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# Greenhouse Gas Emissions – Carbon Capture, Storage and Utilisation

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Additional information is available at the end of the chapter

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## Abstract

According to the recent information, CO<sub>2</sub> concentration in the atmosphere reached 402 ppm at the beginning of 2016. On the other hand, fossil fuels remain as the major source to produce energy. The International Energy Agency estimate that those fuels will remain as the most used source during coming decades.

Carbon capture and storage technology is the most promising technology to significantly decrease CO<sub>2</sub> emissions. Nevertheless, it may be possible to use CO<sub>2</sub> as a raw material for other industrial uses. In this chapter, authors explain both ways to decrease CO<sub>2</sub> emissions.

**Keywords:** CCS technology, CO<sub>2</sub> capture technologies, CO<sub>2</sub> storage, CO<sub>2</sub> uses, macrofouling

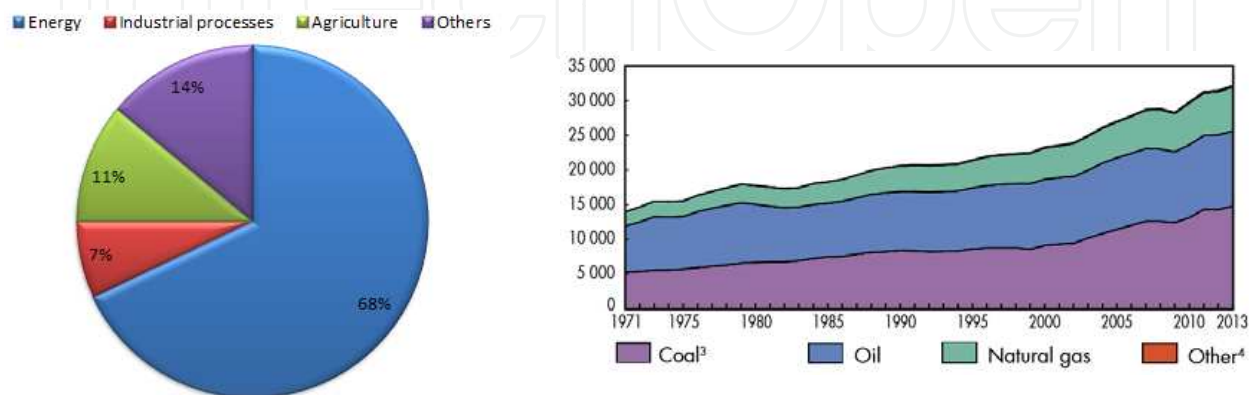
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## 1. Introduction

The Fifth Assessment Report from the Intergovernmental Panel on Climate Change states that human influence on the climate system is clear [1]. The CO<sub>2</sub> concentration in the atmosphere is continuously growing. The latest value is 402.52 ppm (January 2016, Mauna Loa Observatory), which is 2 ppm higher than the value registered in January 2015 [1].

Carbon capture and storage (CCS) is a way of 'decarbonising' fossil fuel power generation. It involves capturing carbon dioxide (CO<sub>2</sub>) emitted from high-producing sources, transporting it and storing it in secure geological formations deep underground, to mitigate the effect of greenhouse emissions on climate change [2].

The transported CO<sub>2</sub> can also be reused in processes such as enhanced oil recovery (EOR) or in the chemical industry, a process sometimes known as carbon capture and utilisation (CCU). CCS can be applied to fossil fuel power plants (coal and gas-fired power stations) and to industrial CO<sub>2</sub>-emitting sources such as oil refineries or cement, chemical and steel plants. Rather than being a single technology, CCS is a suite of technologies and processes. While some of these have been operated successfully for decades, progress in applying large-scale CCS to power generation globally has been slow (Figure 1).



**Figure 1.** Shares of global anthropogenic greenhouse gas emissions (GHG) and world CO<sub>2</sub> emissions from fuel combustion by fuel (Mt of CO<sub>2</sub>) [3, 4].

Carbon capture and storage (CCS) is likely to be a crucial part of the least-cost path to decarbonisation. It can provide a back-up role for variable renewables and help to manage swings in demand. CCS also has a crucial role in decarbonising heavy industry where there are limited options, and in the longer term would help to maximise the emission reduction obtained from scarce supplies of sustainable bioenergy as well as opening up other decarbonisation pathways.

The European Commission has also emphasised that ‘CCS may be the only option available to reduce direct emission from industrial processes at the large scale needed in the longer term’.

In this chapter, authors review the carbon capture, storage technology (including the CO<sub>2</sub> transport through pipeline), and CO<sub>2</sub> utilisation technologies.

## 2. CO<sub>2</sub> capture

This process consists of the separation of CO<sub>2</sub> from flue gas produced during the combustion of fossil fuels and can be applied to large flue gas stationary sources as thermal power stations and industrial processes.

Current CO<sub>2</sub> capture technology (first generation) is adapted from gas separation processes already in industrial use. There are several technologies and strategies to capture CO<sub>2</sub> from stationary sources: pre-combustion, post-combustion and oxy-fuel (Figure 2).

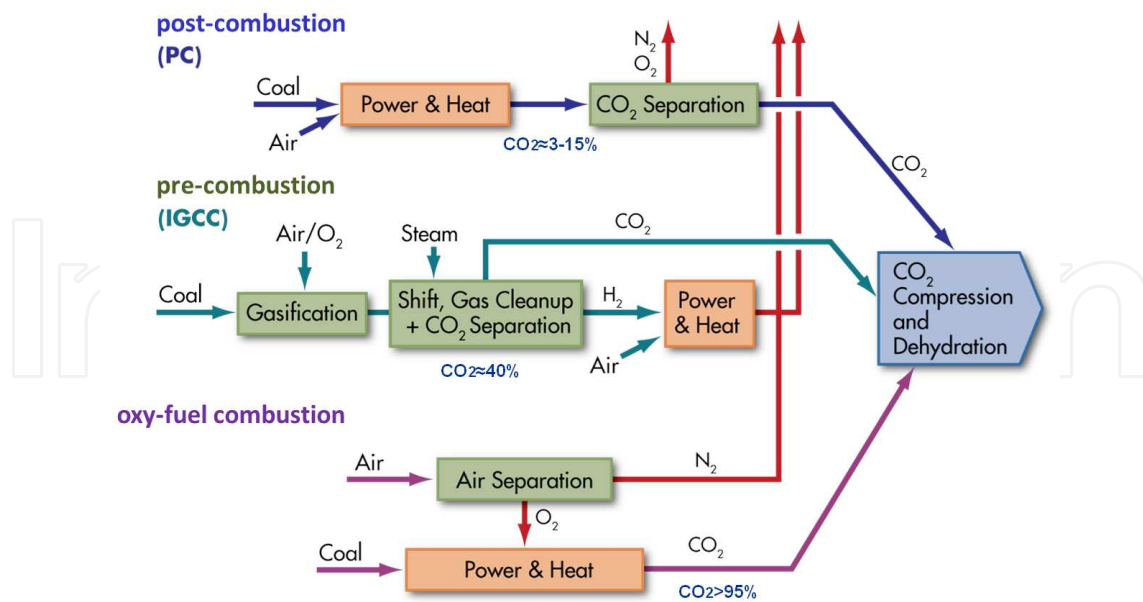


Figure 2. Summary of CO<sub>2</sub> capture technologies (adapted from IPCC) [2].

### 3. First generation of capture technologies

#### 3.1. Post-combustion capture

Post-combustion capture follows the conventional application of a specific purification unit applied for a particular pollutant removal (CO<sub>2</sub> in this case). Figure 3 illustrates a typical block diagram of the post-combustion process that offers a great feasibility and versatility in terms of operating conditions and process integration.

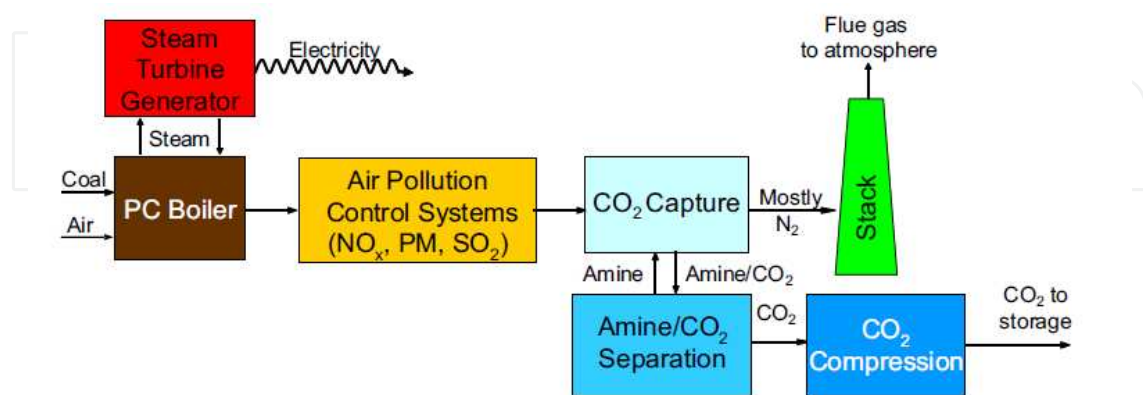


Figure 3. Simplified scheme of a fossil-fuel power plant using a post-combustion capture unit [5].

CO<sub>2</sub> concentration in the flue gas from a combustion process varies from 4 to 14% in natural gas and coal-power plants, while other industries such as cement, iron and steel and petro-

chemical produce flue gas ranging between 14 and 33%. The key drawbacks hindering the large-scale implementation of this technology lies in the large volume of gas that should be treated and the low CO<sub>2</sub> concentration of the flue together with high energy requirements, mainly related to CO<sub>2</sub> desorption process. The presence of large amounts of dust, O<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub> and trace pollutants such as Hg and the relatively high temperature of the flue gas, typically between 120 and 180°C, are also design challenges that have significant impact on the capture costs.

The technologies currently available for post-combustion capture are classified into five main groups: absorption, adsorption, cryogenics, membranes and biological separation. The most mature and closest to market technology and so, the representative of first generation of post-combustion options, is capture absorption from amines.

### 3.2. Chemical absorption from amines

Post-combustion capture using chemical absorption by aqueous alkaline amine solutions has been used for CO<sub>2</sub> and H<sub>2</sub>S removal from gas-treating plants for decades [6]. Amines react rapidly, selectively and reversibly with CO<sub>2</sub> and can be applied at low CO<sub>2</sub> partial pressure conditions. Amines are volatile, cheap and safe in handling. They show several disadvantages as they are also corrosive and require the use of resistant materials. Furthermore, amines form stable salts in the presence of O<sub>2</sub>, SO<sub>x</sub> and other impurities such as particles, HCl, HF and organic and inorganic Hg trace compounds that extremely constrain the content of those compounds in the treated gas.

The most widely used amine is monoethanolamine (MEA), which is considered as a benchmark solvent because of its high cyclic capacity, significant absorption-stripping kinetic rates at low CO<sub>2</sub> concentration and high solubility in water. Some other amine-based solvents such as diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DGA), N-methyldiethanolamine (MDEA), piperazine (PZ), 2-amino-2-methyl-1-propanol (AMP) and N-(2-aminoethyl)piperazine (AEP) have also traditionally been utilised.

A typical chemical absorption scheme is shown in Figure 4. A low CO<sub>2</sub> concentrated flue gas is introduced in the absorber in crosscurrent with lean solvent from the stripper at 50–55°C and ambient pressure. CO<sub>2</sub> reacts with amines in the absorber according to the overall reaction:



As CO<sub>2</sub> is absorbed, rich amine from the absorber bottom is fed into a cross-exchanger with lean amine before it is introduced into the stripper. The stripping temperature varies between 120 and 150°C, and the operating pressure reaches up to 5 bar. A water saturated CO<sub>2</sub> stream is released from the top and is subsequently ready for transport and storage, while lean amine leaving the stripper is pumped back into the absorber.

The high energy penalty related to amines regeneration (a high-intensive energy process because of the stripper operating conditions and solvent used) and solvent degradation are the issues most hindering a large deployment of this technology.

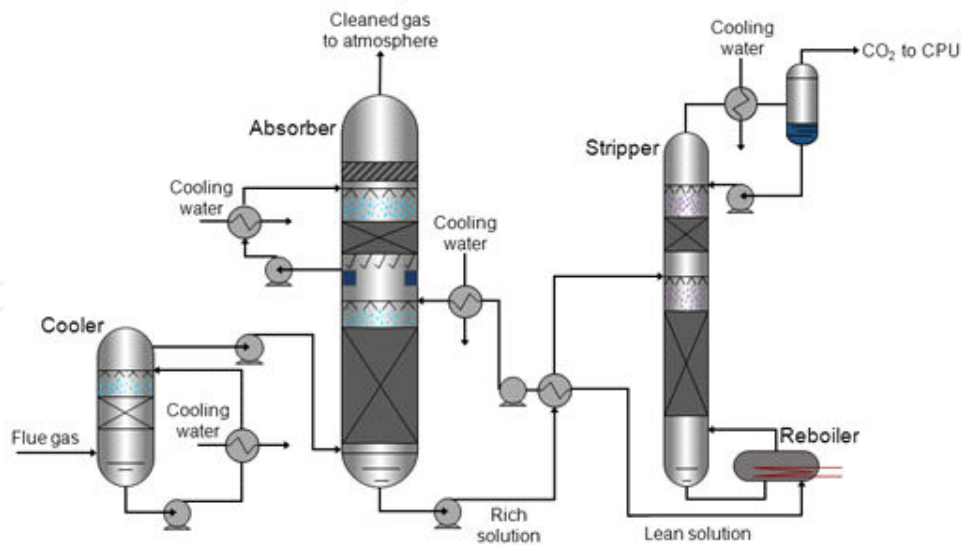


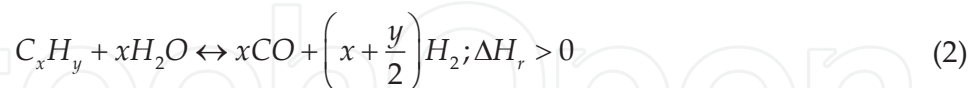
Figure 4. Diagram of a conventional CO<sub>2</sub> capture process using amine-based chemical absorption.

### 3.3. Pre-combustion capture

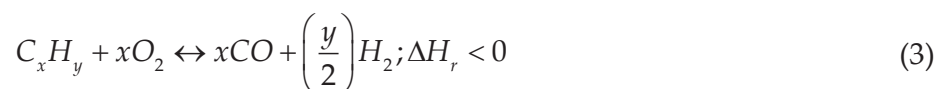
In pre-combustion CO<sub>2</sub> capture, CO<sub>2</sub> separation occurs prior to fuel combustion and power generation (Figure 5). The fuel reacts at high temperature and pressure with either oxygen or/ and steam under sub-stoichiometric conditions, and thereby a gas stream primarily composed of CO and H<sub>2</sub> is obtained. This CO/H<sub>2</sub> gas mixture is commonly known as *synthesis gas* or *syngas*.

In general, steam is utilised in case fuel is solid, namely gasification, whereas sub-stoichiometric oxygen is used with liquid and gaseous fuels. Both reactions occur at elevated temperature (1,400°C) and pressure (3–7 Mpa), as seen in Equations 2 and 3.

Steam reforming:



Partial oxidation:

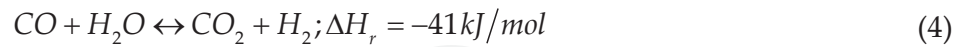


Steam reforming needs a secondary fuel to provide the energy supply necessary for the reaction that occurs and a catalysts to improve the kinetic of this process. In Equation (3), the primary fuel is partially oxidised by a limited amount of oxygen. Partial oxidation produces less H<sub>2</sub> per fuel unit than stream reforming, but the kinetic reaction is faster, it requires smaller reactors and neither catalyst nor energy supply from a secondary fuel.



Once particulate matter is removed, the syngas passes through a two stages catalytic reactor, where CO reacts with steam to produce CO<sub>2</sub> and further yield H<sub>2</sub>: *water-gas-shift (WGS) reaction*.

WGS reaction:

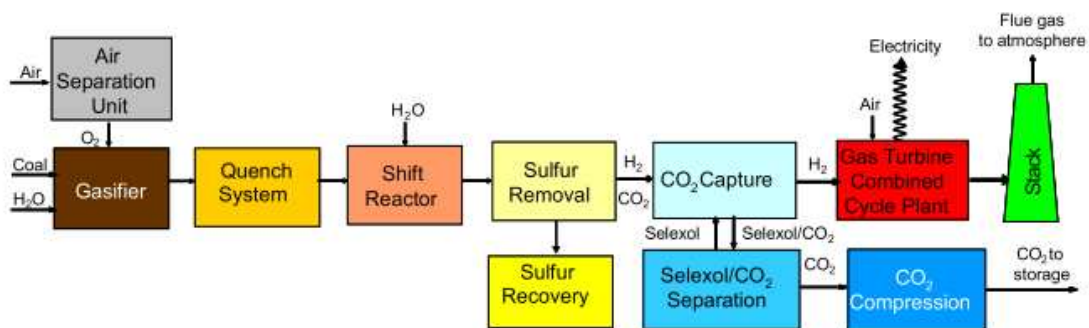


The syngas resulted is mainly composed of CO<sub>2</sub>, ranging from 15 to 40%v/v, and H<sub>2</sub> at elevated pressure from which CO<sub>2</sub> can be easily separated by a physical absorption mechanism and then CO<sub>2</sub> can be easily released by simply dropping pressure.

Before the syngas from WGS reactor is separated into its primary components, the sulphur compounds, mainly in COS and H<sub>2</sub>S form, are removed to avoid its emission to the atmosphere. Sulphur is then recovered in either as solid in a Claus plant or as sulphuric acid.

The sulphur-free syngas has a high CO<sub>2</sub> concentration and an elevated pressure (2–7 MPa), thus making physical absorption highly recommended for CO<sub>2</sub> separation, although adsorption process such as pressure swing adsorption (PSA) is also utilised.

The remaining nearly pure H<sub>2</sub> stream could be burned in a combined cycle power plant to generate electricity, but H<sub>2</sub> turbines require further development. Power fuel cells and transportation fuels are alternative options for using H<sub>2</sub> in the future, currently under development.

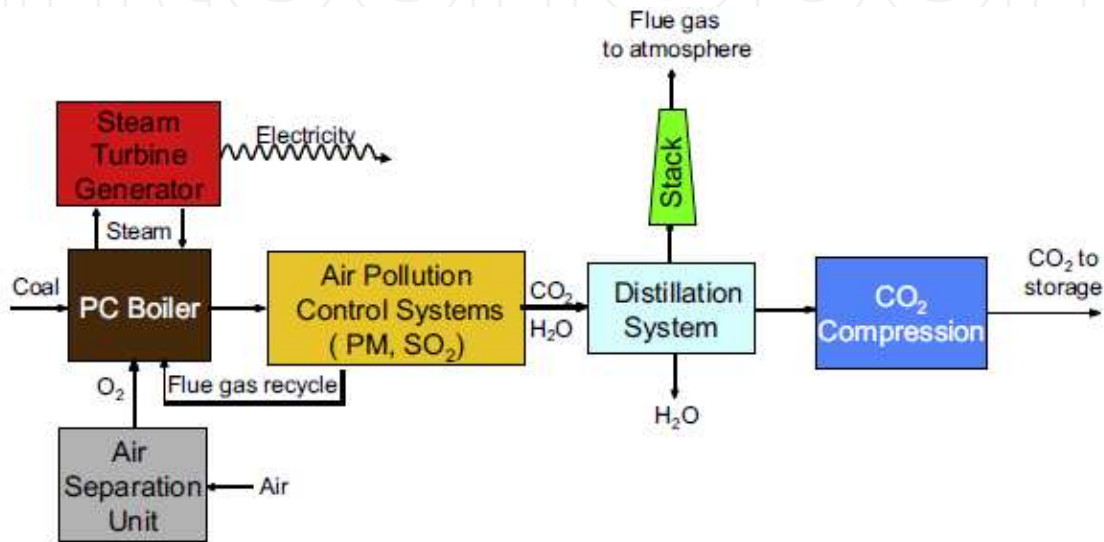


**Figure 5.** Simplified scheme of an integrated gasification combined cycle (IGCC) coupled with a pre-combustion CO<sub>2</sub> capture and storage unit using a physical absorption process [5].

### 3.4. Oxy-combustion capture

Oxy-combustion or oxy-fuel capture is considered as one of the most promising CCS technologies that would be economically competitive in fossil-fuel power plants and industrial facilities. It has been developed for both new designs and retrofitting of existing plants, although it is best adapted to newly designed power plants. A basic process flow diagram is given in Figure 6. Oxy-combustion technology is based on the use of high purity O<sub>2</sub> as oxidiser in an O<sub>2</sub>/CO<sub>2</sub> mixture instead of air during the combustion process. It has been first proposed

for coal boilers and gas turbines but can be applied to any type of fossil fuel utilised for thermal power production. As burning with  $O_2$  at high concentration can produce high flame temperatures in the boiler, part of the exhaust gas from the boiler, mainly  $CO_2$  and water vapour (FGR flue gas recirculation stream), is recycled to control temperatures to levels compatible with available boiler materials. The flue gas obtained from this system consists mainly of  $CO_2$  and  $H_2O$  and are accompanied by minor quantities of  $N_2$ ,  $SO_x$ ,  $NO_x$ , Ar and Hg. Water can be easily removed by condensation, producing a highly  $CO_2$  concentrated flue gas. The  $CO_2$  content varies from 70 to 95%v/v, depending on the process configuration, air in-leakages, fuel characteristics and the purity of  $O_2$ .



**Figure 6.** A simplified scheme of a fossil-fuel power plant based on the oxy-combustion concept [5].

Oxy-combustion requires large amounts of high purity (95–99%)  $O_2$  for power production. A typical 500 MWe fossil-fuel power plant would need 9,000–10,000 t/d to operate under oxy-combustion conditions [7]. Currently, cryogenic distillation is the only available technology that can supply those amounts of  $O_2$ . An air separation unit (ASU) can provide around 4,500–7,000 t/d of oxygen, while other alternative technologies such as vacuum pressure swing adsorption (VPSA) units and membranes can only produce one order of magnitude below ASU production.

The ASU would consume up to 60% of the total electricity required for carbon capture and reduces the overall efficiency of the power plant by about 7–9%, reaching up to 15% in some cases. Furthermore, the availability and rapid response of the ASU to load changes have been noted as crucial challenges for the global oxy-combustion plant operation and feasibility. New technologies for  $O_2$  production as ion transport membranes (ITM) or VPSA have shown promising results related to energy consumption, but the large amounts of  $O_2$  required in power plant operation avoid currently its commercial deployment.

The  $CO_2$  stream obtained from oxy-fuel combustion shows high levels of water vapour, sulphur compounds,  $N_2$ ,  $O_2$  and impurities such as mercury in the flue gas.  $NO_x$  emission is low when compared with air combustion.



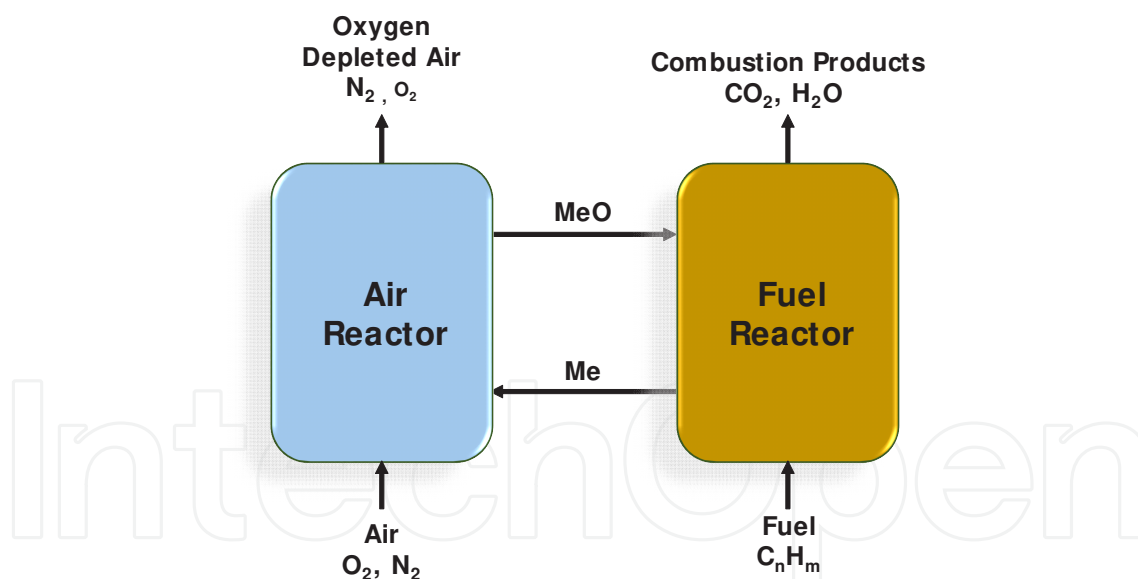
The  $\text{CO}_2$  gas quality has significant impact on the capture cost by this technology, and uncertainties on the future regulatory requirements of  $\text{CO}_2$  quality for its transport and storage has influence on the process configuration of the oxy-combustion plant, gas cleaning unit performance, overall  $\text{CO}_2$  recovery capacity and on the energy requirements for  $\text{CO}_2$  compression and purification.

## 4. Emerging technologies for $\text{CO}_2$ capture

The most promising emerging technologies applied to carbon capture are discussed in this section to complete the overview of the  $\text{CO}_2$  capture technologies currently under research.

### 4.1. Chemical looping combustion

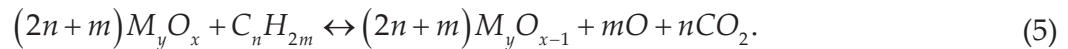
Chemical looping combustion (CLC) is a promising technology for fuel combustion, which can be beneficial in carbon capture applications. It is based on the use of an oxygen carrier, typically a metal oxide, to supply the  $\text{O}_2$  needed for the fuel combustion process, producing a highly  $\text{CO}_2$  concentrated exhaust gas. Iron, nickel, cobalt, copper, manganese and cadmium are commonly used as oxygen carriers in CLC.



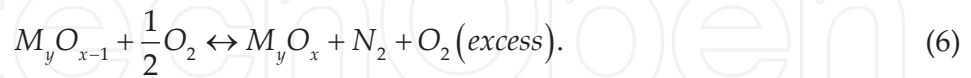
**Figure 7.** A simplified scheme of a chemical looping for oxy-combustion.

CLC consists of two fluidised bed reactors, namely reducer and oxidiser. In the reducer reactor, fuel is fed along with the metal oxide containing oxygen, which is transferred from the metal oxide to the reactor as the combustion occurs (Figure 7). A flue gas containing over 99%v/v of  $\text{CO}_2$  can be obtained by a simply condensation stage because of the fact that the exhaust gas at the reducer outlet is primarily formed by  $\text{CO}_2$  and water vapour. This stream is then sent to further compression and permanent storage.

Reducer:



Oxidiser:



#### 4.2. Hydrate-based separation

This separation approach is based on the hydrate formation from high pressure water in contact with the flue gas containing CO<sub>2</sub>. Hydrates are crystalline under suitable low temperature and high pressure conditions. A pure CO<sub>2</sub> stream is then obtained as CO<sub>2</sub> is released from the hydrates, achieving up to 99% of CO<sub>2</sub> recovery.

#### 4.3. Calcium looping

Calcium looping is based on the reversible reaction between CaO and CO<sub>2</sub> to form calcium carbonate.

Calcium looping consists of two fluidised bed reactors, namely carbonator and calciner. In the carbonator, primary fuel is burned and CaO reacts with the CO<sub>2</sub> formed from the fuel combustion following the reaction seen in Equation (7). Carbonator temperature is within 650–700°C, depending on the system pressure.

Carbonator:



Calciner:



CaCO<sub>3</sub> is then heated by secondary fuel combustion in the calciner. CaO is regenerated and CO<sub>2</sub> is released for storage according to the reaction in Equation (8). The calciner temperature can reach 900°C, depending on the CO<sub>2</sub> partial pressure.

This technology shows benefits for carbon capture. Limestone is cheap and widely available, and there is a potential for process integration, which can lead to low energy penalties, i.e., heat released from carbonisation can be utilised in a steam cycle or the heat used in the calciner reactor can be recovered in the carbonation process.

#### 4.4. Partial oxy-combustion

The energy consumption required for solvent regeneration and high purity oxygen production is the major drawback of post-combustion and oxy-combustion technologies. A new hybrid concept has been proposed to reduce the energy requirements associated with CO<sub>2</sub> capture step combining a partial oxy-fuel combustion (using oxygen-enriched air instead of high purity oxygen as oxidiser) and a CO<sub>2</sub> separation process treating a flue gas with a higher CO<sub>2</sub> concentration than in conventional air combustion (Figure 8).

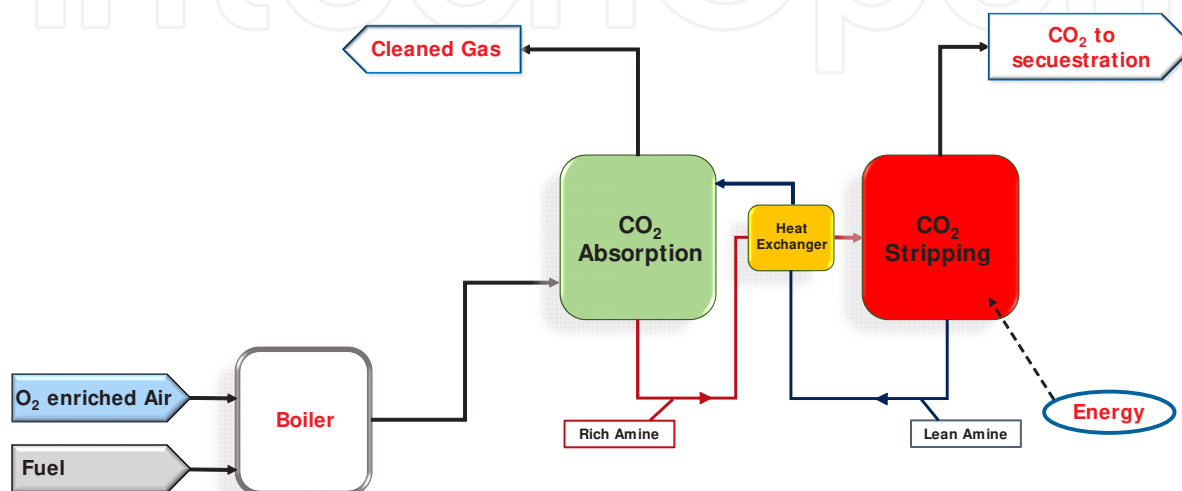


Figure 8. A simplified scheme of a partial oxy-combustion plant.

The combination of a less-constrained ASU for oxygen production and a carbon capture process using membranes instead of amine solvents can conduce to a minimal energy requirement associated with an oxygen purity ranging between 0.5 and 0.6 molar fraction.

#### 4.5. Biological CO<sub>2</sub> capture

Biological CO<sub>2</sub> capture from a gas mixture is based on natural reactions of CO<sub>2</sub> with living organism, mainly enzymes, generally proteins and (micro)algae. Enzymes catalyse CO<sub>2</sub> chemical reaction and enhance CO<sub>2</sub> absorption rate in water. Enzymes can be also immobilised at the gas-liquid interface to promote CO<sub>2</sub> dissolution from the bulk gas. In this sense, carbonic anhydrase enzyme supported in a hollow fibre with liquid membrane has been reported as a potential method applied to CO<sub>2</sub> capture, achieving up to 90% CO<sub>2</sub> capture associated with low energy requirements in the regeneration process at laboratory-scale experiments. Carbonic anhydrase promotes carbonic acid formation from dissolved CO<sub>2</sub> and enhances CO<sub>2</sub> absorption from gas phase using and extremely low CO<sub>2</sub>/enzyme ratio. CO<sub>2</sub> separation using enzymes must incorporate a tailored regeneration process to produce a high concentrated CO<sub>2</sub> exhaust stream. Membrane boundary, fouling, long-term operation and pore wetting are identified as the most relevant technical issues to be addressed before the scale-up of this CO<sub>2</sub> capture approach.

The use of algae is also considered a promising CO<sub>2</sub> capture option among natural occurring reactions. Algae consume CO<sub>2</sub> through photosynthesis mechanism. The use of algae in CO<sub>2</sub> capture would avoid subsequent CO<sub>2</sub> compression and storage stages, but there are some key issues that must be addressed for its large-scale deployment. In fact, algae require excessive amount of water and large gas-liquid interface surfaces that drastically limit their application in carbon capture. Algae are also highly susceptible to changes in operating conditions and to the presence of impurities such as vanadium and nickel.

#### **4.6. Ionic liquid absorption**

Significant progress has been made in the application of ionic liquids (ILs) as alternative solvents to CO<sub>2</sub> capture because of their unique properties such as very low vapour pressure, a broad range of liquid temperatures, excellent thermal and chemical stabilities and selective dissolution of certain organic and inorganic materials. ILs are liquid organic salts at ambient conditions with a cationic part and an anionic part.

ILs have the potential to overcome many of the problems of associated with current CO<sub>2</sub> capture techniques. ILs are particularly applicable in absorption of CO<sub>2</sub> while effectively avoiding the loss of sequestering agents. Other advantage of ILs is that they can be combined into polymeric forms, increasing the CO<sub>2</sub> sorption capacity compared with other ILs and conventional solvents and greatly facilitates the separation and ease of operation.

### **5. CO<sub>2</sub> transport**

Currently there are more than 6,500 km of CO<sub>2</sub> pipelines worldwide. Most of them deliver CO<sub>2</sub> to EOR operations in the United States, but there is also a growing number under development for CO<sub>2</sub> storage projects

The relative development of the infrastructure to transport CO<sub>2</sub> is still in its early stages. This is reflected by the low number of existing infrastructures developed to transport CO<sub>2</sub> from stationary sources into geological structures. Table 1 provides an overview of the current developments for CO<sub>2</sub> transportation globally. All of these examples have been developed in relation to the EOR technique, where the CO<sub>2</sub> source is found mainly in natural reserves. In Europe, only a few projects are in operation, but there are plans to deploy an extended CO<sub>2</sub> pipeline network along Europe to optimise CO<sub>2</sub> storage structures.

These examples may be used to study CO<sub>2</sub> conditions; in addition, many CO<sub>2</sub> pipeline projects are based on well-known designs and materials commonly used in natural gas pipeline specifications. The most profitable way to transport CO<sub>2</sub> is in its dense phase [9].

To avoid two phases, it has been suggested that the most efficient way to transport CO<sub>2</sub> is as its supercritical phase [8, 9], which occurs at a pressure higher than 7.38 MPa and a temperature of more than 31.1 °C. To maintain these conditions, this type of transportation may require the use of booster stations in the pipeline layout to maintain the required pressure and temperature.

Pipeline	Location	Length (Km)	Diameter (inches)	Estimated maximum (10 <sup>6</sup> t/year)
Cortez	US	808	30	23.6
Sheep Mountain	US	656	NA	11.0
Bravo	US	351	20	7.0
Dakota Gasification/Weyburn	US/Canada	328	14	2.6
Choctaw	US	294	20	7.0
Bairoil	US	258	NA	23.0
Central Basin	US	230	16	4.3
Canyon Reef Carriers	US	224	16	4.3
Comanche Creek	US	193	6	1.3
Centerline	US	182	16	4.3
Delta	US	174	24	11.4
Snohvit	Norway	153	NA	0.7
Borger	US	138	4	1.0
Coffeyville	US	112	8	1.6
OCAP	The Netherlands	97	NA	0.4
Beaver Creek	US	85	NA	NA
Anton Irish	US	64	8	1.6
El Mar	US	56	6	1.3
Chaparral	US	37	6	1.3
Doliarhide	US	37	8	1.6
Lacq	France	27	NA	0.1
Adair	US	24	4	1.0
Cordona Lake	US	11	6	1.3

**Table 1.** Current CO<sub>2</sub> pipelines. The first long distance CO<sub>2</sub> pipeline was in the 1970s. Main utilisation of the natural & anthropogenic CO<sub>2</sub> is EOR activities [8].

Material selection should be compatible with all states of the CO<sub>2</sub> stream. They should be defined to prevent corrosion and maximum material stress. In addition, eligible materials need to be qualified for the potential low temperature conditions that may occur during a pipeline depressurisation situation.

The design of a pipeline should meet the requirements set by appropriate regulations and standards. CO<sub>2</sub> pipelines shall be designed according to applicable regulatory requirements. The Recommended Practice for Design and Operation of CO<sub>2</sub> refers to the following pipeline standards: ISO 13623:2009, DNV-OS F101:2012 and ASME B31.4 or ASME B31.8.

Usually CO<sub>2</sub> pipelines are designed using existing national standards for gas and liquid transportation pipes, while additional CO<sub>2</sub> specific design issues are taken into consideration by the pipeline construction/operation companies to guarantee the reliable and safe operation of a given pipeline.

The use of carbon steels (e.g., with API X-60 and X-65) for the transportation of CO<sub>2</sub> streams has been ongoing for more than 30 years, as required in EOR projects. During the 2002–2008 period, 18 incidents were reported with no fatalities and/or injuries.

	Range
Length (km)	1.09–808
External diameter (mm)	152–921
Wall thickness (mm)	5.2–27
Capacity design (Mt/y)	0.06–28
Pressure min (bar)	3–151
Pressure max (bar)	21–200
Compressor capacity (MW)	0.2–68

**Table 2.** Summary of the current parameters considered in the CO<sub>2</sub> transport phase.

The cost of pipeline transportation will be determined by the pipeline route, in which physical and social geography will be crucial conditions.

The three major cost elements for pipelines are (1) construction costs (e.g., materials, labour, booster station, if needed, and others), (2) operation and maintenance costs (e.g., monitorisation, maintenance, energy costs) and (3) other costs (design, insurance, fees, and right-of-way).

## 6. CO<sub>2</sub> storage

At present, there are three possible geological structures that may be considered for CO<sub>2</sub> storage: depleted hydrocarbon and production, deep saline aquifers, and coal seams.

### 6.1. Depleted hydrocarbon fields

The CO<sub>2</sub> can be stored in supercritical conditions, rising by buoyancy and can be physically held in a structural or stratigraphic trap, the same way as the natural accumulation of hydrocarbons occurs. The advantage of the capacity of containment system has been demonstrated by the retention of oil for millions of years. If the site is in production, it is used to increase the recovery of oil or gas (EOR recovery – enhanced oil, gas-enhanced recovery – EGR). These operations, EOR/EGR, provide an economic benefit that can offset the costs of the capture, transport and storage of CO<sub>2</sub>.



## 6.2. Deep saline aquifers

They are the best options for storing large volumes of CO<sub>2</sub> because of its size and found more than 800 meters below the surface. The supercritical CO<sub>2</sub> is 30–40% less dense than typical saline water from these formations, which means that the CO<sub>2</sub> naturally rise by buoyancy through the reservoir until it is caught or becomes longer solution term. They require an impermeable cap rock to ceiling (shales or layers of evaporites) and a porous and permeable rock store (sandstone or limestone) that promotes the injection, migration and trapping.

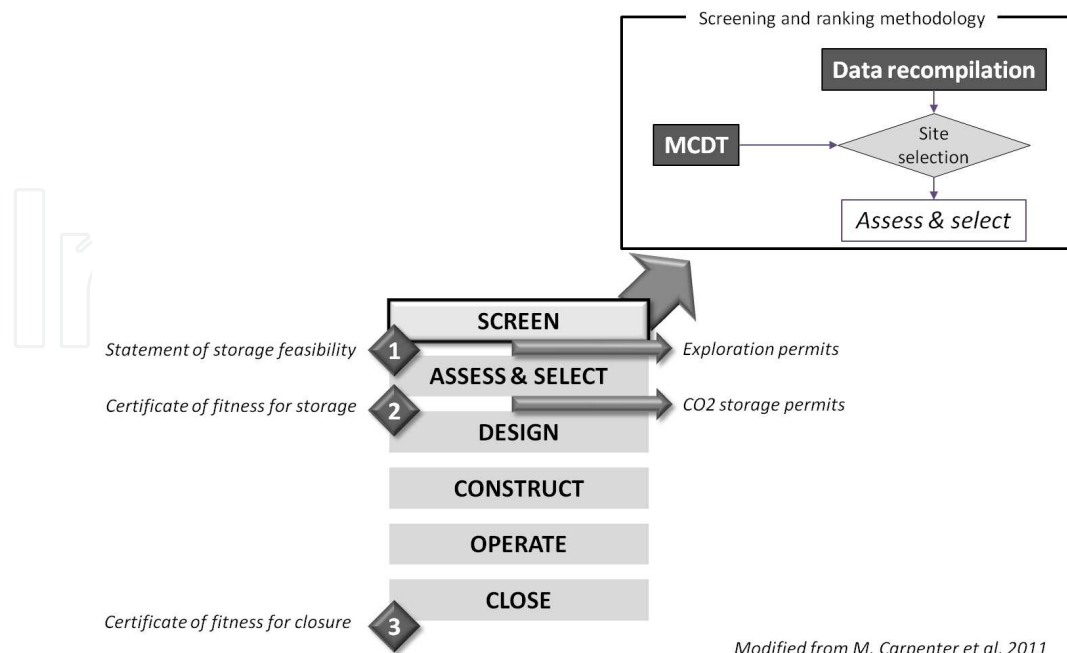
## 6.3. Coal seams

CO<sub>2</sub> in gaseous form is injected into the coalbed, 300 to 600 metre depth, and adsorbed on the matrix pores, releasing the existing CH<sub>4</sub> in the same (two molecules of CO<sub>2</sub> adsorbed by each CH<sub>4</sub> molecule that travels). This has led to the possibility of storing CO<sub>2</sub> in coal seams, while CH<sub>4</sub> recovered is valued. This technique is called 'enhanced coalbed methane production' (ECBM).

Coal properties (range, degree and permeability) determine the suitability of the site, either for storage or storage with only CH<sub>4</sub> recovery.

## 6.4. Site selection and exploration

Figure 9 represents a proposed work flow for any CO<sub>2</sub> storage project. It is possible to determine three mayor phases: pre-injection, injection and post-injection phases.



**Figure 9.** Work flow proposed for basin screening (Definition phase) [10].

In general, most of the areas that could be suitable for storing CO<sub>2</sub> are not well explored geologically. For this reason, pre-injection phase is crucial to decrease the inherent risk in subsurface exploration.

Screen phase could be differentiated by the data recompilation task and the multicriteria decision tool. It is integrated as a preliminary phase, and it is connected with a second phase called *characterisation phase*, which corresponds to site maturation and testing.

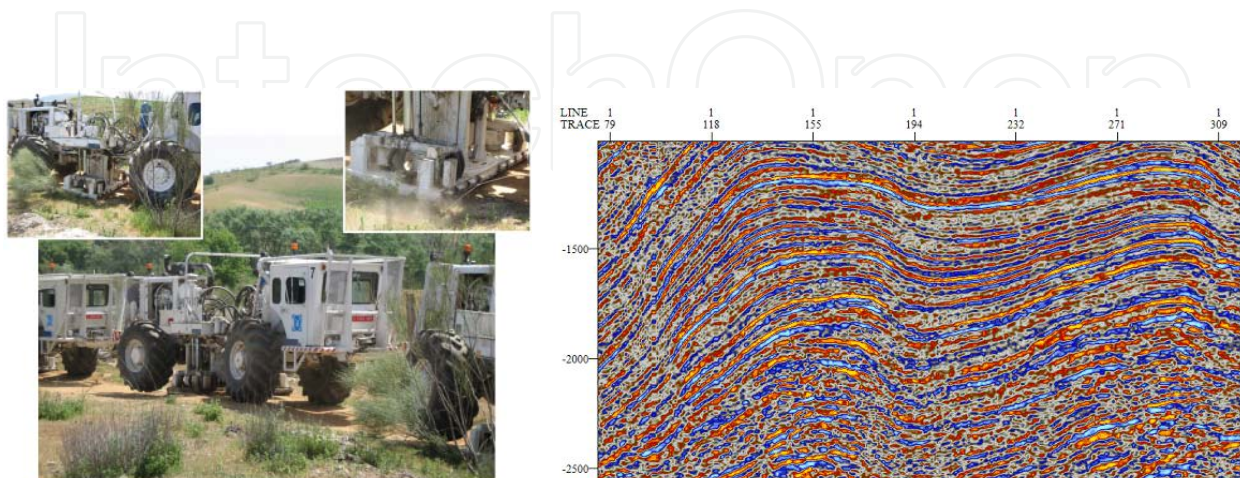
Those criteria should comprise both technique and socio-economic criteria, and they should answer several questions such as where, how much quantity, and which conditions. All of these criteria and questions will contribute to solve and select the most suitable emplacement for storing CO<sub>2</sub> [10].

There are different examples and analogues that can be useful for the definition of criteria. Analogues can be natural (releases and resources) and industrial.

Assess or characterisation task is related to three major ways to explore the sub-surface: outcrops, geophysics and wells.

To decrease the inherent risk of exploration, it is necessary to consider all of the three sub-phases:

- Outcrops exploration provides samples of seal and storage formation, to evaluate some properties such as hydrogeology and geomechanical properties (permeability, porosity, etc.)
- Geophysics survey will provide and describe geological structures, and in some cases hydrogeology parameter (i.e., total dissolved solid, TDS).
- Few techniques may be used if the structure should be 1,000 m deep: seismic reflection is the most important technology (Figure 10), but other technologies such as magneto-telluric or gravimetric may provide relevant information regarding to the geological structure and resistivity of the original fluid.



**Figure 10.** Seismic survey based on vibroseis. Example of a seismic profile.

- Wells will provide real information of the storage and caprock formation in sub-surface conditions. Test will provide information about geomechanical, hydrogeological properties and it may be possible to test interaction between the rock and CO<sub>2</sub>.

## 7. Monitoring techniques

Considering the injection phase, control of the behaviour of injected CO<sub>2</sub> is one of the most important tasks. For instance, the control and monitoring strategy must:

- Demonstrate that the injected CO<sub>2</sub> is stored in the selected reservoir and therefore must be a guarantee that the company responsible for fulfilling its commitment to reducing emissions.
- Check that no intrusion occurs in other exploitable aquifers and water resources.
- Check for surface environmental effects occur, and therefore, you must provide the affected population security and peace on the operations of injection.

The monitoring strategy should not be limited to the operational and post-operational periods but has an important role during the pre-operational stage by conducting the baseline of the injection site [11]. This baseline defines the set of physical, geochemical and biological processes operating in the storage area before any activity injection. The baseline is critical because especially in the early stages of injection, the changes are not evident, both in depth and on the surface, and comparison with the undisturbed condition is needed. The development of the baseline may have added value; for example, building trust and showing the population from the beginning that the project is under control and that any anomaly is detected. Numerous methods have been proposed for monitoring CO<sub>2</sub> in geological repositories. Of these, one can clearly distinguish two types: (a) to detect the evolution of CO<sub>2</sub> injected into deep and (b) for leakage from storage. In the first type, these methods are generally based on geophysical techniques, while in the second type, the range of methods is broader, including geochemical, physical and biological techniques. Therefore, the final selection of the monitoring strategy should take into account the following aspects [12, 13]:

- Efficiency in detecting small changes in behaviour warehouse
- Implementation in large tracts of land
- Reasonable economic cost

Compliance with these requirements will be conditioned by the type of store and its area of influence. Clearly, monitoring techniques will be very different in stores on-shore and off-shore, and within a storage type, geological, hydrological and even ecological characteristics will favour the implementation of a methodology or other.

The monitoring deployment is based on the following aspects: (a) characterisation of the area, (b) establishing a base line CO<sub>2</sub>, (c) establishment of potential areas of migration and release of CO<sub>2</sub> (and other gases) and (d) validation and development of techniques for monitoring CO<sub>2</sub>.

Emission	Leakage	Description/Comments	Phases of the CO <sub>2</sub> Storage
Leak paths through wells and boreholes	Operating or abandoned wells	It is important to identify all abandoned at the site (or close to it) wells. These wells can become the main roads of leakage	· Characterisation · Injection · Post-injection
	Blowouts (uncontrolled emissions from injection wells)	May cause leakage of high flows in short periods of time. It is considered that it is unlikely incidents if safety standards are met during drilling	· Injection
	Future removal of reservoirs of CO <sub>2</sub> can be a problem in the reservoirs of coal deposits	Can be a problem in the reservoirs of coal deposits	· Post-injection
Leak paths and natural migrations through faults and fractures	Through faults and fractures	May origin leak high flows. Proper site characterisation can reduce the risk of leakage	· Characterisation · Injection · Post-injection
	By dissolving CO <sub>2</sub> in a fluid and subsequent transport natural circulation of fluid	Proper site characterisation (evaluation of hydrogeology) can reduce the risk of leakside of gas	· Characterisation · Injection · Post-injection
	Through the pore system in low permeability rocks when the capillary inlet pressure is exceeded or if the CO <sub>2</sub> has been in solution	Proper site characterisation can reduce the risk of leaks. An exhaustive control of the injection pressure is needed	· Characterisation · Injection
	By a stroke if the reservoir	Proper site characterisation overflows can reduce the risk of leakage	· Injection · Post-injection
Another type of leak	Methane release could occur as a result of the displacement of CH <sub>4</sub> by CO <sub>2</sub>	It happens in depleted oil and gas	· Characterisation · Injection · Post-injection

**Table 3.** Possible types of leakage of CO<sub>2</sub> in a geological storage [13, 14, 15].

## 8. CO<sub>2</sub> uses

### 8.1. Current uses of CO<sub>2</sub>

Nowadays different applications are known that can be used for demonstrating that CO<sub>2</sub> is a useful, versatile and safe product. Figure 11 illustrates most of the current and potential uses of CO<sub>2</sub>.

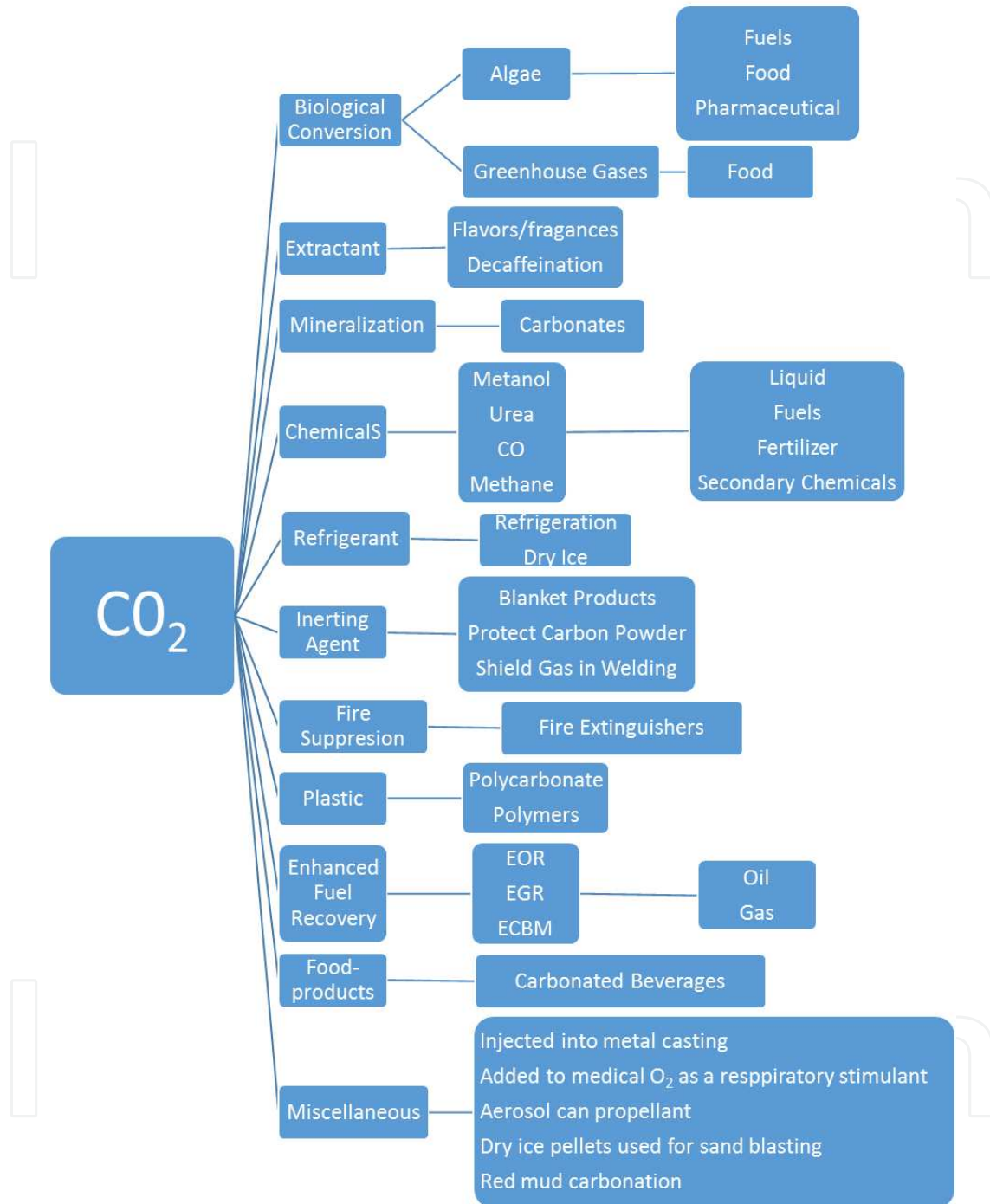


Figure 11. CO<sub>2</sub> uses. Different pathways for utilisation CO<sub>2</sub>.

There are many classifications that can be made about the use or valuation of large-scale CO<sub>2</sub> and including the three categories proposed by Vega [16] for type of uses, which also is used by the PTE-CO<sub>2</sub>, 2013 (Technology Platform Spanish CO<sub>2</sub>). To wit:



1. Direct or technology use: use of CO<sub>2</sub> with different technologies and market applications such as use for oil recovery, for dry cleaning, waste carbonation, food, water treatment or extraction with supercritical CO<sub>2</sub> compounds, including others.
2. Improved biological use: CO<sub>2</sub> fixation in biomass by growing microalgae and carbonic fertigation.
3. Chemical use: artificial photosynthesis and chemical conversion to high added value products and fuels.

## 8.2. Direct use of CO<sub>2</sub>

### 8.2.1. Enhanced oil recovery (CO<sub>2</sub>-EOR)

As much as two-thirds of conventional crude oil discovered in U.S. fields remain unproduced, left behind because of the physics of fluid flow. In addition, hydrocarbons in unconventional rocks or that have unconventional characteristics (such as oil in fractured shales, kerogen in oil shale or bitumen in tar sands) constitute an enormous potential domestic supply of energy.

Carbon dioxide is used in oil wells for oil extraction and to maintain pressure within a formation.

There are many methods for EOR and each has differences that make it more useful based on specific reservoir challenges and other parameters. Choosing the right method by screening the reservoir and fluid properties can ultimately reduce risk by eliminating inefficiencies.

CO<sub>2</sub> EOR is an 'EOR' technology that injects CO<sub>2</sub> into an underground geologic zone (oil/hydrocarbon containing 'reservoir') that contains hydrocarbons for the purpose of producing the oil. The CO<sub>2</sub> is produced along with the oil and then recovered and re-injected to recover more oil.

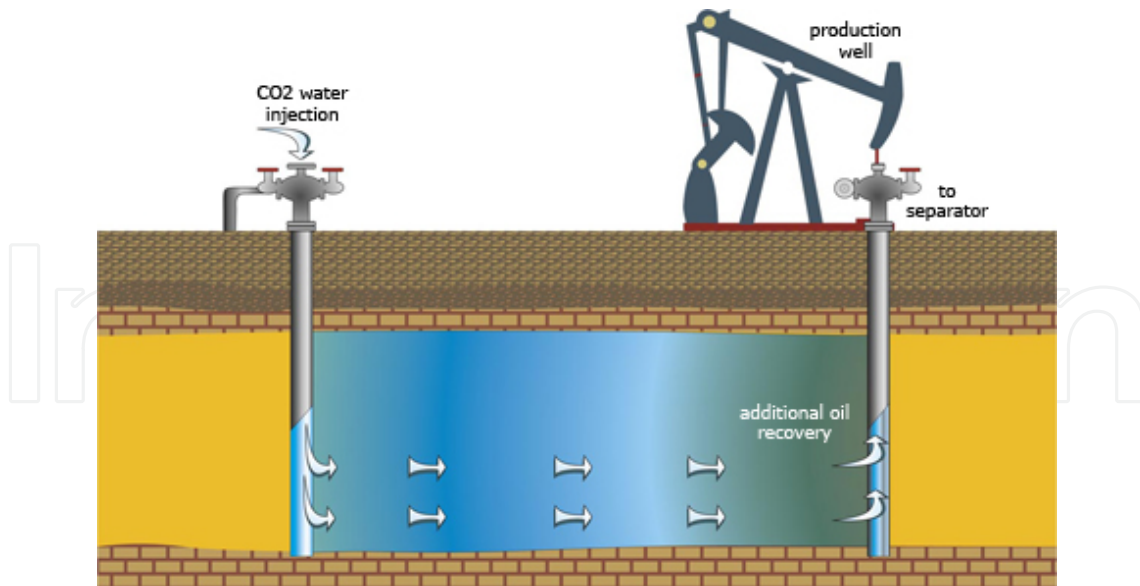
When the maximum amount of oil is recovered from the reservoir, the CO<sub>2</sub> is then 'sequestered' in the underground geologic zone that formerly contained the oil and the well is shut-in, permanently sequestering the CO<sub>2</sub>.

CO<sub>2</sub> injection is a technology successfully used from more than 50 years. The first patent for CO<sub>2</sub>-EOR appeared in 1952 and in 1964 began field trials. In the first commercial project of CO<sub>2</sub>-EOR in Texas, in 1972 (SACROC project), CO<sub>2</sub> was supplied from a gas plant, where the CO<sub>2</sub> was eliminated in the production of ammonia. At present the CO<sub>2</sub> is sent from geological formations (natural) from Bravo Dome in Colorado, and Mc Elmo Dome in New Mexico.

Nowadays, two techniques are largely used for CO<sub>2</sub>-EOR:

- **Miscible water-alternating-gas (WAG) process.** Injection alternates between gas (usually natural gas or CO<sub>2</sub>) and water; the miscible gas and oil form one phase. The WAG cycles improve sweep efficiency by increasing viscosity of the combined flood front (Figure 12).
- **Cyclic gas injection.** Most gas-injection EOR projects today use CO<sub>2</sub> as the injected gas. When CO<sub>2</sub> is pumped into an oil well, it is partially dissolved into the oil, rendering it less





**Figure 12.** CO<sub>2</sub>-EOR operation diagram. CO<sub>2</sub> injection into reservoir to ‘flood’. Diagram courtesy of Dakota Gasification Company.

viscous, allowing the oil to be extracted more easily from the bedrock. The CO<sub>2</sub> used to increase oil recovery can be naturally occurring, or an effective means of sequestering an industrial by-product. In this case, carbon dioxide, under pressure, is injected between oil wells to free the stranded oil. CO<sub>2</sub> is a superior agent in recovering stranded oil as the CO<sub>2</sub> naturally reduces the surface tension that traps the liquid oil in the oil reservoir. When the oil is recovered from the production well, CO<sub>2</sub> is also produced, but is easily separated from the crude oil because the CO<sub>2</sub> reverts back to its gaseous state when the pressure is removed.

### 8.2.2. Fire suppression

Some fire extinguishers use CO<sub>2</sub> because it is denser than air. Carbon dioxide can blanket a fire, because of its heaviness. It prevents oxygen from getting to the fire and as a result, the burning material is deprived of the oxygen it needs to continue burning.

### 8.2.3. Supercritical CO<sub>2</sub> uses

When CO<sub>2</sub> is at suitable temperature and pressure above the critical point (Figure 13), it is called supercritical CO<sub>2</sub>.

This state emphasises its capacity to dissolve chemicals and natural substances of similar way as do different organic solvents such as hexane, acetone or dichloromethane. Therefore, the first applications focused on **the extraction of natural substances** as an alternative to using organic solvents. Thus, **removal of caffeine** (coffee or tea) with supercritical CO<sub>2</sub> is the most mature application at industrial level and is also used in the **extraction of hops or cocoa fat**.

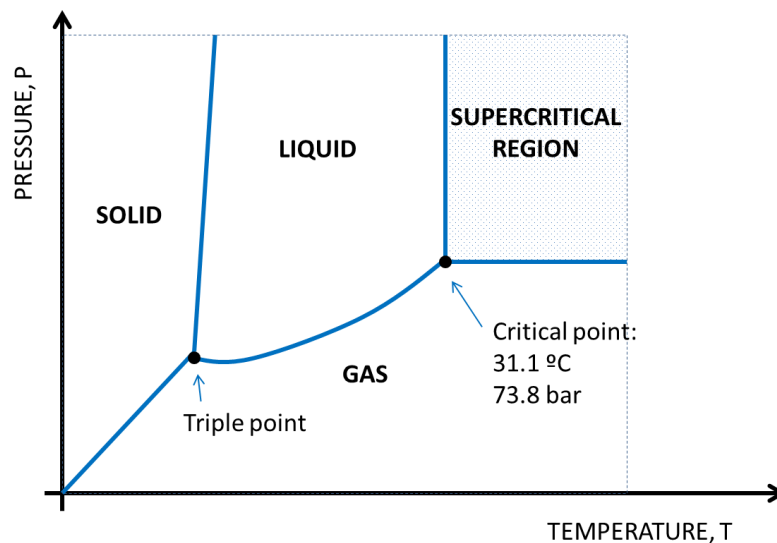


Figure 13. CO<sub>2</sub> phases diagram.

The dry cleaning with CO<sub>2</sub> is one of the most popular applications of supercritical fluids in the textile sector. This method is characterised by removing stains from the fabrics and garments where no harmful organic solvents for the average ambient, such as perchlorethylene (PER), common in conventional dry cleaning processes are used and without causing discoloration or shrinkage and without leaving odour.

One of the main advantages of supercritical CO<sub>2</sub> is that its solubility can easily be controlled suitably adjusting the pressure and temperature, allowing **fractionate mixtures** where all components are soluble.

Supercritical CO<sub>2</sub> extraction coupled with a fractional separation technique is used by producers of **flavours and fragrances** to separate and purify volatile flavour and fragrance concentrates. Like any solvent, supercritical CO<sub>2</sub>, it allows processing chemicals by precipitation or recrystallisation, obtaining particles of controlled size and shape, without excessive fines without thermal stresses and controlling the shape of a polymorphic substance.

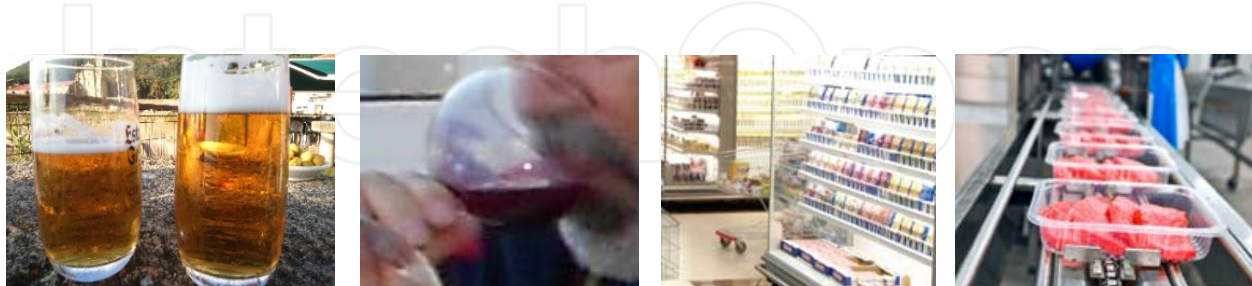
It is, therefore, a cutting-edge technology with great potential, because it is a new way to obtain natural products; it allows the adaptation of new high quality products with appropriate value to consumer habits; enables the development of new non-polluting processes and initiate the development of a tertiary sector led to the new technology.

#### 8.2.4. Food and beverages

Liquid or solid CO<sub>2</sub> is used for quick freezing, surface freezing, chilling and refrigeration in the transport of foods. In cryogenic tunnel and spiral freezers, high pressure liquid CO<sub>2</sub> is injected through nozzles that convert it to a mixture of CO<sub>2</sub> gas and dry ice 'snow' that covers the surface of the food product. As it sublimates (goes directly from solid to gas states), refrigeration is transferred to the product.

Carbon dioxide gas is used to carbonate soft drinks, beers and wine and to prevent fungal and bacterial growth. CO<sub>2</sub> has an inhibitory effect on bacterial growth, especially those that cause discoloration and odours.

CO<sub>2</sub> has an inhibitory effect on bacterial growth, especially those that cause discoloration and odours (Figure 14).



**Figure 14.** CO<sub>2</sub> applications in food.

It is used as an inert ‘blanket’, as a product-dispensing propellant and an extraction agent. It can also be used to displace air during canning.

Cold sterilisation can be carried out with a mixture of 90% carbon dioxide and 10% ethylene oxide, the carbon dioxide has a stabilising effect on the ethylene oxide and reduces the risk of explosion.

#### 8.2.5. Water treatment

Carbon dioxide can change the pH of water because of its slightly dissolution in water to form carbonic acid, H<sub>2</sub>CO<sub>3</sub> (a weak acid), according to Equation 9:



Carbonic acid reacts slightly and reversibly in water to form a hydronium cation H<sub>3</sub>O<sup>+</sup>, and the bicarbonate ion HCO<sub>3</sub><sup>-</sup>, according to Equation 10:



This chemical behaviour explains why water, which normally has a neutral pH of 7 has an acidic pH of approximately 5.5 when it has been exposed to air.

At the moment, CO<sub>2</sub> technology is widely introduced in treatments such as sewage water, industrial water or drinking water remineralisation.

The increased requirements of drinking water in large cities becomes necessary to use sources of very soft water and because of its low salinity and pH are very aggressive and can bring on corrosion phenomena in the pipes of the pipeline, with the appearance of colour and turbidity

when these pipes are made of iron, and by undermining these ones made with cement fibre by dissolving the calcium carbonate ( $\text{CaCO}_3$ ), because of excessive aggressive  $\text{CO}_2$ .

The introduction of carbon dioxide in the pipes regulates a state of equilibrium between dissolved bicarbonates, calcium carbonate inlaid and the  $\text{CO}_2$  added.

Therefore, for the treatment of soft or aggressive waters, the use of  $\text{CO}_2$  in combination with lime or calcium hydroxide is advisable to increase water hardness. This process is called **remineralisation** and is meaningful in water treatment plants, because soft water is indigestible.

The use of  $\text{CO}_2$  in wastewater neutralisation, Figure 15, offers great advantages in the operation and the environment by preventing other chemicals:

- Better working conditions. Eliminate the risk of burns, toxic fumes and other injuries from handling mineral acids
- Safe neutralisation. Avoiding risk of over-acidification with strong acids
- Low initial investment. Simple equipment, insurance and small dimensions
- Automated process. Automation avoids the handling of corrosive acids in the plant, pH control is automatic
- Economy



Figure 15. Dosing system for sewage.

#### 8.2.6. Carbonate mineralisation

The alkaline waste management presents significant problems, mainly because of its volume and its geochemical properties that do not allow disposing in conventional landfills. Therefore, the accelerated carbonation of this waste is another technological uses of  $\text{CO}_2$ .

Carbonate mineralisation refers to the conversion of  $\text{CO}_2$  to solid inorganic carbonates. Naturally occurring alkaline and alkaline-earth oxides react chemically with  $\text{CO}_2$  to produce

minerals, such as calcium carbonate ( $\text{CaCO}_3$ ) and magnesium carbonate ( $\text{MgCO}_3$ ). These minerals are highly stable and can be used in construction or disposed of without concern that the  $\text{CO}_2$  they contain will release into the atmosphere. One problem is that these reactions tend to be slow, and unless the reactions are carried out in situ, there is a large volume of rocks to move. Carbonates can also be used as filler materials in paper and plastic products.

### 8.2.7. Biological utilisation

Green plants convert carbon dioxide and water into food compounds, such as glucose and oxygen. This process is called photosynthesis (Equation 11).



The reaction of photosynthesis is as follows: Biological applications are based primarily on the use of  $\text{CO}_2$  as food for plant growth. In a similar way as the plants take advantage of sunlight and  $\text{CO}_2$  for biomass, or other products, 'imitating' nature, improving its results. Therefore, this technology is also known as biomimetic transformation.

There are two main ways in the biological utilisation process: greenhouses carbonic fertilisation and growth of microalgae.

#### 8.2.7.1. Greenhouses carbonic fertilisation

$\text{CO}_2$  is found naturally in the atmosphere and, therefore, in the **greenhouse** environment. It is essential for plant growth, since it represents the carbon source for organic compounds they need, in short, for compounds that constitute their biomass (leaves, stems, fruits, etc.).

$\text{CO}_2$  is not the only factor involved in photosynthesis, so that for its use, other factors must be at levels that do not limit the process. Light, temperature, amount of available nutrients and the relative humidity are other environmental factors affecting photosynthetic activity.

During photosynthesis, plants capture light energy and  $\text{CO}_2$  through the leaves, and water and nutrients through the roots. Thanks to these elements and chlorophyll leaves, plants get synthesise sugars and various organic compounds required for their development. Photosynthesis is responsible for plant growth. Therefore, favouring photosynthesis we managed to promote the development of the plants and agriculture in our case.

Yields of plant products grown in **greenhouses** can increase by 20% by enriching the air inside the greenhouse with carbon dioxide. The target level for enrichment is typically a carbon dioxide concentration of 800 ppm – or about two-and-a-half times the level present in the atmosphere (Figure 16).

In the CENIT SOST- $\text{CO}_2$  project that includes the entire life cycle of  $\text{CO}_2$ , researching technology uses as chemical and biological uses, the following results were confirmed, among others [18]:





Figure 16. Carbon fertilisation in hydroponics culture greenhouses.

- Rating combustion gases from combined cycle plants to use in vegetable crops in greenhouses, in applications in irrigation pipes to prevent clogging and to balance the pH in nutrient solutions.
- With regard to the quality of gas from CCGT, it can be recommended for direct use in greenhouses or other agricultural uses.
- The carbonic fertilisation allows early crop production along with a greater amount of product with better quality.

#### 8.2.7.2. Growth of microalgae

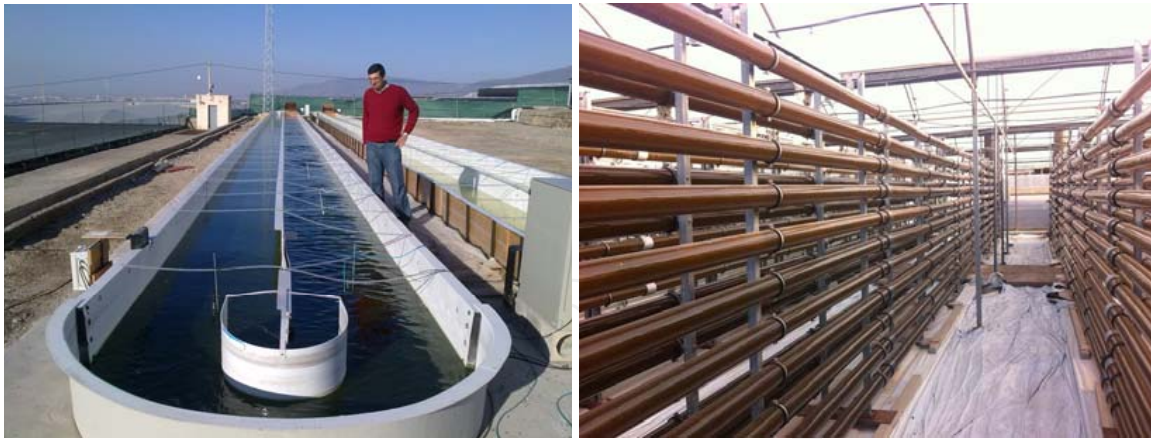
Microalgae are photosynthetic microorganisms that can grow in diverse areas mainly in water media where the forced culture can be carried out in diverse type of reactors in concordance with its design and operation. The advantage of this process is that microalgae are a microorganism with a high production rate (some species are able to duplicate their biomass in 24 hours), and therefore with increased demand for CO<sub>2</sub> conventional terrestrial plants.

The investigation of microalgae culture for different purposes began in the middle of last century, when the United States launched the 'Aquatic Species Program'. At that time, the research focused on the possibility of obtaining biofuels from microalgae: mainly methane and hydrogen, but after the oil crisis in the 1970s the biodiesel was also considered.

Biofixation of CO<sub>2</sub> by microalgae, especially as an option for the utilisation of flue gases from power plants, has been the subject of extensive investigations in the United States, Japan and Europe (IEA-GHG Biofixation Network). However, none of the related projects have demonstrated the feasibility of the concept at a pre-industrial level. What is more, CO<sub>2</sub> fixation efficiency is quite low because of the photobioreactors used in those pilot plants (raceway or open-ponds) (Figure 17).

The current production of microalgae is mainly focused around a few species, such as *Spirulina*, *Chlorella*, *Dunaliella* or *Haematococcus* for nutritional purposes (for humans) and animal feed (especially aquaculture). Other sectors, such as cosmetics, effluent treatment and bioenergy, have shown interest, incorporating these or other species of microalgae and cyanobacteria into commercial products. Currently, 95% of the production of microalgae is based on open systems





**Figure 17.** Microalgae culture in open system (raceway) and close photobioreactor (Almeria University and Palmerillas Research Center).

(raceways or circular open ponds). These systems have a low rate of  $\text{CO}_2$  fixation and it is estimated to be around 20–50% of the injected gas is effectively set by microalgae [17].

#### 8.2.8. Use of $\text{CO}_2$ in chemicals

Carbon dioxide gas is used to make urea (used as a fertiliser and in automobile systems and medicine), methanol, inorganic and organic carbonates, polyurethanes and sodium salicylate. Carbon dioxide is combined with epoxides to create plastics and polymers.

Corn-to-ethanol plants have been the most rapidly growing source of feed gas for  $\text{CO}_2$  recovery.

##### 8.2.8.1. Artificial photosynthesis

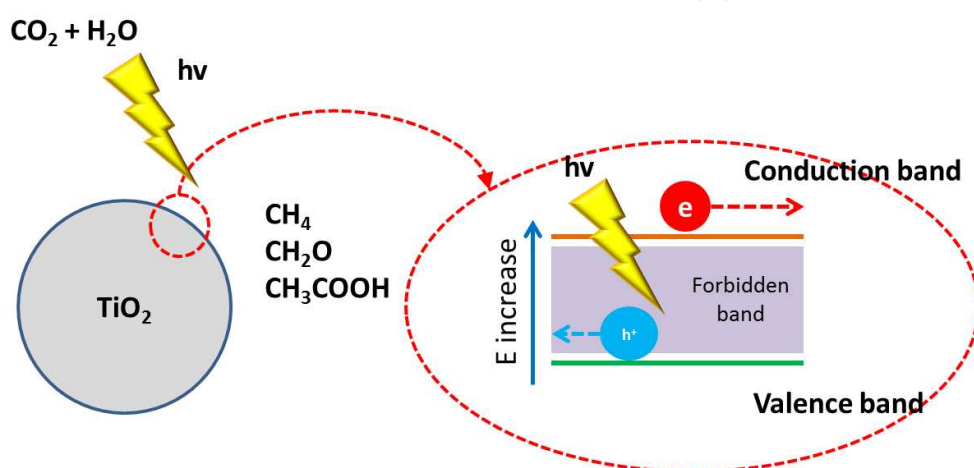
Because  $\text{CO}_2$  is a practically inert molecule, artificial photosynthesis of  $\text{CO}_2$  involves the use of large amounts of energy so it must use a clean source of energy (such as solar radiation). Therefore, the use of catalytic agent to facilitate the process allowing even take place at ambient temperature and pressure is necessary. In this case, it is also called as photocatalysis or photoreduction.

In photocatalysis two processes occur:  $\text{CO}_2$  reduction and oxidation of other compounds. Early works on the photocatalytic reduction of  $\text{CO}_2$  in aqueous solution were published between 1978 and 1979 ([19, 20]), and later numerous investigators have studied the mechanism and efficiency of the process using different catalysts (oxides of titanium, zinc and cadmium, cadmium sulphide, silicon carbide), and reducing (water, amines, alcohols) and R light sources (lamps xenon, mercury, halogen). Thus, it has been shown that by using specific semiconductors and reducing agents, can be obtained a great variety of products (methane, methanol, formaldehyde, formic acid, ethanol, ethane, etc.).

Along with thermodynamics, catalysis is one of the core technologies for an economically interesting use of  $\text{CO}_2$  as feedstock in chemical processes. This is one of the areas most

sophisticated and complex of modern chemical research. It is one of the major challenges for the scientific and technological developments related to the fields of energy and catalysis, as was highlighted in the report to officiate Sciences US Department basic Energy: more than 85% of all products are produced using chemical catalysis [21].

Photocatalysis involve the production of reactions because of the incidence of light on a semiconductor material. Unlike metals, these materials have a forbidden energy band, which extends from the top of the so-called valence band to the bottom of the conduction band (Figure 18).



**Figure 18.** Diagram of behaviour of a semiconductor,  $\text{TiO}_2$ , in light presence and participation in the photocatalytic  $\text{CO}_2$  reduction organic products.

The main disadvantage in these cases remains in the low process efficiency.

In general, the process of photocatalytic reduction of  $\text{CO}_2$  requires a milder conditions and lower energy consumption than chemical reduction [22].

### 8.3. Chemical conversion

Large quantities are used as a raw material in the chemical process industry, especially for urea across  $\text{CO}_2$  reaction with  $\text{NH}_3$  and later dehydration of the formed carbamate. Urea is the product most used as agricultural fertiliser. It is used in feed for ruminants, as carbon cellulose explosives stabiliser in the manufacture of resins and also for thermosetting plastic products, among others.

Methanol production, where  $\text{CO}$  is added as additive, is very a well-known reaction. The production is carried out in two steps. The first step is to convert the feedstock natural gas into a synthesis gas stream consisting of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and hydrogen. This is usually accomplished by the catalytic reforming of feed gas and steam. The second step is the catalytic synthesis of methanol from the synthesis gas. If an external source of  $\text{CO}_2$  is available, the excess hydrogen can be consumed and converted to additional methanol.

CO<sub>2</sub> is also used, to make inorganic and organic carbonates, carboxylic acids, polyurethanes and sodium salicylate. Carbon dioxide is combined with epoxides to create plastics and polymers (Figure 19).



Figure 19. Different products made with CO<sub>2</sub> derivatives.

## 9. New ways for CO<sub>2</sub> uses

In general, the area of CO<sub>2</sub> utilisation for carbon storage is relatively new and less well known compared to other storage approaches, such as geologic storage. Thus, more exploratory technological investigations are needed to discover new applications and new reactions.

Many challenges exist for achieving successful CO<sub>2</sub> utilisation, including the development of technologies capable of economically fixing CO<sub>2</sub> in stable products for indirect storage.

Significant innovation and technical progress are being made across a number of utilisation technologies. The **electrochemical reduction** could be really attractive because it is an excellent way for renewable energy storage.

### 9.1. Power to gas technology (P2G)

In the 3rd Carbon Dioxide Utilisation Summit, October 2014 in Bremen, Germany, ETOGAS GmbH presented its turn-Key plan and technology Power-to-Gas for SNG through electrolysis processes [18].

This technology uses CO<sub>2</sub> as a feed gas for the production of carbon products with Etogas methanation plant (Figure 20), which are reactor systems for conversion of H<sub>2</sub> and CO<sub>2</sub> to methane (synthetic natural gas). The produced gas is DVGW- and DIN-compliant synthetic natural gas and can be used directly, e.g., as a fuel for a CNG vehicle.

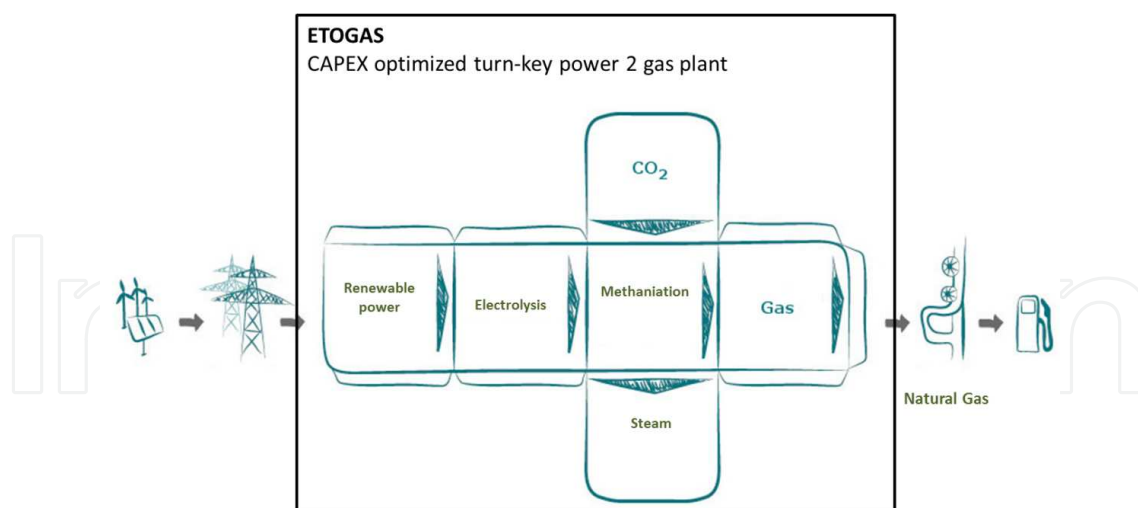


Figure 20. SNG schematic process. Source: ETOGAS Project.

## 9.2. Electrochemical CO<sub>2</sub> utilisation

According to DNV GL, electrochemical CO<sub>2</sub> utilisation presents some advantages as follows:

Production de-coupled from the sun (flexibility in renewable energy source); land use is minimised and no limitation with respect to geography; no competition with food (corn, sugar); flexibility in end fuel – ethanol, butanol or diesel (depending on the organism used); flexibility in electrochemical process (matching to supply/demand of renewable energy); and significant net reduction in CO<sub>2</sub> emission (Figure 21).

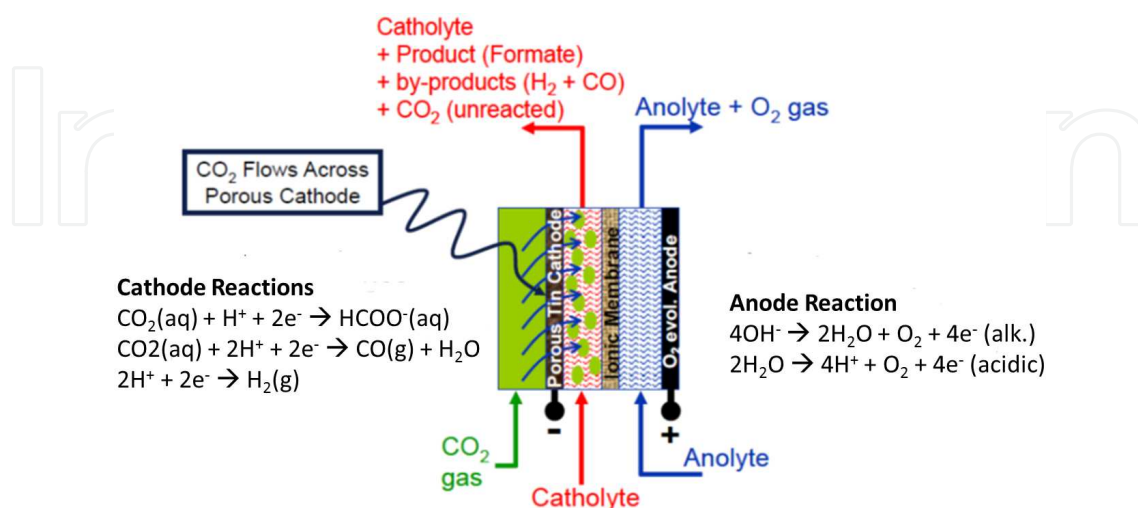
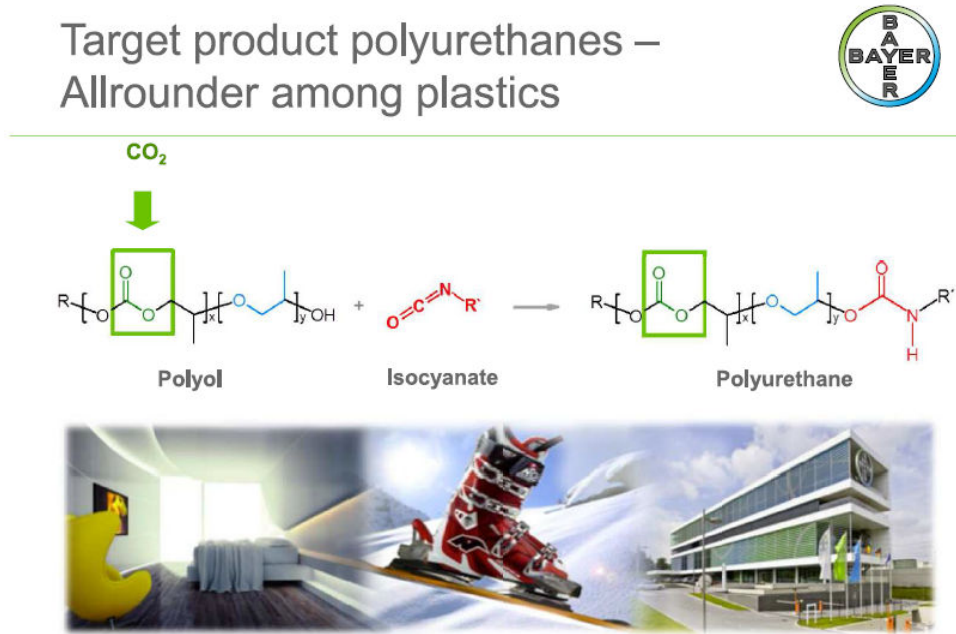


Figure 21. Electrochemical production of formic acid (HCOOH) and CO. Source: third Carbon Dioxide Utilisation Summit. DNV GL.



### 9.3. Polymers production

**Bayer MaterialScience** (Germany) in the Project “Dream Production” combines part of waste streams of coal-fired power plants, CO<sub>2</sub>, with the production of polymers. The target is the design and development of a technical process able to produce CO<sub>2</sub>-based polyether polycarbonate polyols on a large scale. The first step was to convert the CO<sub>2</sub> in new polyols, and these polyols showed similar properties such as products already on the market and can be processed in conventional plants as well (Figure 22).



**Figure 22.** Target product polyurethanes – All rounder among plastics. Source: 3rd Carbon Dioxide Utilisation Summit. Courtesy: Bayer.

The CO<sub>2</sub> thus acts as a substitute for the petroleum production of plastics. Polyurethanes are used to produce a wide range of everyday applications. When they are used for the insulation of buildings, the polyurethane saves about 80% more energy than it consumes during production. Light weight polymers are used in the automotive industry, upholstered furniture and mattress manufacturing.

### 9.4. Macrofouling control in industrial facilities

In the past years, several projects have been focused in the **direct use of flue gases** from Combined Cycle Power Plants for developing different applications. In this way, the project CENIT SOST-CO<sub>2</sub> has demonstrated the use of flue gases from CCPP in a direct way to control the pH in the cooling water systems with refrigeration tower and Iberdrola has developed an application for power plants.

Another application for the future will be “CO<sub>2</sub> for Zebra Mussel Control”. A project developed by Iberdrola and the University of Salamanca shows that carbonic acidification just in the



moment when the larva of zebra mussel are in the adequate phase (pediveliger) causes a much greater lethality than inorganic acids because of the synergistic effect of the lethal hypercapnia by physiological changes in cell metabolism of the larvae. (CDTI Project: Seguimiento de la incidencia del mejillón cebra (*Dreissena polymorpha*) en el Ciclo Combinado de Castejón 2009-2011. Iberdrola – Universidad de Salamanca).

The project LIFE13 ENV/ES/000426. CO2FORMARE [23], "Use of CO<sub>2</sub> as a substitute of chlorine-based chemicals used in O&M Industrial processes for macrofouling remediation", led by Iberdrola Generación, seeks to demonstrate the viability of using CO<sub>2</sub> from combustion gases to control macrofouling (*fouling caused by larger organisms, such as oysters, mussels, clams and barnacles*) in a thermal power plant (Castellon CCPP), cooled by sea water. First estimates indicate that a 400 MW CCPP (Figure 23) may be necessary to use up to 50,000 t CO<sub>2</sub> yr<sup>-1</sup>, [23].



Figure 23. Castellon Power Plant. Courtesy: Iberdrola.

## 10. Others

The Carbon Storage Program of the NETL (National Energy Technology Laboratory) of US Department of Energy supports four main CO<sub>2</sub> utilisation research areas: **cement**, **polycarbonate plastic**, **mineralisation** and **enhanced hydrocarbon recovery**. Several projects on active CO<sub>2</sub> utilisation focused in these areas receive Department of Energy (DOE) funds that aim to obtain the goals for the Carbon Storage Program.

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