematic layout of MOXIE. [19]

6.2 Innovative materials

Carbon nanotube composites from CO2 (C2CNT) represents cutting-edge CO2 utilization. Carbon nanotubes have the strongest tensile strength of any material, greatly lowering the quantity of material required to produce the same structural strength. As a result, the CO2 emitted during the manufacture of CNT is far lower than that emitted during the old procedure. This technology is carbon negative and involves synthesizing CNTs from CO2 by low-energy C2CNT (CO2 to CNT) molten electrolysis. About four tons of CO2 electrolyzed forms one tonne of CNTs. This avoids several hundred tonnes of CO2 by replacing structural materials with CNT composites.

In the traditional process, CNTs can be synthesized by several methodologies including flame-assisted and plasma-assisted CVD techniques. But these processes are complex, costly, and energy-intensive and hence are responsible for the high price of CNTs between $85K-450K per ton [20]. The newly found C2CNT, on the other hand, splits CO2 by electrolysis in molten carbonates in a high-yield, high-purity, low-cost method. In many ways, the physical-chemical environment of traditional CVD CNT synthesis differs from that of the novel C2CNT synthesis. The latter is an electrochemical reaction that uses only CO2 as a reactant, whereas the former is a chemical reaction with organometallics (compounds containing at least one metal-carbon bond) as a reagent. Furthermore, CVD typically takes place at a gas/solid interface, whereas C2CNT takes place at a liquid/solid interface. There are also some noticeable differences. Near the growing interface, C2CNT gives a greater density of reactive carbon (molten carbonate electrolyte). During CVD CNT development, an electric field may or may not be supplied to the substrate. The consumption of CO2 as it is dissolved in molten carbonate and divided by electrolysis to generate the building blocks of CNTs was tracked using Carbon-13 monitoring. C2CNT uses molten electrolysis to convert CO2 into carbon nanotubes. In lithium carbonate, transition metal-nucleated electrolysis produces CNTs, oxygen, and dissolved lithium oxide according to the following:

$$Li_2CO_3 \rightarrow C_{CNT} + O_2 + Li_2O \qquad (1)$$

CO2 dissolved in the electrolyte interacts chemically with lithium oxide to regenerate and rebuild Li_2CO_3:

$$CO_2 + Li_2O \rightarrow Li_2CO_3 \quad (2)$$

The net reaction of (1) and (2) is the electrolysis of CO2 into CNTs and oxygen.:

$$CO_2 \rightarrow C_{CNT} + O_2 \quad (3)$$

This reaction occurs at 750 °C and, in addition to the CO2 absorbed, its production cost is only $1000 per tonne, making it commercially convenient as well.

The carbon footprint and production cost of conventionally produced CNTs are significant. Replacing a big mass of cement with a small mass of CNTs results in a lower mass composite with the same strength as the CNT-free cement, avoiding the replaced cement's huge carbon dioxide emissions. The inclusion of modest amounts of carbon nanotubes, typically less than 0.1% of the total weight, increases the tensile, compressive, and flexural strength of cement by 30-60%. To obtain the same strength, one tonne of carbon nanotubes may replace 938 tonnes of cement.

There have been fewer studies on the strengthening effect of CNTs on metals than on cement, even though they, too, show a large strength increase in the metal with a small CNT additive (composite). When the virgin material displaced by CNTs has a carbon footprint greater than 1, the massive tonnage (844 tonnes) of CO2 avoided per tonne of CNT in a cement composite can be surpassed.

As a CNT-Al composite, inductive heating and melting of aluminium provide an effective media for homogeneously dispersing CNTs. The addition of 0.1% CNT increases the tensile strength of aluminium by 37%. Because of the cascading effect of a large carbon footprint in the manufacturing of Al, the usage of a CNT-Al composite avoids an unusually high value of 4400 tonnes of CO2 upon addition of 1 tonne of CNT, as shown in the table. Aluminium manufacturing is one of the most carbon-intensive industrial processes, producing 11.9 tonnes of CO2 for every tonne of aluminium produced.

CO_2 abatement may be boosted by using structural materials with a high carbon footprint. An uneven dispersion of CNTs in CNT-Mg composites reduces the efficiency of the CNT-metal interaction. Production of magnesium emits 14 tonnes of CO_2 every tonne of magnesium. The CNT-Mg composite saves 1820 tonnes of CO_2 per tonne of CNTs because to its large footprint and the stronger composite created with modest CNT additions.

Because titanium and steel have a greater melting point than aluminium and magnesium structural metals, creating a uniform dispersion of CNTs in the CNT composite is more difficult, and there have been fewer reports of these CNT composites than with other metals. A CNT-Ti composite containing 0.3% CNT increases tensile strength by 102% and substitutes 339 tons of titanium with 1 tonne of CNT. With a carbon footprint of 8.1 tons CO_2 per tonne Ti in titanium manufacturing, 2750 tonnes CO_2 are saved per tonne CNT in the CNT-Ti.

The CNT-stainless steel composite with 0.75% CNT has a 37% better yield strength. Due to the large carbon footprint of stainless steel, which emits 6.15 tonnes of CO_2 per tonne, this saves 302 tonnes of CO_2 per tonne CNT in the CNT-stainless steel composite.

X	wt% CNT	Property	Increase in property	Tonnes X removed per tonne CNT to achieve equal strength	Tonnes CO_2 emitted per tonne X produced	Tonnes CO_2 avoided per tonne CNT	kWh consumed per tonne CO_2 avoided
Cement	0.048%	Tensile strength	45%	938	0.9	**840**	**2.45**
Aluminum	0.10%	Tensile strength	37%	370	11.9	**4400**	**0.47**
Magnesium	0.30%	Tensile strength	39%	130	14	**1820**	**1.14**
Titanium	0.3%	*Yield strength*	102%	339	8.1	**2750**	**0.75**
Stainless steel	0.75%	Tensile strength	37%	49	6.15	**302**	**6.85**

CO_2 avoidance of CNT cement, Al, Mg, Ti, or stainless steel composites. [21]

The net energy required by the C2CNT transformation of CO_2 to CNTs is:

$E_{C2CNT;\ net\ energy\ consumed}$ = 2.0MWh per tonne CO_2 reacted to CNT

Carbon nanoplatelets, graphene, graphene scaffolds, and carbon nano-onions are just a few of the carbon nanomaterials (CNMs) that have recently been created by modifying the conditions of CO_2 molten carbon electrolysis. Each CNM has its form and features.

Through their manufacture by CO_2 electrolysis C2CNT and uses as lighter weight, strong CNT composite structure material, CNTs are shifted from a major (CVD manufacturing induced) carbon footprint material to a huge CO_2 avoidance material. By replacing them with CNT-aluminium, CNT-magnesium, CNT-titanium, or CNT-stainless steel composites, world yearly anthropogenic carbon dioxide emissions will be reduced dramatically, helping to mitigate climate change.

CONCLUSION

In the near term, the CO_2 market is likely to remain small but has great potential to develop in the long term, particularly as a raw material to produce high carbon products like chemicals, fuels, and cement. In fact, despite their high footprint, they are likely to remain among the most manufactured goods and so the only chance to lower their environmental impact is to change their production process to a less polluting one.

However, the CCU consists also of CO_2 capture that can be made through various techniques, depending on stream features like CO_2 pressure and temperature. But the main logistical constraint is the transport of CO_2 in a liquid or gaseous phase. In both cases, the utilization facility must be built near the capture site to abate transport costs. Consequently, most CCU plants will be in large industrial areas where CO_2 supply is cheap and plentiful, raw materials, as well as low-carbon energy, are easily available and existing high-emission plants could be equipped with a Carbon Capture section.

Commercialization of innovative materials that outperform current state-of-the-art materials in each methodology would undoubtedly reduce the energy needs of both the capture and utilization processes in both situations. In terms of usage, the production of fuels and chemicals, as well as the use of renewable energy sources, may reduce overall costs while ensuring a long-term strategy for value-added product creation.

Over the years, the environmental issue will become more and more important, a rewarding green solution like this and therefore more and more funds will be allocated for their implementation. The latter in addition to economic incentives are crucial to reduce the commercial gap between CO_2-derived products and market incumbents. These include direct financial assistance for project expenditures as well as tax incentives.

The thesis has aimed to show and describe in a critical review the cutting-edge technologies for the use of CO_2 considering its entire cycle, starting from its capture, also taking into consideration its more developed alternative (storage). Furthermore, it has proposed to deal with an even more innovative area, beyond the environmental issue, such as the moxie project which represents a great step forward towards the dream of creating a human colony on Mars.

Waiting for developments in this field, each of us, in our small way, can do something with small measures to reduce waste, both of high-impact materials and energy, still produced for the most part with highly polluting processes. A sharp decrease in CO2 emissions in processes will be of no use if the demand for their products increases even more. For example, we can decide to move as much as possible by public transport, avoid the use of single-use plastic, use low-consumption appliances, improve the thermal insulation of our homes to limit the use of heating etc.

Only by adopting all these precautions in addition to the development of technologies to limit the emission of CO2, like the CCU, it will be possible to limit global warming and leave a clean world for future generations as we have received it from our predecessors.

SUNTO IN ITALIANO

Negli ultimi anni, i dati sulle emissioni di gas serra annuali hanno raggiunto i massimi livelli storici accelerando ulteriormente il processo di riscaldamento globale del nostro pianeta, andando quindi ad alterare gli ecosistemi con una conseguente diminuzione di terreno fertile e biodiversità. Per mantenere l'innalzamento delle temperature sotto i 2 °C rispetto ai livelli preindustriali, come suggerito dagli esperti per evitare una catastrofe ambientale, è ormai urgente una seria presa di posizione da parte dei governi nazionali. A tal proposito, con l'accordo di Parigi 190 stati hanno concordaro le azioni da mettere in atto nel breve e lungo termine per contrastare i cambiamenti climatici.

La tesi si propone di descrivere criticamente una delle tecnologie a più alto potenziale, ancora in stato sperimentale: la CCU (cattura e utilizzo del carbonio). Questa, infatti, prevedendo l'utilizzo della CO2 in vari ambiti permetterebbe di trasformare un problema come la CO2 in una preziosa risorsa, permettendo quindi di diminuire le emissioni di quest'ultima rilasciate dai processi.

Il primo stadio della CCU è costituito dalla cattura del carbonio prodotto dal proceso industriale. Questa è realizzata integrando un ristema di cattura a quello dei gas di scarico già esistente, variabile in base alla tecnologia utilizzata per la cattura. Questi sistemi hanno l'obiettivo di catturare la CO2, separandola da altri prodotti chimici come l'idrogeno e l'ammoniaca che possono anch'essi essere utilizzati nei processi o venire espulsi in atmosfera. La tecnologia utilizzata dipende principalmente dalla purezza e lo stato del gas, in funzione delle condizioni ambientali e possono essere classificate in pre e post combustione a seconda che la CO2 sia catturata prima o dopo la combustione. In aggiunta a queste la ossicombustione, ancora nella prime fasi si sviluppo, rappresenta un alternativa a le precedenti.

Le tecnologie di cattura sono quindi le seguenti:

- Assorbimento fisico
- Adsorbimento
- Tecnologia a membrana

- Separazione criogenica

A questo punto la CO_2 è compressa allo stato liquido in modo tale da poter essere trasportata facilmente attraverso le condutture fino al punto di utilizzo o di stoccaggio. Il corpo della tesi è rappresentato dai processi e le tecnologie che permettono l'utilizzo della CO_2. Nonostante, però, gli ingenti fondi stanziati negli ultimi anni a favore di queste tecnologie solo alcune sono ad uno stadio avanzato di sviluppo e competitive nel loro mercato di riferimento. Un esempio è dato dalla produzione di materiali da costruzione che conferisce al prodotto caratteristiche superiori a prezzi inferiori rispetto ai suoi competitors. Le applicazioni della CO_2 in ambito industriale sono molte e possono essere suddivise in:

- Produzione di combustibili tramite il processo Fischer-Tropsch consistente in sei fasi: compressione H_2 e CO_2, reazione RWGS, sintesi FT, idrotrattamento, generazione di energia e **utilità**. Questa soluzione, pero, richiede grossi quantitativi di energia andando ad aumentare i costi di produzione. Di conseguenza, la sua scalabilità è limitata alle zone con bassi costi di elettricità e disponibilità di CO_2 come il Chile, il Nordafrica e l'Islanda. Inoltre, bisogna considerare che questa applicazione riduce realmente la emissioni di CO_2 a patto che l'ingente domanda energetica venga soddisfatta da fonti rinnovabili.
- Produzione di prodotti chimici: la polimerizzazione è il processo più scalabile tra quelli proposti perché richiede un minore apporto energetico e una sostenuta riduzione degli impianti di produzione di plastica, tra i principali emettitori di CO_2 con un'impronta di carbonio di circa 6 kg di CO_2 per kg di plastica. Il risultato del processo è un policarbonato biodegradabile utilizzabile nell'industria del packaging alimentare o in leghe polimeriche. Inoltre, il suo smaltimento mediante incenerimento è pratico e sicuro. Questo processo è già competitivo, a causa della bassa energia di input e del valore commerciale superiore rispetto ai suoi concorrenti, senza considerare che, in alcuni casi, la produzione di polimeri è fino al 30% più economica, a causa della CO_2 a basso costo utilizzata. I benefici climatici che questa soluzione può fornire sono strettamente correlati alla quantità di CO_2 che può essere assorbita dal materiale, che può raggiungere

il 50% della massa del polimero. Bisogna tener conto che la CO_2 è intrappolata nelle sostanze chimiche solo temporaneamente per poi essere rilasciata alla fine del ciclo di vita.

- <u>Produzione di materiali da costruzione</u>: la CO_2 può essere utilizzata per produrre materiali da costruzione, per sostituire l'acqua nel calcestruzzo (polimerizzazione della CO_2) o come ingrediente grezzo nei suoi costituenti (inerti di cemento e costruzione). Questa può essere utilizzata in vari modi ma il può sviluppato è come reagente nel processo di concrete curing dove il calcestruzzo fresco viene posto assieme alla CO_2 in una camera a temperatura e pressione fissate. In questo ambiente avviene una reazione di carbonatazione da cui si ottiene il carbonato di calcio che conferisce al calcestruzzo una maggiore resistenza in tempi inferiori. Tuttavia, poiché il trasporto incide fortemente sul costo complessivo, questi impianti produttivi dovrebbero essere distribuiti su tutto il territorio. Uno dei vantaggi principali è che la CO_2 viene intrappolata permanentemente nel calcestruzzo, oltre ad un prodotto con una maggiore resistenza e minore impatto ambientale. Un'alternativa meno conosciuta prevede l'utilizzo dell'anidride carbonica per trasformare prodotti di scarto ricchi di metalli, provenienti dai settori elettrico e manifatturiero, in carbonati stabili, utilizzabili come aggregati nell'industria edile. Tuttavia, il basso valore di mercato dei materiali da costruzione rende difficile l'entrata nel mercato di questi derivati. L'unico vantaggio è quindi costituito dal minor impatto ambientale.
- <u>Incremento della resa delle colture nelle serre</u> fino al 25-30%. Per evitare di danneggiare le colture, è richiesto un elevato livello di purezza della CO_2 utilizzata combinata a calore a bassa temperatura proveniente da sistemi di cogenerazione. Le aree dove questa applicazione è competitiva sono situate vicino a zone industriali in grado di fornire: CO_2 a basso costo e ad alta purezza, e calore da sistemi cogenerativi. Questo processo può contribuire alla riduzione del carbonio, a condizione che le emissioni causate dalla cattura, dalla depurazione e dal trasporto siano inferiori alle emissioni di CO_2 derivanti dalla combustione tradizionale del gas naturale.

L'alternativa più sviluppata, di cui è solo fornito un accenno, è costituita dallo stoccaggio della CO2 in giacimenti petroliferi e carboniferi esausti o in falde acquifere saline molto profonde. Ad alta temperatura e pressione (circa 500 kg/m3), un sito standard di stoccaggio geologico può immagazzinare molte decine di milioni di tonnellate di CO2. La selezione di luoghi geologici adatti per lo stoccaggio di CO2 deve però essere effettuata con cautela. Un clima geologico sicuro, porosità, spessore e permeabilità sufficienti della roccia del serbatoio e una roccia a cappuccio con buone capacità di tenuta caratteristiche richieste per lo stoccaggio geologico di CO2.

Bisogna, però, considerare che il successo della CCU è fortemente legato all'accettazione pubblica delle sue infrastrutture e dei suoi prodotti. Infatti, in numerosi casi, l'opposizione pubblica ha portato alla cancellazione di progetti innovativi green. Le principali preoccupazioni sono legate a timori di potenziali minacce come perdite di CO2 durante lo stoccaggio e il trasporto, oltre che a domande sulla reale sostenibilità del processo o sul livello qualitativo dei prodotti. Da un sondaggio svolto si è capito che i vantaggi di questo tipo di tecnologie sono compresi dalla popolazione. Per quanto riguarda invece i rischi percepiti e l'incontrollabilità si nota una certa diffidenza, dovuta principalmente ad un livello di conoscenza superficiale delle tecnologie utilizzate.

Una delle applicazioni più avanzate è rappresentata dalla sintesi dell'ossigeno a partire dall'anidride carbonica. Lo sviluppo di questa tecnologia è fondamentale per ridurre la massa e il costo delle missioni spaziali, in particolare quelle su Marte. Infatti, generando ossigeno in loco, è possibile rifornire i razzi di ritorno e fornire aria artificiale a una struttura chiusa vivibile (una futura città marziana). Il MOXIE (Mars Oxygen In-Situ Resource Utilization Experiment) progettato dalla NASA è un concept, su scala ridotta, che produce ossigeno dall'atmosferma marziana ad alto contenuto di CO2 utilizzando l'elettrolisi ad ossido solido. È incorporato nel rover Perseverance, ormai su Marte da febbraio 2021, e produce fino a 10 g di O2 all'ora dall'atmosfera marziana, durante esperimenti intermittenti di un'ora.

Un altro processo all'avanguardia nel quale è possibile utilizzare la CO2 con notevoli vantaggi è la produzione di nanotubi di carbonio. Il loiro principale vantaggio è dato dall'elevata resistenza a trazione che permette di utilizzare quantità inferiori di materiale per ottenere la stessa resistenza strutturale, andando quindi a ridurre drasticamente la CO_2 emessa a parità di condizioni. Il processo C2CNT prevede la sintesi di nanotubi di carbonio (CNT) a partirre dalla CO_2, tramite elettrolisi fusa a bassa energia. Mediamente ogni quattro tonnellate di CO_2 utilizzata si viene a formare una tonnellata di CNT. È possibile evitare l'emissione di grandi quantità di CO_2 sostituendo i materiali strutturali prodotti mediante processi altamente inquinanti con materiali compositi ai nanotubi di carbonio. I materiali con nanotubi di carbonio più utilizzati la momento sono: Alluminio, Magnesio, Titanio e Acciaio inossidabile.

La CCU presenta un elevato potenziale a lungo termine, in particolare per la produzione di materiali alto contenuto di carbonio come prodotti chimici, combustibili e cemento. Questi, infatti, nonostante il loro elevato impatto, con buone probabilità rimarranno tra i prodotti di più largo consumo e quindi l'unica soluzione sembra essere quella di sostituire il loro processo produttivo con uno meno inquinante. Tuttavia, il principale vincolo è quello logistico. Il trasporto di CO_2 in fase liquida o gassosa deve essere previsto su brevi distanze per tenere bassi i costi di trasporto. Di conseguenza, la maggior parte degli impianti che utilizzano la CO_2 è ubicata in grandi aree industriali in cui l'approvvigionamento di CO_2 è economico e abbondante, e materie prime ed energia green sono facilmente reperibili.

Nel corso degli anni, la questione ambientale diventerà sempre più importante, causando un progressivo aumento dei fondi e degli investimenti stanziati in questo tipo di tecnologie che permetterà il loro sviluppo su larga scala. In attesa di sviluppi, ognuno di noi, nel nostro piccolo, può fare qualcosa per ridurre gli sprechi, sia di materiali ad alto impatto che di energia, ancora prodotta per la maggior parte con processi altamente inquinanti. Una forte diminuzione delle emissioni di CO_2 nei processi, infatti, non sarà di alcuna importanza se la domanda dei loro prodotti aumenterà ancor più. Solo adottando una gestione intelligente delle risorse in aggiunta a tecnologie green, come la CCU, sarà possibile limitare il riscaldamento globale e lasciare un mondo pulito alle generazioni future così come l'abbiamo ricevuto dai nostri genitori.

REFERENCES

[1] M. R. Hannah Ritchie, “CO2 emissions.” https://ourworldindata.org/co2-emissions.

[2] I. Gosh, “A Global Breakdown of Greenhouse Gas Emissions by Sector,” *Vis. Capital.*, 2020, [Online]. Available: https://www.visualcapitalist.com/a-global-breakdown-of-greenhouse-gas-emissions-by-sector/.

[3] IEA, “Putting CO 2 to Use,” *Energy Rep.*, no. September, p. 86, 2019, [Online]. Available: https://www.iea.org/topics/carbon-capture-and-storage/policiesandinvestment/.

[4] “The Paris Agreement.” https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement (accessed Mar. 15, 2021).

[5] T. Wilberforce, A. Baroutaji, B. Soudan, A. H. Al-Alami, and A. G. Olabi, “Outlook of carbon capture technology and challenges,” *Sci. Total Environ.*, vol. 657, pp. 56–72, 2019, doi: 10.1016/j.scitotenv.2018.11.424.

[6] M. C. Romano, P. Chiesa, and G. Lozza, “Pre-combustion CO2 capture from natural gas power plants, with ATR and MDEA processes,” *Int. J. Greenh. Gas Control*, vol. 4, no. 5, pp. 785–797, 2010, doi: 10.1016/j.ijggc.2010.04.015.

[7] CockrellSchool, “Flexible Operation of Carbon Dioxide (co2) Capture at Coal-Fired Power Plants Part 1”,” 2010.

[8] C. Dhoke *et al.*, “Sorbents screening for post-combustion CO2 capture via combined temperature and pressure swing adsorption,” *Chem. Eng. J.*, vol. 380, no. July 2019, p. 122201, 2020, doi: 10.1016/j.cej.2019.122201.

[9] A. Alkhudhiri and N. Hilal, “Membrane distillation — Principles , ap- plications , configurations , design , and implementation Developments in Petroleum Science Arsenic Removal by Membrane Distilla- tion Adsorption (Chemical

Engineering),” 2020.

[10] “MTR Membrane Technology & Research.” https://www.mtrinc.com/our-business/natural-gas/co2-removal-from-natural-gas/ (accessed Mar. 30, 2021).

[11] C. Paper, “Advanced Methods of Biogas Purification-a Review,” vol. XLVII, no. November, pp. 470–475, 2017.

[12] G. Zang, P. Sun, A. A. Elgowainy, A. Bafana, and M. Wang, “Performance and cost analysis of liquid fuel production from H2and CO2based on the Fischer-Tropsch process,” *J. CO2 Util.*, vol. 46, no. November 2020, p. 101459, 2021, doi: 10.1016/j.jcou.2021.101459.

[13] “E-fuels: Power of the Future.” https://www.iav.com/en/what-moves-us/e-fuels-power-of-the-future/#:~:text=Synthetic fuels%2C produced from renewable,for sustainable mobility work group. (accessed Oct. 04, 2021).

[14] Amin Taheri Najafabadi, “CO2 chemical conversion to useful products: An engineering insight to the latest advances toward sustainability,” *ResearchGate*, 2013, [Online]. Available: https://www.researchgate.net/publication/260283151_CO2_chemical_conversion_to_useful_products_An_engineering_insight_to_the_latest_advances_toward_sustainability.

[15] T. Compernolle, N. Witters, S. Van Passel, and T. Thewys, “Analyzing a self-managed CHP system for greenhouse cultivation as a profitable way to reduce CO2-emissions,” *Energy*, vol. 36, no. 4, pp. 1940–1947, 2011, doi: 10.1016/j.energy.2010.02.045.

[16] M. He, S. Luis, S. Rita, G. Ana, V. Euripedes, and N. Zhang, “Risk assessment of CO2 injection processes and storage in carboniferous formations: a review,” *J. Rock Mech. Geotech. Eng.*, vol. 3, no. 1, pp. 39–56, 2011, doi: 10.3724/sp.j.1235.2011.00039.

[17] K. Arning, J. O. Heek, A. Sternberg, A. Bardow, and M. Ziefle, “Risk-benefit

perceptions and public acceptance of Carbon Capture and Utilization," *Environ. Innov. Soc. Transitions*, vol. 35, no. July 2018, pp. 292–308, 2020, doi: 10.1016/j.eist.2019.05.003.

[18] "Mars 2020 mission perseverance rover." https://mars.nasa.gov/mars2020/spacecraft/instruments/moxie/.

[19] M. Hecht *et al.*, "Mars Oxygen ISRU Experiment (MOXIE)," *Space Sci. Rev.*, vol. 217, no. 1, 2021, doi: 10.1007/s11214-020-00782-8.

[20] "Industrial Carbon Nanotubes Products," 2021. https://www.cheaptubes.com/product-category/industrial-carbon-nanotubes-products/.

[21] S. Licht, X. Liu, G. Licht, X. Wang, A. Swesi, and Y. Chan, "Amplified CO2 reduction of greenhouse gas emissions with C2CNT carbon nanotube composites," *Mater. Today Sustain.*, vol. 6, p. 100023, 2019, doi: 10.1016/j.mtsust.2019.100023.

AKNOWLEDGEMENTS

Vorrei innanzitutto ringraziare il Prof. Francesco Corvaro ed il correlatore Matteo Vitali per avermi permesso di conoscere ed approfondire questo tema molto interessante e ad alto potenziale, seguendomi con grande disponibilità durante questi mesi di lavoro e fornendomi consigli preziosi.

Vorrei ringraziare la mia famiglia per avermi sempre sostenuto in questi anni, dandomi forza e spronandomi a fare sempre meglio, e per essermi stata vicina nei momenti difficili.

Agli amici di una vita che, anche se lontani per scelte diverse, mi sono sempre stati vicino, hanno condiviso con me momenti importanti e continueranno a farlo.

Agli amici di Fermo, conosciuti all’università e nelle situazioni più disparate con cui ho condiviso questo percorso con allegria e spensieratezza anche quando di spensieratezza ce n’era ben poca, trasformando normali serate in momenti indimenticabili.