MASTER THESIS

MASTER IN INDUSTRIAL ENGINEERING

Reverse emissions: The latest pathways to transform CO_2 into solid carbon and other storable value-added products

REPORT

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SUMMONS: February 2023

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ABSTRACT

Currently, the main cause of climate change are greenhouse gas emissions into the atmosphere. These gases are mostly expelled when fossil fuels are burned for energy. One of the most important ones is carbon dioxide.

The need to avoid CO_2 emissions into the atmosphere increases exponentially as the years go by since its emissions are causing sudden changes in the planetary temperature and global climatic changes. Several approaches and new technologies are being documented to mitigate the increase in these types of emissions. For this purpose, carbon capture, storage and utilization technologies have drawn global attention as a solution to the emission reduction requirement. They presume to be a permanent solution for the CO_2 emissions problem.

In order to find an efficient usage and transformation process of these CO_2 emissions captured, an extended bibliographical research has been made. The main targets of these transformations have been five value-added products that complement several chemical industries: coal, methanol, methane, dimethyl ether, and polymers.

Thus, CO_2 from exhaust gases could be transformed into new products or precursors of many others valuable to the industry. These technologies help to mitigate the impact to the atmosphere and can improve both the global economy and the scarcity of raw materials, as well as helping to create a closed and clean cycle of carbon life.

Keywords: Carbon dioxide, greenhouse gas emissions, carbon capture and storage or utilization technologies, coal, methanol, methane, dimethyl ether, polymers.

RESUM

Actualment, la causa principal del canvi climàtic són les emissions de gasos d'efecte hivernacle a l'atmosfera. Aquests gasos s'expulsen principalment quan es cremen combustibles fòssils per obtenir energia. Un dels més importants és el diòxid de carboni.

La necessitat d'evitar les emissions de CO_2 a l'atmosfera augmenta exponencialment amb el pas dels anys, ja que les emissions estan provocant canvis bruscos en la temperatura planetària i canvis climàtics globals. S'estan documentant diversos enfocaments i noves tecnologies per reduir l'augment d'aquest tipus d'emissions. Amb aquest propòsit, les noves tecnologies de captura, emmagatzematge i ús del carboni, han cridat l'atenció mundial com una solució al requisit de reducció d'emissions. Presumeixen de ser una solució permanent al problema de les emissions de CO_2.

Per tal de trobar un procés eficient d'aprofitament i transformació d'aquestes emissions de CO_2 capturades, s'ha dut a terme una investigació bibliogràfica extensa. Els objectius principals d'aquestes transformacions han estat cinc productes d'alt valor que complementen diverses indústries químiques: carbó, metanol, metà, dimetil èter i polímers.

Així, el CO_2 dels gasos d'escapament es podria transformar en nous productes o precursors de molts d'altres valuosos per a la indústria. Aquestes tecnologies ajuden a mitigar l'impacte a l'atmosfera i millorar tant l'economia global, com l'escassetat de primeres matèries, a més d'ajudar a crear un cicle tancat i net de vida del carboni.

Paraules clau: Diòxid de carboni, emissions de gasos d'efecte d'hivernacle, tecnologies de captura i emmagatzematge o utilització, carbó, metanol, metà, dimetil èter, polímers.

RESUMEN

Actualmente, la principal causa del cambio climático son las emisiones de gases de efecto invernadero a la atmósfera. Estos gases se expulsan principalmente cuando se queman combustibles fósiles para obtener energía. Uno de los más importantes es el dióxido de carbono.

La necesidad de evitar las emisiones de CO_2 a la atmósfera aumenta exponencialmente con el paso de los años ya que sus emisiones están provocando cambios bruscos en la temperatura planetaria y cambios climáticos globales. Se están documentando varios enfoques y nuevas tecnologías para mitigar el aumento de este tipo de emisiones. Con este propósito, las nuevas tecnologías de captura, almacenamiento y utilización de carbono han llamado la atención mundial como una solución al requisito de reducción de emisiones. Presumen de ser una solución permanente al problema de las emisiones de CO_2.

Con el fin de encontrar un proceso eficiente de aprovechamiento y transformación de estas emisiones de CO_2 capturadas, se ha realizado una extensa investigación bibliográfica. Los principales objetivos de estas transformaciones han sido cinco productos de alto valor que complementan varias industrias químicas: carbón, metanol, metano, dimetil éter y polímeros.

Así, el CO_2 de los gases de escape podría transformarse en nuevos productos o precursores de muchos otros valiosos para la industria. Estas tecnologías ayudan a mitigar el impacto en la atmósfera y pueden mejorar tanto la economía global como la escasez de materias primas, además de ayudar a crear un ciclo cerrado y limpio de vida del carbono.

Palabras clave: Dióxido de carbono, emisiones de gases de efecto invernadero, tecnologías de captura y almacenamiento o utilización, carbón, metanol, metano, dimetil éter, polímeros.

CONTENT

ABBREVIATIONS

TFM: Master degree thesis.

GHG: Greenhouse gases.

CCS: Carbon capture and storage.

IEA: International Energy Agency.

EOR: Enhanced oil recovery.

CCU: carbon capture and utilization.

CCUS: Carbon capture, utilization, and storage.

DAC: Direct air capture.

ONU: United Nations Organization.

COP: Conference of the Parties to the United Nations Framework Convention on Climate Change.

ASU: Air separation unit.

MAP: Modified atmosphere packaging gas.

LM: Liquid metal.

DMF: Dimethylformamide.

HTES: High temperature electrochemical synthesis.

ISRU: In Situ Resource Utilization.

SOXIE: Solid oxide electrolysis unit.

MOXIE: Mars Oxygen In-Situ Resource Utilization Experiment.

CRI: Carbon recycling international.

ETL: Emissions-to-liquids.

DMTM: Direct methane to methanol.

SNG: Synthetic natural gas.

EIA: Energy Institute Agency.

DME: Dimethyl ether.

PTFE: Polytetrafluoroethylene.

CFC: Chlorofluorocarbon.

LPG: Liquefied petroleum gas.

LCA: Life cycle analysis.

1. INTRODUCTION

Climate change refers to long-term changes in temperatures and weather patterns. It refers to changes in the climatic conditions of a specific place compared to the normal climatic conditions of that same site. It can be measured and quantified using, for example, m^3 of rainfall, temperatures, among others. As an overview of the problem, burning fossil fuels generates greenhouse gas emissions that act like a blanket that envelops the Earth, trapping the sun's heat and raising temperatures. In comparison, weather changes can occur naturally but only involve changes for a short period of time, meanwhile, climate changes refer to climate conditions changing over a long period of time, like hundreds of years.

First, it is necessary to clarify two concepts that, although they are closely related, are often mistakenly taken as synonymous: climate change and global warming. There is an important difference, global warming is, in fact, the cause of climate change. That means that the increase in the temperature of the planet caused by emissions into the atmosphere of greenhouse gases derived from human activity, are causing variations in the climate that would not occur naturally.

The Earth has already warmed and cooled on other occasions naturally, but these cycles had always been much slower, needing millions of years. Now and as a result of human activity, the levels that are being reached have brought extinctions and important changes in the population and the biosphere in just two hundred years in the past (see Figure 1).

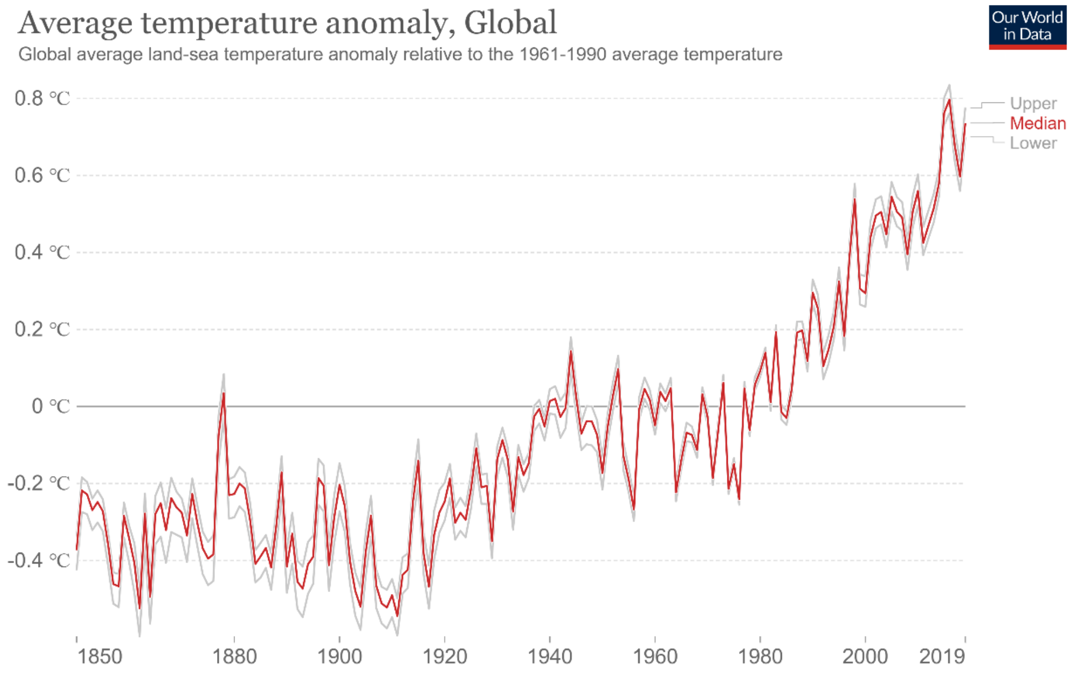


Figure 1: Global average land-sea temperature anomaly relative to the 1961-1990 average temperature (1)

Currently, the main cause of climate change are greenhouse gas emissions into the atmosphere. These gases are mostly expelled when fossil fuels are burned for energy, for example gas, oil, coal.

As discussed above, the consequences of these emissions are more noticeable in long term. There are small year-to-year fluctuations in temperature and the specific temperature increase depends on what year is taken as a reference, but overall, global temperature rise is in the range of 1 to 1,2 ºC (2). The biggest challenge in terms of avoiding this climate change is that all the solutions that can be carried out or found nowadays, will take many decades to be effective and the consequences of environmental mismanagement will continue to be paid for many more years.

It's important to note that there is a lag between atmospheric concentrations and final temperature rise, this means that when population finally manage to stabilize atmospheric CO_2 concentrations, temperatures will continue to slowly rise for years to decades. It's not only the level of change of CO_2 concentrations in the atmosphere that matters, but also the rate that this has changed. Historical changes in CO_2 concentrations tended to occur over centuries or even thousands of years. It took us a matter of decades to achieve even larger changes. This gives species, planetary systems, and ecosystems much less time to adapt (2).

The need to avoid CO_2 emissions into the atmosphere increases exponentially as the years go by. Large quantities of greenhouse gas emissions are causing sudden changes in the planetary temperature and global climatic changes. Specifically, the level of carbon dioxide emissions has increased in recent decades due to the high degree of anthropogenic emissions. This emission has resulted in increased CO_2 concentration from about 270 ppm during the pre-industrial era to over 416 ppm in 2021, which represents an increase of around 50% (3).

According to The Global Carbon Project report (4), in 2021 more than 36.000 Mt of CO_2 were produced, an increase of 4,9% compared to 2020. Analysing previous data, it has been concluded that these data represent a similar rise to the rebound that followed the financial global crisis of 2008, which had a growth of 5% in 2010.

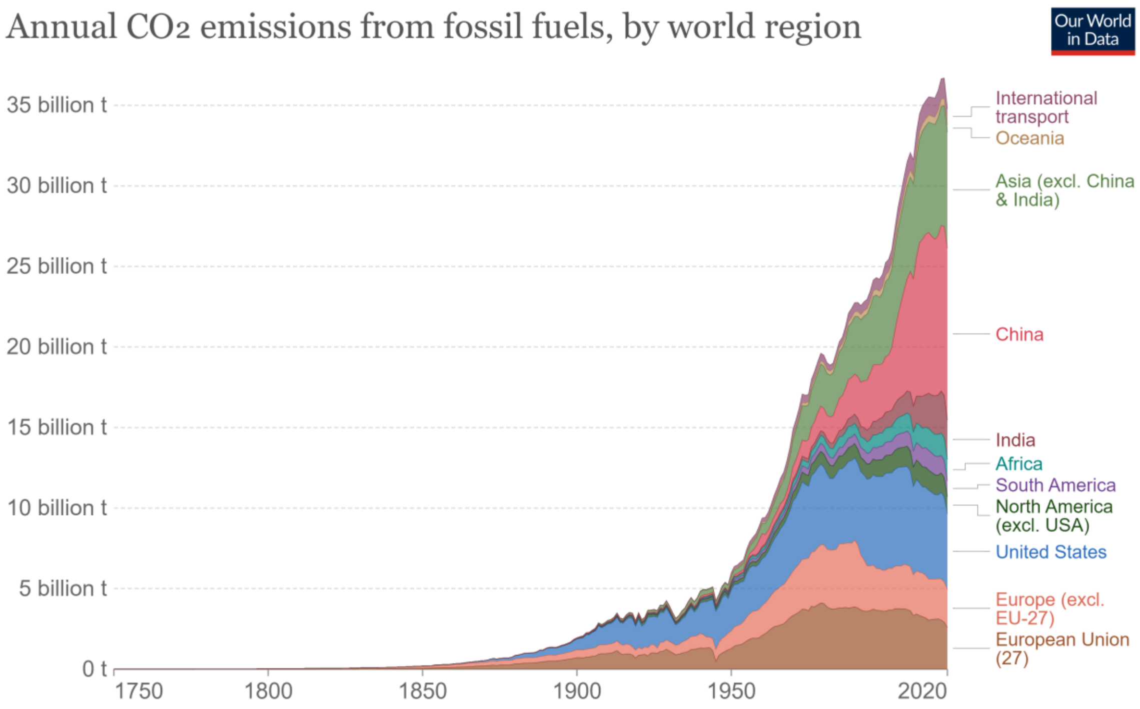


Figure 2: Fossil fuel and industry emissions by world region. (5)

Note that Spain cut back 17,2% of its CO_2 emissions during the first year of the pandemic caused by COVID19. In Spain, emissions in 2020 were 208,9 Mt of CO_2, which represents a decrease of 17,2% compared to 2019 levels. Globally, this reduction was 5,4% in 2020, mainly due to lockdowns during the pandemic year (6).

As shown in Figure 2, Asia is by far the largest emitter, accounting for 53% of global emissions. Nevertheless, the fact that 60% of the world's population is located in Asian territory causes Asia's per capita emissions to be slightly lower than the world average. Specifically, China emits more than a quarter of annual global emissions. In the opposite case it is found Africa or South America, which together only represent approximately 7% of global emissions (5).

For all this reasons, several approaches and new technologies are being documented to mitigate the increase in these types of emissions. Carbon capture technologies have drawn global attention and importance as a solution to the agreed emission reduction requirement (see Figure 3). Firstly, carbon capture and storage, from now on CCS, technology was presented. This technology was first used in the 1970s, even though the capture of CO_2 has been done since the 1920s. It was first implemented in Texas, USA, where CO_2 captured from a gas processing facility was separated and placed into a boost oil recovery. By September 2021, 27 large-scale CCS facilities are operating worldwide with 4 more under construction (7).

Additionally, a total of 67 commercial CCS facilities exist (8):

- 27 are operational.
- 2 have suspended operations due to an economic downturn or due to fire.
- 4 are under construction.
- 13 are in advanced development reaching front end engineering design.
- 21 are in early development.

Projects at advanced stages of planning represent a total estimated investment of more than 27 billion dollars, almost double the investment in projects commissioned since 2010. Even though these numbers have represented an increase of almost 50% compared to the 2019 data, the high costs of CCS technologies have made their commercial deployment quite difficult.

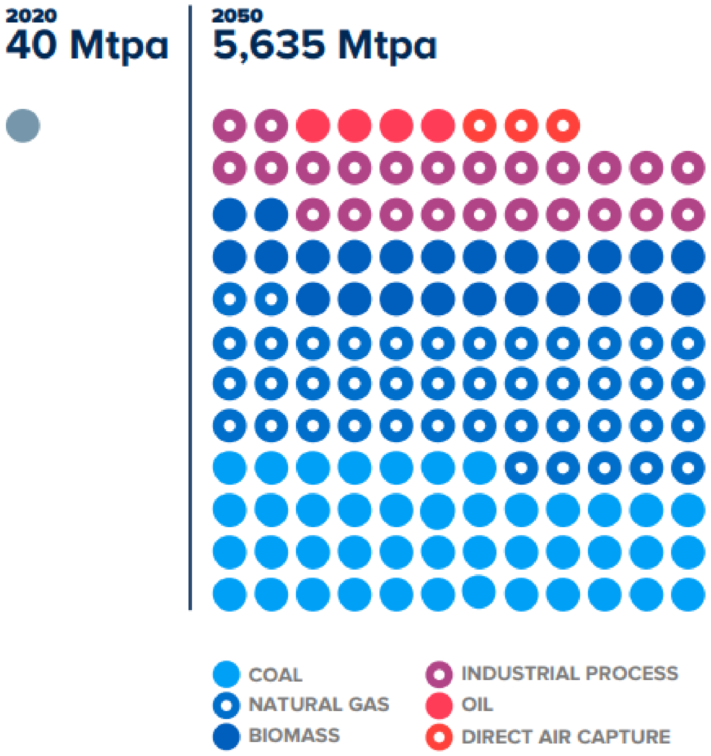


Figure 3: CO_2 carbon capture capacity in 2020 and 2050 by fuel and sector in the IEA sustainable development scenario (8)

Depending on the origin of the CO_2 stored underground, this type of plants can be divided into two large groups, encompassing in them the majority of CCS facilities existing today:

- From gas processing facilities: There they extract natural gas from underground fields. In natural gas refining processes, it is common to remove CO_2 to increase its purity and enhance its properties and thus, be able to sell it.

- From power plants: Fossil fuels are burned and produce, in greater proportion, CO_2 as a product of combustion. In these facilities it is not an essential requirement, as in those mentioned above, to capture these CO_2 emissions. Incorporating a CO_2 capture and separation process increases the overall cost and is a practice purely developed to reduce the environmental impact of the process.

Enhanced oil recovery facilities, from now on EOR, revalue CO_2 and transform it as a by-product of the actual process so it is another monetary source. The CO_2 is often extracted from the oil field along with the oil, but it can be separated and reused to produce yet more oil. Additionally, when all the oil has been produced, the CO_2 can be permanently stored in the depleted oil field. This overall process prevents the emission of the CO_2 used for the extraction into the atmosphere (9).

Regarding the storage options of these CO_2 captured, it can be stored in deep geological formations and solid storage by reaction of CO_2 with metal oxides to produce carbonates. Additionally, it was once suggested that CO_2 could also be stored in oceans, but it has been demonstrated that this process could add to ocean acidification. Geologic carbon sequestration stores CO_2 in deep geologic formations. Carbon dioxide is compressed up to 100 bar to convert into a supercritical fluid and injected around 1 km deep. On the other hand, biological carbon sequestration involves the removal of CO_2 by micro-organisms and store it in vegetation and soils and woody products.

As mentioned before, CCS facilities have very high maintenance and operating costs, this has been the main reason why they have evolved to carbon capture and utilization, from now on CCU, facilities. This is a potential alternative to CCS and presumed to be a permanent solution for CO_2 problem. The CCU option delivers a benefit relative to the CCS pathway regarding the reuse of a once considered waste to become an alternative resource to fossil fuels. Nevertheless, several studies comparing CCS to CCU routes suggested that CCS has a larger CO_2 mitigation potential, however, the additional opportunities offered by CCU are worth studying and exploiting in the near future (10).

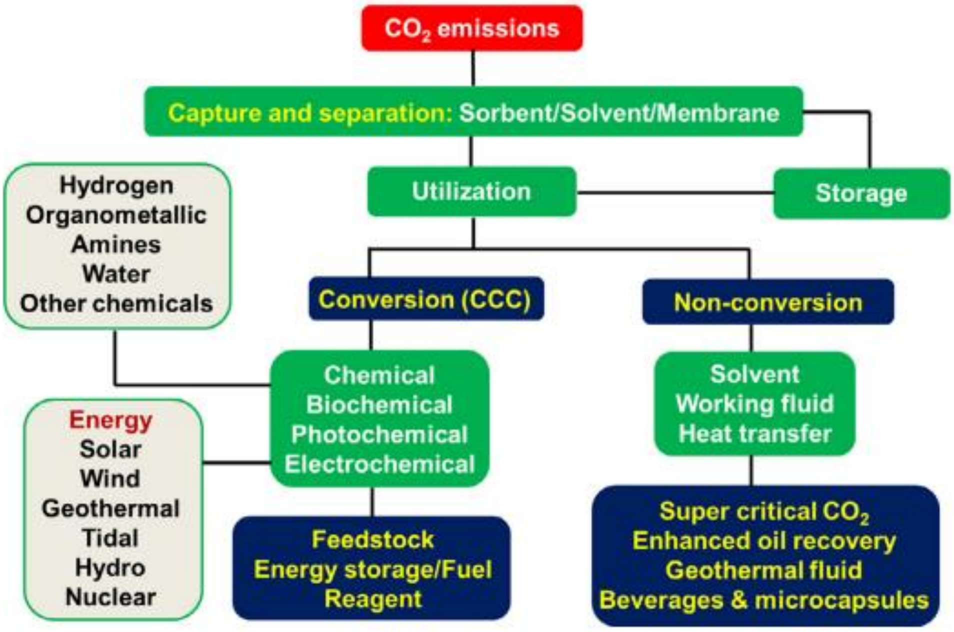


Figure 4: CO_2 capture and utilization (CCU) process (11)

This CO_2 captured and stored, can lately be used as a forerunner of numerous value-added products (see Figure 4). Direct use of CO_2 involves using it at its pure state or alternatively suspended in a solution. On the other hand, its indirect utilization converts CO_2 into chemicals, materials or fuels through different chemical and biological processes (12). These technologies, while reducing the global emission rate of CO_2, also valorise CO_2 to produce various products that complement chemical industries.

The main target to be presently explored, is to transform this captured CO_2 into substances that can be stored and transported easily. This can improve both the global economy and the scarcity of raw materials, as well as helping to close the cycle of carbon life. This technology is known as carbon capture, utilization, and storage (CCUS).

2. OBJECTIVES

The main purpose of this project is to contribute to the study of the latest pathways to transform carbon dioxide emissions into value-added storable products.

The specific goals for the present project are the following ones:

- To conduct a bibliographical search aimed at describing the actual scenario and importance of the carbon dioxide emissions worldwide.
- To conduct a bibliographical study focused on the transformation of these emissions into five main storable products with high industrial interest: coal, methanol, methane, dimethyl ether, and polymers.
- To outline the most innovative projects currently related to carbon dioxide emissions reduction.

2.1. Scope of the project

The aim is to carry out a detailed study considering the hole process and techniques of separating carbon dioxide from industrial flue gases until its final transformation into value-added products. Special interest has been paid to the synthesis of these five products mentioned above due to their special interest both as final products, and for their use as precursors in multiple industries.

This study aims to contextualize, encompass, and summarize the techniques developed to date in order to be used as a source of synthesized information on the subject.

3. FRAME OF THE STUDY

3.1. Carbon dioxide

Carbon dioxide, from now on CO_2, is a colourless gas and one of the most important greenhouse gases linked to global warming. It is a minor component of Earth's atmosphere formed in combustion of carbon-containing materials, fermentation, and in respiration of animals and employed by plants in the photosynthesis of carbohydrates. Its presence in the atmosphere avoids that some of the radiation energy entering the Earth to be returned to space.

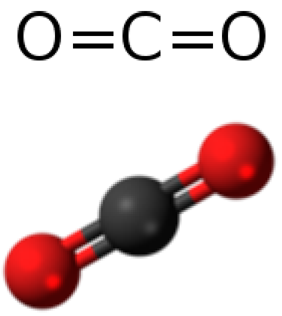
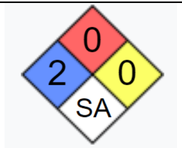


Figure 5: CO_2 structure (13)

CO_2 is soluble in water and is naturally found in groundwater, lakes, ice caps, and seawater. When carbon dioxide dissolves in water, it forms carbonic acid which may cause ocean acidification while atmospheric CO_2 levels increase.

It is widely used in industry as a precursor of several value-added products, as a by-product of various preparations such as hydrogen from ammonia synthesis, in lime kilns, among others. It is also known to be used as a refrigerant, in fire extinguishers, for foaming rubber and plastics, and in carbonated beverages.

Table 1: Carbon dioxide properties

CAS Number	124-38-9
Molar mass [g/mol]	44,009
Solubility in water (at 25 ºC and 100 KPa) [g/L]	1,45
Dipole moment [D]	0
Heat capacity [J/mol·K]	34,135
Hazards	

3.2. Main CO_2 sources

Carbon dioxide comes from a variety of sources, from extensive industrial practices such as energy production, steel, and cement industries, to medium-scale sources emanating from commercial and industrial buildings to small-scale sources such as the transport sector (10).

Most emissions are related to the combustion of fossil fuels, whether for energy production, oil refining or for their use in a wide and diverse number of industrial activities. It is known that 87% of all human-produced carbon dioxide emissions come from the burning of fossil fuels (14). The concentration of carbon dioxide in these flue gases is strongly linked to the type of fuel and combustion conditions. As an example, carbon dioxide from highly concentrated high-pressure flows can be easily separated, while it is more expensive and complicated to capture from low-concentration sources.

Air can be considered as another source of carbon dioxide, where its concentrations are around 400 ppm. Direct air capture, known by its acronym DAC, can be carried out through the process of photosynthesis, the formation of metal carbonates or using adsorbent components. Among them, the technology most used to capture CO_2 uses potassium or sodium hydroxides (KOH or NaOH) that react with carbon dioxide and form a carbonate. The subsequent precipitation of this carbonate in the form of calcium carbonate allows the captured carbon dioxide to be separated.

Additionally, solid amines are also used for the adsorption of CO_2 since their subsequent separation is relatively easier and more energy efficient. This high energy demand of the separation process in DAC technologies is their biggest drawback as it represents most part of the costs of implementing these applications compared to capturing CO_2 from high concentration sources (10).

3.3. Current situation and future horizon of global CO_2 emissions

Over the years, new records for CO_2 concentration in the atmosphere have been broken. With each breath of air that people exhale, CO_2 is released to the atmosphere. This shows that, in general, it is not a toxic gas for people, and yet, it is key in global warming. These emissions not only affect to other atmosphere gases and global warming, but also the oceans temperatures and land conditions. "*Global climate monitoring must cover the entire Earth system, from the atmosphere to the oceans, from the cryosphere to the biosphere, and encompass the water cycle and energy and greenhouse gas budgets*" said World's Meteorological Organization Secretary-General Professor Petteri Taalas (15).

Carbon dioxide is the main greenhouse gas emitted in anthropogenic activities. These human activities have caused an increment of around 1,0 ºC of global warming in comparison to the pre-industrial level. The carbon cycle has become one of the most important biogeochemical cycles in the earth-atmosphere system. This cycle is directly related to climate change because carbon dioxide accounts for about 60% of the heat-trapping effects of all greenhouse gases. This gas has great potential to affect the Earth's biosphere and climate in the future, which is why it draws everyone's attention to prevent unwanted changes.

To contextualize the current situation regarding greenhouse gas emissions, where CO_2 emissions are included, it is necessary to emphasize the Kyoto Protocol and the COP 21. On December 11, 1997, 84 countries signed and 46 ratified the Kyoto Protocol at the Climate Summit, an international agreement sponsored by the United Nations Organization (ONU). Its objective was the commitment of all the signatory parties for the reduction of greenhouse gas emissions.

Later, the 21^{st} Conference of the Parties to the United Nations Framework Convention on Climate Change (COP 21) held in Paris in 2015, concluded with the adoption of the Paris Agreement, which would take effect from 2020. The triple objective agreed at this conference was: to limit the average increase in global temperature to 2 ºC compared to pre-industrial levels, increase measures and regulations so as not to exceed the 1,5 ºC level by the end of this century and achieve climate neutrality in 2050 (16) (17).

These measures are still in force nowadays, however, in 2018, the world reached a record high of 55,3 Gt CO_2 emissions. Currently, even fulfilling all the measures agreed at COP 21 for 2030, greenhouse gas emissions would be more than 35% higher than those necessary to meet the maximum of 1,5 ºC agreed (18). In fact, following current global dynamics, by 2100 the Earth's temperature could increase more than 3 ºC in comparison to pre-industrial levels (19).

As mentioned before, there was a notorious decline in CO_2 emissions due to the COVID19 pandemic occurred in 2020. In 2021 global energy-related CO_2 emissions have rebound and grow as demand for coal, oil, and gas rebounds with the economy. China's CO_2 emissions increased by 750 Mt over the two-year period between 2019 and 2021, it was the only major economy to experience economic growth in both 2020 and 2021 (see Figure 6). The increase of over 1.500 Mt of CO_2 would be the largest single increase since the carbon intensive economic recovery from the global financial crisis from 2008. By the end of 2021, global emissions were 1.2% below the 2018 peak (20) (21).

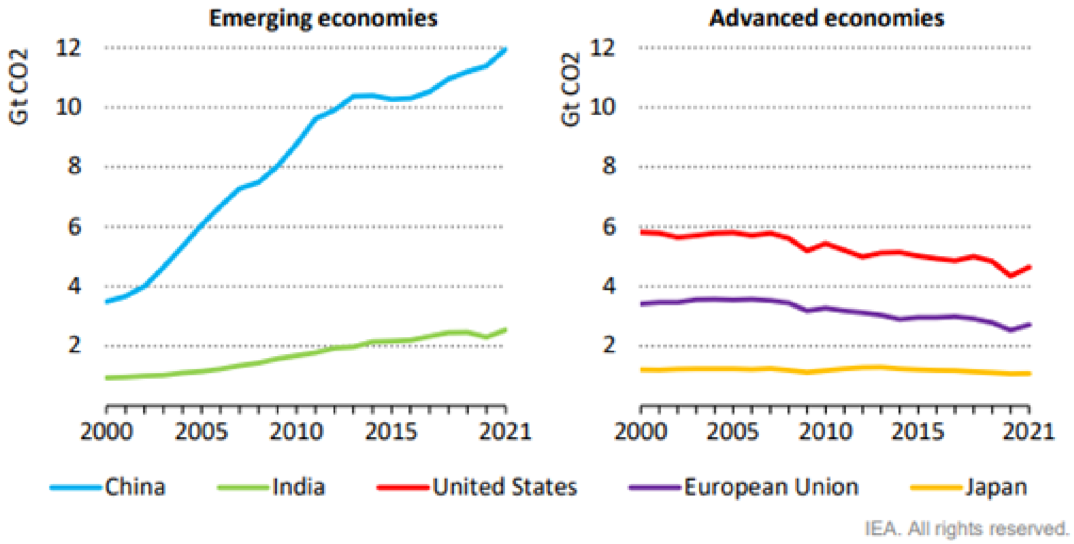


Figure 6: CO_2 emissions in selected emerging and advanced economies data from 2000 to 2021 (21)

The world's largest per capita CO_2 emitters are the major oil producing countries, most of them located in the Middle East. In 2017 Qatar had the highest emissions at 49 tons per person, followed by Trinidad and Tobago, Kuwait and United Arab Emirates. Nevertheless, many of them have small populations and this leads them to have low total annual emissions. On the other hand, one of the most populous countries that have one of the highest per capita emissions are the United States, Australia, and Canada. These countries just mentioned had registered levels of emissions more than three times the global average (5).

It is obvious that depending on the main energy sources that a country has, it will impact in a higher or lower way on the level of global emissions. France is a clear example of a country with mainly renewable and nuclear energy sources. This leads to a much lower percentage of electricity production from fossil fuels, being only 5% in 2015 (5), which causes lower total annual emissions of the country.

Even though energy-related CO_2 emissions may seem to be the most contributing to global warming, it has been proven that the household sector is a major contributor to greenhouse gas (GHG) emissions, accounting for more than 60% of global GHG emissions (19). In particular, the contribution of each country is notoriously different according to its development level, with the largest contributors being the USA, China, and Canada.

The projected horizon for both 2030 and 2050 does not predict a prominent improvement in the amount of GHG emissions. The current crisis of resources and energy sources such as coal or gas due to the Russian conflicts, has not helped governments to focus their attention on reducing emissions. As mentioned before and based on a business-as-usual trend, the objectives proposed at the COP 21 will not be accomplished.

3.4. Hazards of CO_2 emissions

Greenhouse gases, such as CO_2, are necessary to contribute to the Earth to achieve and maintain a tolerable global temperature that allows life to develop. Without CO_2 or water vapor on the atmosphere, the average temperature of the Earth would be about -33 °C, which would make life unviable. However, excess CO_2 emissions accentuate the greenhouse effect, which reduces the dispersion of heat accumulated by solar radiation on the planet's surface into space and causes greater global warming.

The risk of this type of emissions are many. It is estimated that the increase in CO_2 levels has a direct impact on the summer temperature of the northern hemisphere, while extreme tropical precipitation on the southern one. On the other hand, one of the most prominent risks is the melting of glaciers and polar ice caps, causing a notorious rise in sea level and consequently, accelerating the increase in global temperature. This future situation can be seen as a vicious cycle, not only because the frozen surfaces on Earth will no longer exist, but also because that mass of ice nowadays reflects part of the solar radiation, which the planet would otherwise absorb and increase its temperature.

Additionally, climatic phenomena such as storms and even hurricanes could occur more frequently. This type of extreme weather will make it more difficult for some plant and animal species to survive, so that the loss of biodiversity could be another consequence.

In regard to humans, CO_2 is not toxic, in the sense of harm or poisoning by inhalation, since it is really a gas that living beings exhale in their breathing process. CO_2 produces oxygen displacement and in high concentrations, more than 30.000 ppmv, then it can cause suffocation. In these high concentrations it can also cause headaches, lack of concentration, dizziness, and some other respiratory problems.

4. CO_2 CAPTURE AND SEPARATION TECHNIQUES

To capture and separate the carbon form CO_2, it is previously required to partition CO_2 from a mixture of exhaust gases. Techniques such as adsorption, absorption, membrane separation, cryogenic separation or the use of physical and chemical solvents are the most employed to develop this task (22).

The major issue faced lately is to produce a high concentrated CO_2 stream without neglecting the purity requirement. Furthermore, the process must be viable from economic and energy aspects so that the energy consumption must be as low as possible while keeping high CO_2 recovery, always above 90%. Financially, carbon capture projects currently cost around 100 \$/tCO_2 and are expected to drop to around 40 \$/tCO_2 by 2030. This will encourage the rollout of the technology on a commercial scale (10).

Carbon dioxide from flue gases can be captured via three main technologies listed below (23) (24).

- Carbon capture with separation:
    - Pre-combustion capture: Removal of carbon dioxide before combustion. The carbon dioxide is separated and H_2 is used for combustion to produce energy. It leads to carbon-free fuels. Normally via absorption, adsorption or using membranes.
    - Post-combustion capture: Combustion occurs normally, and the carbon dioxide removal takes place in the fuel gas. Normally via chemical absorption or using membranes. Appropriate for exhaust gases with low CO_2 concentrations (4-14 % v/v).
- Carbon capture without separation:
    - Oxy-fuel combustion: Combustion takes place in a pure oxygen environment. Complete absence of NOx and SOx components in the flue gas and high concentrations of CO_2. Normally via adsorption or using membranes.

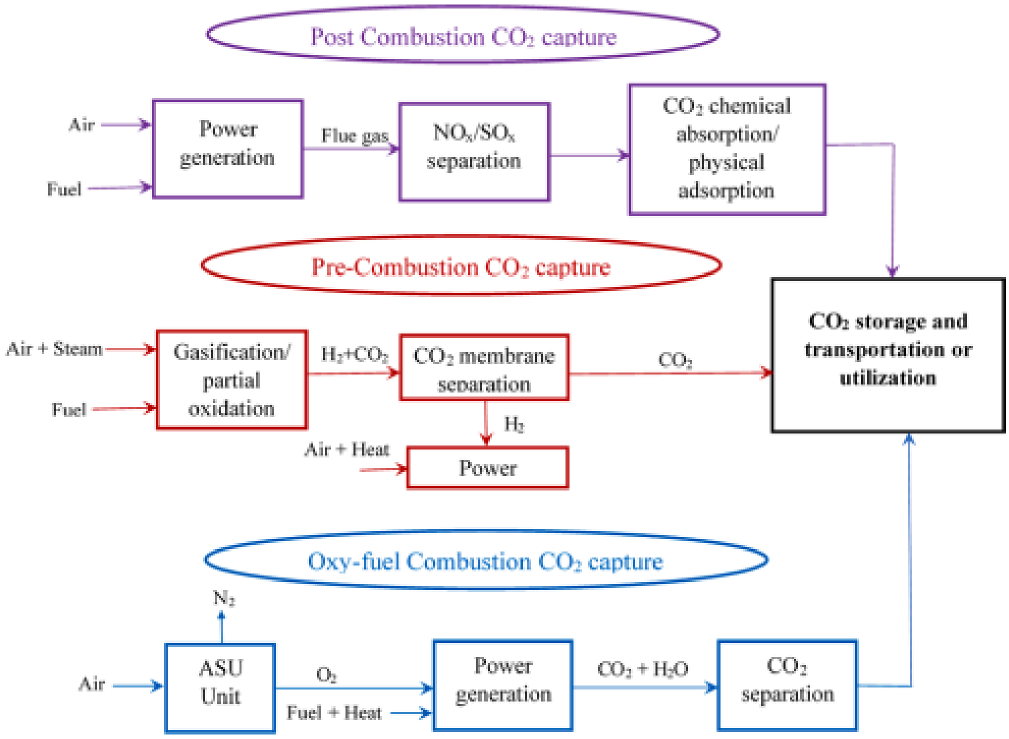


Figure 7: Schematic flow diagram of various CO_2 capture technologies (25)

The first method listed above consists of capturing CO_2 from the synthesis gas stream before combustion. In this case, the carbon is removed directly from the coal before it is used in the gas steam. For this purpose, firstly, a partial oxidation of the coal is done by gasification with oxygen or air being present. A mixture of carbon monoxide, hydrogen and minor traces of methane is produced, also known as syngas or synthetic gas. The produced syngas is passed through a gas purifier reactor where CO converts to CO_2 (see red pathway in Figure 7).

Different separation techniques are used to separate the large amounts of hydrogen produced from the CO_2. The most used ones are absorption, physical and chemical adsorption, and membrane separation processes (24).

For pre-combustion separation via absorption, physical solvents are normally used. The main benefits of this method are the low cost and elevated stability; however, its main drawbacks are the elevated energy demand, high corrosiveness, and high global cost. Currently, ionic liquids have been classified as viable alternatives to the traditional physical solvents used since they present low requirements, including regeneration demand energy. Then again, the adsorption capture process includes the bulk phase transfer of CO_2 molecules in the flue gas to a solid surface, normally performed at atmospheric pressure and high temperatures. This capture technique is the most promising method among others since it presents long-term stability, lowest regeneration cost and is inexpensive. Conversely, membranes technologies are expensive due to the large quantity of energy required to pressurize the gas and more research is needed for material development and composition design (22).

The captured CO_2 can be then dried, compressed, and finally sequestered. Moreover, the hydrogen previously produced can also be used as a source of energy or as a raw material for other industrial processes.

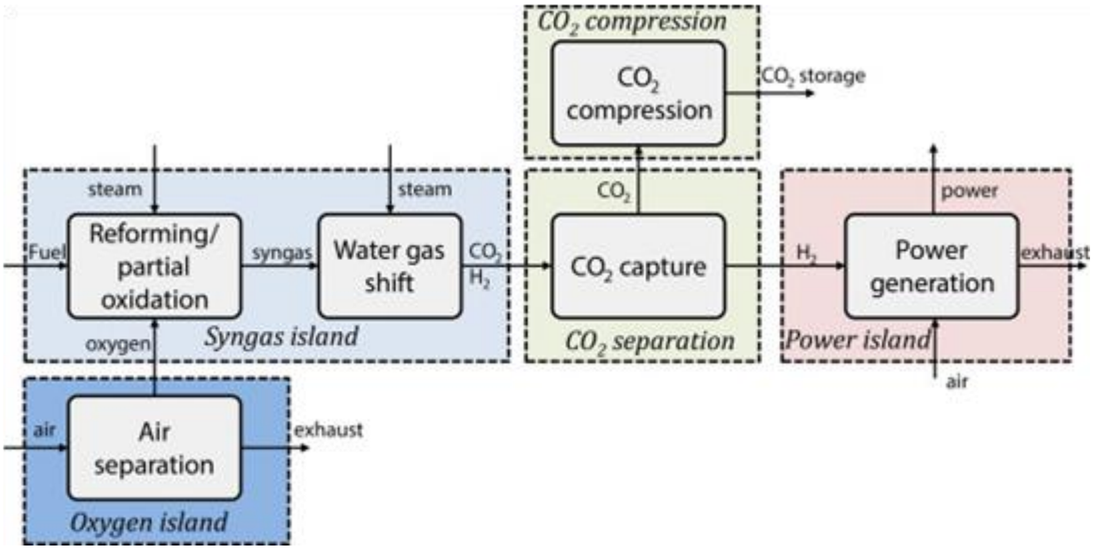


Figure 8: Schematic of pre-combustion capture for power generation (26)

On the other hand, post-combustion capture normally involves the removal of CO_2 from burning fossil fuels, which makes it difficult to be separated due to its high temperatures and severe conditions (see violet pathway in Figure 7). Researchers have shown absorption to be the most complete post-combustion capture technique. Absorption gas separation techniques have been applied mainly in petrochemical industries and power plants.

However, these absorption technologies have some important limitations related to high energy consumption, corrosion, and solvent degradation. Membrane separation has shown a high potential for becoming the most environmentally friendly technology since it does not involve the use of any chemical, high temperature or pressure for its regeneration. Finally, the increase in the use of adsorption technologies relies on the development of new adsorbents with higher CO_2 capacity and low heat capacity. Even though being at an initial stage of research it has shown that these new adsorbents will be able to perform better than other technologies available nowadays (27) (23).

Carbon capture without separation technology does not require any kind of separation technique as the gas stream mainly contains CO_2 and steam. Oxy-fuel combustion is the coal combustion process that take place in an almost pure oxygen environment instead of an air one. The oxygen supplied during the initial stage is done using cryogenic air separation unit. As mentioned before, this combustion generates a flue gas that has a very high concentration of CO_2 and water vapor. Other products formed are particulate matter, such as ashes, and SO_2 which can be eliminated using electrostatic precipitator and a desulfurization respectively (28). It is a big inconvenience if the SO_2 liberated is high in the flue gas because it may result in corrosion of the whole system. In this process cost for CO_2 separation is very low because CO_2 capture can be done from the flue gas by water condensation followed by compressing and storing.

Finally, Oxy-fuel combustion consists of three main components (see blue pathway in Figure 7): air separation unit (ASU) which provides oxygen needed for combustion, the furnace and heat exchangers for combustion and heat exchange, and the CO_2 compression and separation unit. The CO_2 capture and the compression unit normally consist of multi-stage compression and cooling procedures (25).

Researchers have now turned their interest into this last method presented due to CO_2 emission and climate change. Technical feasibility is the major advantage of this process, but the quantity of oxygen required is more which results in high cost (29).

4.1. Overview of captured CO_2 utilization

When CO_2 is used either directly or as a raw material for future materials, the actual number of emissions that will be sent into the atmosphere varies depending on the durability of these products. Each process of CO_2 utilization has a different environmental impact that must be determined in a prior assessment of the life cycle ensuring that the global environmental balance is positive (30).

While CCS is a recognized emission reduction instrument, it is not accounted as a direct emission reduction solution. If CCU can lead to reductions in fossil raw material use, it is possible that CCU indirectly affects emission accounting just as other efficiency measures and its feasibility increases.

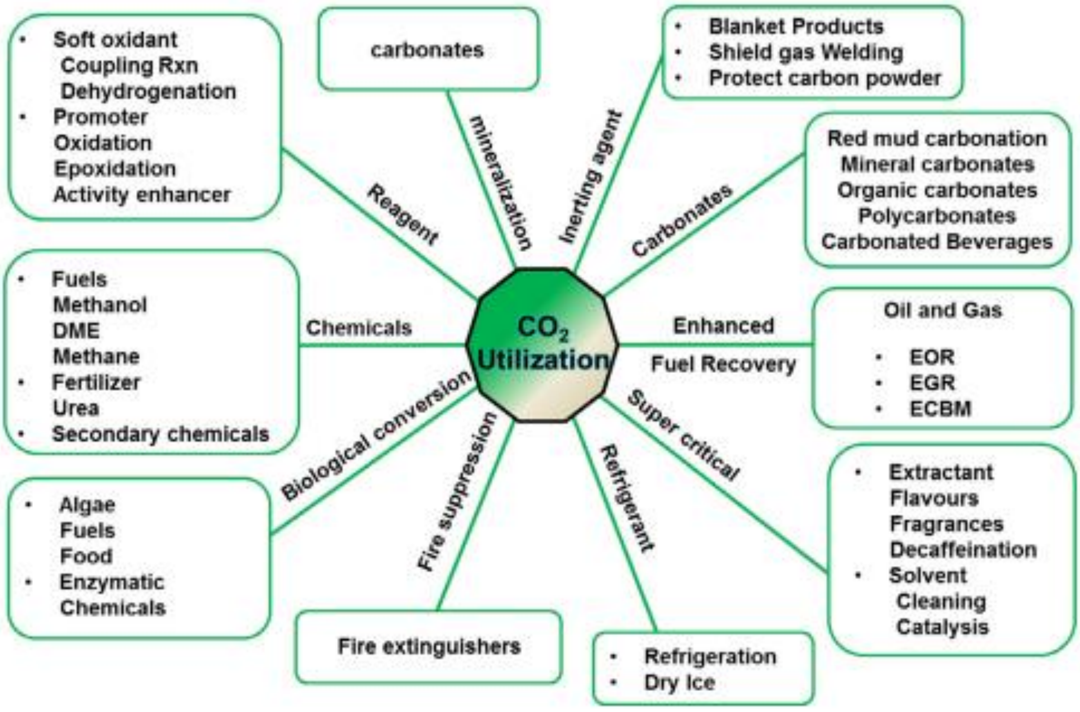


Figure 9: Overview of CO_2 utilization (11)

Figure 9 shows the most common ways to use CO_2. As can be seen, CO_2 is used for carbonated drinks, as a precursor for many value-added products, in cleaning industries, in syngas production from dry reforming, as a promoter, among others. The most familiar use for carbon dioxide is in carbonated drinks such as sparking water, many soft drinks, carbonated alcohols, etc. These carbonated beverages contain between 2,5 to 4,5 % v/v of carbon dioxide.

Furthermore, it is also a substance widely used as a refrigerant, mainly in industrial steam purchasing systems. As far as the food industry is concerned, carbon dioxide has been used lately as a modified atmosphere packaging gas, also known as MAP. Its antimicrobial properties have been used to help preserve fresh foods such as meat and fish. The use of CO_2 atmospheres that displace oxygen in spaces where fresh or packaged food is stored, ensures a more exhaustive control of its biochemical metabolism, and significantly extends its useful life.

Continuing on the direct CO_2 utilization, it is known to be widely used in alternative medical sciences such as carboxytherapy or angiography. Moreover, it is also used extensively in the oil industry to promote the recovery of other gases.

On the other hand, as mentioned before, there are several pathways to use CO_2 as a C1 resource and precursor of many value-added chemicals (see left part in Figure 9). In addition, it is known that its chemical utilization as feedstock or reagent has positive ramifications on efforts towards carbon management (11). The main challenges, or disadvantages, of its use lie in its low reactivity, thermodynamic stability, and high oxidation state (30) (31). There are several ways to deal with these obstacles, for example, by selecting the appropriate reactions that can lead to a negative Gibbs free energy of the reaction or by shifting the equilibrium to the product side.

For instance, the synthesis of urea and its derivates, such as carbamates, isocyanates and quinazolines involves the use of CO_2 as raw material. These derivates are known to be used as anticancer agents, plastic additives, and dyes. Additionally, in the field of electrochemistry, electrical energies from renewable sources are being used for the electrochemical reduction of CO_2. In this way, it can be subsequently transformed into fuel and organic materials by a renewable energy source.

The greatest interest regarding the transformation of CO_2 into value-added products, is to use it as a raw material for methanol, dimethyl ether, and its derivatives (32). These can then be used as fuel and thus help offset their high demands of recent years. By dehydrating methanol, dimethyl ether is produced and can be used as a potential alternative to gasoline and diesel. On the other hand, methanol can also be used for the subsequent production of olefins, such as ethylene or propylene, which are also used to produce synthetic hydrocarbons.

The most common uses mentioned above of CO_2 as a raw material and the transformation technology of each value-added product obtained have been summarized and shown in Table 2 (12).

Table 2: Application and chemical reaction of products from CO_2 conversion

Product	Technology	Application
Syngas	Reforming	Intermediate for the synthesis of various chemicals and fuels
	Hydrogenation	
	Electrochemical	
Urea	Carboxylation	N_2 source for fertilizers, feedstock for adhesives, plastics, and resins
Methanol	Hydrogenation	Additive, feedstock for dimethyl ether, acetic acid, and formaldehyde
	Electrochemical	
	Photochemical	
Algae	Photosynthetic	Synthesis of biodiesel, biogas, biofuel, bio-alcohols, bio-H_2, cosmetics
Dimethyl ether	Hydrogenation	Fuel alternative
Methane	Hydrogenation	Production of compressed natural gas and syngas
	Electrochemical	
	Photochemical	
Formic acid	Hydrogenation	Disinfection and cleaning solution, raw material for perfumes and chemicals such as amides, ketones, and aldehydes.
	Electrochemical	
	Photochemical	
Polyurethane	-	Coatings, sealants, adhesives, foams, and elastomers.

One of the less known uses of captured CO_2 is the underground CO_2 sequestration mechanism. Carried out mostly in the northern European countries, this procedure consists of liquating CO_2 separated from combustion processes and then transporting it by ship to stations where it is injected into depleted oil and gas fields and into the main regional aquifers. For example, in the Sleipner gas field, Sweden, CO_2 is being injected into Utsira Sand, a large saline aquifer. Currently, more than 6 Mt of CO_2 have been injected, with a projected end target of around 20 Mt. Another of Europe's most important aquifers, Bunter Sandstone, stretches from Britain to Poland (33) (34). Reykjavik-based company Carbfix is known as one of the first start-up companies that addresses this problem. "*Basically, we're doing the same thing that nature has been doing for millions of years, so we're helping nature help itself*", declared in 2021 the ones responsible for the company (35).

5. STORABLE VALUE-ADDED PRODUCTS SYNTHESIS FROM CAPTURED CO_2

This section will present the mechanisms, technologies, and applications of CO_2. Paying special attention to the transformation pathways into five value-added substances which can lately be used as raw material for new industrial processes: **coal, methanol, methane, dimethyl ether, and polymers.**

5.1. Coal

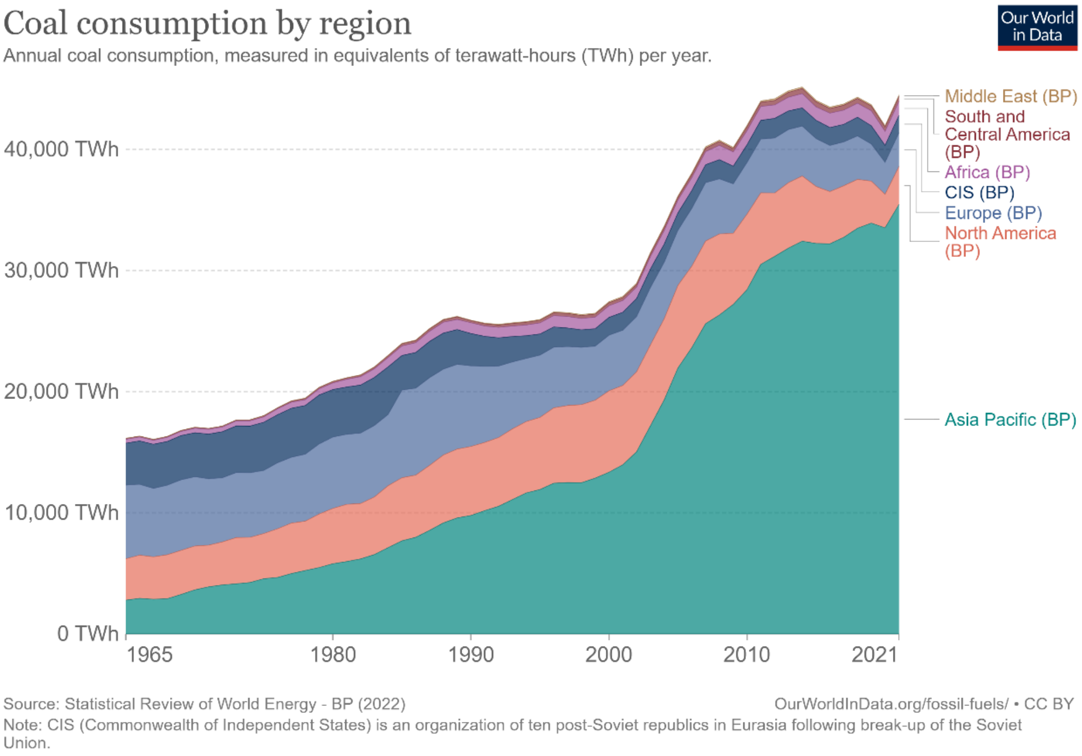
To facilitate the effective storage of captured carbon, reduced products should preferably be solid to prevent accidental release into the environment. That is why the ideal catalyst should allow the reduction of CO_2 to elemental coal materials at high efficiency of the thermodynamic process, thus reversing the combustion of fossil fuels in a minimum energy consumption.

This CO_2 transformation into solid products is one of the most important focuses of research since reducing CO_2 to small molecules such as CO, C_2H_4, CH_4, etc. is not suitable as a solution for the indefinite removal of CO_2 from the atmosphere since they are also volatile compounds and potential pollutants.

Table 3: Coal properties

CAS number	65996-77-2
Chemical formula	C
State at room temperature	Metallic gray solid stones
Density [g/cm^3]	~ 42,27
Molecular weight [g/mol]	12,01
Sublimation point [°C]	3642
Heat of fusion [kJ/mol]	117
Safety pictograms	

In particular, the coal transformation has gained popularity in recent years among the scientific community due to its energy interest. It is a globally known energy source, of which more than 44.000 terawatt-hour equivalents (TWh) were consumed in 2021, being the second most consumed fossil energy source worldwide (36). "*While we can't literally turn back time, turning carbon dioxide back into coal and burying it back in the ground is a bit like rewinding the emissions clock*" Daeneke, an Australian Research Council DECRA Fellow, said (37).



Source: Statistical Review of World Energy - BP (2022) OurWorldInData.org/fossil-fuels/ • CC BY
Note: CIS (Commonwealth of Independent States) is an organization of ten post-Soviet republics in Eurasia following break-up of the Soviet Union.

Figure 10: Annual coal consumption by region, measured in equivalents of terawatt-hours (TWh) per year (38)

The main use of coal is as a fuel. Specifically, in 2020, coal supplied around a quarter of the world's primary energy and more than a third of its electricity (39). The largest consumer and importer of coal in 2020 was China (see Figure 10), accounting for almost half of the world's annual coal production, followed by India with around a tenth. Indonesia and Australia are the countries that export the most, followed by Russia. As mentioned before, coal is currently the largest source of electricity globally and for many countries remains the dominant source.

Due to its high global interest just mentioned, several processes of transformation, or synthesis, of CO_2 into coal have been documented. The most innovative and viable processes are explained in detail below.

5.1.1. Via LM-based catalysts

The CO_2 transformation into solid materials is challenging as the solid products obtained from the reaction, can then cover the surface of the catalysts used, and cause the yield reaction to decrease drastically, it could be classified as a self-sabotage. The attachment of the solid products on the surface due to Van der Waals forces, block access to the active sites of the catalyst and then diminish catalytic activity.

This adhesion process is known as coking. Coke deposits may amount to 15% or even 20% w/w of the catalyst and accordingly they may deactivate the catalyst either by covering of the active sites, and by pore blocking. Sometimes a distinction is made between coke and coal, but the difference is however somewhat arbitrary: usually coal is considered the product of CO disproportionation, whereas coke is referred to the material originated by decomposition or condensation of hydrocarbons (40).

The solution found to solve this coking problem is to use liquid catalysts, specifically in this case that concerns us, liquid metal (LM-based) catalysts, which have proven to have resistance to deactivation via coking (41) (40). The fact that the reaction takes place in a liquid state, eliminates any possibility of adhesion from the produced carbonaceous materials on its surface by eliminating the impact of adhesive Van der Waals forces between the by-products and the surface of the LM.

As a result, LM-based electrocatalysts are expected to be ideally suited for the continuous reduction of CO_2 to carbonaceous and graphitic products, since surface adhesion of the products and subsequent deactivation are expected to be a major challenge (42) (41) (43). The metallic nature of these liquids also ensures excellent conductivity which is crucial when designing electrocatalytic processes like the desired reduction of CO_2 (44).

In general, one of the most used metals for these LM-based electrocatalysts is gallium, it is suitable for liquid catalysts since it remains liquid at room temperature, and it is non-toxic. Cerium-containing LM catalyst has also been used and successfully proven to convert CO_2 into carbonaceous and graphitic products at room temperature (42).

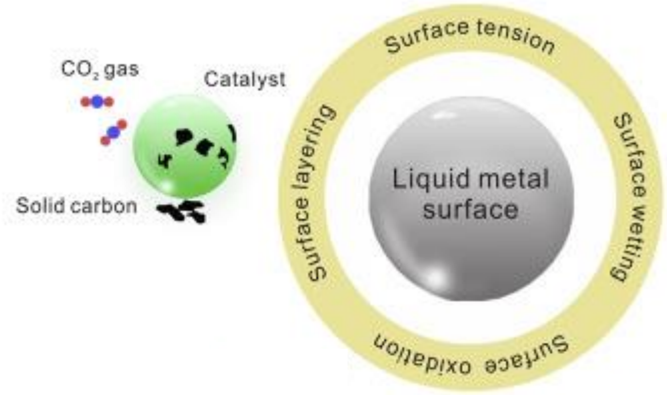


Figure 11: Visual surface characteristics of liquid metals (45)

These recent used catalysts use droplets of a liquid metal alloy attached to a porous support in contact with gaseous reagents. These microscopic alloy droplets are liquid because they contain, in their majority, a large proportion of gallium, an element with a very low melting point, although as mentioned above, different metals of low melting point can be used for this same purpose. The high concentration of metal in the dispersed droplets is responsible for the catalytic effect of the solution. These catalysts have demonstrated to be able to combine the benefits of customized molecular reaction accelerators with the advantage of a faster and easier way to separate the catalyst from the final product (46) (47) (45).

Various LM-catalysts have been documented to be efficiently used (45):

- Gallium catalysts: The surface of the microdroplets oxidizes spontaneously forming a surface heterostructure of Ga/Ga_2O_3. This heterostructure shows a resonance of tunable plasmons, which refers to a variation of surface charge density of the microdroplet and it has shown to improve the catalytic activity up to triple it with respect to the use of WO_3 catalyst, one of the best photocatalysts known.

- Silver and gold catalysts: Modifying the droplets surface with metal particles is another method used to obtain LM-based catalysts. Using electrochemical substitution, silver and gold nanoparticles can displace gallium atoms, which possess lower standard reduction potential. The metallic nanoparticles promote electron charge transformation, thus improving the activity of catalysis.

- Cerium catalysts: It has become popular for the CO_2 reduction reaction since the reduction of Ce^{3+} to metallic Ce^0 occurs at low potentials, very close to the CO_2 reduction potentials. On the other hand, the use of cerium as a catalyst may allow new catalysis pathways that were previously inaccessible, due to its pyrophoric nature.

Regarding CO_2 reduction, several authors have proposed different reduction mechanisms using several of the LM-catalysts just mentioned. The most innovative and that implement the greatest number of methodological differences with respect to the rest are the Australian researchers Dorna Esrafilzadeh et al. that have documented the reduction of CO_2 to solid coal at room temperature (42). They are a group of researchers of the RMIT University in Melbourne, Australia. Until now, the biggest drawback of all CO_2 reductions was its high energy demand because this is a very stable molecule in nature and its decomposition requires high levels of energy. They have exploited the formation of a cerium oxide catalyst at the liquid metal/electrolyte interface, which, due to the cerium nanoparticles, promotes CO_2 reduction at room temperature. The nature of this reaction is to break the carbon dioxide into oxygen gas, as well as carbonaceous products which float to the surface of the container due to differences in density and can therefore be easily extracted.

The reduction of CO_2 to CO occurred using the cycle from Ce^{3+} to Ce^{4+}. Ce_2O_3 dominates the surface of the LM-catalyst forming a thin 2D layer due to its high reactivity at the metal-air interface. For this synthesis, the electrochemical reduction of CO_2 was performed using this mentioned LM-Ce catalyst in an electrolyte based on dimethylformamide (DMF), due to the high solubility of CO_2 in this solvent. In this reduction, carbonaceous material was produced which formed black floating debris in the electrolyte after prolonged electrolysis. This product was then collected and purified for further analysis and characterization. Later analysis of these carbonaceous materials determined that the produced materials were mainly composed of carbon (84,49%) while containing 14,99% of oxygen and predominantly contained C–C and C=C bonds.

On the other hand, the scientists Zarma Zuraiqi et al. have encountered another pathway to convert this CO_2 emissions to solid carbon by using the same LM-catalyst technology (48). Unlike the aforementioned process, this one proposes a mechanism using a LM-catalyst with an alloy of gallium and indium and carrying out the synthesis at 200 ºC.

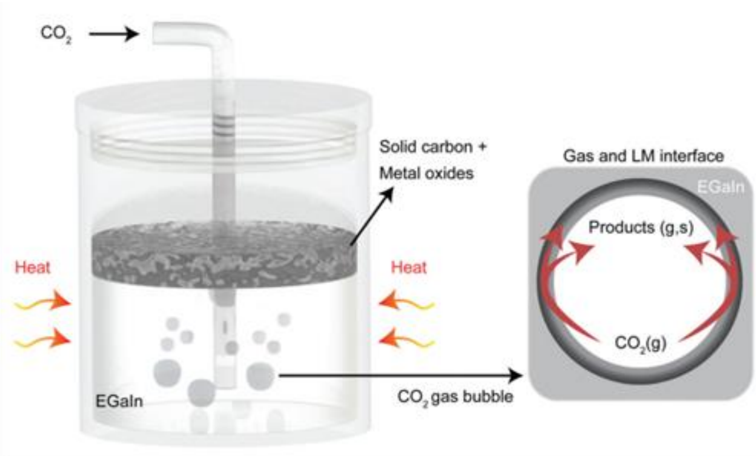


Figure 12: Overview of the CO_2 dissociation process over liquid EGaIn. Representation of the interaction between gaseous CO_2 and the molten metal (48)

The proposed catalyst is formed of 75 wt% Ga and 25 wt% In and thus achieves a melting point of 15,5 ºC. These scientists themselves also demonstrate the ease of preparation of this LM-catalyst, a great advantage due to its easy replicability. They proved that the use of Ga without any alloy obtained similar conversion results but had the disadvantage that pure Ga solidifies at room temperature. In this way they improved the properties of the catalyst by adding In avoiding unwanted solidification of the metal.

The undesirable reaction in this type of synthesis is the production of CO from CO_2 in contact with the synthesized solid C. This group of scientists showed that the selectivity of the reaction decreased from 100% when exceeding 400ºC of temperature, since these conditions favoured the synthesis of CO.

Other scientifics, such as Mohannad Mayyas et al. have also demonstrated this improvement of catalysts activity and selectivity when doped with other metals such as indium, mentioned above, or tin (Sn) (49). In their paper, the research team show an efficiency of 92% in converting a ton of CO_2 as described, using just 230 kWh of energy. They estimate this equates to a cost of around 100 dollars per ton of CO_2 (50).

5.1.2. Via molten salts

Molten salts are salts that are in a solid state at standard temperature and pressure but have the ability to enter the liquid phase at high temperatures. A salt that is normally liquid, even at standard temperature and pressure, is usually called an ionic liquid, so molten salts are a class of ionic liquids (51). Douglas et al. and Ren et al. have previously demonstrated CO_2 reduction to nanotubes and nanofibers but using high temperatures and energy demanding processes with molten salts (52) (53). Both used electrolysis pathways but they perform the carbonaceous nanotubes synthesis using temperatures above 600 ºC. This type of electroreductions at high temperatures are also known as high temperature electrochemical synthesis (HTES). High yields were obtained in both cases, as well as the formation of highly valued, compact, and readily stored form of carbon.

On the other hand, Novoselova et al. from the Ukrainian National Academy of Sciences, has developed a novel electrolytic synthesis method for carbon nanomaterial generation from ionic melts (54). The proposed reduction mechanism consists of a cathodic reduction of CO_2 to elemental C in metal electrodes. It should be noted that due to the low solubility of CO_2 gas in molten chloride, the only possible way to increase the rate of reduction is to generate excessive gas pressure. This electroreduction, such as those proposed by Douglas et al. or Ren et al. are also carried out at high temperatures, in this case around 550 ºC. They finally prove to successfully produce carbon nanotubes with a content up to 40 vol% in the cathode.

Additionally, Otake et al. have also proven to decompose CO_2 gas in molten salts, such as $LiCl\text{-}Li_2O$ or $CaCl_2\text{-}CaO$, to produce carbonaceous materials (55). After the electrolysis in both salts, the aggregations of nanometre-scale amorphous carbon and rodlike graphite crystals were observed by transmission electron microscope. The current efficiency was evaluated to be up to 78,5%. In this case to avoid CO transformation from C and CO_2 reaction, they decided to lower the temperature to approximately 500 ºC when using the molten LiCl-Li_2O as solvent. Unfortunately, this temperature reduction was impossible to carry out using the molten $CaCl_2$-CaO since its working temperature is around 1.200 ºC and the undesired production of CO was more difficult to control in this case.

5.1.3. Via MOXIE combinated process

MOXIE is a technology used for Mars 2020 Perseverance Rover. It demonstrates to be able to perform an In Situ Resource Utilization (ISRU) by dissociating atmospheric CO_2 into O_2. It is known that this process will be able to autonomously provide at least 24 metric tons of liquid oxygen for ascent vehicle propellant in the 16 months preceding launch of a human crew to Mars. This process involves conversion of CO_2 into O_2 using a solid oxide electrolysis unit, known by its acronym SOXE, developed by Ceramatec (see Figure 13). The SOXE is configured as a single mechanical stack of 10 cells, electrically configured as two stacks of 5 cells each, sufficient to produce O_2 at a rate of 1,2 g/hr/cell (56).

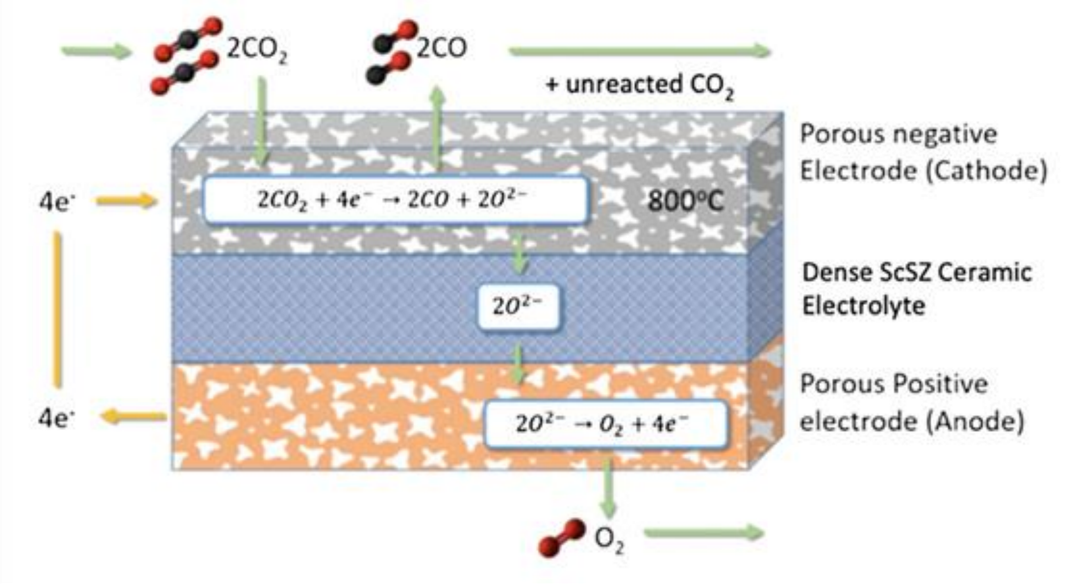


Figure 13: Cross-section of a single SOXE cell layer (56)

$$2\,CO_2 \rightarrow 2\,CO + O_2 \quad (Moxie\ reaction) \qquad \text{Equation 1}$$

The stack is constructed from scandia-stabilized zirconia (ScSZ) ceramic electrolytes with thin screen-printed electrodes, coated with a catalytic cathode on one side and an anode on the other. When CO_2 flows over the catalysed cathode surface at 800 °C under an applied electric potential, it is electrolyzed to produce

CO and oxygen ions. The ions are electrochemically drawn through the solid oxide electrolyte to the anode, where they combine to produce gaseous O_2 (57) (58).

By implementing this mechanism in the field of the study of this project, it could be used as a technology to efficiently obtain CO from CO_2.

The CO obtained by the MOXIE process can be later transformed into CO_2 and carbonaceous products, so that the overall reaction would be the desired transformation of CO_2 into carbonaceous products and oxygen (see the global mechanism below).

$$2\,CO_2 \rightarrow 2\,CO + O_2 \quad (Moxie\ reaction) \qquad \text{Equation 1}$$

$$2\,CO \rightarrow CO_2 + C \quad (Chatterjee\ et\ al.) \qquad \text{Equation 2}$$

$$CO_2 \rightarrow C + O_2 \quad (Global\ reaction\ desired) \qquad \text{Equation 3}$$

This Equation 2 was documented by Chatterjee et al. in 1954, using an iron catalyst at an average temperature of 550 ºC (59). It has been claimed that both metallic iron and iron carbide are a useful catalyst for this reaction. On the other hand, Baukloh et al. also investigated the decomposition of CO forming free C (60). They assured that the rate of decomposition depends on the nature of the catalysts and is greater at 500 ºC. Fe_2O_3 mixed with SiO_2, CaO, Al_2O_3 or Cr_2O_3 caused a decrease in the catalytic breakdown of CO, while mixing it with Cr_2O_3 was found to be the most effective.

They paid particular attention to the influence of various metals and metal oxides in this reaction (61). CO was passed through Fe_2O_3, Fe_3O_4, Fe, Co_3O_4, Co, Ni_2O_3, NiO, Ni, Cr_2O_3, Cr, Mn_3O_4, Mn, Al_2O_3, Al, ZnO, Zn and Cu at temperatures between 350 ºC and 850 ºC. The amount of separated C was raised to a maximum at 550 ºC for oxides of Fe and Fe, at 650 ºC for oxides of Co and Co, at 450 ºC for oxides of Ni, but at 750 ºC for Ni, at 650 ºC for Cr and at 850 ºC for Mn. No C was synthesized using Mn_3O_4, Al_2O_3, Zn or ZnO, nor CuO. They conclude that not oxides, but the metals produced from them, cause the efficient decomposition of CO into carbonaceous substances. Additionally, they also investigated the effect of metal carbides formation that decreased the reaction rate, since metal carbides have a much lower activity than pure metal. To avoid this inconvenience, H_2 was used so that the activity of the initial metal was restored (62).

5.1.1. Via methane decomposition combinated process

Catalytic methane decomposition, also known as CDM, is a promising process that simultaneously produces COx-free hydrogen and carbonaceous nanomaterials. Methane can be obtained from CO_2 as will be explained detailed later in Section 5.3. The reaction stages that this synthesis follows are shown below.

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O \qquad \text{Equation 4}$$

$$CH_4 \rightarrow C + 2\,H_2 \qquad \text{Equation 5}$$

Being the overall reaction shown in Equation 6.

$$CO_2 + 2\,H_2 \rightarrow C + 2\,H_2O \qquad \text{Equation 6}$$

The mechanisms of synthesis of the Equation 4 are detailed in the Section 5.3.

The decomposition reaction of methane, Equation 5, is of high interest since there is no formation of CO or CO_2 as by-products, so it is not necessary to use additional equipment for the separation of these. On the other hand, the final products can be easily separated since the coal produced is in solid state, so the hydrogen can be used directly without the need for prior purification. To obtain conversions close to 100% it is necessary to carry out the decomposition at a temperature close to 1.000 ºC which can cause sintering of the catalyst. Furthermore, as expected, the formation of solid carbon during the reaction decreases the useful life of the catalyst due to the formation of coke (63).

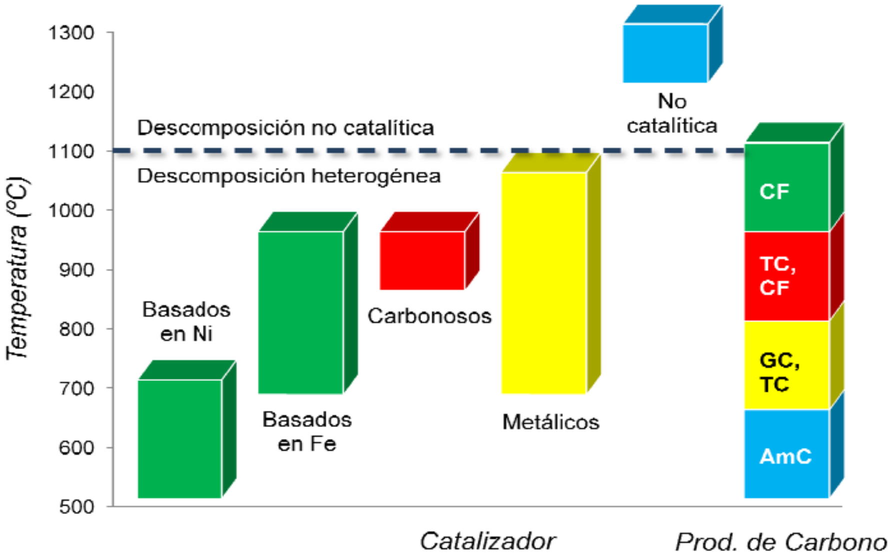


Figure 14: Temperature range by catalyst type and carbonaceous products obtained. CF: carbon filaments; TC: turbostratic carbon; GC: graphitic carbon; AmC: amorphous carbon (64)

This decomposition reaction requires the presence of a metal catalyst, usually Ni, Co, Fe or Pt (see Figure 14). In addition to being able to break the strong C-H bonds of the molecule, it must possess great activity and stability at high temperatures for long periods of time. Specifically, as many reports prove, nickel is the most used because it can work at low temperatures, between 400 and 600 ºC, and has a low operating cost (65) (66). Supported Ni catalysts produce carbon nanofibers with a Ni metal particle at the tip of them.

On the other hand, Fe-based catalysts have also shown high activity and elevated capacity for carbon production. Zhou et al. assure that is known to be more environmentally friendly, and its price is 200 times lower than that of nickel (67). Iron catalysts are also more attractive since due to their high melting point, they can operate at higher temperatures, between 700 and 950 ºC. Moreover, Avdeeva et al. showed that Co-based catalyst performance is very similar to that of Ni-based ones (68). They demonstrated that the best performances are exhibited by the coprecipitated high loading Co-alumina catalysts.

Thermal properties of this catalyst are not good over time at high temperatures, the use of bimetallic catalyst is then explored for this reaction since it can improve activity, selectivity, and thermal stability (66). Takenaka et al. proved that the addition of Cu into Ni-based catalysts enhanced the catalytic activity and life for the methane decomposition reaction desired (69). Additionally, they demonstrated that Pd modified catalysts also showed higher activity and longer life for methane decomposition, even in the higher temperature range around 750 ºC.

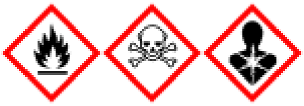
To avoid the problem of removing the carbon deposited in the catalysts, carbon substrates have also been used as a catalyst, ranging from activated carbon to graphite. Muradov showed that activated carbon has shown the highest activity, while graphite performance was poor and show the lowest carbon formation (70). Carbon has several advantages over metal-based catalysts, such as low cost, easy availability, and no regeneration needs. Moreover, the reaction can be catalysed by the carbon produced in the process, so that an external catalyst is not required except for start-up. The main problem with this type of catalyst in DCM is that lower solid carbon conversions are obtained compared to metal catalysts (66).

5.2. Methanol

Methanol (CH_3OH) is a basic chemical component used in the production of other commodities that are widely used in our daily lives (see

Figure 15). It is the simplest alcohol, at room temperature it is presented as a low-density, colourless, flammable, and toxic liquid that is commonly used as antifreeze, solvent, and fuel.

Table 4: Methanol properties

CAS number	67-56-1
Chemical formula	CH_4O
State at room temperature	Colourless liquid
Density [g/cm^3]	0,792
Molecular weight [g/mol]	32,04
Melting point [°C]	-97,6
Boiling point [°C]	64,7
Heat of combustion HHV [kJ/mol]	725,7
Safety pictograms	

Methanol is nowadays presented as one of the greenest fuels, since it can be obtained from CO_2 previously separated from industrial combustion gases. It is a fuel of non-fossil origin and the obtaining of which entails a compensation of CO_2 emissions. The use of methanol as a transport fuel is growing progressively due to its versatility and for being an economical alternative fuel thanks to its efficient combustion, ease of distribution and wide availability around the world. Increasing the use of methanol as an energy source will help reduce, or even eliminate, dependence on fossil fuels. In the same way, it also promotes a carbon neutral cycle so that the carbon emissions themselves are converted into new value-added chemicals.

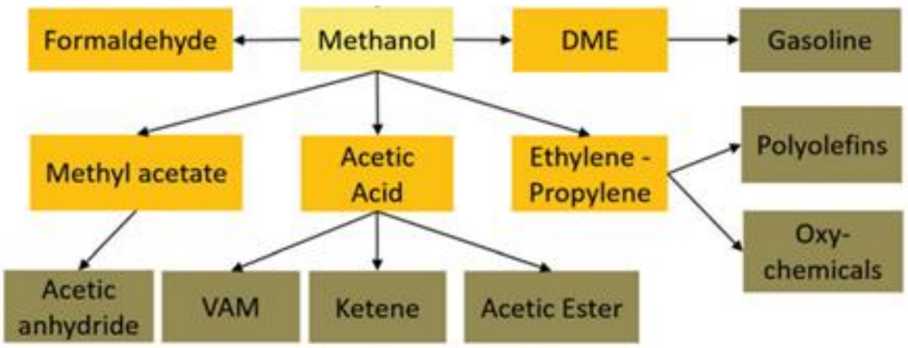


Figure 15: An overview of methanol derivatives (71)

Currently, more than 90 methanol production plants are operating worldwide. They had a combined production capacity of approximately 160 million metric tons in 2021 (see Figure 16) and, furthermore, their production capacity is expected to increase by more than 80% until 2030 (72). Additionally, global demand has been largely driven by emerging energy applications that have been found for the use of methanol, which currently account for approximately 40% of methanol consumption globally. It is known that every day, almost 200.000 tons of methanol are used as a chemical feedstock or as transport fuel worldwide (73).

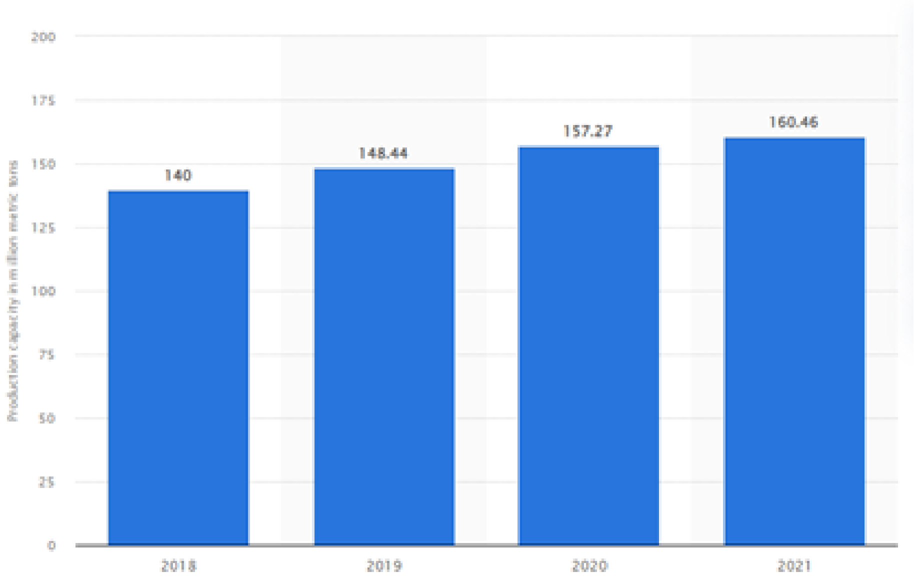


Figure 16: Production capacity of methanol worldwide from 2018 to 2021 (in million metric tons) (72)

This methanol produced is stored in fully enclosed containers, designed to prevent ignition or human contact. The tanks must be on the ground, with ventilation and have controls for the emission of vapours. Although it has a high storage danger, it is a totally stable product to store, which makes it a value-added product with respect to its forefather, CO_2.

Irina Tsukerman, president of strategic advisory Scarab Rising, is confident that the total global market for renewable methanol will grow from 122 million dollars in 2021 to more than 3 billion dollars by 2031 (74). The main expansion of the use of this fuel is due to the interest on the part of major logistics sectors such as China Merchants Group and Maersk, which are investing in large tonnage cargo ships fuelled with methanol.

Methanol is mainly produced by reacting CO and CO_2 with H_2. Normally, this synthesis occurs in a two-step process, first the production of synthesis gas is carried out and then the final production of methanol. A major limitation associated with this CH_3OH production route is the requirement of a very large amount of carbon-free hydrogen supply, which makes the development of this large-scale production process complicated.

5.2.1. Via CO_2 hydrogenation

The conventional CH_3OH production route is by hydrogenation, following the Fischer-Tropsch process where synthesis gas, a mixture of H_2, CO and CO_2, reacts on the surface of the catalyst. The equation followed in this synthesis is shown below:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \text{Equation 7}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \text{Equation 8}$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad \text{Equation 9}$$

The hydrogenation of CO_2 for CH_3OH synthesis (Equation 7) results in two side reactions of reverse water gas shift reaction (Equation 8) and CO hydrogenation (Equation 9). CO_2 hydrogenation with H_2 via a reverse water gas shift process produces methanol at a capacity of approximately 75 Mt per year (75).

As can be seen, CO is still an intermediate in this CO_2 hydrogenation process that later leads to methanol and other fuels synthesis. The main problem in this two-step synthesis is that the first part of CO synthesis requires high temperatures and low pressures, unlike the consecutive synthesis of methanol. Due to this large difference in the reaction conditions of the two mechanisms involved, a single-step commercial process to produce methanol from CO has not yet been designed.

To obtain synthesis gas from sequestered CO_2, catalysts need to exhibit high activity and selectivity due to the high energy demands of the reaction. It has been shown that there are metals supported in metal oxides that act as highly active and stable catalysts in the hydrogenation reaction of CO_2 to produce CO. Among them, Au, Ag and Mo have been shown to promote selective CO production through a non-dissociative C-O bonding mechanism. Bobadilla L. F., Yang S. C., Xu H. and Kattel S. among other scientists, have shown that the size of the metal nanoparticles of the monometallic and bimetallic catalysts used in this reaction play a very important role against the selectivity of CO (76). For example, although Pd is not generally used for the synthesis of CO from CO_2 due to its selectivity towards CH_4, it was found that a monometallic and atomically sufficiently dispersed Pd/Al_2O_3 catalyst can selectively produce CO through CO_2 hydrogenation (77).

Copper (Cu) has shown to be the only metal catalyst suitable for both binding the initial CO_2 molecule and reduce CO into higher molecular weight products such as alcohols and hydrocarbons (see Figure 17). However, the major drawback of using Cu is its low thermal stability, which leads to fast deactivation of the catalyst particularly at high temperatures (76). Other metals, such as Ni, Fe, Pt, and Ti have not been used for this hydrogenation in aqueous media since they are highly active in reducing water and thus favours the H_2 subproduct production. One of the most studied modifiers for the improvement of the Cu/ZnO catalyst is ZrO_2. This system is considered more catalytically effective than the Cu/ZnO/Al_2O_3 typically modified catalyst, showing higher CO_2 conversion methanol productivity at mild reaction conditions (78).

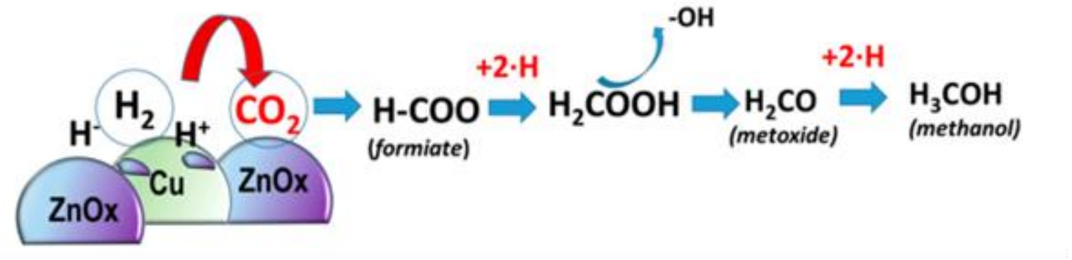


Figure 17: Schematic representation of the elementary steps involved in the hydrogenation of CO_2 to methanol over Cu/ZnO catalysts (78)

Following Simelys Hernández et al. reviews, it has been proven the feasibility of the electrochemical reduction of CO_2 to CO, and subsequently to syngas, using heterogeneous catalysis (71). As mentioned above, Au and Ag are the most favourite metals for the electrochemical selective reduction of CO_2 to CO, due to their inability to reduce CO to other side products. Therefore, the use of noble metals has a high operating cost, which represents the main problem for its development. This is the main reason why extensive research is being done on the development of new more economical nanoparticle metal catalysts. A team at the University of South Wales in Sydney was among the latest to propose a zinc oxide catalyst from flame spray pyrolysis (79). The catalyst proves to be more economically viable, as well as its production much easier since it is simply the pyrolysis of the material. It can be then used to convert CO_2 into synthesis gas, and later into methanol, through an electrolyser.

These metal catalysts promote a change in the stable geometry of CO_2 from its linear form into a curved structure. This first structural transformation is a limiting step in the synthesis of CO and at the same time conditions the subsequent production of CO. The next step for the nonlinear molecule is its interaction with water. This second step is considered energetically instantaneous compared to the first one due to the energy needed to modify the molecular structure of the initial CO_2. Therefore, the stabilization of this intermediate plays a key role in both the efficiency and reaction rate of the CO_2 reduction process (76) (80) (75).

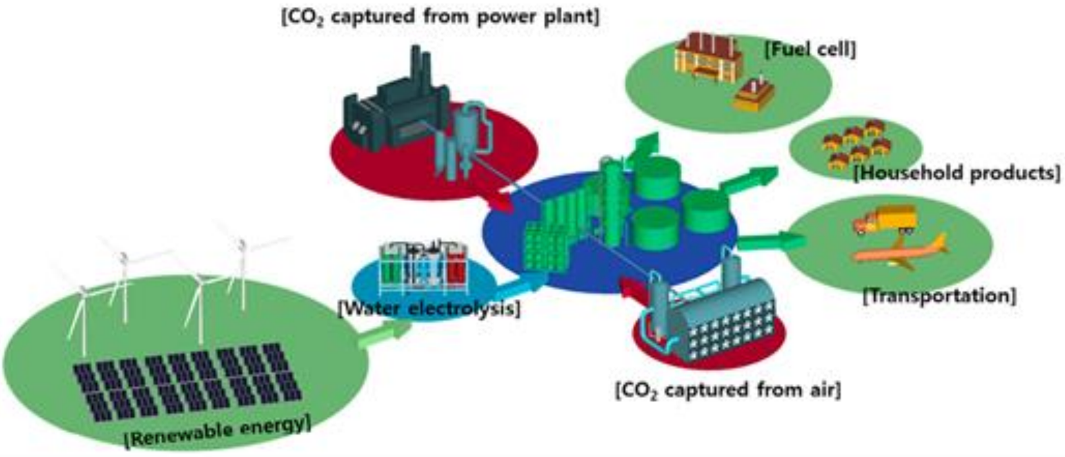


Figure 18: Overview of the renewable methanol synthesis based on the CO_2 hydrogenation technology (81)

Moreover, Carbon Recycling International (CRI) has recently patented and developed an efficient industrial-scale process for transforming CO_2 from blast furnace flue gases into methanol (82). The technology has been patented as Emissions-to-Liquids (ETL) technology. This plant is located in Anyang, in the Henan province from China. This facility is the first of its kind using this technology based on the hydrogenation of captured residual CO_2. Additionally, the hydrogen used is sustainably obtained through the electrolysis of water using electricity from 100 % renewable sources (see Figure 18). Construction was completed in mid-2022 and its start-up took place during the third quarter of 2022, being the first of many projects of this type proposed by the company (83).

5.2.2. Via direct methane to methanol transformation (DMTM)

Carbon dioxide, captured from the combustion of natural gas and other sources, can be combined with H_2, and transformed with the help of catalysts, into synthetic natural gas (SNG) or methane. This process is called methanization and the main reaction of the system is shown below.

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O \qquad \text{Equation 10}$$

The process of synthesizing methane from CO_2 gases is explained in more detail in Section 5.3.

Once methane has been synthesized, it can be used as a direct source of energy, stored for future use or can be a precursor to other value-added substances such as methanol. This direct transformation allows to avoid the passage of high energy consumption required to transform the CO_2 molecule into CO and H_2, and therefore represents an economically advantageous and noticeably more environmentally friendly option.

Technologies for DMTM conversion could be catalytic oxidation processes, photocatalysis technologies, plasma technologies, supercritical water oxidation technologies, and membrane technologies, among other methods (84). The main drawback for the application on an industrial scale of these processes is the complicated stability of CH_3OH compared to CH_4 since the former is more prone to oxidation. That is why the control in the overoxidation of CH_3OH plays an indispensable role in this type of synthesis.

The reactivity of methane is lower than methanol because its C-H bonds are stronger and that causes the CH_4 molecule to be highly stable. For example, the energy required for the dissociation of the C-H bond of methanol is 393 kJ/mol, while that of methane is 440 kJ/mol (85). It then takes more energy to oxidize methane than methanol, which is why the coexistence of both in an oxidation reaction is complicated. It becomes difficult to control the selectivity of the single-step process from methane to methanol oxidation since the oxidation route of methanol to stable over-oxidation products such as CO or CO_2 is easier than the oxidation route of methane itself.

The use of solid catalysts in this direct synthesis is widespread, since, due to the structure of the molecules' spins, oxygen itself is not a recommended oxidizer of the reaction. However, there are different existing routes of direct transformation, using both solid catalysts and oxygen. It is important to note that the use of oxygen as an oxidant facilitates the implementation of the process at a bigger scale, since it is a homogeneous process that does not need additional reagent recovery processes, which leads to be a more economically viable process.

The use of oxygen causes the reaction mechanism to be strongly guided by the reactions of radical chains in the gas phase. The partial oxidation of methane to methanol in the presence of oxygen involves more than 1.000 elemental reactions with numerous reactive species involved (below are shown the main ones). Among them, Verma et al. demonstrated that the limiting reaction of the mechanism is that of abstraction of the first hydrogen from methane to form the methyl radical, that has high reactivity (86).

$$CH_4 + 0{,}5\ O_2 \leftrightarrow CH_3OH \qquad \text{Equation 11}$$

$$CH_3OH + 0{,}5\ O_2 \leftrightarrow HCHO + H_2O \qquad \text{Equation 12}$$

$$HCHO + 0{,}5\ O_2 \rightarrow CO + H_2O \qquad \text{Equation 13}$$

$$CO + 0{,}5\ O_2 \rightarrow CO_2 \qquad \text{Equation 14}$$

These secondary steps are highly exothermic and that, causes a high difficulty to stop the reaction where desired, which requires strict control of the reaction at all times. Several researchers in this field claim that high methane pressure can prevent deep oxidation if appropriate temperatures and pressures are used (85) (86) (87) (88) (89). For example, Zhang et al. indicated that the best reaction conditions were 723–773 K and pressures of 30–60 bar; while Holmen concluded that the best yields were obtained at temperatures of 450-500 °C and pressures of 30–60 bar, with a methanol yield up to 40% (88) (89). Many of these scientists have experimentally demonstrated that it is impossible to obtain high transformation yields of methanol since an increase in the methane conversion is linked to a decrease in selectivity towards CH_3OH.

On the other hand, solid catalysts have also been used for this direct synthesis, causing the reaction mechanism to occur on the surface of these, being then a heterogeneous catalysed reaction. The temperature and pressure requirements are much lower in this case since the control of the reaction is easier. The first catalysts used were supported on iron and molybdenum. Next, the solid catalysts of V_2O_5/SiO_2 were introduced, which in adding a flow of N_2O or NO significantly improved the selectivity and conversion of the system. The reactions transported on Cu-Fe zeolites have also achieved high conversions and selectivity of CH_3OH. Finally, tungsten and iron catalysts have been investigated and have demonstrated high selectivity at temperatures around 800 K (85).

A field yet to be explored regarding this reaction is the homogeneous catalysis of CH_4 in solution. Periana et al. have developed catalysts based on platinum, palladium and mercury salts that have demonstrated good performance in this partial oxidation (90). The catalyst catalyses methane into fuming sulfuric acid to obtain methyl bisulphate, then it is hydrolysed to methanol.

$$CH_4 + 2\,H_2SO_4 \rightarrow CH_3OSO_3 + SO_2 + 2\,H_2O \qquad \text{Equation 15}$$

$$CH_3OSO_3 + H_2O \rightarrow CH_3OH + H_2SO_4 \qquad \text{Equation 16}$$

Unfortunately, the use of H_2SO_4 as a solvent makes it difficult to later separate methanol from solvent and is not a standard practice at industrial level since the reaction takes place in a multi-step and difficult to control environment.

5.3. Methane

Methane is the simplest alkane hydrocarbon, whose chemical formula is CH_4, where each hydrogen atom is bonded to carbon by a covalent bond. It is a non-polar substance that occurs in the form of a gas at ordinary temperatures and pressures. Its use as an energy source is widespread since it is the main compound present in natural gas (usually 87–97%).

Table 5: Methane properties

CAS number	74-82-8
Chemical formula	CH_4
State at room temperature	Colourless gas
Density in normal conditions [kg/m^3]	0,717
Molecular weight [g/mol]	16,043
Melting point [°C]	-182,456
Boiling point [°C]	-161,5
Heat capacity [J/K·mol]	35,7
Safety pictograms	

Although being one of the main greenhouse gases, it provides a great environmental benefit, producing more heat and light energy by mass than other hydrocarbons or fossil fuels. In addition, in its combustion it produces significantly less carbon dioxide and other pollutants that contribute to smog and unhealthy air.

It can create controversy then, the fact of transforming CO_2 into CH_4 since both promote the greenhouse effect and, therefore, help global warming; but methane apart from being a direct source of energy, is a precursor to many other chemicals highly used in industry and with much less environmental impact. The routes of transformation of CO_2 to CH_4 that are interesting, as far as the environment is concerned, are those that do not end in the synthesis of CH_4, but subsequently transform it into storable value-added products.

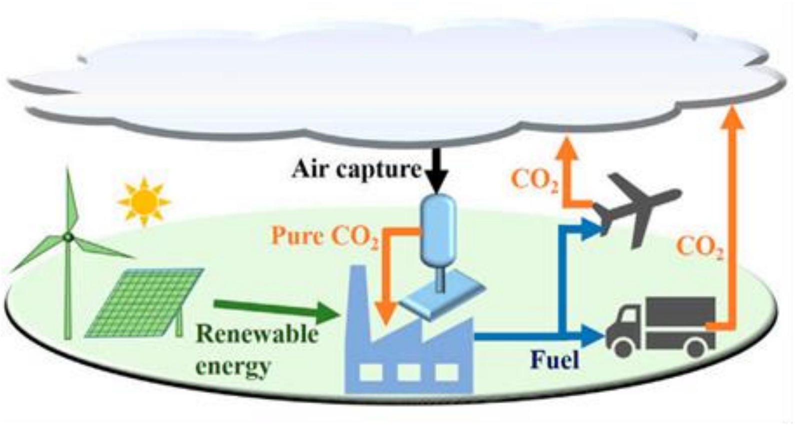


Figure 19: Example of the closed carbon cycle emissions from exhaust from vehicles and other sources to recycled fuel synthesis sources (91)

The transformation to methane of carbon dioxide emissions trapped from combustion, and then the use of this methane as a new energy source, creates a closed carbon cycle. Thus, as shown in Figure 19, the final CO_2 emissions from CH_4 used as energy are trapped and used for the synthesis of this CH_4 again and their emissions are not net to the atmosphere.

Hydrochloric acid, one of the most common acids used in laboratories, is manufactured with methane gas as the main ingredient. On the other hand, trichloromethane, also known as chloroform, is another compound that requires methane gas, and it is used extensively both as a solvent and as anaesthetic. Additionally, methane can be liquefied after its synthesis at a temperature of approximately -161,7 °C and atmospheric pressure conditions to be an easier storable substance. When used as automotive fuel, it can be stored in onboard cryogenic tanks (vacuum-insulated stainless-steel vessels).

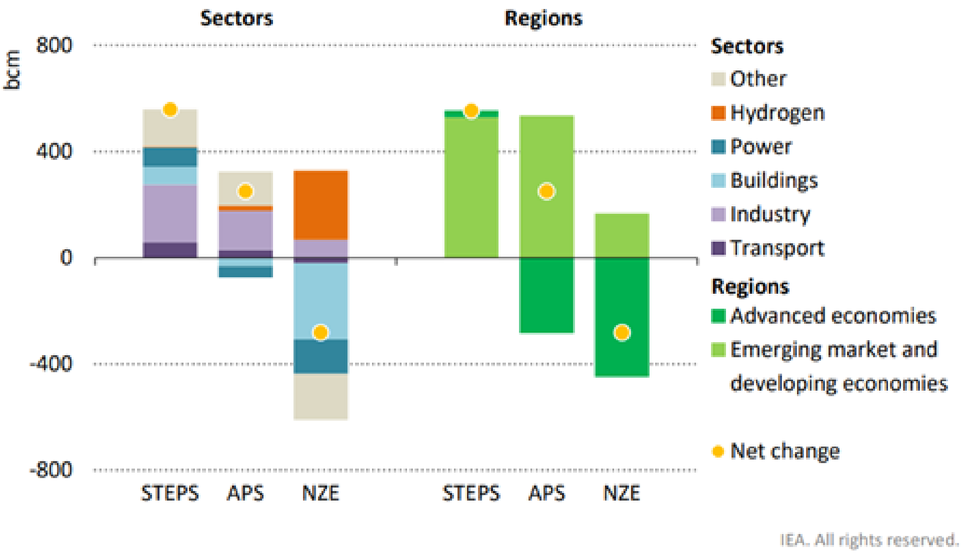


Figure 20: Changes in natural gas demand between 2020 and 2030 (92)
STEPS: Stated Policies Scenario; APS: New Announced Pledges Scenario; NZE: Net Zero Emissions by 2050 Scenario

Being a difficult storage substance and gas in normal conditions, the main drawback of its transport and consumption are the possible leaks to the atmosphere, which are highly polluting. If all the methane leaks estimated in 2021 had been captured and sold, it is known that natural gas markets would have received an additional 180 billion cubic meters of natural gas. To get a more quantitative idea, this amount is equivalent to all the gas used in the European electricity sector (93).

According to the Energy Institute Agency (EIA) estimations, global natural gas consumption will grow from 340 billion cubic feet per day (2015 data) to 485 billion cubic feet per day in 2030 (see Figure 20). The main contributors to this increase are expected to be countries in Asia and the Middle East. Specifically, it is estimated that the growth in the use of this fuel in China in the aforementioned period represented more than a quarter of its total (92) (94). For all these reasons it is of important interest to investigate the transformation of CO_2 into CH_4 in order to be able to use this synthetic methane for this expected increase in the global demand.

Depending on the origin of the hydrogen used, the production routes of synthetic methane can be classified into three large blocks: via purely thermochemical processes where industrial syngas is used as raw material in a catalytic reactor, via combined thermo-electrochemical processes where hydrogen is produced from electrolytic cells and lastly, via purely electrochemical processes of methane synthesis in situ at high temperature. In all these three main routes, the synthesis pathway for the transformation of CO_2 into CH_4 is commonly known as methanation.

5.3.1. Via methanation

Methanation is referred to the catalytic hydrogenation of CO_2 into CH_4, also called the Sabatier reaction (Equation 17). It is thermodynamically favourable, since the Gibbs energy at room temperature is negative, if catalysed with some precious metals such as palladium (Pd), ruthenium (Ru) or rhodium (Rh).

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O \qquad \text{Equation 17}$$

The most effective catalysts in this reaction are those mentioned above and supported in inorganic oxides such as SiO_2, Al_2O_3 or CeO_2, among others, that provide important performance characteristics like thermal and chemical stability of the synthesis. The main drawback, as has been discussed in other catalytic processes mentioned earlier in this work, is the high cost of these precious metals. Therefore, the truly most used catalysts in this hydrogenation reaction are non-noble metal ones such as copper (Cu), cobalt (Co) or nickel (Ni), specifically the last one has become the focus of most studies for the optimization of this hydrogenation reaction. In any case, the problem of Ni-based catalysts is its deactivation at low temperatures which promotes a high interaction between the metal particles and CO, if it is created as an intermediate of the reaction.

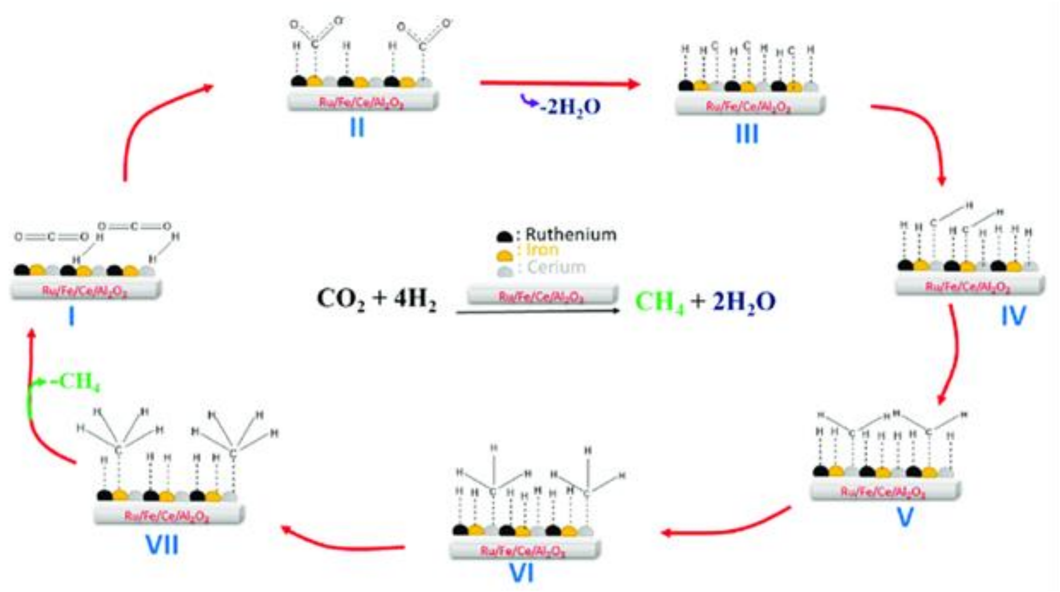


Figure 21: Proposed reaction pathways for CO_2 methanation on Ru/Fe/Ce/γ-Al_2O_3 catalyst with plausible intermediates (95)

An Le et al. have determined Ni/CeO_2 to be the most active for CO_2 methanation since it can be used at low-temperature reactors and thus achieve high CO_2 conversions (96). This methanation reaction has demonstrated to be significantly sensitive to the catalyst structure and its preparation method since they influence its performance (97) (96). The catalytic activity of Ni/CeO_2 increased if increasing the surface area of CeO_2 as the strong CO_2 adsorption on CeO_2 has shown to be beneficial for the reaction. For this report, the metal catalyst was prepared by the co-precipitation method.

On the other hand, Liu et al. demonstrated that using a Ni/TiO_2 catalyst obtained a conversion of carbon dioxide of 96 % and a selectivity against methane of 99% working at a temperature of 260 ºC. For this experimentation, the Ni in TiO_2 was synthesized by the deposition-precipitation method followed by a calcination-reduction process (98).

Zang et al. also trailed the CO_2 catalytic conversion to CH_4 using Ni catalyst supported in Al_2O_3 at low temperatures (99). They tested the evolution of this reaction at different temperatures to see its effect on the performance of the reaction and the formation of coke species. The catalyst was prepared by impregnation with the support previously calcined at temperatures from 600 ºC to 1.000 ºC. It was shown that the interaction Ni-Al was much stronger, the nickel dispersion was also higher, and it provides more active sites for the reaction over the catalyst synthesized at 600 ºC than the one at 1.000 ºC. Additionally, Daroughegi et al. also designed a Ni/Al_2O_3 catalyst for this reaction (100). In this case, the preparation method of the catalyst was by co-precipitation with a load of Ni between 15 and 30%. CO_2 conversions of CO_2 of more than 80 % were achieved with a CH_4 selectivity of

100%. They also experimentally demonstrated that for this hydrogenation reaction higher H_2/CO_2 ratios improved the catalytic performance.

Along with the use of Ni as the catalyst metal of the reaction, Pandey et al. focused their research on SiO_2-supported catalysts for CO_2 methanization (101). In this case, catalysts with a second metal such as iron (Fe) have shown to provide better results than with a single main metal. The Ni-Fe alloy presented a synergistic effect that resulted in increased catalytic activity and enhanced transformation performance to CH_4. On the other hand, Wu et al. proposed the use of a Fe-Ni catalyst also supported in SiO_2 by hydrothermal method (102). They achieved conversions of 95.2% and CH_4 selectivity of 68.7% at temperatures of 320 ºC. Finally, Moghaddam et al. obtained a Ni/Al_2O_3 catalyst using the one-pot sol-gel synthesis and adding a promoter (Fe, Co, Cu, Zr and La) (103). It was observed that the Fe-promoted catalyst showed the best performance with 71% of CO_2 conversion and 99% of selectivity for methane at 350 ºC, demonstrating the desirable resistance against sintering.

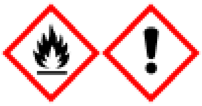
Focusing now on the use of noble metals as catalysts, it is known that Ruthenium (Ru), although being more expensive and difficult to obtain than Ni, has better properties for CO_2 methanation (97). The most used supports for this metal are Al_2O_3 and TiO_2, the last one has shown to have a high catalytic activity due to the increased encapsulation of Ru in TiO_2 particles that help the dissociation of CO_2 (104). Various researchers have demonstrated good catalytic performance for Pd-based catalysts in this CO_2 hydrogenation reaction. However, the drawbacks of Pd-based catalysts include higher cost, lower activity below 400 °C, less CH_4 selectivity, and greater selectivity towards methanol and heavier hydrocarbons which are not desired for this reaction (105).

To conclude, Debek et al. have demonstrated Rh to be among the most reactive catalysts for methanation of CO_2 at low temperatures (100–200 °C) (106). The main benefit of Rh-based catalyst is its lower reduction temperature, less than 400 °C, compared to the commonly used Ni-based catalyst, which is typically more than 500 °C. They also showed that the plasma-catalytic CO_2 methanation has a great potential of industrial application due to the high efficiency of the process.

5.4. Dimethyl ether

Dimethyl ether (DME) is made up of two methyl groups joined by an oxygen molecule. It is a volatile organic compound but has no carcinogenic, mutagenic, or toxic properties. Its storage is one of the critical aspects of the synthesis of DME since it dissolves most polymers, except for example polytetrafluoroethylene (PTFE). It has a high flammability, being this the greatest risk of the product. Its average lifetime in the atmosphere of 5,1 days is very low, compared to other greenhouse gases seen so far such as CH_4 or CO_2, and has a lower global warming potential than the rest (107).

Table 6: Dimethyl ether properties

CAS number	60-29-7
Chemical formula	$C_4H_{10}O$
State at room temperature	Colourless liquid
Density [g/cm^3]	0,7134
Molecular weight [g/mol]	74,123
Melting point [°C]	-116,3
Boiling point [°C]	34,6
Heat capacity [J/K·mol]	172,5
Safety pictograms	

Its use as a propellant gas is widespread and it has also served as a replacement for chlorofluorocarbon (CFC) gases since it has no harmful impact on the ozone layer. Moreover, it is potentially used as fuel since it has a high H/C ratio, low oxygen content, absence of C-C bonds and a high energy density without emitting NOx or SOx pollutants into the atmosphere. Its chemical and physical properties are similar to those of liquefied petroleum gas (LPG: propane and butane) and it has the potential to be a future alternative fuel for the same uses as LPG. DME can be directly used as fuel, with a thermal efficiency like the one for diesel, through small modifications in conventional diesel engines.

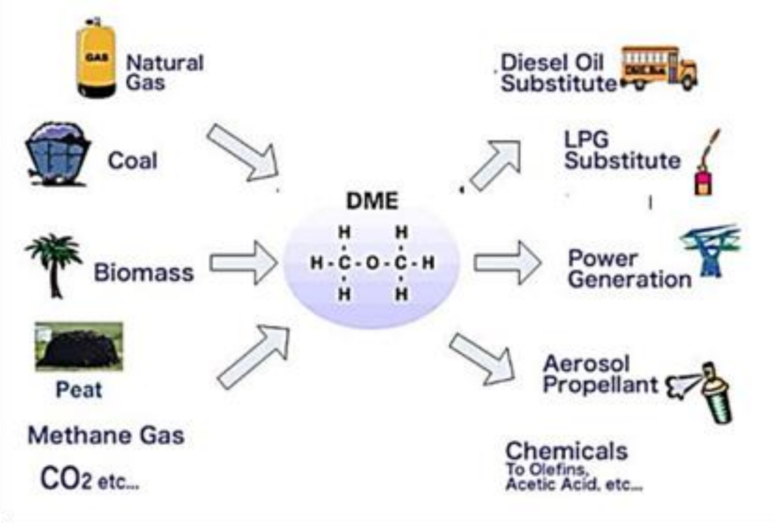


Figure 22: Different pathways for DME production and its later possible utilization (108)

As just mentioned, DME is being used as a mixture with LPG as an additive to improve combustion and reduce hazardous emission but unfortunately it is not yet an expanded-use fuel to completely reduce dependence on LPG. It has been shown that when added as an additive, it reduces the low calorific value and the kinematic viscosity, and increases the number of cetane, thus assisting the combustion. Nowadays many eastern countries such as China, India, and Indonesia, with a high dependence on LPG imports, are vigorously promoting the globalized use of DME as an alternative fuel (109). China started in 1990 with the production of methanol, and then they made the leap to the production of DME, firstly Shandon Jiutai Chemical Co. built a 5000 tons/year plant, after a year it was proven that it was a reliable technology and production was increased. From a worldwide perspective, DME production is mainly focused on the United States, Germany, the Netherlands, Japan, and China.

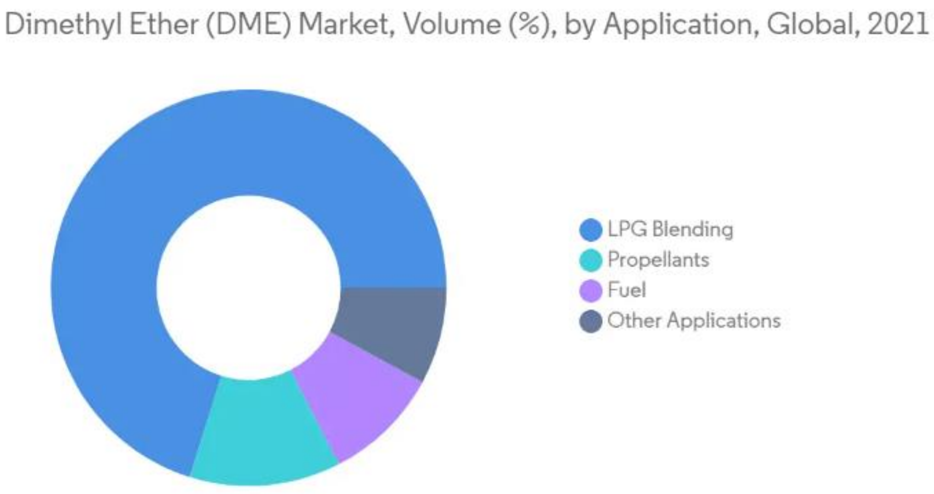


Figure 23: Dimethyl ether market volume (%) by application, global 2021 (109)

Furthermore, it is known to be an intermediate in the synthesis of many high-value chemicals such as gasoline, light olefins, methyl acrylate, among others. From the use of DME as a precursor arises the concept of thermochemical biorefinery, which encompass a wide variety of possibilities of transform DME into different final products. Specifically, in the synthesis of olefins, DME plays a very important role since CO_2 could be the raw material for its transformation into plastics.

In addition to the applications already mentioned, one of the most interesting transformation routes corresponds to the synthesis from DME of chemicals currently produced from methanol. This provides a cheaper, less toxic, and corrosive solution than by using CH_3OH. The replacement of CH_3OH by DME therefore makes these processes less harmful to the environment.

DME cannot be synthesized directly from CO_2 recovered from flue gases. It actually occurs from the dehydration of methanol followed by a second rectification process. If this methanol is obtained from CO_2 by the mechanisms mentioned in Section 5.2, then a transformation route from CO_2 to DME can be designed (see

Figure 15 of Methanol Section).

$$2CO_2 + 6\,H_2 \rightarrow CH_3OCH_3 + 3\,H_2O \qquad \text{Equation 18}$$

The transformation route begins with the hydrogenation of CO_2 to methanol, where CO is also produced. This CO is hydrogenated back to methanol. The methanol is then dehydrated and DME is formed. The detailed mechanism of the overall reaction specified above is shown below.

$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O \qquad \text{Equation 19}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \text{Equation 20}$$

$$CO + 2\,H_2 \rightarrow CH_3OH \qquad \text{Equation 21}$$

$$2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \text{Equation 22}$$

As can be seen from the overall mechanism of the reaction (Equation 18), a high proportion of hydrogen (6:1) is needed and this causes the reaction to be energetically unfeasible unless this hydrogen is produced from renewable sources. Yes, it is technically feasible that 100% of the energy needed to produce DME comes from renewable sources such as solar or wind energy (110). This includes the electrolysis of H_2O using electricity from renewable sources in order to obtain the hydrogen needed for the synthesis.

The large-scale synthesis of DME from CO_2 imply the requirement of a mixture of CO_2, CO and H_2 (syngas) as raw material. This process can be carried out by an indirect or direct way, the second one being the most innovative method and the first one being the traditional method already established.

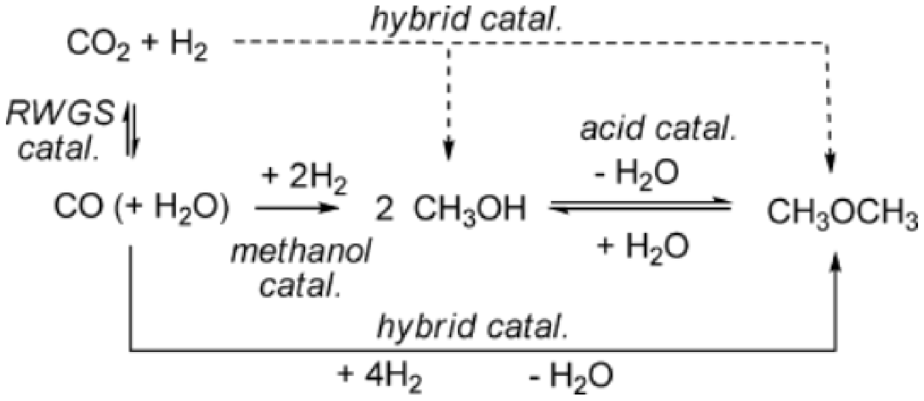


Figure 24: One step and two-step process for DME synthesis (111)

5.4.1. Via two-step process

The conventional process consists of a two-step method (see middle part in Figure 24) that first comprises the production of methanol from synthesis gas obtained from CO_2 sequestered from the flue gases, it is then purified and dehydrated to DME in another reactor in series.

For the first step of CO_2 transformation to methanol the routes explained in detail in Section 5.2 can be followed. As mentioned by Bahmanpour et al., as well as the University of South Wales, among others, the catalysts that showed to have the best properties for this hydrogenation reaction are copper and zinc oxides (76) (77) (71) (80) (75) (82) (83) (79). As an alternative route, the transformation of CO_2 to methane and the subsequent transformation from methane to methanol (DMTM) explained in detail in Section 5.2.2 is also feasible.

The mechanism of the reaction that take place in this first step follows the equations showed below.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \text{Equation 23}$$

$$CO + 2\,H_2 \rightarrow CH_3OH \qquad \text{Equation 24}$$

The CH_3OH is then separated and purified by rectification. The second stage runs from the inlet of the purified methanol into the second reactor to the output of the DME as the final product. Depending on the properties of the catalyst used in this reactor, the dehydration of methanol can occur in either gas or liquid phase. The crucial factor in this dehydration is the use of an acid catalyst that promotes the desired reaction, such as acidic zeolites, heteropoly acids or oxide compounds. The acid catalysts cause the protonation of the alcohol molecule (CH_3OH) and thus make it susceptible to be attacked by another alcohol molecule creating then the ether. The reaction mechanism of this stage of the synthesis follows the equation showed below:

$$2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \text{Equation 25}$$

The use of γ-Al_2O_3 as a catalyst has been extensively researched due to its low cost, high selectivity, mechanical strength, and time life. It is considered the benchmark catalyst for this dehydration of methanol to DME. In addition, apart from being used in the DME synthesis, γ-Al_2O_3 is widely used in the production of alkanes and other ethers from alcohols due to its excellent acidity. Sun et al. demonstrated that besides the acidity, the structure type of alumina catalyst is also a key factor for this dehydration reaction, as well as the texture, degree of crystallinity and number of acid sites of the catalyst (112). The main drawbacks of alumina are the low hydrothermal activity and the numerous side reactions, among others, but above all, the strong adsorption of steam that causes its own deactivation. It has been shown that catalytic activity can be enhanced by modifying the surface of γ-Al_2O_3 with silica, aluminium-phosphates, titanium, niobium, boron, or other species (113).

On the other hand, the use of zeolites as catalysts in this dehydration reaction has also been extensively researched due to its high hydrothermal stability and low-temperature availability. The problem with the use of zeolites is that they also favour numerous side reactions such as the formation of hydrocarbons or coke that can cause a decrease in the productivity of the DME reaction. To avoid this, the acidity of the zeolite used must be modified so that it favours dehydration to DME (75) (113). Several investigations have demonstrated that lowering acidity in the zeolite surface may prevent unwanted side reactions and modifying the pore size may minimize the coke formation (112) (113) (114) (115) (116). One of the most used and researched ones is ZSM-5, which offers a high conversion of methanol at relatively low temperatures. To reduce acidity, it has been modified by adding different metals or ions, such as Na^+, AlF^{3-}, La, Ce, among others (75) (113) (112).

It is an exothermic reaction, that is why the effect of temperature is of greater importance since lower temperatures favour the reaction to the production of CH_3OCH_3 and not vice versa. The most frequent operating temperatures are between 200 and 400 ºC keeping the pressure in a range between 10 and 20 bar (75) (117).

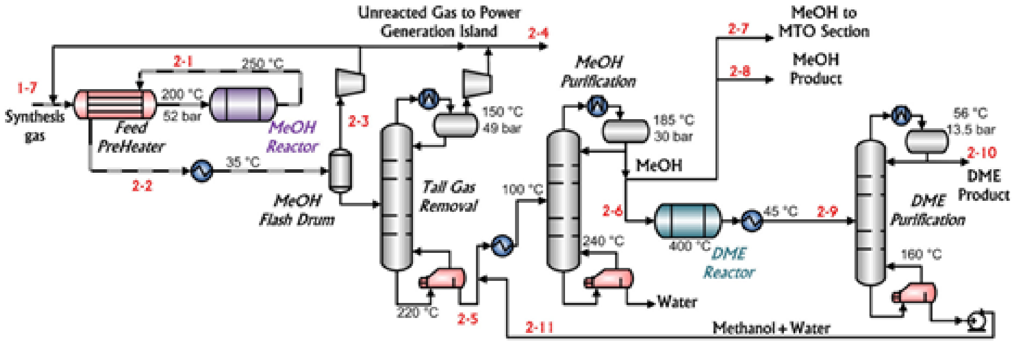


Figure 25: Flow diagram of the conventional process in two stages of obtaining dimethyl ether (118)

5.4.2. Via direct synthesis

The process of direct transformation in a single step to DME (see low part in Figure 24) can use CO_2 or CO as raw materials, each process being known as CO_2-to-DME and syngas-to-DME processes. Syngas-to-DME process is not suitable for commercial purposes since the water gas shift reaction is also simultaneously involved, which means consumption of CO to form CO_2. However, thermodynamics for the CO_2-to-DME process is not as favourable as that of the syngas-to-DME process, so the yield of DME is lower (78).

The overall reaction followed considering the compounds that enter and leave the reactor is:

$$2\,CO_2 + 6\,H_2 \rightarrow CH_3OCH_3 + 3\,H_2O \qquad \text{Equation 26}$$

It is a process with greater energy efficiency and more thermodynamically favourable than the one presented in the previous subsection. Direct synthesis of dimethyl ether is carried out in fixed-bed reactors or slurry. Depending on the catalytic activity and the composition of the initial synthesis gas, the reaction normally takes place in a temperature range of 200-320 °C and pressures from 30 to 100 bar (119).

The catalyst for the direct conversion to DME should be able to efficiently catalyse both reactions and, at the same time, minimize the yield of CO and hydrocarbons formed as sides reactions. Thus, the catalyst should exhibit a redox function able to hydrogenate CO_2 to methanol and an acid function able to convert the alcohol in the ether desired (see Figure 26). Usually, the catalyst that fulfil all these specific requirements are bifunctional/hybrid catalysts, with a metallic function that acts as a catalyst for the synthesis of methanol and, additionally, an acid function that catalyses its dehydration.

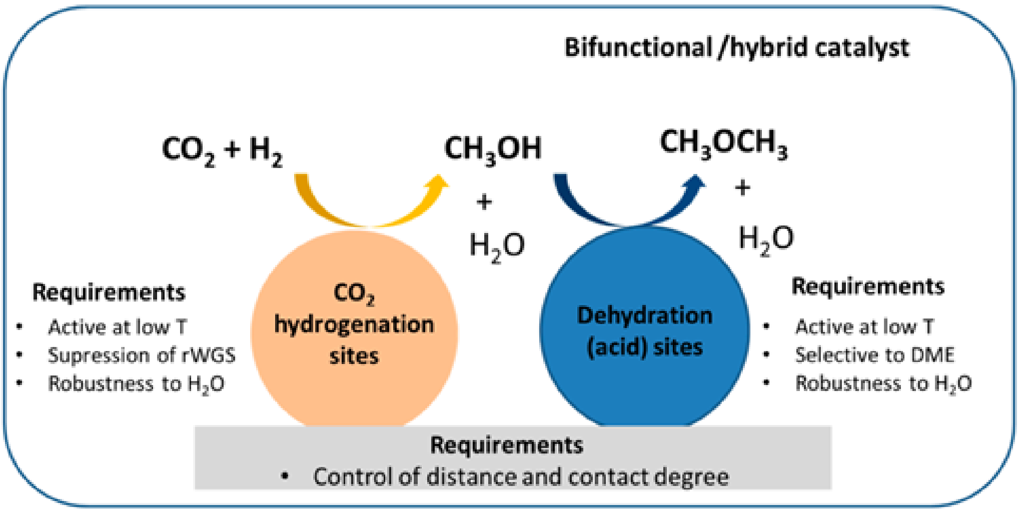


Figure 26: Scheme of bifunctional/hybrid catalysts and requirements for hydrogenation and dehydration functionalities for direct synthesis of DME from CO_2 (78)

The catalyst function necessary for the hydrogenation of CO_2 to methanol should have a high activity at low temperature. The hydrogenation function must also minimize the formation of CO during hydrogenation by suppressing the reverse water gas shift reaction and must be resistant to deactivation by water. On the other hand, acid sites must also be stable in water and should be able to work at temperatures compatibles with the thermodynamic requirements for the methanol synthesis first step.

The catalytic requirements for this reaction have been previously explained in Section 5.4.1 above. The difference in this case is the fact that it is a bifunctional catalyst that must combine the two main qualities mentioned early on (see Figure 26).

Whatever the method of preparation for the hybrid/bifunctional catalysts is used, the main objective is to control the dispersion of the active phases, the metal, and the acid ones, and to control the contact between them. In any case, the use of bifunctional/hybrid catalysts showed a higher DME formation in a single fixed-bed reactor than the DME synthesis on catalysts segregated in two fixed beds by the two-step synthesis.

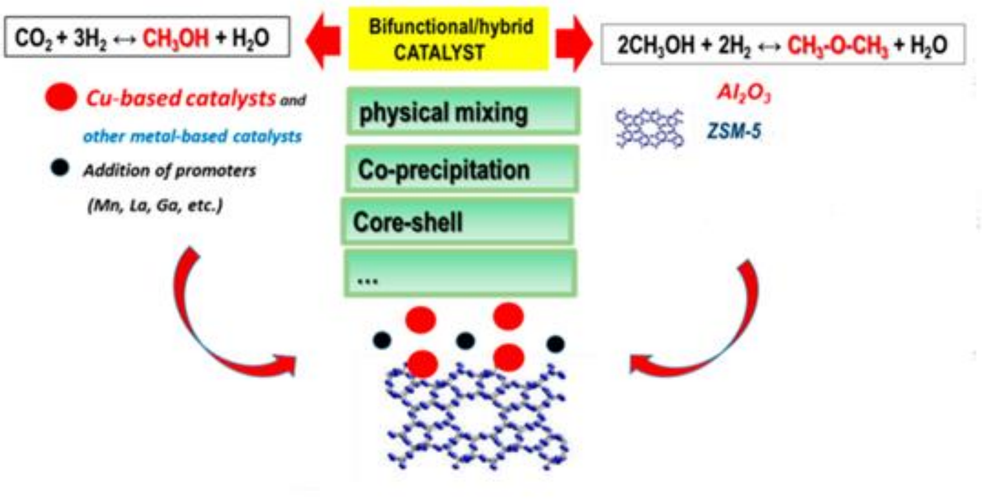


Figure 27: General scheme of the preparation of bifunctional/hybrid catalysts for direct CO_2 hydrogenation to DME (78)

5.5. Polymers

A polymer is any of a class of natural or synthetic substances composed of macromolecules, also known as repeating monomers. Polymers make up many of the materials in living organisms and are the basis of many minerals and man-made materials. Both the natural and the synthetic ones, are synthetized via polymerization, which refers to the process of combining many small molecules into a covalently bonded chain. Their large molecular mass leads to unique physical properties such as toughness, high elasticity or even viscoelasticity. Moreover, polymers are widely used thank to their low cost, low-energy demanding manufacture and facile processing into final products. The structure of a polymeric material can be described using different length scales, from the sub-nm one up to the macroscopic length scale (120).

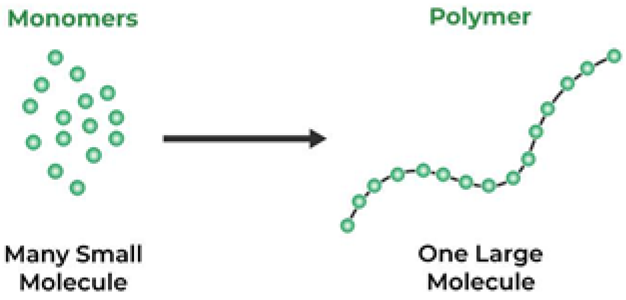


Figure 28: Illustration of polymer molecules (121)

Nowadays, synthetic polymers are used in almost all walks of life. Its properties can be enhanced by combination with other materials or polymers. Their application allows to save energy by building lighter cars and planes pieces or by improving thermal insulations of buildings, use more efficient packaging of food and drinks, preserve materials and superficies while coating them, and helps in many medical applications improvements.

The concepts of plastics and polymers can be confusing and easily confused with each other. Every plastic is known to be a polymer, but not all polymers are plastics. Specifically, plastic is an appropriate polymer for modelling since it is fluid when heated and solid at room temperature. In 1950 the world produced only 2 million tons of plastic per year, while, in 2019, annual production increased almost 230 times, reaching 460 million tons. During this period, cumulative production reached 9.500 million tons of plastic, more than a ton of plastic for every person alive today (122).

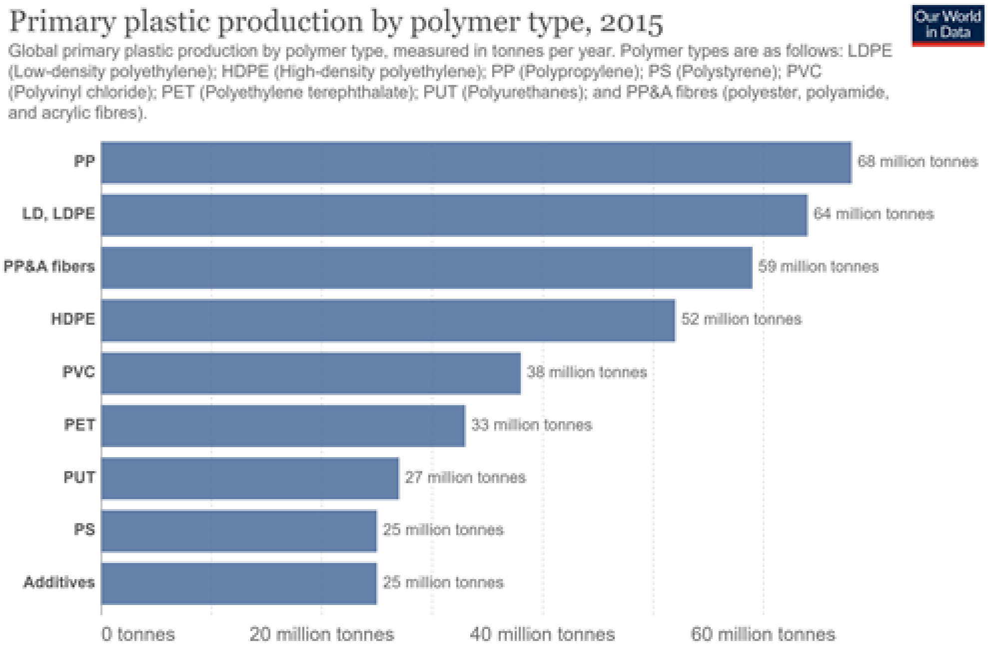


Figure 29: Global primary plastic production by polymer type, measured in tonnes per year, 2015 (122)

The most commonly used polymers include polyethylene terephthalate (PET), a strong, transparent and lightweight plastic used to make fabrics and commonly known as polyester. Among the most used ones, polyvinyl chloride (PVC) is also found, mainly used for its chemical and weather resistance, high dielectric properties or abrasion resistance. Moreover, there is polypropylene (PP) one of the high-volume commodity thermoplastics used for packaging, automotive, appliances and carpets, among other uses. Lastly, polystyrene (PS) is used in packaging, known as Styrofoam, is also available as a naturally transparent solid used in soft drink lids or medical devices.

Despite all their useful and versatile material properties, polymers face a major problem: 90% of them are produced from fossil carbon and finally end up as CO_2 emission. The improvement proposed is to obtain the carbon source necessary to form the monomer macro chains from CO_2 emissions from other industrial processes, thus helping to close the carbon cycle.

CO_2 utilisation could be the solution to meet the demand of virgin polymers in the future (see Figure 30). A total of at least 40 companies and research projects from Asia, Europe and North America are working on CO_2-based polymers nowadays.

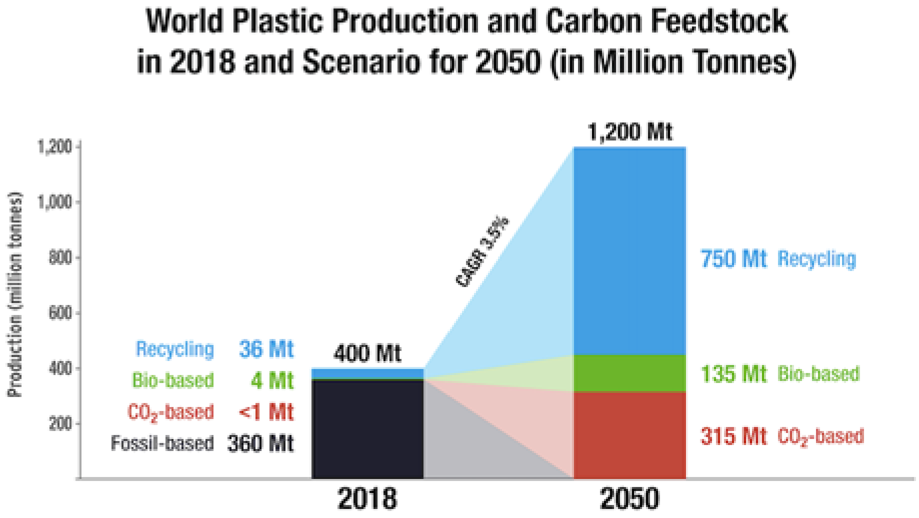


Figure 30: World Plastic Production and Carbon Feedstock in 2018 and Scenario for 2050 (in million tonnes) (123)

CO_2 can be used as a raw material for obtaining intermediate products, such as methanol, for the subsequent production of polymers; or directly replacing raw materials initially derived from fossil fuels. In the first case, the high energy demand makes the process quite expensive and unviable. On the other hand, the second case is a more commercially viable production process (124).

5.5.1. Via direct CO_2 combination

To convert CO_2 into a polymer, a polymerization agent needs to be used. This is a chemical that is added to CO_2 molecules to allow them to bond together and form a polymer. Without this agent, it would not be possible to convert CO_2 into a polymer. In addition, in some cases heat or pressure can also be used to facilitate the polymerization process.

There are many chemicals that can be used as polymerizing agents to convert carbon dioxide into a polymer. Some common examples include acrylic acid, titanium dioxide, and phthalic acid. In general, any chemical that can promote the binding of CO_2 molecules can be used as a polymerization agent.

In the reaction of CO_2 with cyclic monomers, ring-opening polymerization, also known as ROP, led to the polymer synthesis desired. Epoxides are among the first substances to be combined with CO_2 to create CO_2-based polymers. The groundbreaking ones in this field were Inoue et al., who found in 1969 that the use of diethyl zinc mixed with water could catalyse the polymerization of propylene oxide (PO) and CO_2 to generate poly(propylene carbonate) (PPC) (see Figure 31) (125). Other transition metals catalysts have been investigated to enhance this polymerization reaction. Moreover, some recent bifunctional organoboron catalysts have emerged as a kind of metal-free catalyst with notorious higher efficiency. Furthermore, Darensbourg and Wilson used a bifunctional Co(III) catalysts for the copolymerization of indene oxide and CO_2 to produce poly(indene carbonate) (PIC) (126).

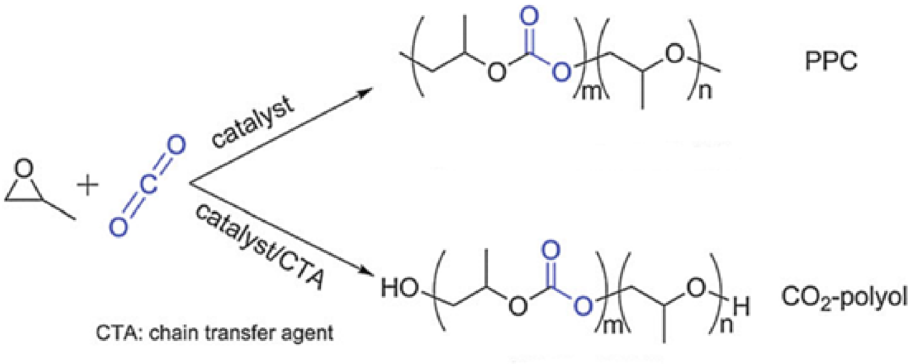


Figure 31: Two kinds of polymers from the copolymerization of CO_2 and PO (127)

Research groups such as those of Lu, Coates and Nozaki have done in-depth research works in this field (128). Only Cr, Co and Zn compounds have shown significant activities in copolymerization so far. Several researchers have shown that homogeneous catalysts allow faster and more selective CO_2-epoxide copolymerization than heterogeneous catalysts, as well as a precisely defined architecture of the synthesized polymers (129). The company Novomer was founded in 2004 as a result of Coates' research and implemented a technology that allows the synthesis of polymers containing up to 47 wt% of CO_2.

On the other hand, olefins polymerization with CO_2 is known to be the most popular route toward CO_2-sourced polyesters, which demonstrated to have high performance and degradability. Price et al. studied the thermodynamics and kinetics of this polymerization. They conclude that due to its endothermicity, ethylene and CO_2 polymerization was difficult to achieve, and butadiene has relatively higher reactivity with CO_2 (130).

Furthermore, multiple reactions based on CO_2 and triple-bond compounds have been reported, but only a few of them were polymerization reactions. Qin and Tang groups developed various multi-component polymerizations based on CO_2 and triple-bond monomers towards a wide variety of functional polymers. Additionally, Song et al. developed an efficient one-pot polymerization of CO_2, diynes, alkyl dihalides, and primary/secondary amines (128).

6. INDUSTRIAL VIABILITY OF THE CO_2 UTILIZATION PATHWAYS PRESENTED

In the first place, in order to address a complete environmental assessment of the CO_2 utilization techniques set out in Section 4 and Section 5 of this project, a complete life cycle analysis, from now on LCA, must be made (131) (132). This approach allows the assessment to be modelled for each of the subsystems of the CCU network and adds them to a global assessment of the overall impact of the technology on the environment (see Figure 32 below).

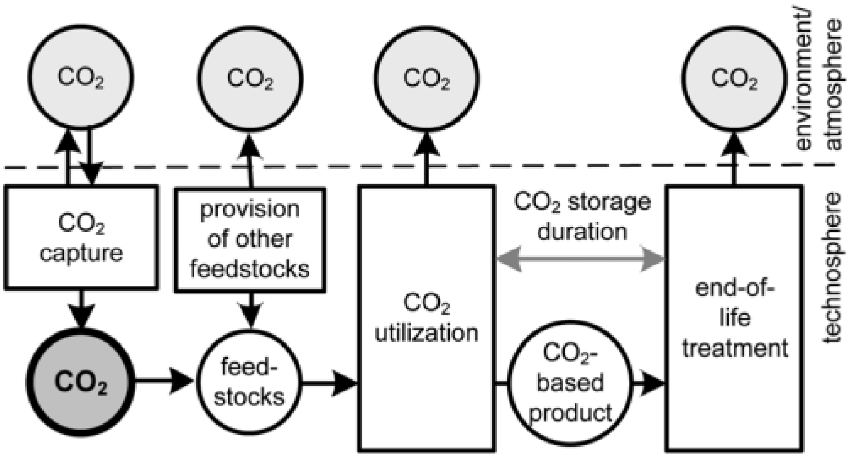


Figure 32: Flow chart of the entire CCU system (133)

As can be seen from the proposed generalized LCA flow chart above, the carbon dioxide that is treated as a feedstock is considered an economic flow related to its capture process emissions. The metric used in terms of global warming impacts incorporates the criterion of the duration of CO_2 storage. Applying the LCA results as an environmental assessment of CCU technologies can be used as a reliable basis for decisions about CCU implementations (133).

The impact of these CCSU plants cannot be generalized, but the vast majority demonstrate that CCSU technologies can provide substantial opportunities that extend beyond their sector of application and towards cross-sectoral synergies within more global systems. From an industrial point of view, this type of CO_2 capture and distribution facilities are technically viable. A market price for CO_2 at about 60 to 450 $/t for a market of about 2,7 billion $/year, combined with a CCS and CCU elevated potential means that CO_2 might become more and more available as a raw material source (111).

Let's focus on the CO_2 transformation processes mentioned so far. Table 7 shows a brief comparison of the viability of the different technologies used in the synthesis processes presented above (23).

Table 7: Comparison of different technologies for CO_2 transformation

Technology	Benefits	Drawbacks
Chemical	Large quantities production. Possibility of direct hydrogenation with higher Gibbs' energy chemicals.	Low global selectivity. High costs due to the use of noble metals for catalysts. Catalyst deactivation.
Thermal	Liquid fuel production due to syngas formation.	High temperature requirement. Catalyst deactivation due to coke formation. High costs due to the use of noble metals for catalysts.
Photochemical	Low input energy and temperature requirements. Lower operational costs. Wireless configuration process.	Low photovoltaic activity and product selectivity. Low yields obtained. Complex photoreactor designs.

As mentioned before, the possible transformation of emissions into solid coal as a new energy source has caught the attention of the scientific community in the recent years. The use of liquid metal catalysts is, however, very novel and is not implemented on an industrial scale. In any case, it opens up new and promising horizons on CO_2 conversion technologies. Additionally, synthesized carbonaceous products are generally produced at low costs, which indicates that it can be an economically competitive bet. These products have wide applications as building materials, fillers for composites, supercapacitor ingredients, and even as catalytic supports.

The combinated MOXIE process or the combinated methane decomposition are viable, hitherto undocumented, proposals for the synthesis of carbonaceous products. The new emerging MOXIE technology can expand its uses not only to obtain oxygen as the main product, but also promote the production of CO that can later be used to synthesize carbonaceous products. Additionally, as seen above, methane synthesized from CO_2 emissions can be viably transformed into coal afterwards. This combination of reactions, so far developed separately, may lead to the opening of a new field of research on CO_2 conversion. In any case, its economic and technical viability is still to be established since an exhaustive laboratory scale test and study is firstly required.

Regarding the synthesis of methanol, seems to be an attractive option due to methanol versatile application and exceptional physical and chemical characteristics. CCU-to-methanol plants are technically feasible and can operate under operating conditions and equipment similar to currently existing natural gas-based methanol synthesis plants (134). As mentioned above, there are already plants of this type spread around the world, such as the one located in Anyang, China, which is currently in operation and recycles about 160.000 tons of CO_2 per year (83). As an energy-viable proposal, this type of industrial-scale plants could be located in an industrial port, where electricity from offshore wind and CO_2 from industrial emissions are available. Such industries could compete with current fossil methanol market prices in the future.

However, processes in which large amounts of H_2 are needed can only be beneficial in mitigating CO_2 emissions if all, or most part, of the hydrogen used comes from non-fossil sources. A possible viable source of obtaining H_2 is the electrolysis of water. The disadvantage of using this technology to obtain H_2 is its high cost since it is usually the most significant in those plants where it is installed. The cost of hydrogen is commonly the bottleneck of this type of synthesis process (134).

On the other hand, the synthesis of methanol from methane has been little researched and has not attracted the attention of the scientific community due to its high difficulty of implementation on an industrial scale. The difference in the stabilities of the two compounds makes continuous production very difficult and makes reaction conditions and selectivity very complicated to control to date.

The synthesis of methane itself, is also part of the possible CO_2 transformation pathways. This creates a power-to-gas system. The effective costs of generating methane from CO_2 are expected to be two to three times higher than current industrial costs for natural gas, even in long-term scenarios. Therefore, an effective price on carbon emissions must be put in place to allow these synthetic fuel substitutes to be competitive with fossil fuels. It has been shown that a carbon price of 150 €/tCO_2 can enable beneficial business cases for large-scale deployments (135). Recently, a Norwegian company has developed a pilot-scale process based on the recovery of CO_2 from flue gas and its conversion to methane using renewable H_2. Additionally, the Tohoku University of Technology in Japan, have developed a pilot plant based on the Sabatier reaction with very high selectivity that uses hydrogen from seawater electrolysis (111). As shown, several approaches have been made to optimize the use of CO_2 for methane production.

Regarding the synthesis of DME, it has been previously established that, even though it is not the conventional approach, the direct synthesis process is more efficient and thermodynamically favourable than the two-stage mechanism. The process that involves H_2 and CO_2 as raw materials instead of syngas has a better performance from the point of view of deactivation by the formation of coke. These types of plants have been modelled with simulators and demonstrated to reach an energy efficiency of almost 50%.

Korea Gas Corporation, also known as KOGAS, has developed a new DME plant that uses CO_2 as a raw material using the one-step process. Unitel Technologies was recently awarded a contract by KOGAS to prepare the basic engineering and design for a plant that will make 300 kt/year of DME. KOGAS is the first organization in the world to successfully develop and demonstrate a commercially viable one-step process (111). As far as economic viability is concerned, several cash flow analyses have shown that the minimum selling price of DME is 2.193 €/t. This value is approximately 5 times higher than the selling price of conventional diesel (136).

CO_2 industrialization for polymeric materials production is mainly focused on polycarbonate and polyether carbonate polyols synthesis. Several production plants placed in China, Korea y Rusia, have managed to produce up to 65 kt/year of polycarbonates. The biggest breakthrough was in March 2011, when the Saudi Kayan Petrochemical Company, star-up a 260 kt/year production plant (111). The transformation of CO_2 into polymeric materials, offsetting the related demand for petroleum-based resources, has matured to a point where it is being used in specific instances, albeit on a limited industrial scale. These processes require low metal residues in the polymer as well as good recyclability and recovery and the ultimate products aim to be degradable CO_2 polymers.

In short, the economic returns of using, rather than wasting, CO_2 emissions are, in most cases, positive. Additionally, the treatment of CO_2 as a raw material at an industrial level, requires fewer precautions with a lower economic and energy cost compared to a wide variety of other chemical products. It has been proven that CO_2 can be a useful molecule for an efficient, viable and sustainable production of chemical and energy resources.

7. CURRENT INNOVATIVE PROJECTS RELATED

As have been seen so far, CO_2 reuse technologies have attracted the attention of both the scientific community and private companies aware of the potential use of these emissions. There are numerous projects from both private and government companies that have set their sights on the use of CO_2 emissions as a raw material. Those most known, not only in the Spanish territory, are presented below.

Repsol Technology Lab is one of the most avant-garde private R+D models in Spain, based on open innovation and networking in alliances with technology centres, companies and universities around the world. They participate in the development of CCS and CCU technologies as members of the Oil and Gas Climate Initiative (137).

On the other hand, in the Basque Country, the LOWCO2 project has been created as an alternative to mitigate climate change and improve the competitiveness of Basque Industry. It is an R+D project launched by a consortium of 11 entities that are committed to sustainable innovation. They have a budget of almost 5 M€ and base their research on new materials and processes for CO_2 capture, methane and methanol production from CO_2 and the development of technologies for the carbonation of waste (138).

Outside the peninsula, Porthos, from its english acronym Port of Rotterdam CO_2 Transport Hub and Offshore Storage, is a Dutch project that aims to store CO_2 under the North Sea. The CO_2 produced by the port of Rotterdam would be transported and stored in empty gas fields under the sea. It is a collaborative project between the Port of Rotterdam Authority, Gasunie and EBN, and co-financed by the Connecting Europe Facility of the European Union. The CO_2 will be transported by underwater pipeline to a platform in the North Sea, approximately 20 km from the coast. From the platform, CO_2 will be pumped into empty gas fields. The empty gas fields are located in a closed reservoir of porous sandstone, more than 3 km below the sea level. It is expected to store approximately 37 Mt of CO_2, which is approximately 2,5 Mt of CO_2 per year for the duration of the project (139).

Using the same underwater storage technology, the Northern Lights project was created, which is intended to be launched by mid-2024. It is expected to have a capacity of 1,5 Mt of CO_2 per year (140).

Continuing with the international scene, in 1994 the XPRIZE foundation emerged, which promotes a massive project that encourage innovation and entrepreneurship. A problem that affects worldwide is proposed by a jury and the first team to build and demonstrate a feasible solution, wins a monetary prize. In 2015 they announced the launch of the NRG COSIA Carbon XPRIZE. The award challenges COSIA member companies, current technology partners and innovators around the world to reimagine CO_2. The prize is 20 M$ and several proposals have been submitted, such as the transformation of CO_2 into vodka, hand sanitizer, sunglasses, purses, straws, crayons, and a wide variety of other products. Both winning teams in 2021 developed solutions that aimed to reduce CO_2 emissions associated with traditional concrete production, which is currently the world's most abundant human-made material and accounts for 7% of all global CO_2 emissions (141). The Asturian scientist F. Pelayo García de Arquer reached the final of the contest designing a nanomaterial based on copper and capable of converting CO_2 into ethylene (142).

Moreover, there is the Carbon4PUR program, a research and innovation project that aims to transform industrial waste gases, such as CO and CO_2 flows, into intermediate products for polyurethane plastics for rigid foams, insulation and building coatings. The consortium is made up of 14 participants from 7 different European countries. This multidisciplinary consortium aims to achieve the objectives of the Horizon 2020-SPIRE-8-2017 by the EU (143).

8. PROJECT PLANNIFICATION

Below is the Gantt diagram used for the initial planning of this project. The tasks have been grouped considering the main sections of the project.

It should be pointed that most of the planning firstly appointed has been fulfilled, and the project has been satisfactorily completed within the time margin established by the university

Table 8: Gantt diagram proposed for the project

.

	Sept.	**Oct.**	**Nov.**	**Dec.**	**Jan.**	**Feb.**
Project definition	■					
Proposed index	■					
Previous bibliographic research	■	■				
Writing the report		■	■	■	■	
Partial delivery			■	■		
Addition of new sections				■	■	
Overview				■	■	
Final delivery					■	■

9. ECONOMIC STUDY OF THE PROJECT

The cost of the development of the present project is detailed below. Since it is a systematic review type of project, the main tasks developed have been research and data collection, as well as the composition of this report. The activities have been carried out in their entirety by the author of this project, a junior engineer, with an average economic remuneration of 15 €/hour.

The cost and hours dedicated to each of the tasks carried out during the project are detailed below:

Table 9: Economic study of the project detailed

	Detail	**Total [€]**	**Observations**
Bibliographic research	150 hours at 15 €/h	2.250	In specialized libraries and online information databases
Report composition	100 hours at 15 €/h	1.500	
Transport (for assisting to the college)	7,95 € each for a total of two	15,90	Price for the 10 journeys tickets in Barcelona
Administrative material	250 €	250	Photocopies, writing material and computer equipment included
Project university registration	18,46 € for each credit	221,52	Equivalent to a 12-credit subject at UPC
TOTAL	**4.237,42 €**		

Thus, the total cost of the project is 4.237,42 € without applying any taxes. If a 21 % *IVA* is applied, this would be 889,86 € and the total cost would amount to **5.127,28 €**.

10. ENVIRONMENTAL STUDY OF THE PROJECT

The carbon footprint generated for the realization of the project is determined below.

The tasks developed in this project are mainly those of searching and writing the report, as mentioned above. These activities are strictly linked to an energy consumption of light both in the workspace and for the technological devices used, this consumption being the most significant ones. It has been considered that 225 hours of the total 250 worked, have been at the workplace. The remaining 25 hours constitute to external research in libraries.

It has also been considered the number of times that has been travelled from the workplace, Avinguda del Parc de Can Mercader (Cornella) to the university located at Avinguda Diagonal, 647 (Barcelona). It is a 5,2 km journey that is carried out in a combination of two public transports, metro (L5) and tram. The total journey time is approximately 25 minutes.

With all this information, the results detailed are explained in the table below:

Table 10: Environmental study of the project detailed

	Detail	**Total [kg CO_2]**	**Observations**
Lighting energy consumption at workplace	0,03 kW for 225 hours applying a 50 % off security factor (considering 0,26 kg CO_2e/kWh)	0,87	Two bulbs of 15 W each have been considered having a light use factor of 50% assuming that the rest of the hours natural light has been used
Lighting energy consumption at libraries	19,8 W/m^2 using approximately 2 m^2 of space for 25 hours (considering 0,26 kg CO_2e/kWh)	0,26	Assuming 33 VA/m^2 illumination rate with an average load factor estimate of 0,6 for schools and study places (144)
Technological devices energy consumption	0,05 kW for 225 hours (considering 0,26 kg CO_2e/kWh)	2,90	Considering specifications of the computer used
Transport (for assisting to the university)		0,00	*Nexus Energía* has been awarded the contract for the supply of electricity to the TMB companies and it is a 100% renewable energy marketer (145)
TOTAL	**4,03**		

The calculation tool offered by the Ministry for the Ecological Transition and the Demographic Challenge of the Government of Spain has been used (146). This calculator allows to easily estimate the greenhouse gas emissions associated with the activities of an organization, considering both direct and indirect emissions from electricity consumption.

This project could easily become a zero-carbon impact investigation if the kg of CO_2 produced were offset. For this purpose, companies specialized in emission offsets can be hired, such as ClimateTrade (147). This type of companies offer the possibility of contributing economically to several projects to achieve carbon neutrality. The price range of Spanish projects is between 1 and 50 euros per ton of CO_2 compensated. Considering an average price of most projects of approximately 35 €/tCO_2 and the project impact that has been calculated (see Table 10), this compensation would only entail an economic outlay of 0,14 €.

11. SOCIAL AND GENDER EQUALITY STUDY OF THE PROJECT

In the field of research concerned with this project, as in many others, men have generally predominated. It is clearly reflected in the bibliography of the project since most of the articles consulted, as well as cited, have male authors. In any case, it should be noted that in most of the university research groups consulted, the number of women members is also remarkable.

The emission recovery technologies presented do not discriminate against any gender group since, with this project, it is intended to bring knowledge about this technological advance to anyone, no matter how far from the scientific world they are. The work has been written with inclusive and non-sexist language. In addition, the topic is initially presented so that anyone can understand the entire project without having to understand all the detailed complexity of it.

On the other hand, the gender aspect has been considered in the authorship of the publications cited throughout the project. No differences have been made in the validity of articles authored by women and men and have been cited by their surname, in most cases, so as not to create possible discrimination by readers.

Regarding the sustainable development objectives, this project is related to six of them:

- Increase in health and well-being.
- Economic growth.
- Innovation in industry and infrastructure.
- Creation of more sustainable cities and communities.
- It promotes sustainable consumption and production.
- Climate action.

Figure 33: Sustainable development objectives related

12. CONCLUSIONS AND FUTURE RESEARCH

The real need to establish an industry based on the reuse of CO_2 and thus contribute significantly to the production of value-added products from CO_2 has been demonstrated. All these processes would have a positive impact on global emissions, as well as curbing global warming and climate change. However, the use of just one of the synthesis technologies presented would not be enough to achieve, in any way, the requirements established by the Kyoto protocol, so a multi-track approach is needed.

The biggest drawbacks in these transformation pathways presented are the costs of capturing and separating CO_2, transporting it to the synthesizing plants, and, above all, the energy, and resources necessary for its conversion. That is why greater investment in the incorporation of green energies into these synthesis processes is also needed. It would decrease the dependence on fossil fuel sources and the real impact of the whole process would be beneficial. The development of an integrated system of industries for in situ conversion of CO_2 using renewable energy can be considered as an ideal strategy for CO_2 global mitigation.

In the present project, several possible pathways for the transformation of CO_2 into value-added products have been defined. It has been demonstrated the wide use of this gas as a precursor of many different characteristics' products and applicable to a multitude of additional processes.

Among all the processes seated, the transformation of CO_2 into coal is one of the most novel and promising. This technology presents a conversion of CO_2 to a new energy source with multiple uses. Regarding this new synthesis process, the major challenge is the inherent risks involved in building commercial-scale production and distribution facilities before the market is fully developed. Current approaches should be focused on the choice of catalyst and appropriate reaction conditions, since the catalyst is considered the main factor in resolving the reaction rate, selectivity, and yield.

Furthermore, the rest of the synthesis routes presented, have been shown to be technologically viable. Further attention must then be focused on promoting and helping their economic viability. Moreover, efforts should be increased to develop and design new materials that can be used as catalysts that reduce the need for precious metals.

This report brings knowledge of carbon separation techniques, transformation details and future perspectives on the CO_2 use. It is aimed to help provide guidance to the current market situation regarding the use of emissions as a source of feedstock, as well as to open up new future directions of research and development.

In conclusion, it can be demonstrated that the use of CO_2 as a precursor is broad by employing different synthetic pathways that have a cumulative effect on its mitigation and an overall positive impact on the environment.

ACKNOWLEDGMENTS

I would like to thank all those who have collaborated in some way in the development of the present project.

First of all, I wish to thank all my teachers with whom I have shared class during the last six years, for accompanying me on this journey that has been my university education.

Secondly, I want to thank my friends, both the new and the old ones, for going along with me in the development of this project.

I also wish to express my gratitude to my teacher in this project Jordi Bou Serra, for placing his trust in my abilities.

This project closes a stage but surely it opens many future ones.

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