



Technical analysis of CO₂ capture pathways and technologies

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ABSTRACT

The reduction of CO₂ emissions to minimize the impact of the climate change has become a global priority. The continuous implementation of renewable energy sources increases energy efficiency, while the reduction of CO₂ emissions opens new options for carbon capture technologies to reduce greenhouse gases emissions. The combination of carbon capture with renewable energy balancing production offers excellent potential for fuels and chemical products and can play an essential role in the future energy system. This paper includes a critical review of the state of the art of different CO₂ capture engineering pathways and technologies including a techno-economics analysis and focusing on comparing these technologies depending on the final CO₂ application. The current cost for CO₂ capture is in the range of 60–110 USD/t, likely to halve by 2030. This review offers technical information to select the most appropriate technology to be used in specific processes and for the different carbon capture pathways, i.e., Pre-combustion, Post-Combustion and Direct Air Capture. This comparison includes the CO₂ capture approach for biomethane production by biogas upgrading to substitute fossil natural gas and other alternatives fuels production routes which will be introduced in future works performed by this review authors.

1. Introduction

1.1. Background

In the last decades, fighting the climate change produced by anthropogenic emissions of Greenhouse Gases¹ (GHGs) has become an urgent priority [1,2]. The excessive emission of these GHGs is disastrous for the earth's climate, ecosystems, and species [3–6]. Current CO₂ atmospheric concentration is near 420 ppm (first third of 2022). This concentration must be reduced below the safe level of 350 ppm (reference by 1990) in order to reach the goal established in 2015 at the Paris Climate Conference of limiting an average global temperature increase of 1.5 °C with respect to pre-industrial temperature [7,8].

The fraction of electrical energy produced by renewable sources is increasing as a strategy to reduce GHGs emissions [9]. However, most countries still rely on combustion power plants to compensate the

fluctuations of renewable power generation. The future of energy technology lies on flexible energy generation and storage to ensure the energy supply and efficient transition. Thermal power plants provide a backup to renewable and provide control services.

CO₂ is the main product generated in every combustion process. Fig. 1 shows how CO₂ emissions from fuel combustion have been increasing in recent decades. By 2021, about 47 % of the emissions were generated in the electricity and heat sector, and around 25 % by the transport sector. The industrial sector (e.g. chemicals, petrochemicals, iron and steel, aluminium, cement or paper) generates about 18 % of the total CO₂ emission [8,10,11].

Carbon Capture and Storage (CCS) consists of storing CO₂ in a suitable geological sink. The options available for this are mainly underground: exhausted oil and gas fields, deep coal beds, aquifers, and salt caverns. In this case, CO₂ might react chemically with minerals in the rock. Thus, CO₂ control over geological time is needed [12]. The total capture capacity for installed CCS globally is currently around 40 Mt per

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¹ The most representative GHG producing global warming is carbon dioxide (CO₂). The Global Warming Potential (GWP) index, is a measure of how much energy the emissions of 1 ton of a gas will absorb, relative to the emissions of 1 ton of CO₂ over a given period of time (usually 100 years). Methane is estimated to have a GWP of 28–36 over 100 years, Nitrous Oxides has a GWP 265–298, while fluorinated gases can be in the thousands or tens of thousands [1]. The term CO₂-equivalent stands for the heat absorbed by any greenhouse gas in the atmosphere, referred to the heat that would be absorbed by the same mass of CO₂.

Nomenclature

AAP	Aqueous Ammonia Process.
AISS	Amine-Impregnated Solid Sorbent.
ASU	Air Separation Unit.
BECCS	Bio-Energy with CCS.
CAPEX	Capital expenditure.
CCGT	Combined Cycle Gas Turbine.
CCS	Carbon Capture and Storage.
CCU	Carbon Capture and Utilization.
CHP	Combined Heat and Power
CMS	Carbon Molecular Sieves.
DAC	Direct Air Capture.
DEA	Diethanolamine.
DGA	Diglycolamine.
EDA	Ethylenediamine.
EGR	Enhanced Gas Recovery.
EOR	Enhanced Oil Recovery.
GHG	Greenhouse Gas.
HHV	High Heating Value.
IGCC	Integrated Gasification Combined Cycle.
IPCC	Intergovernmental Panel Climate Change.
LCOE	Levelized Cost of Electricity.
LNG	Liquefied Natural Gas.

MEA	Monoethanolamine.
MDEA	Methyldiethanol-amine.
MTES	Methyltriethoxysilane.
NGCC	Natural Gas Combined Cycle.
O&M	Operation and Maintenance.
OPEX	Operative Expenditure.
PFAP	Poly-fluoroalkoxyphosphazene.
PSA	Pressure Swing Adsorption.
PWS	Pressurized Water Scrubbing.
SCPC	Supercritical Pulverized Coal.
SEWGS	Sorption Enhanced Water-Gas Shift.
SGSI	Shell Global Solutions Inc.
SLM	Supported Liquid Membrane.
SNG	Synthetic Natural Gas.
SRCCS	Special Report on CCS.
TEA	Triethanolamine.
TEOS	Tetraethoxysilane.
TRL	Technology Readiness Level.
TSA	Temperature Swing Adsorption.
UAN	Urea Ammonium Nitrate.
VOC	Volatile Organic Compound.
VSA	Vacuum Swing Adsorption.
WGS	Water-Gas Shift.

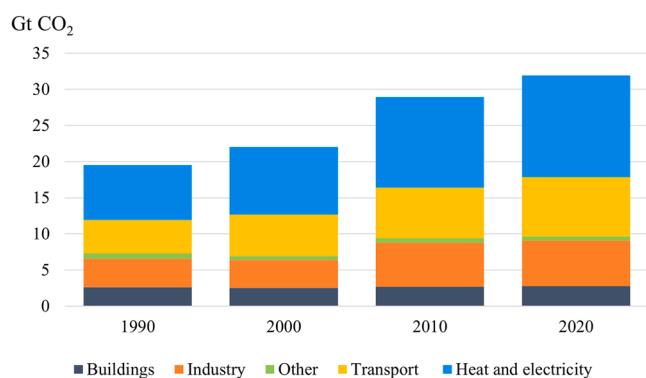


Fig. 1. Global CO₂ emissions from fuel combustion by sector. Adapted from [8].

year [13].

Storing CO₂ is, therefore, limited by the global geological capacity. Alternatively, CO₂ can be transformed into a valuable product using excess of electricity from renewable sources. As the electricity produced by renewable sources increases, it is necessary to take into account energy storage strategies for the overproduction of electricity in periods of, e.g., solar or wind energy production beyond the current demand. In general, energy storage technologies can be classified depending on the form of stored energy:

- **Power-to-Power:** Electrochemical energy storage is based on batteries. Mechanical storage technologies include flywheels, compressed air energy storage, and pumped hydro energy storage [14, 15].
- **Power-to-Heat:** Thermal storage technologies such as combined heat and power plants, small-scale decentralized heat applications, or liquid air energy storage technologies for heat recovery and electric generation.
- **Power-to-Fuels and Power-to-Chemicals:** Excess of electricity can be used to produce green H₂ through water electrolysis. H₂ can be

directly used as fuel (either for combustion or for hydrogen fuel cells), or converted to other fuels or chemicals such as synthetic methane, methanol or dimethyl carbonate.

Power-to-Fuels and Power-to-Chemicals (sometimes also classified as Power-to-Gas or Power-to-Liquid, depending on the product) are based on the reaction of H₂ and CO₂ through, for example, the Sabatier reaction:



This approach is referred as Carbon Capture and Utilization (CCU) [14], and it provides an opportunity to obtain economic and environmental incentives [16–19,20].

The combination of both approaches is called Carbon Capture Utilization and Storage (CCUS), which is a recognized technology to meet the requirement set in the Paris Climate Conference. CCUS include pipelines for transportation, injection in geological formation for storage and final utilization for fuel, chemical or material production. CCUS has the potential to reduce about 19 % of global CO₂ by 2050. This corresponds to increase the CO₂ capture to 4000 Mt until 2040 [21,22].

1.2. Goals, innovation and organization

This paper includes a critical review of the state of the art of different CO₂ capture engineering pathways and technologies including a techno-economics analysis and focusing on comparing these technologies' applications depending on the final CO₂ application. Despite many reviews on CO₂ capture have already been published, this critical review offers a new perspective that includes the CO₂ capture approach for biomethane production by biogas upgrading to substitute fossil natural gas. Currently, the main usage for the capture CO₂ is Enhanced Oil Recovery (EOR) and Enhanced Gas Recovery (EGR), which consist of injection CO₂ into gas and/or oil fields to extract fossil fuels. Both systems are competing with a renewable energy transition, thus, other alternatives use such as synthetic fuel production should be implemented in the years to come. The authors will address the technical analysis of CO₂ utilization technologies as a continuation of this work, including alternative fuel production, which is one of the most environmentally-friendly

routes for the utilization of the captured CO₂.

The paper is organized as follows: In Section 2, the different engineering pathways for CO₂ capture are discussed. In section 3, different technologies used in those pathways are described and compared. Section 4 reports techno-economics data of the implemented CO₂ capture technologies in existing power plants. Finally, Section 5 discusses current restrictions of CO₂ capture and includes possible recommendations for future research plans.

2. CO₂ capture pathways

In this paper, CO₂ capture is divided into three general routes: (1) Atmospheric Capture, (2) Post-Combustion Capture, and (3) Pre-Combustion Capture. In order to explain the differences between the pathways, Table 1 list 5 different CO₂-containing gaseous currents likely to be submitted to CO₂ capture.

2.1. Atmospheric CO₂ capture

The latest report by the UN's Intergovernmental Panel on Climate Change [1] states that, in order to keep global warming below the 1.5°C limit by 2030, reducing the current emissions will not be enough. This means that it is not only necessary to decrease current emissions, but also to decrease the concentration of atmospheric CO₂ already emitted.

Atmospheric CO₂ capture consists of capturing the CO₂ directly from the atmospheric air in order to reduce the concentration (around 420 ppm by the time this manuscript is written). Atmospheric CO₂ capture has the potential to achieve not only net zero, but also net negative emissions, capturing CO₂ that has already been emitted in the past.

2.1.1. Natural carbon sinks

Carbon sinks, such as the forests, the oceans or the soil, are directly and indirectly related to the carbon balance and they capture and emit CO₂ in their natural processes. Furthermore, some CO₂ can also be fixed in the form of wood, algae or other natural materials [23–26].

This paper focuses on the engineering solutions and therefore it does not cover in detail CO₂ capture through natural carbon sinks.

2.1.2. Direct air capture

Direct Air Capture (DAC) consists of capturing the CO₂ directly from the atmosphere by circulating air through regenerative filters. DAC was first used in 1930 in cryogenic air separation plants, and it has been applied in submarines and space stations. As a method to decrease atmospheric CO₂ concentration, DAC has been used since 1999 [27,28] and it currently has a Technology Readiness Level (TRL) of 7 [29]. Several companies such as Climeworks, Global Thermostat and Carbon Engineering are building pilot and commercial plants [29,30].

The main difficulty of DAC is that the concentration of CO₂ in air is very low compared to other air components (see Table 1). Still, the efficiency of DAC has increased rapidly in the last years. In the study developed by [31], in 2007, the capture ratio was about 50 %. The

Table 1

Approximate average composition of different gas currents containing CO₂: Dry air, Flue gas from the combustion of methane with stoichiometric dry air, Exhaust gas from the Oxy-fuel combustion of methane with a mixture of stoichiometric O₂ and recycled CO₂ in 1:1 O₂:CO₂ proportion, Desulfurized Biogas from anaerobic digestion, and CO₂-Hydrogen produced by steam reforming and Water-Gas Shift of pure methane.

Composition	CO ₂	O ₂	N ₂	H ₂	H ₂ O	CH ₄
Dry air	0.042 %	20.9 %	78.1 %	–	–	–
Standard flue gas	9.5 %	–	71.5 %	–	19 %	–
Oxy-fuel flue gas	60 %	–	–	–	40 %	–
Biogas	40 %	–	–	–	–	60 %
Hydrogen	20 %	–	–	80 %	–	–

company Carbon Engineering obtained recently a capture ratio of 74.5 %. In 2014, Climeworks, in a partnership with Sunfire and Audi, captured in a pilot plant in Dresden around 80 % of the CO₂ in air [32].

Fig. 2 shows a scheme of the Climeworks LT DAC small commercial plant, using a low-temperature unit based on an amine solution. Atmospheric air is introduced into the filter where CO₂ is removed from the air. CO₂ is then separated from the filter by a sorbent that covers the filter's maximized surface area. Once the filter is saturated, the fans are switched off, and the remaining air is swept out either by steam or by a vacuum. Afterwards, the sorbent is regenerated at different levels of pressure, temperature, and moisture depending on the sorbent used [32, 33].

DAC has great flexibility as it can be applied anywhere. Theoretically, this technology would allow reaching zero or even negative net emissions. The low concentration of acid gases such as SO_x and NO_x in the atmospheric air results in moderately low degradation of the sorbents [27]. However, CO₂ concentration in ambient air is also low, compared for example with the concentration in flue gases at power plants [34]. As a consequence, operational DAC costs are high. Currently, the cost of a DAC pilot plant is the range of 94–232 USD/t, which is predicted to go down to 60 USD/t by 2040 increasing the competitiveness of this technology [35].

2.1.3. Technologies for direct air capture

Chemical absorption process with amines (Section 3.1.1), hydroxides, and other chemical sorbents are more efficient than physical adsorption (Section 3.3) at low temperatures, such as activated carbon, metal-organic, and zeolites [27]. High-temperature units are based on NaOH and KOH aqueous solution, producing carbonates that are later regenerated in a closed-loop process. The separation in low-temperature systems are normally based on amine solutions and takes place at around 100°C [32].

2.2. Post-combustion capture

2.2.1. Combustion with air

Post-combustion refers to the capture of CO₂ from the flue gases emitted after the combustion of fossil fuels, biomass, or waste in industries and power generation plants. Post-combustion capture is the most suitable approach for retrofitting the current fossil-fuel burning power plants and industries.

The efficiency of the CO₂ capture is also limited by the high temperature of flue gas. In addition to this, the flue gas may contain contaminants such as NO_x, SO_x or fly ashes, which increase the separation cost with existing technologies [36,37]. Examples of commercial-scale coal power plants incorporating post-combustion capture technologies are Petra Nova (Texas, USA) [38] and the Boundary Dam 110 MW (Saskatchewan, Canada) [39].

2.2.2. Oxy-fuel combustion

Oxy-fuel combustion refers to the combustion of a fuel using pure O₂ instead of air. As shown in Table 1, flue gas from air combustion can be

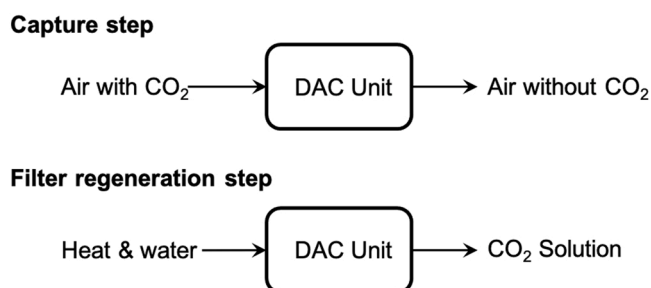


Fig. 2. Climeworks LT Direct air capture system.

considered a mixture of $\approx 70\%$ N_2 and $\approx 20\%$ H_2O and $\approx 10\%$ CO_2 . In turn, the flue gas from oxy-fuel combustion is a mixture of H_2O and CO_2 . Fig. 3.a) illustrates the oxy-combustion process with CO_2 capture applied to a combined-cycled power plant.

Combustion with pure O_2 produces a flame with much higher temperature than air combustion, which can have certain advantages for industrial processes or energy production. If necessary, the flame temperature can be reduced and kept within a specific range by injecting steam or recycled CO_2 in the combustion chamber [40,41]. A further advantage is that NO_x formation is hindered.

This process has energy losses in a range of 7–13 %, which is an equivalent of 20 % additional fuel consumption [42]. Retrofitting a coal-fired power plant will cause a net efficiency loss between 10 % and 12 % [43,44]. Different alternatives have been proposed to reduce energy losses: improved layout designs, optimization of flue gas recycling, optimization of the carbon processing and the Air Separation Unit (ASU) [45] and combination with other capture technologies as calcium looping (see Section 3.1.4) [42]. Oxy-combustion can provide favorable conditions to burn fuels with low heating value, such as biomass or solid urban waste, as the flue gas recycling rate can be adjusted to control the flame temperature [29,46].

Oxy-combustion was developed at the beginning of the 1980s and gained interest in the 1990s due to the environmental impact of fossil fuels [47]. Nowadays, there are a few pilot plants (TRL-7) operating on a commercial scale. Some examples are the 30 MW coal plant promoted by Endesa, CS energy, and Vattenfall; or the 35 MW oil plant of Total SA [48].

2.2.3. Chemical looping combustion

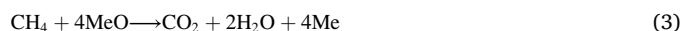
Combustion enhanced by chemical looping is an alternative way to

carry out oxy-combustion without the difficulty associated to the ASU for O_2 production. Chemical looping combustion consists of dividing the process into two reactions performed separately using a solid oxygen carrier. Small particles of metal oxides, such as Mn_2O_3 , Fe_2O_3 , CuO or NiO , are suitable oxygen carriers [49,50].

An standard chemical looping system has two reacting chambers, one for fuel and other for air. In the air reactor, fine particles of reduced metal resulting from the ash of the combustion chamber are oxidized:



The metal oxide current is then injected in the fuel combustion chamber where they get reduced back to elemental metal particles. For example, for methane combustion:



Similarly to oxy-combustion processes, the separation of CO_2 can be easily achieved by water condensation and there is no thermal formation of NO_x .

An enhanced alternative to this system consists of a three-reactor chemical looping configuration [51]. The three reactor configuration includes fuel, steam and air reactors, and H_2 is co-generated together with power [52]. Thus, this configuration offers a promising route for high purity hydrogen production by implementing a steam reactor. Fig. 3.b) describes the combustion of a fuel through a three-reactor chemical looping system for hydrogen and power generation. In the scheme, the fuel is fed into the combustion chamber together with a bimetallic oxygen carrier. Reduced oxygen carrier is partially oxidized in the steam reactor to produce H_2 . Afterwards, the partially oxidized bimetallic oxygen carrier is completely oxidized in the air reactor with

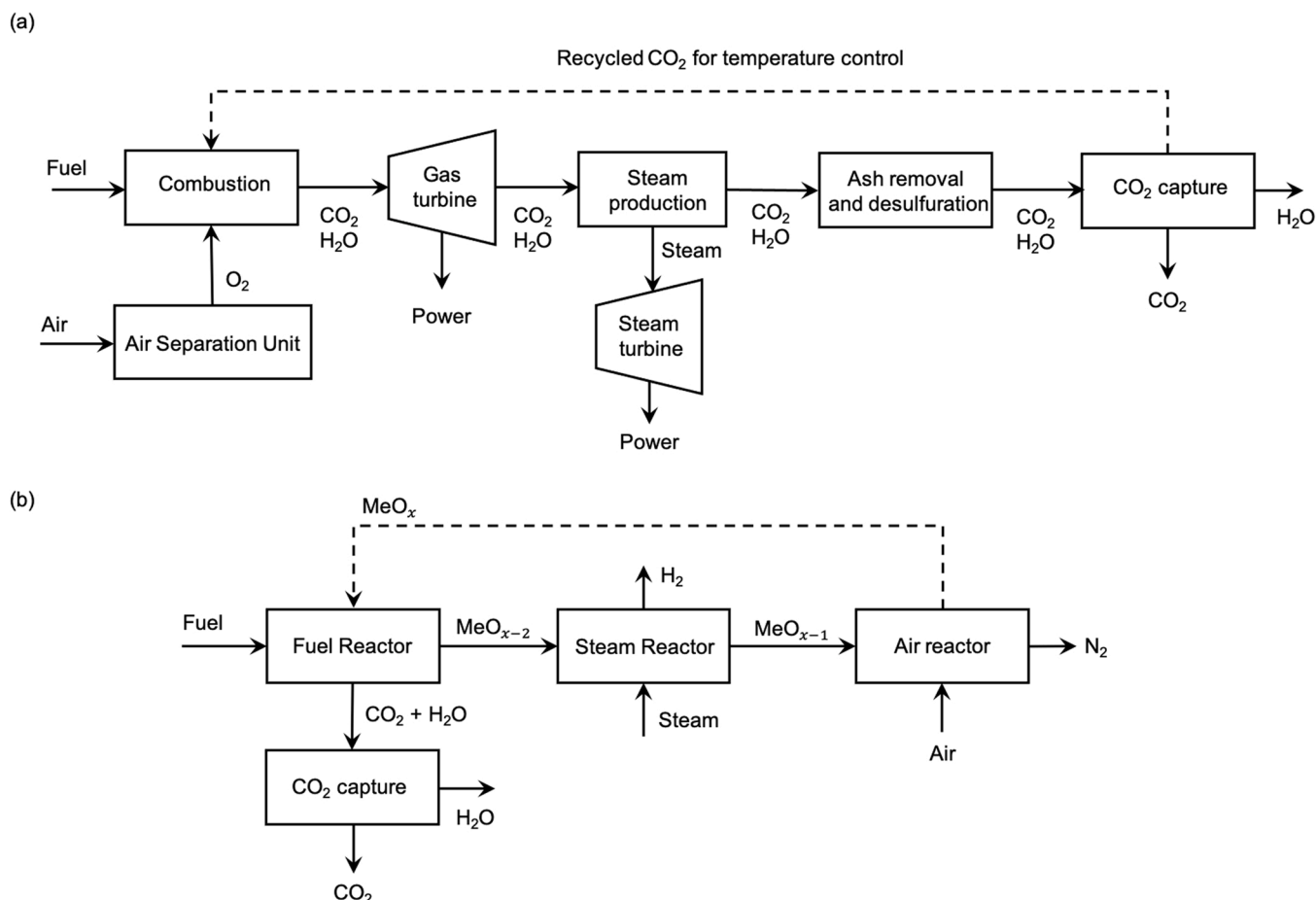


Fig. 3. (a) Oxy-combustion with CO_2 capture applied to a combined-cycled power plant. (b) Chemical looping combustion in a three-reactor configuration.

air [53].

Even though there is no large-scale demonstration, models predict that a power system applying metal oxide air separation has significant advantages. This pathway presents lower irreconcilability associated with the regeneration stage than conventional combustion and lowers energy requirement compared to the separation of CO₂ from nitrogen. The technology is still at a pilot plant scale (TRL-6), and, to the extent of our knowledge, there is no commercial plant operating so far [29,44]. It was reported in the study developed by [54] that the energy penalty could be low as 400 kJ/kg CO₂ for combined cycle power plants.

2.2.4. Technologies for post-combustion capture and oxy-fuel combustion

The capture of CO₂ from the exhaust gas can be carried out using amine absorption (Section 3.1.1), aqueous ammonia absorption (Section 3.1.2), gas hydrate formation, adsorption materials (Section 3.3), membranes (Section 3.4), and cryogenic process (Section 3.5). Chemical absorption with carbonate or amine solution as solvents is one of the best technologies for post-combustion systems. [55,56]. Physical adsorption by Temperature Swing Adsorption (TSA) is also recommendable due to the low CO₂ concentration and it present a TRL of 7. However, polymeric (see Section 3.4.2) or ceramic membranes (Section 3.4.1) could also be used, as they provide enough separation efficiencies for the concentration range of CO₂ in the flue gas. Other novel technology for post-combustion is based on absorption by ionic liquid, but at the moment this alternative is still at lab test scale with a TRL of 3 [23].

Pure O₂ generation for oxy-fuel combustion is provided by the ASUs, which are usually based on Pressure Swing Adsorption (see Section 3.3) or cryogenic separation (Section 3.5) [29,57]. The high operational cost for O₂ production is the main disadvantage of the oxy-combustion capture pathway [58].

Oxy-fuel combustion CO₂ capture can be achieved by chemical absorption or by physical adsorption process for CO₂ generation and CO₂ capture (see Section 3.1 and Section 3.3 respectively). Therefore, using solvents and/or reagents is avoided in physical adsorption, reducing the operation cost and environmental disposal of any related solid or liquid wastes.

As the flue gas from oxy-combustion is mainly composed by CO₂ and H₂O, it is possible to obtain pure CO₂ by cryogenic condensation of the H₂O. In the study developed by [59], it was argued that membranes are more economical than the cryogenic method for air separation.

2.3. Pre-combustion capture

Pre-combustion capture process is based on the transformation of carbon-based fuel (e.g. CH₄) into carbon-free fuel (e.g. H₂).

2.3.1. Biogas upgrading

The clearer example of the pre-combustion pathway is the upgrade of biogas, i.e., the separation of methane and CO₂ to produce biomethane.

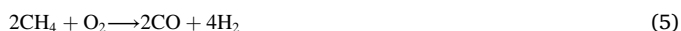
2.3.2. Hydrogen production by methane reforming

It is possible to decrease the carbon content of methane by transforming it to hydrogen, by means of, for example, steam reforming:



$$\Delta H_{298K} = 225.4 \text{ kJ/mol}$$

or methane partial oxidation:



$$\Delta H_{298K} = -22.6 \text{ kJ/mol}$$

Steam reforming is endothermic and requires temperatures in the range of 700–850 °C, while partial oxidation is exothermic. Auto-thermal reforming is a combination of the two previous methods [8].

The CO in the produced syngas can be catalytically reacted with steam through the so-called Water-Gas Shift (WGS) reaction to produce CO₂ and increase the yield of H₂.



$$\Delta H_{298K} = -41.2 \text{ kJ/mol}$$

Ideally, a full conversion of pure methane would produce a current with 20 % CO₂ and 80 % H₂ (see Table 1). CO₂ is then separated producing a highly purity H₂ current [60,61].

2.3.3. Gasification of solid fuels

Fossil fuels can be gasified using a sub-stoichiometric amount of O₂ and/or steam at high pressure (30–70 atm) to produce syngas [55]. In an Integrated Gasification Combined Cycle (IGCC) process for power generation, solid fuel, such as coal or biomass, is partially oxidized with O₂ and steam to produce syngas prior to the electricity generation cycle [62,63]. Typical reactions for IGCC are:



$$\Delta H_{298K} = 131.3 \text{ kJ/mol}$$

The WGS reaction can also be applied to convert the CO into CO₂ for the production of carbon-free H₂ fuel, that can be used for power generation by a gas turbine, gas boiler, or fuel cell. It can also be applied in Power-to-Gas (by Sabatier reaction) for CO₂ methanation or Power-to-Fuel (by Fisher-Tropsch). That is the reason why this capture system is subject to hydrogen pathways [64].

Fig. 4 describes an IGCC with Carbon Capture process. In the figure, the bold boxes are additional processes for CO₂ capture in the design of IGCC. Due to the high partial pressure of CO₂, the physical absorption method demonstrates better performance than chemical absorption for IGCC facilities [65].

The H₂O is removed, and the mixture of CO₂ and H₂ are separated in the Selexol acid gas removal step. The main energy losses occur in the ASU for O₂ and nitrogen (N₂) separation [29,41,62,64].

Several pilot plants are operating to address the feasibility of the IGCC system, such as the ELCOGAS plant (Puertollano, Spain), Vattenfall Group plant (Buggenum, Netherlands), or TECO plant (Florida, USA). Many commercial-scale plants have been developed worldwide with a TRL of 9 for coal gasification and natural gas reforming. In Kemper County IGCC 524 MW (Mississippi, USA), CO₂ from lignite gasification is captured by physical absorption by the Selexol process. In Dongguan Taiyangzhou IGCC 800 MW (Guangdong, China), CO₂ from coal gasification is captured by cryogenic separation [60].

2.3.4. Technologies for pre-combustion capture

The main technologies for biogas upgrading are discussed in Table 2: amine scrubbing 3.1.1, pressurized water scrubbing (PWS) 3.2.1, physical adsorption (PSA) 3.2, polymeric membranes 3.4.2 and cryogenic separation 3.5[66–68]. This critical review is also focused on discussing these technologies in the CO₂ capture approach context.

The most used technology for CO₂ separation in a pre-combustion pathway is via absorption, in which the solvent can be a chemical (Section 3.1) or a physical such as Selexol and Rectisol (see Section 3.2.2) [12]. Physical adsorption by PSA is also a feasible technique due to the high CO₂ partial pressure (Section 3.2) and it is fully implemented in the industrial sector with TRL of 9. As, in this case, CO₂ concentration is normally equal to or greater than 20 %, membranes are also suitable (see Section 3.4).

CO₂ pressure and concentration are higher in pre-combustion technologies than in post-combustion capture technologies, thus, the capture equipment is much smaller, and different solvents can be applied with lower energy losses for regeneration. The energy requirement for CO₂

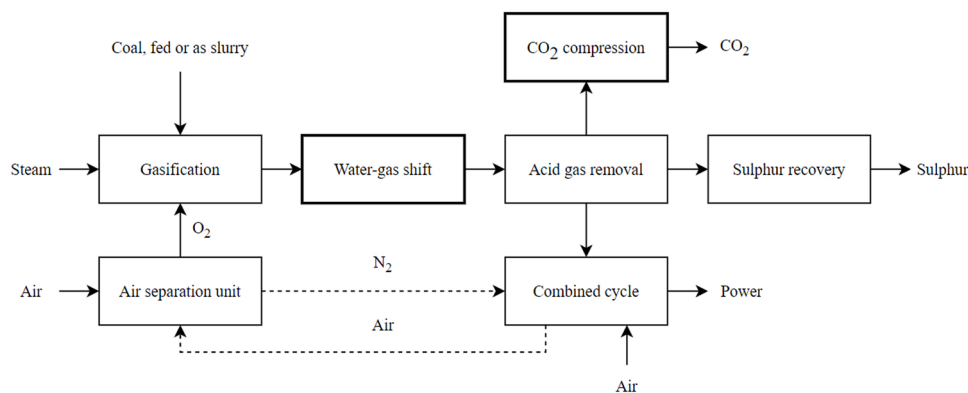


Fig. 4. IGCC with CO₂ capture. Adapted from [41].

Table 2
Characteristics of biogas upgrading technologies [69].

Parameter	PWS	PSA	Amine Scrubber	Memb.
Electricity (kWh/m ³)	0.2–0.3	0.2–0.25	0.15	0.25
Energy efficiency (%)	96–99	93	99	98
Pressure (bar)	5–10	4–7	0.1	5–10
CH ₄ recovery (%)	98	99	99.9	80–99.5
CH ₄ purity (% mol)	>97	>96	>99	>95
CH ₄ leak (%)	2	2	0.04	0.5–20
Exhaust gas treatment	Yes	Yes	No	Yes
Water demand	Yes	No	Yes	No
Chemical demand	No	No	Yes	No
Difficulty	High	Medium	High	Low
CO ₂ pressure (bar)	1	>1	1.8	>1
Heat integration	No	No	Yes	No
CAPEX (€/m ³ CH ₄)	0.13	0.25	0.17–0.28	0.12–0.22

capture and compression can be in the order or half of that required for post-combustion capture [70]. Nevertheless, the energy requirement for the pre-combustion process is high due to the gasification process, air separation or reforming.

The application of Sorption Enhanced Water Gas Shift (SEWGS) offers a reduction in this energy penalty. SEWGS removes CO₂ from the WGS reaction product, increasing the conversion rate of CO and reducing CO₂ emissions [71]. The main disadvantage is that it requires a chemical plant next to the turbines. A complicated chemical process can generate extra shut-down of the plant, affecting the power production.

Table 3
Advantages and disadvantages of different CO₂ capture pathways [29,34,57,72].

Capture pathways	Advantages	Disadvantages
Direct Air Capture	<ul style="list-style-type: none"> High CO₂ removal efficiency Can achieve net-zero or even net-negative emissions 	<ul style="list-style-type: none"> The concentration of CO₂ in air is low (\approx 420 ppm), which makes the process energy intensive
Post-combustion	<ul style="list-style-type: none"> CO₂ concentration in flue gas is higher than in air Applicable for retrofitting existing power plants Extra removal of NO_x and SO_x 	<ul style="list-style-type: none"> Moderately low CO₂ concentration in flue gas (\approx 10 %) Energy penalty due to sorbent/solvent regeneration high CAPEX and OPEX
Oxy-fuel combustion	<ul style="list-style-type: none"> The CO₂ concentration in flue gas is high (\approx 60 %) Mature ASU systems The CO₂ separation is easier without N₂ Low volume of gases involve smaller equipment size NO_x-free emissions Options for compact boiler and other equipment with reduced volume of flue gas output 	<ul style="list-style-type: none"> Energy penalty due to the Air Separation Unit CO₂ recycle required to control combustion temperature May present corrosion problems
Chemical Looping	<ul style="list-style-type: none"> Same advantages than Oxy-fuel combustion Does not need an ASU system Low-cost O₂ carrier materials A three-reactor configuration allows H₂ production 	<ul style="list-style-type: none"> Still in pilot plant stage Abrasion by the metal particles Fuel must be fully desulfured
Pre-combustion	<ul style="list-style-type: none"> Possible for retrofit to existing plants Biogas and H₂ from syngas have high CO₂ concentration Fully developed technologies Potential for compression costs reduction 	<ul style="list-style-type: none"> Challenging operation conditions High energy requirements for sorbent regeneration Extensive support systems requirements High CAPEX and OPEX for current sorption systems

Additionally, other disadvantages are the requirements to clean the gas stream, non-gaseous feed stocks, and the possible need for scrubbing systems for NO_x emission control [55]. However, the main disadvantage is the high total capital cost [57]. Pre-combustion capture technology presents a moderated energy penalty of 10 % based on steam reforming or gasification.

The higher efficiency has been presented in a Biomass-based Integrated Gasification Combined Cycle (BIGCC) using air and amine scrubber capture process to capture CO₂. The efficiency is improved by applying air to avoid the need of the ASU and by introducing heat recovery steam generation [29] (Table 3 collects the main advantages and disadvantages of each pathway).

3. CO₂ capture technologies

Generally, CO₂ capture consists of a combination of energy or fuel conversion and a number of separation steps, involving different physical or chemical methods. The selection of the proper CO₂ capture technology depends on several factors, such as the effect of the impurities, the desired CO₂ purity, the CO₂ concentration in the gas stream, the solvent regeneration, and the capital and operative costs [73].

3.1. Chemical absorption

Since CO₂ is an acid gas, the chemical absorption of CO₂ from gaseous streams is normally based on acid-base neutralization [57].

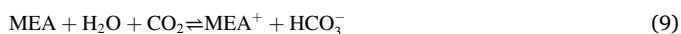
Chemical solvents for CO₂ absorption from natural gas were developed more than 60 years ago. Nowadays, several power plants and other industrial processes use similar solvents. Chemical absorption is effective for low CO₂ partial pressures. Therefore, chemical absorption, using carbonates or amine solutions as solvents, is the most suitable for post-combustion systems [55,56].

3.1.1. Amine

Amine scrubbing is a mature and commercially viable technology that is widely used for the post-combustion treatment of flue gas from natural gas or coal [74]. It consists in the use of an amino-based absorbent, generally in aqueous solution of alkanolamines, that binds CO₂ forming a chemical complex. Amino-based absorbents are added in the flue gas from the top of an absorber (see Fig. 5).

The Amine-CO₂ complex is then led into a desorption unit where the absorbed CO₂ is stripped from the solvent by counter-flowing steam at 100–200°C [57,76]. The process works at atmospheric pressure [74], and the efficiency can be up to 98 % of CO₂ recovery. The sorbent is then cooled down to 40–65°C and recycled into the absorption column [77]. The absorbent regeneration implies an energy penalty up to 30 % [29]. The cost of regeneration is reduced during low electricity periods [78].

The amines used in the scrubbers are commercially available as primary, secondary, and tertiary. Primary forms show the higher reaction rates, while tertiary has higher loading capacities and less energy consumption in the regeneration step [37]. The most applied absorbent is 20–30 wt% monoethanolamine (MEA), as primary amine is especially suitable for low CO₂ partial pressure. Reaction 9 describes the chemical absorption with MEA:



Typical energy consumption of a minimum stripper re-boiler (with 10–15 kPa CO₂, 40°C, 30 wt%) for 90 % CO₂ removal, is in the range of 3.6–4 GJ per tonne of CO₂ captured. The main advantages of this process are low cost of the solvent, good absorption efficiency (>90 % v/v CO₂), high capacity operation at high pressure and low temperature, the solvent is regenerated by heat and easily biodegradable chemicals. However, MEA is corrosive at high concentrations and presents moderate toxicity and degradation by acid gases in the flue gas, which requires previous removal of NO_x and SO₂ from the flue gas stream. Additionally, it has high CAPEX and present low capacity at low pressure and high temperature [23,79].

Chemical absorption with MEA is also one of the most desirable technologies for biogas upgrading after pressurized water scrubbing (see Section 3.2.1) since it offers high methane recovery (> 99 %). For the amine-based scrubber, the CO₂ outlet pressure after biogas upgrading is around 1.8 bar, which offers a relative benefit because less electricity consumption is needed for CO₂ compression before methanation by Sabatier reaction compared to other upgrading technologies. Amine scrubbing produces the formation of chemical bonds between CO₂ and MEA. The main difference to pressurized water scrubbing is that, in the case of the amine-based scrubber, CO₂ and H₂S are more soluble in organic solvents than in water. In addition, a smaller upgrading plant

can be built for the same gas capacity. The main inconvenience of this technology is the heat requirement at the regeneration step [57,69]. Therefore, this technology is more feasible when a district heating source is available.

Carbonated MEA solution have been tested for their potential at harvesting mixing energy using capacitive cells. In capacitive cells, ions pass through ion-exchange membranes and accumulate in porous carbon electrodes producing electrical current [80]. The efficiency of this process was 32 % with a 0.25 M MEA solution as the electrolyte, with an average power density of 4.5 mW/m² and peak power density of 31.7 mW/m² [81].

Tertiary amine aqueous ethylenediamine (EDA) and methyldiethanol-amine (MDEA) show a reduction in energy demand of 8–11.5 % and 15 % respectively, in comparison with 30 wt% MEA [34]. Other amines used for CO₂ capture are diethanolamine (DEA), diglycolamine (DGA), and triethanolamine (TEA) [76]. Using amines mixtures have reported substantial energy demand reduction [82].

The application of sterically hindered amines includes amino alcohols, amino ethers, 2-substituted piperidine alcohols and piperazine derivatives. These options have been the focus in chemical absorption technologies [83]. Compared with other amine-based systems, sterically hindered amines present significant advantages due to the low corrosion, thus does not require a corrosion inhibitor. It also shows lower circulation rates, lower degradation, and less solvent loss, and higher CO₂ absorption and regeneration.

Examples of sterically hindered amines include the solvents offered by Mitsubishi Heavy Industries (MHI), KS-1, KS-2, and KS-3, and 2-amino-2-methyl-1-propanol [73]. The state of the art of MHI process, KM-CDR Process® (Kansai Mitsubishi Carbon Dioxide Recovery), has been already implemented in several commercial plants. KM-CDR Process® with the solvent KS-1 has an energy consumption of 2.44 MJ/kg CO₂ from natural gas boiler flue gas [84].

Amine-impregnated solid sorbent (AISS) is a promising option to reduce energy losses due to the higher absorption capacity, about 140 g CO₂/kg, and the lower energy consumption for regeneration (1.5 GJ/tCO₂). The efficiency in 1.5 points saves 32 % of energy requirements for a natural gas combined cycle (NGCC) and 3.7 points for pulverized coal power plants. The efficiency penalty is reduced by 6.7 points with heat integration [85].

As mentioned before, the largest commercial post-combustion capture plant applying KM-CDR Process® in the power industry is, by 2022, the Petra Nova Carbon Capture Project at the Parish Generating Station in Texas. MHI operates a CO₂ capture demonstration test facility at Southern Company subsidiary Alabama Power's Plant Barry in Mobile county, with a capacity of 500 t per day from coal-derived flue gas. The capture CO₂ is stored underground with a capacity of 1 Mt. MHI CO₂ capture technology reported an improvement of 30 % or more efficiency in power generation compared to existing competitors with the implementation of 90 % CO₂ capture, waste-heat recovery, and MHI's flue gas treatment process [14]. The international CO₂ capture center in Regina, Saskatchewan, Canada, has designed solvent designated as PSR solvents [86]. PSR solvent presents lower regeneration temperatures, lower degradation, lower circulation rate, and lower corrosion rate.

Other commercial processes based on MEA are the Econamine FG Plus™ for high O₂ content flue gas, the Hitachi H3-1 solvent with anticorrosion behavior with an energy demand of 2.4 MJ/kg CO₂ for coal-fired flue gas, and the Shell Cansolv Technology with the DC-101, DC-103 and DC-103B tertiary amine solvent capable of removing both CO₂ and SO₂. This last example is the technology implemented in Saskatchewan, Canada [87,88]. Sinopec has also developed the MEA post-combustion system at Dongying, Shangdong Province, China [88].

The Athabasca Oil Sands Project venture in Canada is capturing more than 1 million tonnes of CO₂ per year applying the ADIP®-X process licensed by Shell Global Solutions Inc. (SGSI). This process is based on MDEA. This facility is the largest CCS project in the oil industry operating since 2015, reducing by 35 % the CO₂ emissions of the plant [89,

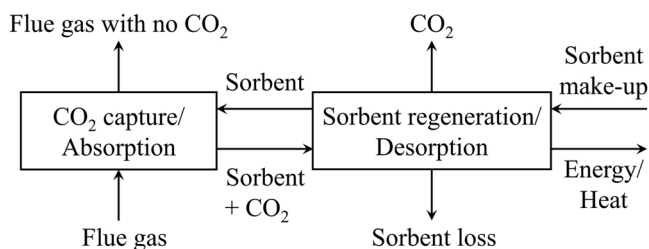


Fig. 5. Amine scrubber schematic: absorption-desorption of CO₂ and sorbents regeneration.

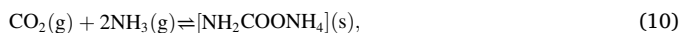
Adapted from [75].

90]. The Tomakomai project capture CO₂ with an amine scrubbing process in an oil refinery, which produces high purity H₂ for hydro-treating by PSA system (see Section 3.3). This facility is the first CCS project led by Japan CCS. Ltd, capturing 100,000 tons of CO₂ per year [91]. The Gorgon project is capturing CO₂ from the Gorgon (14 % vol CO₂) and the Jansz-Lo gas fields (0.15 % CO₂) before further gas processing and liquefaction. This facility is the major world's operation CO₂ capture project in the gas industry. The system applies ADI®-X process, and it can capture 3.4–4 million tonnes of CO₂ per year [92].

3.1.2. Aqueous ammonia

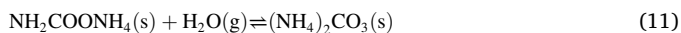
Amine-Based Chemical absorption with MEA could be replaced with Aqueous Ammonia Process (AAP) to capture acid gases such as CO₂, SO₂, NO_x, HF and HCl. Unlike amine scrubbing, AAP does not show absorbent degradation or equipment corrosion by SO₂ and O₂. The energy requirement for absorbent regeneration is much lower than in the MEA process [57]. In addition to this, the major by-products from AAP are ammonium bicarbonate NH₄HCO₃, ammonium sulphate (NH₄)₂SO₄ and ammonium nitrate NH₄NO₃, that are well known fertilizers [93].

The reaction between NH₃ and CO₂ occurs in dry conditions to form ammonium carbamate (NH₂COONH₄),



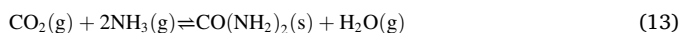
which is very soluble in water, and dissolves into carbamate and ammonium ions.

In the presence of moist air and at room temperature, it can produce also ammonium carbonate and bicarbonate [94], as follows:

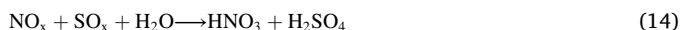


The backward reversible reactions occurs at temperatures in a range of 38–60°C, while the forward reactions occurs at room temperature [95–97].

At temperatures higher than 140°C and high pressure, the CO₂-NH₃ reactions produce urea (CO(NH₂)₂) [98].



Urea production needs a large amount of NH₃ to capture CO₂ from flue gas, which leads to a high operation cost. At high CO₂ concentration in the flue gas, over 15–18 %v/v [99], the CO₂-NH₃ reaction may be explosive. As weak base, the ammonia is also capable of absorb traces of acid gases such as NO_x and SO_x from the flue gas.



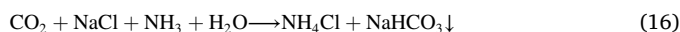
(NH₄)₂SO₄ and CO(NH₂)₂ have a fertilization effect similar to NH₄HCO₃ [100].

Studies reporting the use of ammonia for CO₂ capture are scarce. This technology was compared with the maximum loading capacity of MEA in NH₄OH solution on an equal weight of absorbent basis [101]. It was concluded in previous studies that the maximum CO₂ removal efficiency by NH₃ absorbent could reach 99 %, with a CO₂ loading capacity of 1.2 g CO₂/g NH₃. On the other hand, MEA has a maximum CO₂ removal capacity of 94 % with a loading capacity of 0.409 g CO₂/g MEA. More recent studies like [102], minimized the capital cost and energy demand of the process. The work developed by [103] compared the aqueous ammonia process with amine based technology resulting in a regeneration duty reduction by 36 % in comparison with the reference NH₃ process.

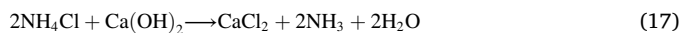
3.1.3. Dual-alkali

The Solvay process uses a dual-alkali approach with ammonia as catalyst to facilitate the reaction between sodium chloride and CO₂ to

generate sodium bicarbonate and ammonium chloride:

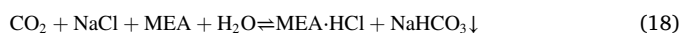


The ammonia is recovered by reacting the generated NH₄Cl with Ca(OH)₂:



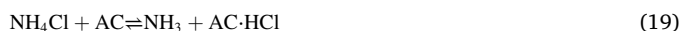
Calcination of limestone is the main source of Ca(OH)₂. In this process, one mole of CO₂ is released for every two moles of CO₂ captured from flue gas in the form of NaHCO₃. Therefore, the process is ineffective due to the limestone and energy consumption during calcination [57].

It is also possible to absorb CO₂ using dual-alkali with MEA instead of ammonia:



The maximum absorption capacity of amines is 0.5 mol-CO₂/mol-amine when the reaction product is carbamate and 1 mol-CO₂/mol-amine if the product is bicarbonate. Therefore, by increasing the bicarbonate in products, the amines' CO₂ absorption capacity doubles [57].

The second stage of this process involves a secondary alkali to regenerate the first alkali. Limestone is replaced by activated carbon to regenerate ammonia at room temperature, absorbing the HCl molecules from NH₄Cl and releasing ammonia:



3.1.4. Reversible carbonation

Calcium Looping is a novel technology based on the carbonation/calcination cycle of calcium oxide (CaO) in a separated gas-solid fluidized bed reactor at high temperature [104]. The exhaust gas contains 15 % CO₂ in volume. The fluidized bed reactor operates at atmospheric pressure, and at 650°C, CO₂ is captured by carbonation of CaO to form CaCO₃. The CaCO₃ particles are introduced in a second reactor for its calcination producing regenerated CaO at 900°C, releasing pure CO₂. The reversible reaction of this process is explained below [105]:



The carbonation reaction is exothermic and the calcination is endothermic. The heat produced in the carbonation reaction can be introduced in a stream cycle to generate more power reducing the energy requirements [106].

This technology can be applied in both post-combustion and pre-combustion processes [105]. Nevertheless, the main use for calcium looping is in post-combustion [34]. This technology has been categorized at a pilot-scale (TRL-6). Coal-fired plants have reported energy losses of 5–12 %. Nevertheless, these losses can be reduced by adding a bottom temperature cycle of AISS, besides, reduces the equipment size and the capital cost [107].

Lithium zirconate (Li₂ZrO₃) has been investigated to capture CO₂ at high temperatures [108]:



The carbonation reaction takes place at approximately 450°C - 590°C. The backward reaction occurs at around 750°C.

The carbonation reaction can be accelerated by the use of eutectic salts formed by, for example, lithium and potassium carbonates. A variety of binary and ternary eutectic salt-modified Li₂ZrO₃ sorbents have been evaluated and identified to capture CO₂ at high temperatures [109]. The formation of eutectic molten carbonate layer on the Li₂ZrO₃ surface facilitates the transfer of gaseous CO₂ during the adsorption process.

Lithium silicate (Li₄SiO₄) has also been studied for the absorption of CO₂ through reversible carbonation [110,111]. These studies proved that Li₄SiO₄ has higher absorption capacity than Li₂ZrO₃. The process is

explained in the following reaction:



Li_4SiO_4 absorbs CO_2 below 720°C and released it above that temperature. Li_4SiO_4 has strong opportunities for commercialization for CO_2 adsorption due to the characteristics such as range of temperatures and CO_2 concentration and stability, rapid adsorption, and large capacity.

3.2. Physical absorption

CO_2 , and other acid gases such as H_2S , can be physically absorbed in different solvents. As absorption does not involve chemical reaction, the regeneration of the solvent is generally easier than in adsorption or chemical absorption processes. The solubility of CO_2 in the solvent increases with the pressure and decreases at higher temperatures. The captured CO_2 is released after depressurization.

Physical absorption is commercially used to remove acid gases from natural gas and capture CO_2 from syngas during ammonia, methanol, and hydrogen production. Some CO_2 capture methodologies combine physical and chemical solvent. The most commonly applied examples are Amisol, a mixture of methanol and secondary amines, and Sulfinol, a mixture of amines such as diisopropyl amine or methyl diethanolamine (MDEA) and the physical solvent sulfolane.

3.2.1. Pressurized water scrubbing

Pressurized Water Scrubbing (PWS) is one of the most desirable technologies for biogas upgrading or CO_2 pre-combustion capture from biogas, as it can also remove H_2S and has low methane loss [66,67,112].

This process operates with compressed biogas, which enters at the bottom of the absorber column, while water is introduced at the top to achieve a liquid-gas counter flow. The operational pressure is in the range of 5–10 bar, and the methane recovery is about 98 % [69,113].

However, this process needs a high amount of water and generates large amount of waste water, it has low flexibility of different biogas flow inputs, and it has the disadvantage of clogging from bacterial growth [112,114–116].

3.2.2. Organic solvents

The Selexol process uses the Union Carbide Selexol solvent (dimethyl ether polyethylene glycol) [117,118]. The solvent can capture CO_2 , water, and sulfur and aromatic compounds. The absorption process occurs at low temperatures, at around $0\text{--}5^\circ\text{C}$. The solvent regeneration can work either by stripping with air, steam or inert gases, or by reducing the pressure.

Some examples applying the Selexol process are the Coffeyville project, which captures 1 million tonnes of CO_2 per year at a petroleum coke-based nitrogen fertilizer production process in Kansas, USA. Synthetic gas is used for urea-ammonium-nitrate fertilizers synthesis. The captured CO_2 is then dehydrated and compressed for the injected into the North Burbank Unit for EOR. A similar approach is followed in the Enid project in Oklahoma, USA, where urea, liquid fertilizers, and ammonia are produced and the dehydrated and compressed CO_2 is transported to an EOR facility with a capacity of 680,000 tonnes of CO_2 per year [119,120].

The Rectisol process uses chilled methanol as a absorbent, and operates at temperatures between -30 and -75°C . This method has been applied mainly to purify syngas or to remove impurities from hydrogen. It is also widely applied in the natural gas industry to reduce CO_2 content [121]. There are different possible configurations for this process depending on the scalability, specification, and requirements.

The FLUORTM process uses propylene carbonate as solvent to capture CO_2 [57]. The FLOURTM process is a good choice for treating gases with high CO_2 partial pressure (above 400 kPa). See Table 4.

Table 4

Advantages and disadvantages of different organic absorbents.

Absorbent	Advantages	Disadvantages
Selexol (dimethyl ether polyethylene glycol)	<ul style="list-style-type: none"> The sweet gas comes out dry Low temperature changes in the absorption process Regeneration by air stripping does not require heating The initial investment and operating cost are low 	<ul style="list-style-type: none"> The process has higher efficiency at high pressure High affinity to a heavy hydrocarbon The feed gas needs to be dehydrated before the process
Rectisol (chilled methanol)	<ul style="list-style-type: none"> High chemical and thermal stability, not corrosive, and has high solubility with water Can be easily regenerated by flashing at low pressure Carbon steel can be used for the equipment 	<ul style="list-style-type: none"> Can absorb metallic traces of mercury, forming amalgams Solvent refrigeration increase the capital and operating cost of the plant
FLUORTM (propylene carbonate)	<ul style="list-style-type: none"> Has high CO_2 solubility, and does not require regeneration heat or make-up water Requires low modification to increase CO_2 in the feed gas Good performance at low temperatures The sweet gas comes out dry 	<ul style="list-style-type: none"> High affinity to a heavy hydrocarbon Expensive

3.3. Adsorption

The use of physical adsorbents (zeolite or charcoal) for CO_2 capture has received significant attention during the last years. However, this method is at demonstration level, with a TRL of 7 [29]. The adsorption process depends on the thermodynamic properties to shift for the flue gas to attach to a solid material. This adsorption can be either chemical (chemisorption) or physical (physisorption) [57].

The adsorption process required removing sulfur dioxide (SO_2) from the flue gas before the CO_2 adsorption process. Additionally, the flue gas must be cooled down to $40\text{--}70^\circ\text{C}$ to ensure adsorption conditions. There are multiple designs for the adsorber vessel: continuous or batch reactor process, bubbling or fixed beds reactors, and potentially integrated both CO_2 adsorption and desorption stage in a single unit. The regeneration process involves pulling the gas stream out under a mild vacuum using a CO_2 booster fan, leading to dehydration and compression. The sorbents can be recycled and led back to the adsorption process. The spent sorbents can be replaced with new sorbents in the adsorption process [122]. The process is described in Fig. 6:

Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA), and Temperature Swing Adsorption (TSA) are feasible technologies for carbon capture. PSA operates at high pressure while VSA works at atmospheric pressure or even lower [123].

The gas mixture flows through a bed at low temperature and high pressure until the capture of CO_2 achieves equilibrium conditions at the bed output [124]. In PSA, the bed is regenerated by reducing the pressure. PSA has demonstrated the best performance due to its simplicity in the application at different pressures and temperatures. Besides, PSA presents the lower energy demand and lower investment cost [123]. In TSA, the regeneration is achieved by means of a hot gas stream. Therefore, the heat requirements make TSA more expensive than PSA.

A combination of TSA and PSA is called PTSA (Pressure and Temperature Swing Adsorption). PTSA reduces the energy consumption required for separation by around 11 % in comparison with the PSA system [125]. PSA is desirable when the partial pressure of CO_2 is high, otherwise TSA is more suitable, as PSA needs longer operation time if the CO_2 concentration is low [126].

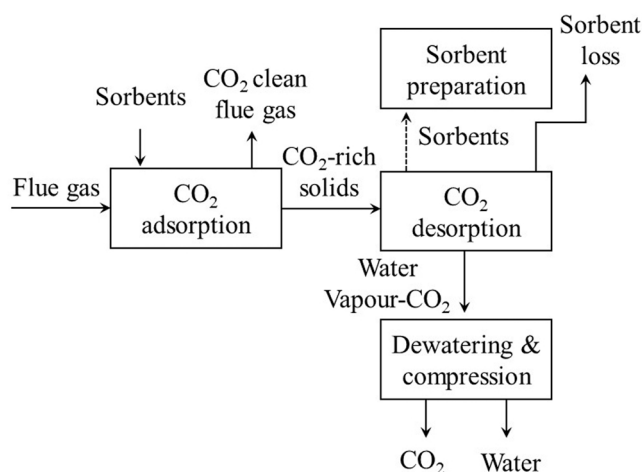


Fig. 6. Adsorption process for CO₂ and sorbent regeneration. Adapted from [122].

Electro Swing Adsorption (ESA) is a new promising technology that is expected to be more competitive (more cost-effective) in the future [127]. In ESA, a low-voltage electric current is passed through the adsorbent [57,128,129].

Solid adsorbents such as activated carbon, mesoporous silicates, alumina, zeolites, and metal oxide have been widely applied for gas separation [130]. CO₂ adsorption from a gas stream is a dry process and thus has no by-products such as the waste water produced in absorption systems. This method requires low energy in comparison with cryogenic and absorption methods. It is more desirable since it has high capacity at normal temperature and pressure, low regeneration cost, high stability and high adsorption rate [131]. CO₂ adsorption has, however, some limitations related to the capacity and selectivity for CO₂ of the adsorbents, and the lower removal efficiency compared to other technologies.

There is an interest in developing new adsorbents or modifying the surface so the adsorbents can operate at higher temperatures in steam presence with improved selectivity and increased capacity.

The advantages of the adsorption are based on the fact that it is a reversible process and the adsorbent can be recycled, generating low amount of waste. The adsorbent has less corrosion than other processes and presents high efficiency (>85 %v/v CO₂). The adsorption process shows high capacity at low temperature and high pressure for physical adsorbents, and at low CO₂ pressure for solid amine adsorbents. Nevertheless, the process shows low CO₂ selectivity if it is based on physical adsorption, and the capacity decreases with temperature and presence of moisture. The chemical adsorption based on lithium compound has high energy consumption due to the high temperature for CO₂ adsorption and adsorbent regeneration [23].

3.3.1. Activated carbon

Activated carbon has been applied in a wide range of industrial processes [132]. The surface of activated carbon has heteroatoms that exist in the form of acidic, basic, or neutral organic functional groups [133]. The activated carbon surface can be modified by incorporating heteroatoms like nitrogen to improve the specific adsorbate-adsorbent interaction. Nitrogen increases the number of primary groups, which changes the charge in the graphene layer. Therefore, the capacity of activated carbon to adsorb CO₂ can be increased by introducing nitrogen functional groups into their structure [134,135].

Previous studies [136] analyzed the CO₂ capture performance with steam-activated anthracite. Raising the temperature decreased the adsorption capacity rapidly. The highest CO₂ loading capacity was 65 mg CO₂/g adsorbent for activated anthracite at 800°C with a surface area of 540 m²/g and 2 h of operation. This moderately low capacity adsorption was improved using anthracite with higher surface area

(over 1000 m²/g). CO₂ capture capacity of the activated anthracite can be increased by chemical modification with NH₃ and polyethyleneimine at a higher temperature due to the introduction of alkaline nitrogen groups on the surface. In the study [137], it was reported that any surface modification of activated carbon should be carefully performed without altering the textural properties.

3.3.2. Molecular sieves

A molecular sieve is designed to separate molecules based on their molecular size. The molecular sieve is a material with small pores of uniform size, and thus molecules larger than the pores diameter cannot enter the porous structure to be adsorbed (see Table 5).

Molecular sieve is a costly technology, but it can be adapted to almost every carbon capture process [77]. There is a particular interest in adsorbents based on high surface area inorganic support that incorporates basic organic groups (typically amines). The interaction between acidic CO₂ and the basic surface results in the formation of surface ammonium carbamates at anhydrous conditions and the formation of NH₄HCO₃ and other carbonate species in the presence of water [139]. Mesoporous substrates, such as SBA-1, SBA-15 [140,141], MCM-41 and MCM-48 [141–144], and silica [139,145] are attractive due to their large porous which can be accessed by molecules with amino groups.

Molecular sieves adsorbents can operate at above ambient temperatures and are insensitive to moisture. Some inorganic substrates with a high surface area and substantial pore volumes have been developed in order to attach basic organic groups [139,145–148]. CO₂ reacts with the amine group in the absence of water to produce surface-bound ammonium carbamates (zwitterionic ammonium carbamate) with the stoichiometry of 2 N atoms for every CO₂ molecule. Nevertheless, in the presence of water, the adsorption capacity is sometimes improved with a ratio of 1 N atom for every CO₂ molecule by forming ammonium bicarbonates after proton exchange. Therefore, the process is similar to the absorption method.

Carbon molecular sieve is also applied as adsorber with PSA due to the long lifetime, of around 7–10 years, since it can be regenerated with vacuum pumps to collect the captured CO₂.

Carbon Molecular Sieves (CMS) is a typical molecular sieve adsorber used for biogas upgrading by PSA. In comparison with other upgrading technologies like amines 3.1.1, PSA only needs electricity supply with no need or heat demand. As other biogas upgrading technologies PSA with CMS also requires a biogas pre-treatment stage to remove volatile organic compounds (VOCs) and H₂S. However, CMS presents a bit more tolerance for VOCs pollution than membranes where all VOCs must be previously removed. Additionally, the CMS can be easily regenerated by vacuum pumps to extract the captured CO₂ from the PSA system increasing the lifetime of the CMS.

3.4. Membranes

Membranes work as semi-permeable barriers that can separate components from a gas stream by concentration, electric potential or pressure gradients [149]. Membranes are available in different materials (inorganic or polymeric), and can be either porous or dense (non-porous). Porous membranes act somehow similar to the molecular sieves described before. Dense membranes have no porous and the transport

Table 5
Reference values for kinetic diameters [138].

Species	Diameter (Å)
H ₂	2.89
CO ₂	3.3
O ₂	3.46
N ₂	3.64
CO ₂	3.76
CH ₄	3.8

occurs via diffusion through the membrane material.

The membrane performance depends on its permeability for a specific chemical species to pass through the membrane. In this case, the performance for separation of CO₂ with respect to the other species (see Fig. 7).

Most of the research plans are trying to improve the driving force across the membrane by, for example, increasing the pressure drop between the feed gas and the permeate streams [150,151]. About 27 % of the patents within CO₂ technologies are membrane-based [152].

Membranes present several advantages over the absorption and adsorption processes: Membranes do not require regeneration energy, have low CAPEX, have no waste streams, show high capture efficiency (> 85 % CO₂) and are moderately simple modular. However, membranes have several disadvantages: The membranes are expensive and need to be replaced periodically due to the limited lifetime. The modules can deteriorate if the stream output present high temperature, and their permeability can be reduced by fouling. Thus, the flue gas must be cooled down before it enters the membrane. Membranes are also sensitive to traces of acidic compounds and moisture [23,57,125].

As a reference, it can be stated that membranes are efficient for CO₂ separation in those cases when CO₂ concentration in flue gas is ≥ 20 % (see Table 1). For lower concentrations, multiple re-circulation stages are needed to achieve high degrees of separation. In recirculated systems, the permeate re-circulation is about 30 % of the input stream from the first membrane. The other 70 % of the permeate stream is led to a second membrane where only 5 % is recirculated as a sweep in the second membrane [43]. Fig. 8 illustrates a two-step membrane separation with permeate re-circulation:

The energy requirement per mass of CO₂ captured is in the range of 0.5–6 GJ/tCO₂ [153].

3.4.1. Inorganic membranes

Inorganic membranes for CO₂ capture are still at lab-scale concept with a TRL of 3 [23]. Porous membranes are the most commonly applied for CO₂ capture. Non-porous membranes are generally used for O₂ separation through perovskite system [154] or H₂ separation through palladium alloys [155].

Porous inorganic membranes consists of a metal or ceramic support with a cast porous thin top layer. They have lower cost but are usually less selective. Zirconia, zeolite, silicon carbide, alumina, glass, and carbon are mainly used as porous inorganic membranes supported on different substrates such as zeolite, α -alumina or γ -alumina. One convenient method to improve their performance is modifying the surface by covalent bonds between a layer of selected compounds with a proper functional group that must have a high chemical affinity for CO₂.

Amorphous silica membranes are appropriate for highly selective membranes with pores > 1 nm. Nevertheless, diffusion through such narrow pores is slow. Several research have focused on membrane pore structure to improve selectivity and performance of silica membranes. Sol-gel methods and chemical vapor deposition are applied to prepare silica membranes with suitable properties for gas separation. Sol-gel methods are usually used for membrane synthesis or for modifying the homogeneity and control of the membrane pores [156,157]. The studies

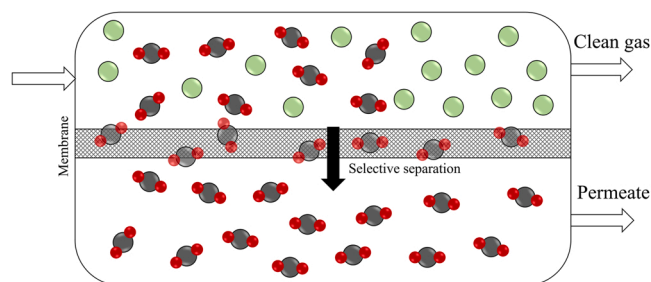


Fig. 7. Schematic of gas separation membrane.

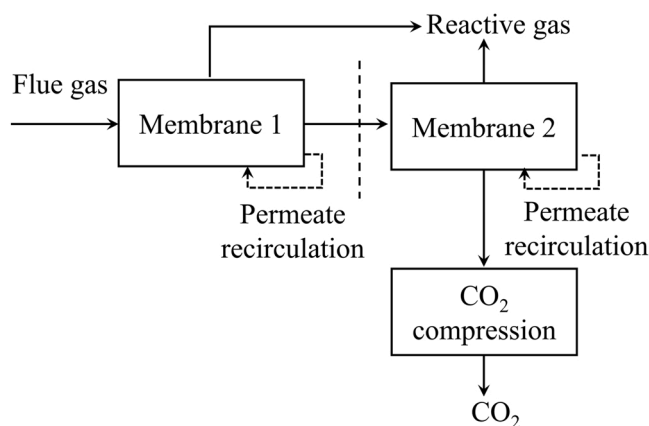


Fig. 8. Membranes for CO₂ capture with permeate re-circulation. Adapted from [43].

of [158] and [159] applied methyltriethoxysilane to modify silica membranes that were formed by applying tetraethoxysilane. The resulting membranes demonstrated both high CO₂/CH₄ selectivity and permeability.

Zeolites present uniform-sized pores of molecular dimensions based on a crystalline inorganic structure. Small-pore, medium-pore and large-pore zeolites have been used to prepare membrane to separated CO₂ from CH₄ [160–163,164]. CO₂ separation from a CH₄ flow is based on competitive adsorption since both CH₄ and CO₂ molecules are smaller than the zeolites pores. CO₂/CH₄ separation selectivity at room temperature for ZSM-5 membranes was in a range of 2.4–5.5 [165], while for Y-type was about 10 [166] and for X-type membranes was as high as 28 [162]. Contrarily, SAPO-34 (0.38 nm pore diameter), zeolite T (0.41) and DDR (0.36–0.44 nm) have small-pore molecular sieves. These membranes showed higher CO₂/CH₄ selectivity due to both differences in competitive diffusivity and adsorption. The study presented by [161] results with a CO₂/CH₄ selectivity of 67 and a CO₂ permeance of 1.6×10^{-7} mol/(m² s Pa) at 297 K working with SAPO-34 membranes. Permeance is the ratio of the permeability coefficient to the membrane thickness. Adsorption isotherm demonstrated SAPO-34 crystals absorbs CO₂ better than CH₄. In [167], it was reported a CO₂/CH₄ selectivity of 48 and a CO₂ permeable of 0.88×10^{-7} mol/(m² s Pa) at 297 K in presence of N₂, H₂O, C₂H₄, C₃H₈ and n-C₄H₁₀ impurities. In [168], it was achieved a CO₂/CH₄ selectivity of 400 and CO₂ permeance of 4.6×10^{-8} mol/(m² s Pa) at 308 K using T-type zeolite membrane with a pressure drop of 0.1 MPa and a vacuum of the permeate side. DDR zeolite membranes on porous alumina tubes were applied in the study developed by [169], resulting in a CO₂/CH₄ selectivity of 220 and CO₂ permeance of 7×10^{-8} mol/(m² s Pa) at 301 K for a pressure drop of 0.5 MPa.

3.4.2. Polymeric

Polymeric membranes have low energy requirements, absence of dangerous emissions and harmful chemicals [170]. Polymeric membranes have a TRL of 6 in post-combustion capture from power plants and TRL of 7 for natural gas pre-combustion processes [29].

Polymeric membranes are classified as glassy or rubbery, whether the preparation and processing temperature are either below (for glassy) or above (for rubbery) the transition temperature of the polymer [171].

Polymer rearrangement in glassy membranes never reaches a thermodynamic equilibrium since it happens at a long time scale. Consequently, the polymer chains are linked imperfectly, heading to excess free volume in the form of microscopic voids in the polymer matrix. Langmuir adsorption occurs within these voids, increasing the solubility.

The membrane area required for separation is inversely proportional to the membrane permeability. Therefore, high permeability displays

lower cost. There is a close relationship between permeability and selectivity for most of the membranes. Higher permeability leads to lower selectivity and vice-versa. This relationship is called the Robeson upper bound or Robeson limit [170,172].

The performance of polymeric membrane can be improved by increasing the CO₂ diffusion (e.g., altering the polymer packing within the membrane) and by increasing the CO₂ solubility (e.g., changing the polymer composition). These improvements have generated a broad range of polymeric membranes with reasonable selectivity and permeability for CO₂ capture. Polymers studied by researchers include poly-aniline [173], polyimides [174], polyetherimides [175], poly(ethylene oxide) [176], polyphenylene ethers [177], polyacetylenes [178], polyacrylates [179], poly(arylene ether)s [180], polysulfones [181], polycarbonates and, polypyrrole [182]. Table 6 summarized the performance of some polymeric membranes, mainly used for post-combustion separation of CO₂ and N₂ from the flue gas [149]. Single-stage membranes systems cannot offer high capture efficiency, thus a second membrane module is required.

The main disadvantage of polymeric membranes is their degradation. High pressures and temperatures can cause swelling of the polymer material, resulting in a lower selectivity since it increases the permeability of all gases. Therefore, to improve efficiency, it is necessary to optimize the balance between temperature and pressure [29].

Polymeric membranes can be used for CO₂/H₂ separation or biogas upgrading in pre-combustion systems, CO₂ capture from exhaust gas in different post-combustion processes as well as air separation unit for O₂/N₂ separation for oxy-combustion processes.

Polymeric membranes offer a practical alternative to other traditional biogas upgrading. This is achieved by circulating pressurized biogas through CO₂ selective membranes where H₂S can also be removed. One of the main advantages is the flexibility to different biogas flow input due to the modular system. Besides, membranes can achieve high methane recovery reaching levels near 99 % [69]. Membrane can be a desirable option for biogas flow $\leq 1000 \text{ Nm}^3/\text{h}$, however, for higher flows the operation cost can be high since the modules must be replaced regularly.

3.4.3. Membranes combined with chemical absorption

To improve a single-stage membrane system it has been proposed the combination of selective membranes and chemical absorption [183, 184]. The study developed by [185] measured and modelled the separation factor and permeability, applying different CO₂ partial pressures of liquid membrane to capture for a CO₂-N₂ system. The process used an aqueous solution of diethanolamine (DEA) and an immobilized liquid membrane (ILM), also referred to as supported liquid membrane (SLM). DEA aqueous solution used helium gas as the sweep, and DEA was immobilized in the hydrophobic micro-porous polypropylene membrane pores. CO₂ absorption and desorption occurs in a single membrane module without external energy requirement. The model developed by [185] was adopted by [186]. They tried both numerical and experimental methods, applying hollow fibre contained liquid membrane permeator to capture CO₂ from a CO₂-air mixture, using a DEA aqueous solution as the liquid membrane. Selectivity for CO₂/N₂ was of 115 and

Table 6
Performance of polymeric membranes separating CO₂/N₂ [149].

Material	Permeability (barrer)	Selectivity (CO ₂ /N ₂)
Polyimide	735	43
Polydimethylphenylene oxide	2750	19
Polysulfone	450	31
Polyethersulfone	665	24.7
Poly(4-vinylpyridine)/polyetherimide	52.5	20
Polyacrylonitrile with polyethylene glycol	91	27.9
Poly (amide-6-b-ethylene oxide)	608	61

a CO₂ permeance of $1.51 \times 10^{-8} \text{ mol}/(\text{m}^2 \text{ s Pa})$ with a gas flow of 15 % CO₂ in the CO₂-air mixture, 20 wt% DEA liquid membrane and atmospheric pressure.

3.5. Cryogenic separation

Cryogenic separation of a gas mixture consists of the fractional condensation and distillation at low temperatures. There is a wide range of low-temperature cryogenic carbon capture technologies, which have been applied in natural gas for CO₂ removal, and it is a mature technology (TRL-9) [44]. This technology is widely used for commercial applications for high CO₂ concentration (usually more than 50 %). Cryogenic is barely used in dilute CO₂ streams such as flue gas from coal or natural gas-fired boiler since the energy required for refrigeration is economically prohibited for a plant [125].

Low temperatures methods enable CO₂ removal with higher purity levels than other technologies. Some cryogenic systems have achieved purity of 99.99 % [43]. The flue gas is cooled down to below the CO₂ boiling point (around -75°C) [57]. The advantage of this process is that it allows recovery of pure CO₂ in liquid form, which can be easily transported [125]. Additionally, the process does not require chemical absorbent and can operate at atmospheric pressure.

The water content in the gas mixture can form solid CO₂ clathrates and ice, producing major plugging problems [124]. Thus, several costly processes need to be added to remove water traces from the flue gas. The formation of solid CO₂ into the heat exchanger surface during the capture cycle affects the heat transfer reducing the process efficiency [187]. Additionally, the electricity demand for cooling is also thermodynamically disadvantageous. Therefore, it is recommendable to have access to existing sources of excess cooling. This source could be a co-located liquefied natural gas (LNG) re-gasifier due to the high cooling capacity in the LNG vaporization process [188]. The most promising application for this technology is pre-combustion or oxy-combustion, in which CO₂ has high concentrations in the flue gas [125]. There are different cryogenic technologies: cryogenic distillation, dynamic packed bed, mechanical cooler using Stirling cycle, and hybrid membrane/cryogenic process [29].

Fig. 9 describes a packed bed cryogenic system that applies the LNG vaporization process as a cooling source to cool down the flue gas. Once the flue gas reaches cryogenic temperatures, CO₂ and H₂O are separated simultaneously. The CO₂ removal efficiency is 99 %, with impurities composition of around 10 % CO₂, 89 % N₂ and 1 % H₂O. This technology is also applicable for biogas upgrading, nevertheless, the high cost offers low feasibility for this technology [43].

The study developed by [189] reported CO₂ capture from natural gas. The research team tested the CryoCell CO₂ removal technology in a field trial. This system avoids water consumption, the usage of chemicals, and corrosion issues. The test demonstrated the technical viability of solid-phase CO₂ separation and economic viability compared to the

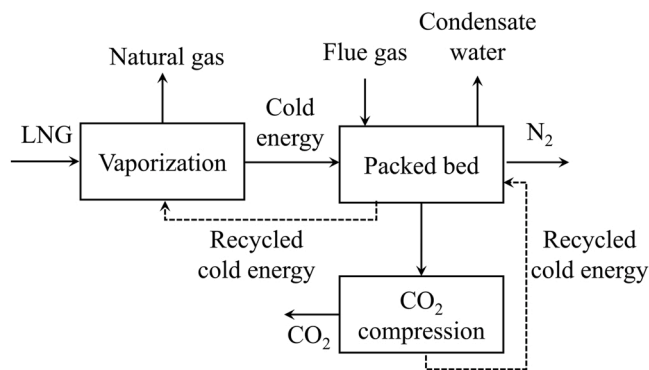


Fig. 9. Packed bed cryogenic system with LNG vaporization integration. Adapted from [43].

amine absorption process for high CO₂ gas field development.

4. Techno-economic analysis of CO₂ capture pathways

Currently, the cost of capturing CO₂ globally is about 60–110 USD/t and it is considered to decrease by 2030 to 30–50 USD/t. This cost reduction would increase the implementation of this technologies at industrial scales [35]. This section presents comparative data of the CO₂ capture costs reported in the latest IPCC Special Report on Carbon Dioxide Capture and Storage (SRCCS) [75]. The intention is discussing the cost of implementing CO₂ capture technologies in heat & power plants, which are, as mentioned before, the main source of global CO₂ emissions.

Tables 7 and 8 present techno-economic data sheets and process descriptions from the carbon capture technologies applied at: low temperature DAC; post-combustion for Supercritical pulverized coal (SCPC), natural gas combined cycle (NGCC) and bioenergy carbon capture and storage (BECCS) and oxy-fuel combustion for SCPC and pre-combustion for IGCC coal plant. Novel post-combustion system based on membranes or adsorption are still in development stage and might offer capture cost reduction. Thus, estimation cost are uncertain and are not discussed in this section.

This analysis includes measures of cost such as the levelized cost of electricity (LCOE), the cost of avoided CO₂, and the cost capture CO₂. The cost measures applied in this section are defined as follows [190]:

• Levelized cost of electricity

$$LCOE = \frac{(T_{CC}F_{CF}) + F_{OM}}{8760C_F M_W} + V_{OM} + (H_R F_C) \quad (23)$$

where LCOE (€/MWh) is the levelized cost of electricity generation, T_{CC} (€) is the total capital cost, F_{CF} (fraction/yr) is the fixed charge factor, F_{OM} (€/yr) is the fixed operating and maintenance (O&M) cost, V_{OM} (€/MWh) is the variable non-fuel O&M cost, H_R (MJ/MWh) is the net power plant heat rate, F_C (€/MJ) is the unit fuel cost, C_F (fraction) is the plant capacity factor, M_W (MW) is the net plant capacity, and 8760 (h/yr) accounts for the total hours in an average year.

All of the parameters in Equation represent their levelized values and it is assumed to remain constant over all the plant lifetime.

• Cost of avoided CO₂.

$$A_{CO_2} = \frac{LCOE_{CCS} - LCOE_{NCCS}}{\eta_{NCCS} - \eta_{CCS}} \quad (24)$$

where A_{CO_2} is the cost of avoided CO₂ (€/tCO₂), η (tCO₂/MWh) is the CO₂ mass emission rate to the atmosphere based on the net capacity of each power plant, CCS and NCCS refers to plants with and without CCS, respectively.

• Cost to capture CO₂

$$C_{CO_2} = \frac{LCOE_{CCS} - LCOE_{NCCS}}{\eta_{captured}} \quad (25)$$

Table 7
Low temperature DAC.

Parameter	Value	Unit
Capacity	360,000	tCO ₂ /y
Lifetime	20	years
CO ₂ capture efficiency	80	%
Electricity demand	250	kWh/tCO ₂
Fuel (heat) demand (typically, natural gas)	1750	kWh/tCO ₂
CAPEX	730	€/tCO ₂ /y
OPEX	4	%CAPEX

Table 8
Post-combustion for SCPC plant with MEA using bituminous coal.

Parameter	Unit	SCPC Post- Comb.	NGCC Post- Comb.	SCPC Oxi- Com.	IGCC Pre- Comb.
Maturity	TRL	9	9	7	7
Reference net power output	MW	587	549	684	581
Emission rate without CC	tCO ₂ /MW	0.762	0.37	0.83	0.773
Emission rate with CC	tCO ₂ /MW	0.112	0.05	0.08	0.109
CO ₂ reduction per MWh	%	88	86	92	86
Plant efficiency without CC, HHV	%	43	50	39	40
Plant efficiency with CC, HHV	%	34	43	32	34
CAPEX without CC	€/W	1.86	0.81	2.36	1.95
CAPEX with CC	€/W	3.03	1.42	4.49	2.68
LCOE without CC	€/MWh	70	51	59	74
LCOE with CC	€/MWh	110	75	101	97
Cost of captured CO ₂	€/tCO ₂	44	63	48	29
Cost of avoided CO ₂	€/tCO ₂	62	76	57	36

where C_{CCO_2} is the cost to capture CO₂ (€/tCO₂), $\eta_{captured}$ (tCO₂/MWh) is the total mass of captured CO₂ per net MWh for the plant with CCS (equal to CO₂ produced minus emitted). The cost of captured CO₂ exclude storage and transport.

The technological maturity can be analysed by the Technological Readiness Level (TRL), which indicates the technology maturity on a simple scale [191]. This critical review includes the TRL of several technologies for CO₂ capture so it can be applied for the maturity analysis. The scale has nine levels: from TRL 1 - basic principles observed and reported, to TRL 9 - actual system has proven through successful mission operations. TRL 6 - system/subsystem model or prototype demonstration in a relevant environment, represents a turning point in technological maturity development by achieving a demonstration level. The TRL development from lab scale to fully implemented scale in CCS technologies is about 10–15 years [192–194]. According to this, it is assumed that CCS technologies to be implemented in 2030 must at least have a TRL 6 in 2020. Currently, the CO₂ capture technologies with TRL 6 are chemical looping, membranes for post-combustion application and calcium looping. Secondly, DAC, oxy-fuel combustion, IGCC, membrane for pre-combustion application and physical adsorption have a TRL of 7. Finally, cryogenic capture presents a TRL of 9. Therefore base on the TRL scale, several CCS technologies could be ready by 2030 and 2050.

Low temperature DAC system offer high capture efficiency, but CAPEX and OPEX are quite high in comparison with other capture processes. As mentioned before, optimistic predictions state a decrease of DAC cost to around 100\$ per ton by 2030.

Most of public data for post-combustion capture pathways are based on amine scrubbing using MEA. The CAPEX of reference power plant with and without carbon capture process have increased since the SRCCS publication due to inflation and economic factor changing. Additionally, the cost of coal has also risen in the last years. IGCC pre-combustion systems present higher CAPEX that other post-combustion systems based on NGCC or BECCS proving an improvement of competitiveness of post-combustion versus pre-combustion process.

Most coal power plants apply bituminous coals and the majority of the research plans about CCS in coal power plants have been focused on bituminous coal. Nevertheless, there has been an increase in low-rank coal applications due to their lower mining cost, high reserves and low sulfur content. The mean energy requirements for low-rank coal

power plants is 37 %, higher than for bituminous coal power plants, this is mainly due to the higher amount of CO₂ captured per net MWh of electricity. Bituminous coal power plants present a lower average capital cost, about 14 %. However, low-rank coal power plants demonstrate only a 3 % more average LCOE than bituminous coal power plants due to the lower fuel price. The average cost of avoided and captured CO₂ are practically the same for both coal types because of the higher costs are offset by the higher amount of CO₂ avoided and captured per net MWh of electricity [190].

Recent studies are also focused on post-combustion capture for NGCC plants. Post-combustion for NGCC with CO₂ capture process present lower CAPEX and LCOE than coal power plants, but higher cost to avoid and capture CO₂.

Current research plans about oxy-fuel combustion focus on SPCP using low-rank coals as an alternative to post-combustion process. Oxy-fuel combustion plants apply conventional cryogenic air separation for oxygen/nitrogen separation. This process has higher overall CO₂ capture efficiency than post-combustion CCS. Nevertheless, the oxy-fuel combustion pathway require 25 % higher energy penalty for compression and capturing CO₂ per net MWh of electricity production than the best current post-combustion CCS. The oxy-fuel combustion CCS system shows 91 % higher CAPEX and 72 % higher LCOE related to a post-combustion system without CCS. The main reason for this LCOE difference is due to the lower price of sub-bituminous coals than the bituminous coals applied in the post-combustion system. Therefore, the LCOE data from both system cannot be directly compared [190].

Pre-combustion pathways continue focusing on IGCC power plants. The pre-combustion system for IGCC with CCS has 6 % higher LCOE than the post-combustion system for SPCP. This shows an important change in the relative economic competitiveness of both technologies. However, it is important to mention that the IGCC has lower CAPEX, avoided and captured CO₂ cost than the post-combustion system with SPCP [190].

Table 8 shows the efficiencies of some CO₂ capture pathways, including some energy penalties to run the system and LCOE data for different coal power plants. In this regard, however, the recent studies available for this review do not fully reflect the lower energy penalties achieved by the more efficient capture and power generation systems now emerging and available for post-combustion CO₂ control. The post-combustion plant and oxy-fuel combustion plant use different types of coal for the CCS system and therefore, the LCOE data oxy and post combustion cannot be compared due to the different coal prices applied.

Chemical absorption with MEA is the most commonly used solvent for DAC, post-combustion and oxy-combustion. Furthermore, it can also be applied for a pre-combustion process such as biogas upgrading. Other chemical adsorption technologies like AAP can reduce the future cost of implementation for carbon capture pathways. Physical adsorption technologies like PSA can be applied in post-combustion, oxy-combustion processes and biogas upgrading, while TSA is more recommended for post-combustion. Membranes are mostly recommended to be applied in pre-combustion pathways. However, other membranes technologies like ceramic or polymeric membranes can be implemented in post-combustion processes. Cryogenic CO₂ capture is mainly recommended for oxy-combustion and pre-combustion due to the high CO₂ concentration in the flue gas.

5. Conclusions

To achieve the Paris Agreement's targets, CCS technologies must reduce CO₂ emissions to reach zero-net CO₂ emissions by 2050. This target will be achieved with the combination of CCS and CCU technologies.

The alternative fuel production by CCU must be used by 2030 to reduce the current conventional fuel emissions. Nevertheless, both the TRL scale and the emissions reduction present several limitations. The TRL scale offers information of a individual technology and not for a

whole industrial system. Besides, the scale does not cover the trans-disciplinary actions on innovation, so it does not offer information about what innovation is needed to advance technologically. Therefore, the TRL scale could lead to an overestimated maturity. Some CCS technologies such as EOR and EGR are not compatible with the Paris Agreement's targets but several CCU technologies could offer the application of alternatives fuels and products, and play an important role in the energy sector to reduce CO₂ emissions, as it will be discussed in future works. It is relevant to mention that further research plans could focus on including CCU product to reduce CO₂ emissions in other different sectors.

The future energy system has to integrate CO₂ capture technologies to reduce GHGs' emissions while assuring the supply of energy and the proper integration between heat, electricity, and transport sectors. New promising technologies still require research, development and implementation on a commercial scale. Research plans should focus on finding new ecological and economical materials, that could improve the efficiency and reduce the cost. This review covers the most applied CO₂ capture technologies for different pathways, including novel technologies to be implemented in the future.

CO₂ capture processes lead to CCS and CCU. This work is part of a larger research project intended to describe and implement CCU technologies over CCS. As a result, CO₂ based materials and alternative fuels like biomethane, methanol or dimethyl ether can be produced and be implemented in the future energy system.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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