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Current status of carbon capture, utilization, and storage technologies in the global economy: A survey of technical assessment

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ABSTRACT

The latest tremendously rapid expansion of the energy and industrial sector has led to a sharp increase in stationary sources of CO_2. Consequently, a lot of concerns have been raised about the prevention of global warming and the achievement of climate mitigation strategies by 2050 with a low-carbon and sustainable future. In view of this, the current state of various aspects of carbon capture, utilization, and storage (CCUS) technologies in general technical assessment were concisely reviewed and discussed. We concentrated on precisely identifying the technology readiness level (TRL), which is beneficial to specifically defining the maturity for each key element of the CCUS system with a commercialization direction paths. In addition, we especially presented and emphasized the importance of CO_2 capture types from flue gases and CO_2 separation methods. Then, we determined valuable data from the largest R&D projects at various scales. This paper provides a critical review of the literature related to challenges of the CCUS system that must be overcome to raise many low TRL technologies and facilitate their implementation on a commercial scale. Finally, our work aims to guide the further scaling up and establishment of worldwide CO_2 emission reduction projects.

1. Introduction

1.1. *Recent trends in global CO_2 emissions: The energy–climate challenge*

The main reason for the increase in anthropogenic emissions is the drastic consumption of fossil fuels, i.e., lignite and stone coal, oil, and natural gas, especially in the energy sector, which is likely to remain the leading source of greenhouse gases, especially CO_2 [1]. The new analysis released by the International Energy Agency (IEA) showed that global energy-related CO_2 emissions soared sharply by 6% in 2021 to 36.3 gigatonnes (Gt) compared to last year [2]. In 2020, fossil CO_2 emissions reached approximately 34.81 Gt [3], a 7% drop from levels in 2019 [4], and in 2021 hit the highest level ever in history, as a result of the tremendous rebound from the COVID-19 pandemic crisis, which stifled international economic and social activities. This rise was fueled in large part by coal power plants, which coal itself represented >40% of the total increase in worldwide CO_2 emissions in 2021, achieving a new peak, surpassing all previous records (15.3 Gt). For natural gas this value also grew considerably, to 7.5 Gt, over 2019 levels. In the case of oil, CO_2 emissions remained notably lower than before the pandemic, reaching 10.7 Gt, which was mainly caused by limited global air transport [2].

Considering all these issues, optimizing the combustion of fossil fuels used for energy production and the application of renewable energy sources cannot counteract the phenomenon of increasing CO_2 emissions and therefore climate change is likely to continue in the coming decades. Given the above, one of the most important goals of the energy policy of the European Union is to reduce greenhouse gases, such as CO_2, methane, nitrous oxide, and F-gases, which absorb and release thermal infrared radiation, resulting in an increase in the temperature of the Earth (the greenhouse gas emissions by gas in 2018 are presented in Fig. 1). Within the last 100 years, human-caused skyrockets in greenhouse gas concentrations have led to a surge of 0.87 °C (2006–2015 relative to 1850–1900) in the global mean surface temperature of the Earth (GMST) [5]. Only in the last three decades before 2012 the temperature has increased by 0.6 °C [6]. In addition, other environmental issues caused by excess greenhouse gas levels in the atmosphere include increasing seawater levels, as well as the number of ocean storms; stronger melting of ice sheets and glaciers; oceanic storms; species extinction; and disturbance of ecosystems [7]. Therefore, the reduction of CO_2 emission has become one of the priorities of highly developed countries, as well as sectors of private industry around the world (Kyoto

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Nomenclature

Acronyms

ASU	Air separation unit
BECCS	Bioenergy with carbon capture and storage
CaL	Calcium looping
CAP	Chilled ammonia process
CCC	Cryogenic carbon capture
CCMC	Carbon capture and mineral carbonation
CCS	Carbon capture and storage
CCT	Clean coal technologies
CCU	Carbon capture and utilization
CCUS	Carbon capture, utilization, and storage
CCUS	Carbon capture, utilization and storage
CEP	Clean Energy Package
CLC	Chemical looping combustion
CMR	Catalytic membrane reactor
CUP	CO_2 utilization potential
DAC	Direct air capture
ECBM	Enhanced coal bed methane
EFs	Emission factors
EGR	Enhanced gas recovery
EOR	Enhanced oil recovery
ESA	Electric swing adsorption
ESS	Energy storage system
EU	European Union
FEED	Front-end engineering design
FGD	Flue-gas desulfurization
GDP	Gross domestic product
GHG	Greenhouse gas emissions
GMST	Global mean surface temperature
HSE	Health, safety, and environment
IEA	International Energy Agency
IGCC	Integrated gasification combined cycle
IGCC	Integrated gas combine cycle
IPCC	Intergovernmental Panel on Climate Change
KM CDR	Kansai Mitsubishi carbon dioxide recovery process
LCA	Life cycle assessment
MCFCs	Molten carbonate fuel cells
MOFs	Metal-organic frameworks
NETL	National Energy Technology Laboratory
NG	Natural gas
NGCC	Natural gas combined cycle
OC	Oxygen carriers
PSA	Pressure swing adsorption
R&D	Research and development
RES	Renewable energy sources
RTIL	Room temperature ionic liquid
SEWGS	Sorbent-enhanced water–gas shift
TES	Total energy supply
TGR-BF	Top-gas recycling blast furnace
TPSA	Temperature pressure swing adsorption
TRL	Technology readiness level
TSA	Temperature swing adsorption
USA	United States of America
VCSA	Vacuum concentration swing adsorption
VPSA	Vacuum pressure swing adsorption
VSA	Vacuum swing adsorption
WGSR	Water-gas shift reaction
ΔH	Standard enthalpy of reaction
% vol.	By volume

Chemicals

Al_2O_3	Aluminum oxide (III)
C	Carbon
$CaSiO_3$	Wollastonite
CO	Carbon oxide (II)
CO_2	Carbon dioxide
DEA	Diethanolamine
DIPA	Di-2-propanolamine
H_2	Hydrogen
H_2S	Hydrogen sulfide
K_2CO_3	Potassium carbonate
MDEA	*N*-methyl diethanolamine
MEA	Monoethanolamine
Mg_2SiO_4	Forsterite
$Mg_3Si_2O_5(OH)_4$	Serpentinite
$Mg_3Si_4O_{10}(OH)_2$	Talc
NOx	Nitrogen oxides
O_2	Oxygen
SO_x	Sulfur oxides
TiO_2	Titanium dioxide

Units

Gt	Gigatonne
kJ	Kilojoule
kWe	Kilowatt electric
MPa	Megapascal
Mt	Megatonne
Mtpa	Metric tonnes per annum
MWe	Megawatt electric
MWth	Megawatt thermal
PPM	Part per milion

Protocol from 1997, EU Emission Trading System from 2005, Climate and Energy Package - “3x20% Package” from 2008, Energy Roadmap 2050 from 2012, and Paris Agreement form 2015). Accordingly, over the past two decades, global CO_2 emissions from fossil fuel combustion from the European Union have already declined, and in 2020 reached 7.29% on the global scale (Fig. 2).

Consequently, the protection of Earth’s atmosphere against the emission of pollutants is one of the most important research directions in the field of environmental engineering [8,9]. The policy in the field of air protection against harmful gaseous impurities, especially CO_2, CO, SO_x, NO_x and volatile organic compounds, is dominated by the following forward-looking trends: increasing the amount of chemical compounds covered by international regulations, which limits the negative impact on the natural environment, consistent capture of pollutants at the source of emissions, and standardizing pollutant emissions in industry, energy, and transport sector. As a result, the reduction of CO_2 emissions from flue gas mixture streams is a necessary operation in many important, high-tonnage technological processes and a perspective in the power industry and ecology. Distant areas of industrial activity should be mentioned, such as fossil fuel power plants that generate electricity (the removal of CO_2 released by burning coal, synthetic natural gas and biomass), and industrial processes, including cement industries, petrochemical industries (oil refineries), iron and steel mills, and the production of hydrogen by steam reforming methane or gasification of other hydrocarbons [10]. In 2020, CO_2 emissions reached almost 36.6% from electricity and heat production worldwide (Fig. 3). The other largest carbon dioxide emitters were industrial manufacturing and fuel production (21.8%); transportation (road transport, non-road transport), domestic aviation and inland waterways (20.1%); buildings - small-scale non-industrial stationary combustion (9.4%); and other

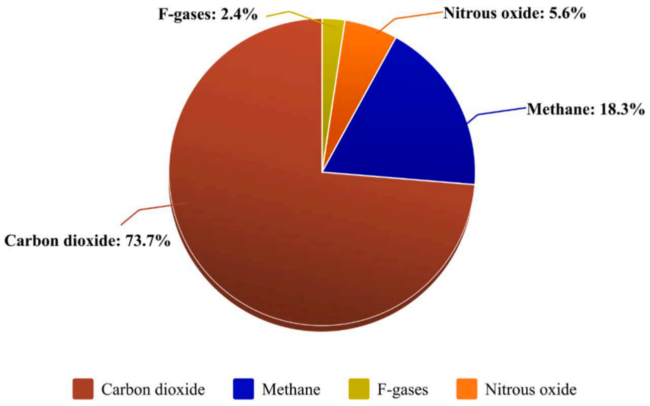


Fig. 1. Global greenhouse gas emissions in 2018 by gas [11].

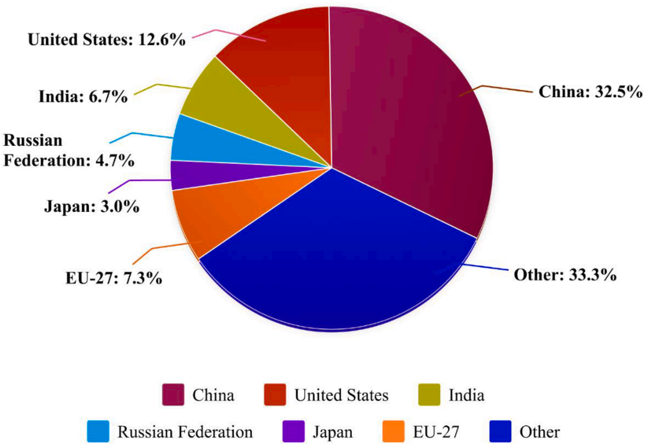


Fig. 2. Global CO_2 emissions from fossil fuel combustion in 2020 by country [11].

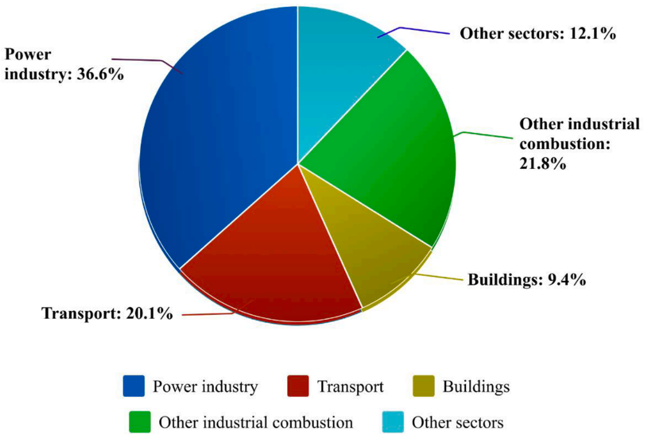


Fig. 3. Global CO_2 emissions in 2020 by sector [11].

sectors - industrial process emissions, agricultural soils and wastes (12.1%) [11].

1.2. *Current and future legislation on CO_2 emission standards*

Scientific institutions, using independent reports, have shown that the CO_2 emission problem cannot be underestimated due to the potential threat resulting from disturbance of the natural balance in nature. According to the Intergovernmental Panel on Climate Change (IPCC), CO_2 levels in the atmosphere will reach 570 parts per million (PPM) in 2100, resulting in an increase of 1.9 °C in the world average temperature [12]. The special report of IPCC from 2018 proves that global warming is likely to reach 1.5 °C between 2030 and 2052 if it continues to increase at the current rate [5]. In view of the above, in 2019, the European Union (EU) worked on the "Clean Energy for All Europeans" regulation package, in short, referred to as the Clean Energy Package (CEP). In the same year, the European Council published a communication on the European Green Deal, i.e., a strategy whose ambitious goal is for the EU to achieve climate neutrality by 2050, as a global leader in this area, and approved it in 2020. In 2021, the European Council adopted a binding EU objective to reduce net target greenhouse gas emissions by at least 55% by 2030, compared to 1990 levels (increase of the 40% target). Then, the EU regulation package called "Fit for 55" was introduced, which covers climate change, energy production, land use, transportation, taxes, and aims to provide a coherent and balanced framework to achieve the climate goals of the EU and reach the 2030 target.

Beyond introducing specific regulations within a timeframe, considering issues of financial input to achieve the goals of net zero emissions and the Paris Agreement, as the first global climate agreement, is also crucial. According to the report named "The Emitting 7: the time and cost of climate neutrality", released in 2022, the seven largest CO_2 emitters (E7): China, the United States, the European Union, India, Russia, Japan, and Brazil were responsible for 66% of global CO_2 emissions in 2018 and made up 72% of the world's gross domestic product (GDP) in 2019. It has been determined, in light of the way things are heading in their current lines of activity, that the EU will reach the point of net zero emissions in 2056 (6 years after the objective that was officially set), USA in 2060 (10 years after the objective), Brazil in 2061, China in 2071, Japan in 2076, India in 2085, and Russia one year later [13].

1.3. *CCUS technologies: effective ways to reduce CO_2 emissions*

Considering the predicted increase in global energy consumption driven mainly by developing economies, the content of CO_2 in the atmosphere will be increased significantly in the next decades. For these reasons, various methods are being searched by which it would be possible to minimize this phenomenon. One of them is the way of clean coal technologies (CCT), which are a new generation of sophisticated coal utilization methods. They are intended to improve the efficiency of coal extraction, preparation, and use, while also improving the environmental acceptability of the process in terms of stopping the increase in CO_2 emissions [14].

The most widely acknowledged CCT by experts, including IEA officials, is carbon capture, utilization, and storage (CCUS) that refers to a group of technologies that can satisfy climate objectives in a variety of ways and become a key alternative for the decarbonization of the world's industrial industries. Among them, CCS is well known process of capturing CO_2 from stationary sources of carbon emissions and permanently storing it, before it is released into the atmosphere [15]. CCS can be defined in more detail with reference to the characteristic stages that follow each other, such as: capture, including CO_2 separation from flue gases (also regarded as a peculiar technique); followed by transport; and long-term storage, which should be harmless to the environment. This is directly related to the storage of CO_2 in the lithosphere, biosphere, and oceans, i.e. rock formations by injection into the ground or below the ocean surface, to prevent it from being emitted and remaining in the atmosphere. After sequestration, the storage location must be considered as a "sealed vessel of CO_2", therefore, various aspects of CCS, including leakage and monitoring. In addition to CCS, the IPCC recognizes the related concept CCMC, which stands for carbon capture and mineral carbonation, as a viable technology in the CCS spectrum, which is still being intensively developed [16,17]. Although there is some opinion that CCMC should not only be seen as a CCS storage solution, but as a separate technology, due to the possibility of CO_2 utilization.

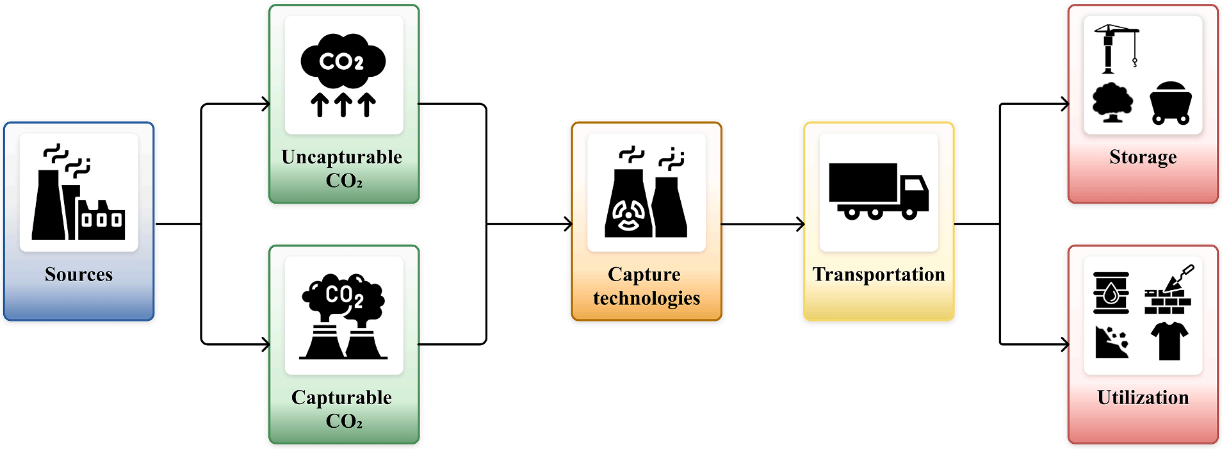


Fig. 4. Methodology of operation of CCS, CCU, CCMC, BECCS, and DAC technologies.

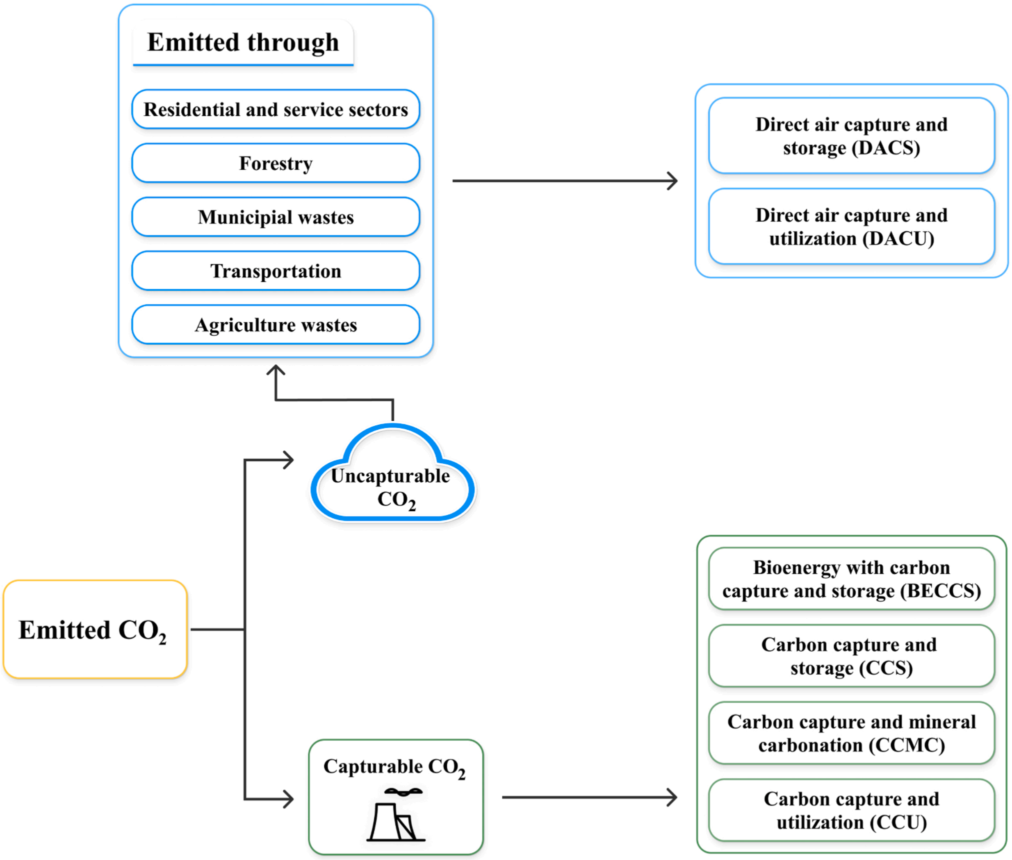


Fig. 5. Technologies currently used for reduction of CO_2 emissions.

Another equally valuable strategy as a modification of CCS is bioenergy with carbon capture and storage (BECCS), as a combination of obtaining energy from biomass with the simultaneous capture and storage of CO_2. The IPCC Climate Change and Land report states that BECCS is one of the most effective mitigation activities related to land use, which would lower emissions by 0.4–11.3 $GtCO_2$ per year between 2020 and 2050 [18]. On the other hand, there is competitive technology for CCS that rather than storing carbon dioxide, can reuse it as raw material in industrial processes by contributing to the replacement of fossil fuels and chemicals, as well as the production of completely new valuable products – carbon capture and utilization (CCU) [19].

Unfortunately, the CO_2 emitted from certain sources is impossible to capture; they are first and foremost agricultural waste, residential and service sectors, forestry, municipal waste and, especially, transportation. Therefore, the technology to extract already emitted CO_2 directly from the atmosphere, called direct air capture (DAC), was also developed. In conjunction with the storage and utilization of CO_2, it is, respectively, referred as DACS or DACU. Nowadays, to extract CO_2 from the atmosphere, two different technical techniques are being used: liquid DAC and solid DAC (solid sorbents). There are 19 direct air capture facilities in operation around the world, capturing >0.01 Mt of CO_2 per year [20]. The schematic methodology and technologies used to reduce the capturable and uncapturable CO_2 emissions are presented in Fig. 4 and Fig. 5.

1.4. CCUS: A solution for global energy economy crisis

A matter of comparable importance to a stable energy economy is the conversion, accumulation, and transformation of stored energy into work. Today, energy production mostly includes the usage of fossil fuels, less, renewable energy sources (RES), and nuclear fuels. The fact that fossil fuels remain the dominating source of energy and automatically cause tremendous CO_2 emission, is due to the potential of a very simple, affordable, and direct conversion of energy into work in important branches of economy. Those are transportation (heat engines or internal combustion engines), heating in industry and households, which utilized various types of thermal systems (gas, oil, heat pumps).

The measure of the problem is clearly illustrated, in particular, by the utilization of large amounts of energy from those sectors. In 2019 the European Union used almost 30.9% of the final energy consumption for transport, 26.3% for households, and 25.6% for industry [21]. Over and above to that, in the same year according to the International Energy Agency (IEA), the world total energy supply (TES) was approximately 606 EJ, where 30.9% of this value was made up of oil, 26.8% of coal, 23.2% of natural gas, 9.4% of biofuels and waste, 5% of nuclear energy, 2.5% of hydro, and only 2.2% of the rest of RES (geothermal, solar, wind) [22]. The percentage breakdown in TES by source is shown in Fig. 6.

With fossil fuel reserves becoming more depleted or a marginal share of RES in TES (~23.5%) associated with a relatively high dependence on weather conditions, rational management of energy production and consumption in various regions has emerged as one of the most pressing concerns of the 21 century and the prospects for accelerated energy transitions. Therefore, the developments that have occurred because of worldwide environmental objectives, the impacts of the COVID-19 pandemic, and the growth in oil costs discussed in recent years suggest that the local and global energy sectors are in desperate need of modernization [23]. In this sense, specific solutions to energy management systems must be adopted to address these issues, with the goal of rationally monitoring the state of fossil fuel resources and gradually increasing the share of renewable energy sources. However, it is impossible to abandon the use of fossil fuels at present; besides, the completely implementation of TES on an industrial scale will take several decades. Hence, CO_2 emission reduction continues to be a worldwide priority, and the only most promising way for that purpose are CCUS technologies. As an outcome, CCUS plays a critical role in attaining carbon neutrality, addressing the challenge of global climate change, and meeting global energy goals.

Accordingly, advancing the establishment of a low carbon economy will become substantially more difficult without a sufficiently flexible energy system that allows the energy producing process to operate independently of its consumption over a certain time period. The word "flexibility" refers to the efficiency of the energy system throughout continuous operation, in situations of substantial variations in energy production and consumption (allowing for both the area and the temporal stability of the system) [24]. Energy storage appears as a critical idea to solve the challenges associated with unstable energy production and to enable the fulfillment of current and future energy demands as a consequence of the energy sector transformation. It is widely considered a viable solution, which during off-peak times can store energy and release it during times when there is great demand [25]. In general, this tends to help electrical grids overcome the major drawbacks (the uncertainty of load dynamics and contingency [26]) that allow modernization and development of the energy system, reducing the start-up time of the power plant, and less troublesome energy production due to light-load operation [25,27].

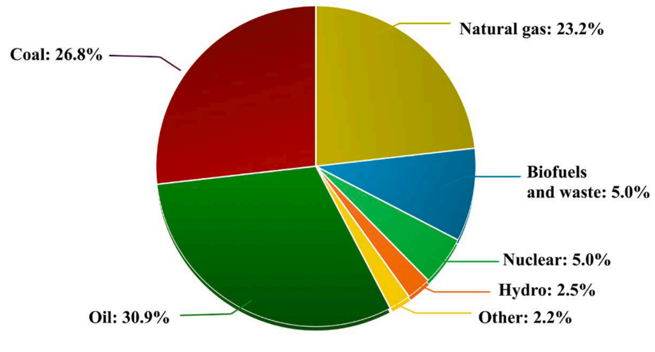


Fig. 6. World total energy supply by source in 2019 [22].

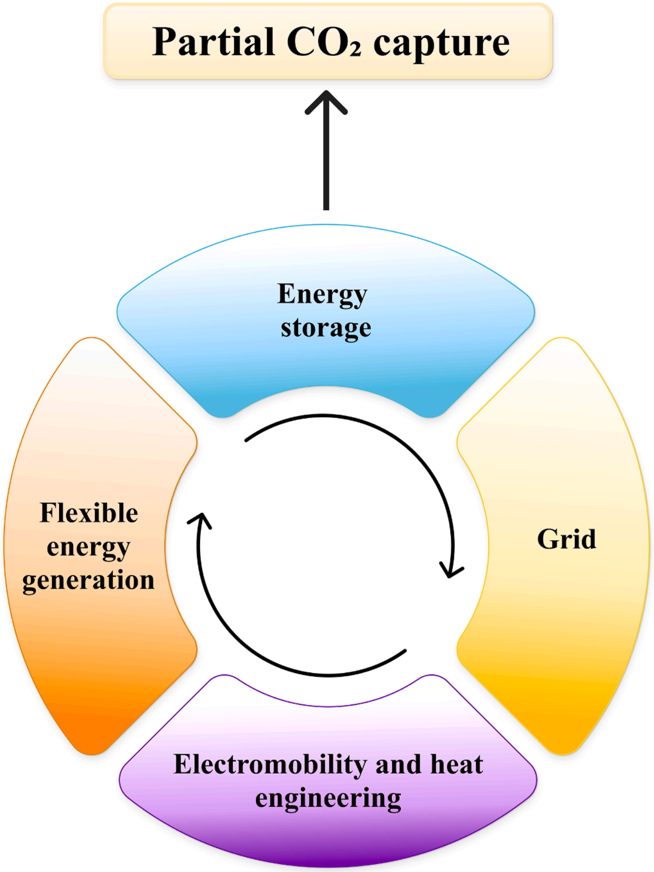


Fig. 7. The flexibility of the energy system.

What is more, additional factor related to the dynamic maturation of RES, their extremely increasing importance in the future energy industry, and the energy storage system (EES) have been shown to be essential to reduce CO_2 emissions into the atmosphere. It is the flexible operation of plants combined with partial CO_2 capture in CCUS that has a significant impact on the reduced costs of the capture step (Fig. 7). Process simulations and economic evaluation proved that carbon capture processes based on absorption [28,29] or adsorption [30] could use excess electricity produced by RES in the most crucial technologies to trap CO_2 emitted from large point sources, when the price for it is above the standard level.

To address the previously identified and noted issues, this review aims to provide a comprehensive exploration of the CCUS generic technical assessment. The main objective of this work is to analyze the technological maturity of CCUS crucial elements that directly influences their deployment phase on a commercial scale and achieves carbon neutrality. Toward this, the paper is organized as follows: Section 2 describes an overview of current CCUS facilities development across the globe; Section 3 explores three main CO_2 capture ways from flue gases (pre-combustion capture, post-combustion capture, and oxy-fuel combustion) and summarizes CO_2 separation method (absorption, membranes techniques, cryogenic method, chemical looping combustion, and adsorption); Section 4 focuses on CO_2 transport, including pipeline and ship transport; Section 5 evaluates CO_2 utilization and storage along with CCMC; Section 6 characterizes BECCS, as a novel connection of biomass energy production with CO_2 reduction. Ultimately, Section 7 outlines future research opportunities for CCUS systems.

2. An overview of CCUS development progress: state of the art

Currently, the number of commercial CCUS facilities in the world increased to 135 with a total mean CO_2 capture capacity of 149.3 Mtpa, according to the report published by the Global CCS Institute in September 2021 (27 are operational, 4 are in construction, 58 in advanced development, 44 in early development, and 2 suspended operations (Fig. 8)) [31]. Most of plants that implemented CCUS technology are based in North America, Europe and East Asia and Pacific, which account for 63%, 22% and 9% of global maximum capture capacity, respectively (Fig. 9). Compared to 2020 and 2019, these values were totally different, the number of large-scale CCUS facilities was 65 and 51, with a maximum CO_2 capture capacity of around 114.3 [32] and 96 $MtCO_2$/year [33]. Nevertheless, even the current performances of CCUS systems allows for sequentially lowering CO_2 emissions into the atmosphere, to achieve Paris Agreement climate targets by 2050 as outlined in the IEA’s Sustainable Development Scenario, >2000 facilities will be required. That entails building between 70 and 100 new facilities every year [34].

In the case of the division of CCUS facilities due to key global maximum CO_2 capture capacity industry sector, the following can be particularly distinguished: power generation (26 facilities with 62.51 $MtCO_2$/year), natural gas processing (20 facilities with 42.95 $MtCO_2$/year), chemical production (9 facilities with 13.72 $MtCO_2$/year), hydrogen production (16 facilities with 13.45 Mt CO_2/year), ethanol production (39 facilities with 10.85 $MtCO_2$/year), fertilizer production (7 facilities with 7.45 $MtCO_2$/year), and cement (3 facilities with 3.2

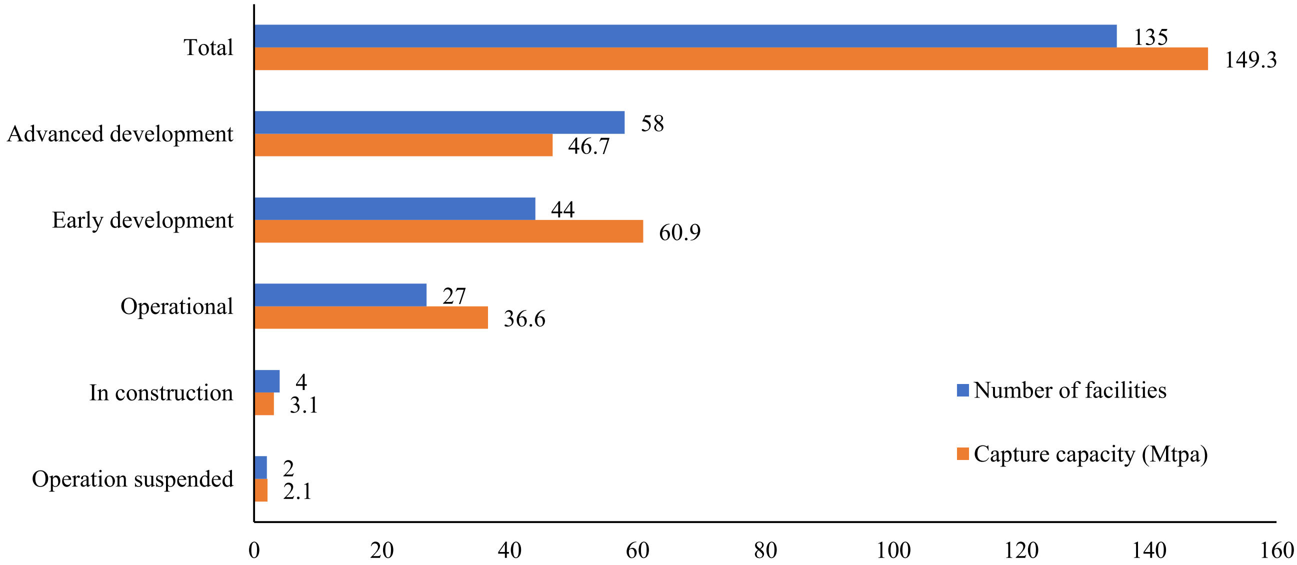


Fig. 8. Numbers of global commercial CCUS facilities and their mean CO_2 capture capacity by different stage of development in 2021 [31].

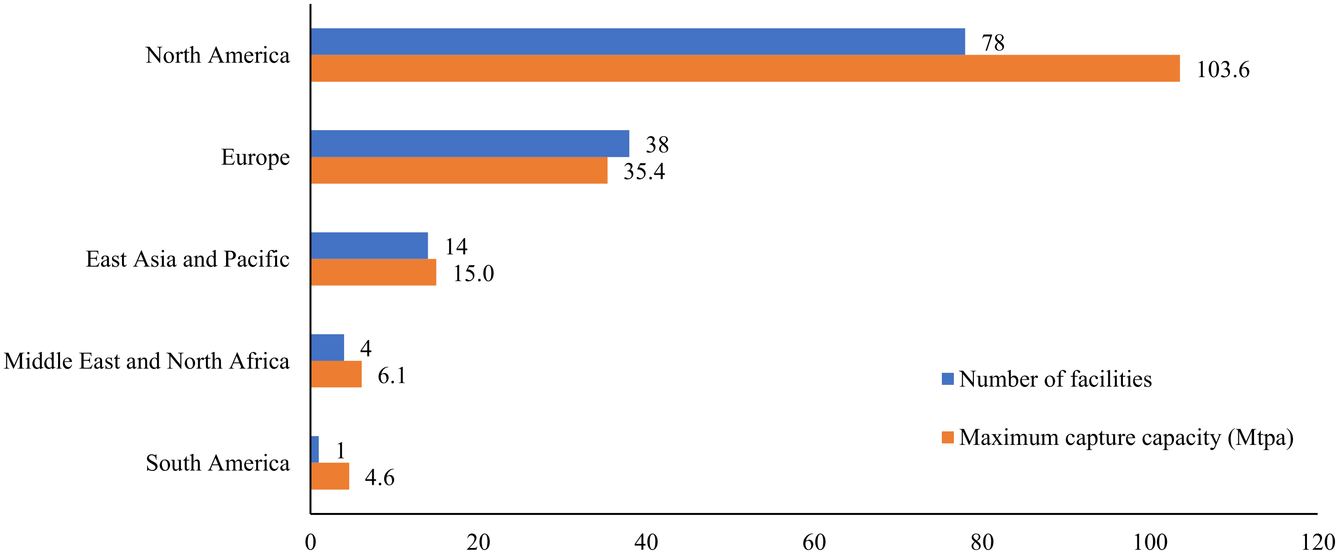


Fig. 9. Numbers of global commercial CCUS facilities and their maximum CO_2 capture capacity by world region in 2021 [31].

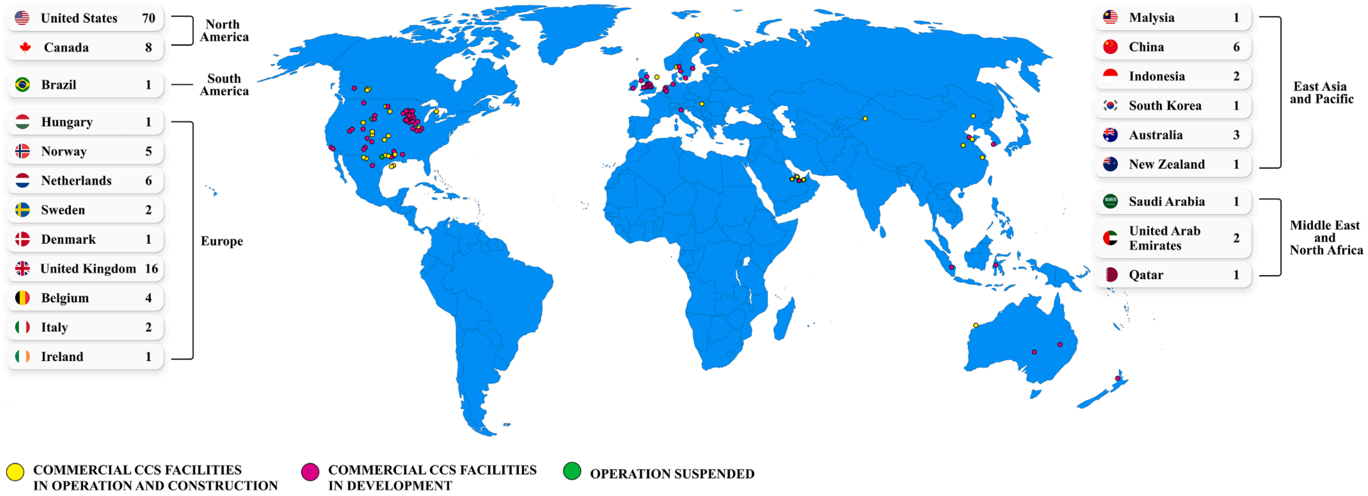


Fig. 10. World map of commercial CCUS facilities in various stages of development in late 2021 [31].

Table 1
Comparison of CCUS facilities with operational status in late 2021 (based on [31]).

Name of the CCS facilities	Country	Operation date	Industry	CO_2 capture capacity [Mtpa]		CO_2 storage method
				Min	Max	
Terrell Natural Gas Processing Plant	United States	1972	Natural Gas Processing	0.4	0.5	CO_2-EOR
Enid Fertilizer Plant	United States	1982	Fertiliser Production	0.1	0.2	CO_2-EOR
Shute Creek Gas Processing Plant	United States	1986	Natural Gas Processing	7	7	CO_2-EOR
MOL Szank field CO_2 EOR	Hungary	1992	Natural Gas Processing	0.059	0.157	CO_2-EOR
Sleipner CO_2 Storage	Norway	1996	Natural Gas Processing	1	1	Saline formations
Great Plains Synfuels and Weyburn-Midale Plant	United States	2000	Synthetic Natural Gas	1	3	CO_2-EOR
Core Energy CO_2-EOR	United States	2003	Natural Gas Processing	0.35	0.35	CO_2-EOR
Sinopec Zhongyuan Carbon Capture Utilization and Storage	China	2006	Chemical Production	0.12	0.12	CO_2-EOR
Snøhvit CO_2 Storage	Norway	2008	Natural Gas Processing	0.7	0.7	Saline formations
Arkalon CO_2 Compression Facility	United States	2009	Ethanol Production	0.23	0.29	CO_2-EOR
Century Plant	United States	2010	Natural Gas Processing	5	5	CO_2-EOR
Petrobras Santos Basin Pre-Salt Oil Field CCS	Brazil	2011	Natural Gas Processing	4.6	4.6	CO_2-EOR
Bonanza BioEnergy CCUS EOR	United States	2012	Ethanol Production	0.1	0.1	CO_2-EOR
Coffeyville Gasification Plant	United States	2013	Fertiliser Production	0.9	0.9	CO_2-EOR
Air Products Steam Methane Reformer	United States	2013	Hydrogen Production	1	1	CO_2-EOR
PCS Nitrogen	United States	2013	Fertiliser Production	0.2	0.3	CO_2-EOR
Boundary Dam 3 Carbon Capture and Storage Facility	Canada	2014	Power Generation	0.8	1	CO_2-EOR
Quest Carbon Capture And Storage	Canada	2015	Hydrogen Production	1.2	1.2	Saline formations/ depleted oil fields
Uthmaniyah CO_2-EOR Demonstration	Saudi Arabia	2015	Natural Gas Processing	0.8	0.8	CO_2-EOR
Karamay Dunhua Oil Technology CCUS EOR Project	China	2015	Methanol Production	0.1	0.1	CO_2-EOR
Abu Dhabi CCS (Phase 1 being Emirates Steel Industries)	United Arab Emirates	2016	Iron And Steel Production	0.8	0.8	CO_2-EOR
Illinois Industrial Carbon Capture and Storage	United States	2017	Ethanol Production	0.55	1	Saline formations
CNPC Jilin Oil Field CO2 EOR	China	2018	Natural Gas Processing	0.35	0.6	CO_2-EOR
Gorgon Carbon Dioxide Injection	Australia	2019	Natural Gas Processing	3.4	4	Saline formations
Qatar LNG CCS	Qatar	2019	Natural Gas Processing	2.2	2.2	CO_2-EOR
Alberta Carbon Trunk Line (ACTL) with North West Redwater Partnership's Sturgeon Refinery CO_2 Stream	Canada	2020	Hydrogen Production	1.3	1.6	CO_2-EOR
Alberta Carbon Trunk Line (ACTL) with Nutrien CO_2 Stream	Canada	2020	Fertiliser Production	0.2	0.3	CO_2-EOR

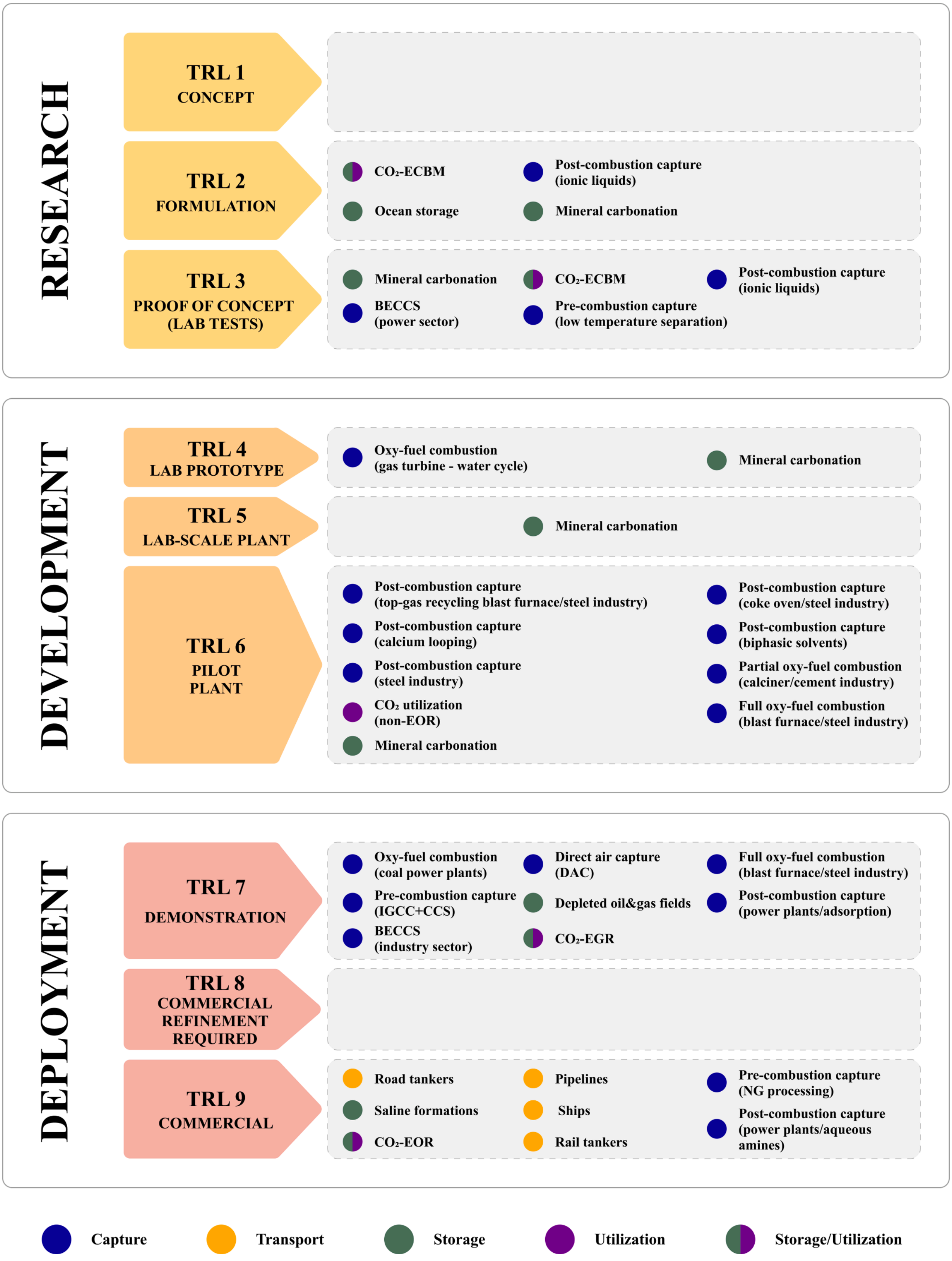


Fig. 11. Overall status of the most crucial element for CO_2 emission reduction technologies measured in terms of the TRL scale [44,45,166].

$MtCO_2$/year). The rest of industry branches are expanding their use in a wide variety of fields and applications, including the ones that follow: synthetic natural gas, power generation and refining, direct air capture (DAC), methanol production, waste incineration, iron and steel production, bioenergy, power generation and hydrogen production (achieving at the same time 12.53 $MtCO_2$/year) [31]. The world map of the current status of CCUS facilities is presented in Fig. 10 and the comparison of operational ones in Table 1.

The most important considerations in the use of CCUS technologies are the CO_2 generation process, the technical readiness level (TRL) of the particular steps of CCUS, the effectiveness of CO_2 separation, the capital/operating costs, the environmental performance (Life Cycle Assessment – LCA), as well as the ability to store or use CO_2 on site or in adjacent places of a plant [35]. The significantly crucial of the above is TRL, which is a nine-point scale system, used to define the degree of maturity of the advancement of CCUS technology and to track the state of technological development of the work (the same concept is also used for CCU and CCMC ways, as well) [36]. Referring to forecasts carried out by scientific centers around the world, it is indicated that the amount of captured and stored CO_2 will reach a value of at least 4 Gt/year in 2040 and 8 Gt/year in 2050 (in 2017 this value was only 40 Mt/year) [37,38]. Therefore, a faster implementation of CCUS technology in many branches of industry at the commercial level will undoubtedly be of fundamental importance in the long-term reduction of CO_2 emissions [39]. In account of this, it is typical for the technological progression of CCS to proceed in a succession of scaling phases, which correspond to the respective levels of TRL. From initial concept and basic principles (TRL 1), formulation of the application (TRL 2), starting with laboratory scale (TRL 3-5), progressing to pilot scale operation (TRL 6), demonstration scale (TRL 7), the need for commercial refinement requirements (TRL 8), and finally commercial scale (TRL 9) [40]. In summary, TRL 1-3 characterize the research, TRL 4-6 the development, and TRL 7-9 the deployment phase [41]. Fig. 11 illustrates every crucial part of CCS technologies on the TRL scale, which will be deeply discussed later in the next sections.

3. CO_2 capture

In CCUS technology, there are three main capture configuration that can be implemented in power plants and allow obtaining a concentrated stream of CO_2 from fuel combustion. They are classified into pre-combustion capture, post-combustion capture, and oxy-fuel combustion (Fig. 12). However, there is another technique, such as capture from industrial process streams (steel, cement and chemical) that is often considered the fourth [42]. In addition to the above four, there is also a competitive CO_2 capture from the atmosphere, as mentioned earlier (DAC). They will be described in more detail in Section 3.1.

Here in this step, carbon dioxide is separated at the same time from the use of fossil fuels and/or biomass from other gaseous media by many of the existing technologies for gas separation that are integrated into CO_2 capture systems, such as absorption, adsorption, membrane separation, cryogenic distillation, or solid looping (calcium looping (CaL)), chemical looping combustion (CLC)). This step of CCS is ambivalent crucial, as flue gases may consist of additional pollutants such as: H_2S, CO, CH_4, SO_x, and water vapor, which alter the gas stream's physicochemical characteristics (density, equilibrium limit of the vapor–liquid), causing ineffective storage. Consequently, the direct influence of these pollutants on the cost, safety, and efficiency of CCS technology is an

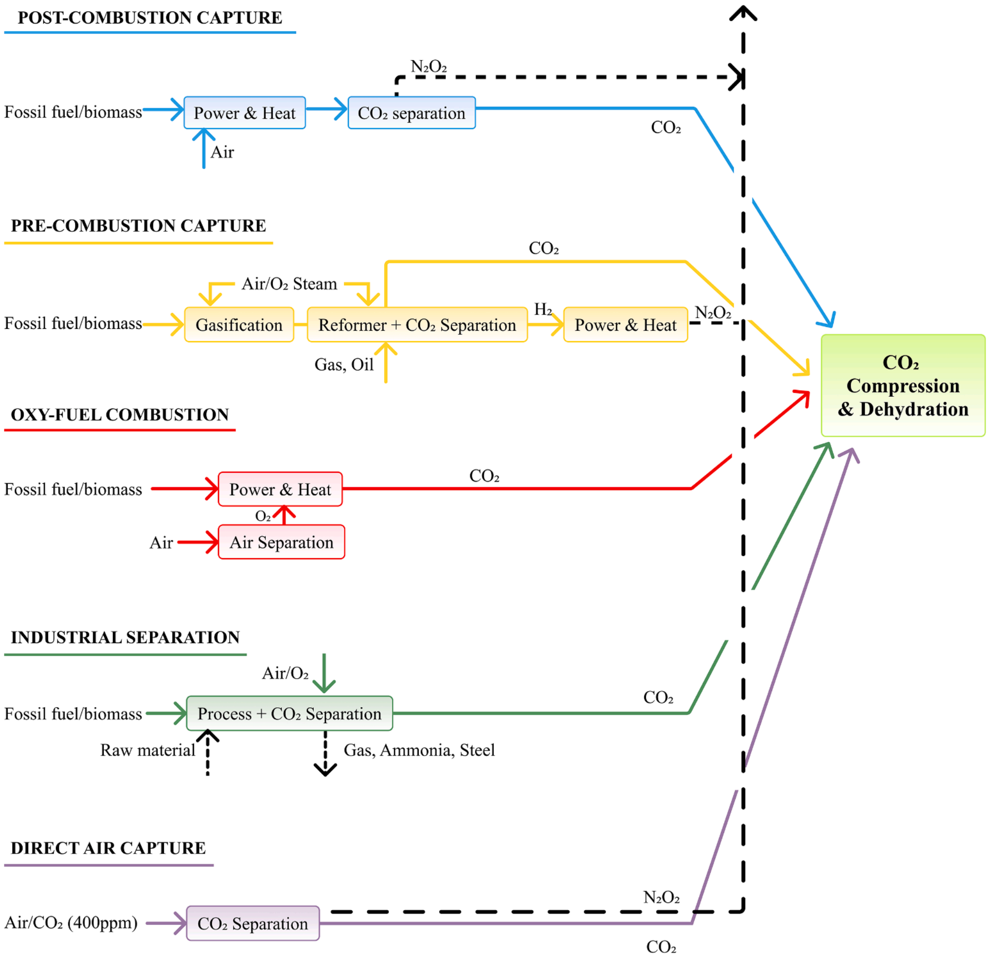


Fig. 12. Generic comparison of existing CO_2 capture systems [42,46].

elemental consideration throughout its commercial deployment. The CO_2 capture process is expected to account for nearly 70–80% of the overall cost of CCS; therefore, obtaining a purified gas stream with the necessary level of CO_2 through a highly effective process is significantly important [43].

As the separation process is part of the capture technology, TRLs depend mainly on their combination, the type of CO_2 generating plant/industry, and the fuel used. CO_2 separation technologies are comprehensively described in Section 3.2, where the TRL will be discussed in detail for each. Considering above, there is only two capture methods that has reached a commercial scale (TRL 9), which is pre-combustion capture (widely used in natural gas processing plants) and post-combustion capture (power plants/aqueous amines) [44]. As for the demonstration scale (TRL 7), the listed capture methods are in that stage, such as: pre-combustion capture (IGCC - integrated gasification combined cycle + CCS), oxy-fuel combustion (coal power plant), and post-combustion (solid sorbent). For comparison, the direct air capture (DAC) possesses TRL of 7. They might also perhaps reach the stage of commercialization in the not-too-distant future. The other CO_2 capture methods range between pilot scale (TRL 6) – post-combustion capture (calcium looping), lab prototype (TRL 4) – oxy-fuel combustion gas turbine (water cycle), and lab test, as proof of concept (TRL 3) – pre–combustion capture with low temperature separation [44].

In addition, capture methods can have various technological configurations, including: post-combustion capture (top-gas recycling blast furnace (TGR-BF)/steel industry), post-combustion capture (coke oven/steel industry), partial oxy-fuel combustion (calciner/cement industry) with TRL 6, or full oxy-fuel combustion (blast furnace/steel industry) with TRL 6–7 [45].

3.1. CO_2 capture from flue gases: A comparison of three existing capture technologies

3.1.1. Pre-combustion capture

Pre-combustion CO_2 capture technology converts solid coal fuel or petroleum residues (heavy oil fractions) into gaseous fuel that is hydrogen-rich by gasification of coal at high pressures. Where, the CO_2 obtained is a by-product [47,48]. In the discussed CO_2 capture method, the fuel can react with oxygen or air, which results in the production of a mixture of carbon monoxide and hydrogen, i.e., synthesis gas, after prior cleaning of exhaust gases. The above process is called gasification [47,49]. Then, in the catalytic reactor, the reaction between the synthesis gas and steam takes place with the reduction of temperature, which promote CO conversion to CO_2 and an additional amount of hydrogen is produced (water–gas shift reaction - WGSR) [50]. The concentration of carbon dioxide in the gas mixture (CO_2/H_2) with little impurities is approximately about 15–60% and is much higher than in the combustion gases of conventional power plants [51]. As a result, the high concentration of CO_2 and high pressure (typically 2–7 MPa) facilitates its separation from the exhaust gases, which means that the energy expenditure for the process is significantly lower and a capture method is less expensive [7,51]. The reactions taking place during the process are presented below [49,52]:

- Synthesis gas production reaction

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H = 118.9\frac{kJ}{mol} \tag{1}$$

- Boduard's reaction

$$C + CO_2 \rightarrow 2CO \qquad \Delta H = 160.9\frac{kJ}{mol} \tag{2}$$

- Hydrogassing reaction

$$C + 2H_2 \rightarrow CH_4 \qquad \Delta H = -87.4\frac{kJ}{mol} \tag{3}$$

- Incomplete combustion reaction

$$2C + O_2 \rightarrow 2CO \qquad \Delta H = -246.3\frac{kJ}{mol} \tag{4}$$

- Conversion of carbon monoxide with water vapor (water-gas shift reaction)

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{5}$$

- Methanization

$$CO + 3H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H = -42.3\frac{kJ}{mol} \tag{6}$$

Table 2
Pre-combustion capture characterization.

Advantages/Opportunities	References
✓ Used extensively in the industry sector (existing technology which has been utilized for higher than 95 years).	[19,47,54,55]
✓ Emission of CO_2 is quite low (92–93% CO_2 recovery).	[47,53]
✓ Requires less energy for CO_2 separation and compression steps – high CO_2 concentrations and partial pressure (<50% of post-combustion capture).	[12,53–55]
✓ Less expensive - requires smaller capital costs and equipment size.	[53]
✓ The pre-combustion approach could be less expensive than the post-combustion and oxy-fuel technologies, by 38–45% and 21–24%, respectively.	[56]
✓ Utilization of physical solvent used in CO_2 separation, which are available at low cost and require low energy for regeneration (mature physical absorption technology)	[12,55]
✓Possibility to switch between H_2 production and electricity generation with ease, which allows for more flexibility in the outputs.	[19]
✓ Synthesis gas can be used as an alternative fuel to the turbine cycle.	[54]
✓ After further purification, H_2 may be utilized in fuel cells, transportation, and as a building ingredient in the synthesis of high-value chemicals.	[57]
✓ Compared to post-combustion capture, this method uses less amount of water.	[54]
Disadvantages/Challenges	**References**
➢ Energy loss is significant compared to post-combustion capture method (energy is required for the reforming process, air separation).	[19,54]
➢ Improvements of efficiency of energy recovery throughout the manufacturing process needs to be pursued.	[19]
➢ Requires a chemical plant in front of the turbine.	[12]
➢ Retrofitting existing facilities increases the cost and complexity of the set-up process, which prevents it from being commercialized.	[19]
➢ High pressure operation.	[53]
➢ Complex chemical processes often result in further plant shutdowns.	[12,53]
➢ Non-gaseous feed stocks (demand for a cleaned gas stream and the possibility of costly scrubbing to control excessive NO_x emissions).	[12]
➢ Improvement of the gasification stage.	[54]
➢ Temperature associated with heat transfer problems due to H_2-rich gas.	[53,55]
➢ The cooling of the flue gas to CO_2 capture is necessary.	[47]
➢ Requires a extensive supporting systems (e.g. an air separation unit).	[53,54]
➢ Efficiency loss in water–gas shift section.	[47]
➢ In the absorption method, to avoid any reduction in solvent quality, the regeneration temperature should be lower than that used currently. To resolve this problem, ionic liquids are being utilized, which possess negligible volatility.	[19]

In the next step, CO_2 is separated from the gas mixture by physical solvents, such as rectisol and selexol, which are readily accessible and inexpensive. Subsequently, CO_2 passes through the conditioning process (condensate and moisture removal, separation of solid particles, cooling or heating of the gas, removing unwanted gaseous components) and is compressed for final storage [46–48,52]. On the other hand, the remaining gas with a high concentration of hydrogen is used as fuel in boilers or gas turbines in a combined IGCC (integrated gas combine cycle) system to generate electricity. Despite the possibility of achieving a fairly high level of carbon dioxide capture efficiency up to 80% before the combustion process, the very implementation of the technology is closely associated with high capital and operating costs. These costs are generated primarily by the obligatory gas synthesis process, which reduces the economic attractiveness of the CO_2 capture method itself [46,47].

The characterization of pre-combustion capture method is included in Table 2. The main opportunities and challenges of this technology are related to improving the gasification stage, the CO_2 separation step (absorption), and new strategies for cleaning syngas, in order to reduce energy consumption and associated costs [53]. In Table 3 is included information on active, proposed, and terminated CCS projects worldwide with pre-combustion capture technology between 2013 and 2019.

3.1.2. *Post-combustion capture*

The technology of capturing CO_2 after the fuel combustion process is considered a mature technique that consists of the direct removal of carbon dioxide from the flue gas, which comes from the thermal power plant combustion chamber [12]. Additionally, it is compared in many ways with the equivalent of flue-gas desulfurization (FGD), which is widely used to capture SO_2 from flue gases in coal and oil-fired power plants [47]. The advantages and disadvantages of post-combustion capture are given in Table 4. Table 5 presents selected global CCUS projects from 2013 to 2018, which utilized this CO_2 capture technology.

The key purpose of post-combustion capture is to capture and separate CO_2 from other products contained in the resulting flue gas mixture, such as nitrogen, sulfur dioxide, and nitrogen oxides, mainly due to the inability to sequestrate flue gases, taking into account the costs of their compression and storage [47]. Therefore, prior to CO_2 capture, the flue gas is subjected to denitrification, desulphurization, and dust removal, among other processes [59]. The flue gas, which is primarily composed of CO_2, H_2O, and N_2, is then fed into the CO_2 separation unit. The choice of the appropriate separation method depends mainly on several physicochemical properties of the exhaust gases and the process conditions, that is, temperature, pressure, carbon dioxide concentration, and the size of the gas mixture stream. Currently, among post-combustion approaches, absorption based on monoethanolamine (MEA) is the most widespread and only commercially available technique [19]. The adsorption approach is also employed in post-combustion capture, in the form of either temperature swing or pressure swing adsorption processes, as well as calcium looping combustion (CLC) [60]. It is also possible to implement membranes as an appropriate separation technique to reduce capital costs associated with post-combustion technology. To achieve low energy needs, a low carbon footprint, and low operating expenses, membrane technology is straightforward to adapt and scale up with the existing power plant [61]. In addition, it is worth emphasizing that the above methods of separating CO_2 itself do not influence other processes that occur during fuel combustion [62–64].

The flue gases from post-combustion technology themselves with relatively high temperature are discharged into the atmosphere under low pressure, close to atmospheric pressure (corresponding to the boiler flue gas pressure), where the carbon dioxide concentration is quite low. It reaches 7–14% in coal-fired power plants, and in the case of gas-fired power plants it reaches a value of about 4%. That is a serious design challenge, with respect to a thermodynamic driving force for low CO_2 capture [46,47,62]. Therefore, the installation and process apparatus must process large amounts of flue gases, resulting in their large size and generating high capital costs [47]. Furthermore, the amount of energy

Table 3
Selected worldwide CCUS projects from 2013 to 2020 with pre-combustion capture technology [58].

Project name	Country	Project start date	Overall status	Plant size	Amount of CO_2 capture/stored	Capture/stored unit	Project cost	Currency
Riley Ridge Gas Plant	United States	2020	Potential	–	–	–	–	–
Shenhua Ningxia CTL Project	China	2020	Potential	10,000 MW	–	–	–	–
E.ON Ruhrgas Killingholme IGCC	United Kingdom	2019	Terminated	470 MW	6,850	Metric Tons Per Day	1,000,000,000	British Pound
Captain Clean Energy Project	Scotland	2017	Hold	570 MW	10,412	Metric Tons Per Day	1,000,000,000	Euros
Kentucky NewGas project	United States	2017	Terminated	–	13,700	Metric Tons Per Day	3,000,000,000	US Dollar
Bent County IGCC Plant	United States	2016	Hold	600 MW	4,200,000	Metric Tons Total	1,000,000,000	US Dollar
FutureGen - Jewett	United States	2015	Terminated	275 MW	–	–	1,500,000,000	US Dollar
FutureGen - Mattoon	United States	2015	Terminated	275 MW	–	–	1,200,000,000	US Dollar
FutureGen - Odessa	United States	2015	Terminated	275 MW	–	–	1,500,000,000	US Dollar
FutureGen - Tuscola	United States	2015	Terminated	275 MW	–	–	1,000,000,000	US Dollar
Great Lakes Energy Research Park	United States	2015	Active	250 MW	90	% Reduction	2,000,000,000	US Dollar
Hydrogen Power Abu Dhabi Project	United Arab Emirates	2015	Hold	420 MW	4,658	Metric Tons Per Day	2,500,000,000	US Dollar
Masdar CCS Project	United Arab Emirates	2015	Potential	–	11,782	Metric Tons Per Day	15,000,000,000	US Dollar
DKRW Energy LLC	United States	2014	Hold	–	20,000	Barrels Per Day	2,000,000,000	US Dollar
Kwinana Project	Australia	2014	Terminated	500 MW	10,960	Metric Tons Per Day	2,000,000,000	Australian Dollar
RWE IGCC Plant with CO_2 Storage	Germany	2014	Hold	450 MW	7,124	Metric Tons Per Day	2,000,000,000	Euros
Taylorville Energy Center	United States	2014	Terminated	630 MW	55	% Reduction	2,500,000,000	US Dollar
Wallula IGCC Plant	United States	2014	Terminated	700 MW	65	% Reduction	2,200,000,000	US Dollar
Belle Plaine Polygen Capture	Canada	2013	Hold	500 MW	2,740	Metric Tons Per Day	5,000,000,000	Canadian Dollar
Huntley IGCC Project	United States	2013	Terminated	680 MW	65	% Reduction	1,500,000,000	US Dollar

needed for the capture and separation of CO_2 related to the above mentioned problems is quite high and must be included as potential costs for electricity production (increases them by 32% for a gas-fired power plant and 65% for a coal-fired power plant) [63,64].

3.1.3. *Oxy-fuel combustion*

Oxy-fuel combustion technology is significantly different from conventional methods because fuel combustion itself occurs in a mixture of high purity oxygen and recirculated exhaust gas, rather than in air. Therefore, the primary objective is to reduce nitrogen in the atmosphere through separation processes, consisting of the initial separation of oxygen (to obtain its purity above 95%) and nitrogen from the air supplied to the boiler, leading to its partial or complete elimination [12,66]. It is closely related to the fact that due to the high nitrogen content in the atmospheric air, ranging from about 79%, the carbon dioxide content in the resulting boiler flue gases fluctuates in the range of 3–15%, depending on the type of fuel used [42]. In this situation, the separation of CO_2 from the rest of the exhaust gas components is quite troublesome. Furthermore, part of the flue gas is recirculated to lower the combustion temperature, its implementation in pure oxygen would be practically impossible, and therefore it is diluted with the exhaust gas taken from the boiler (recirculation) [12]. This is important because the materials presently available are incapable of withstanding the enormous temperatures generated by the burning of coal in pure oxygen (the combustion temperature reaches approximately 3500 °C). Research shows that the optimal composition of the stream fed to the boiler should contain 30–35% O_2 and 65–70% CO_2 [42,67]. That is why a certain research direction of this technology is the development of high-temperature resistant materials, especially for the adsorption process.

The great interest in the oxy-fuel combustion method in power systems is mainly due to its key advantages, i.e., the decrease in the amount of flue gas and nitrogen gas emissions, together with improved boiler energy conversion efficiency, and the possibility of direct CO_2 sequestration (CCS). Where the concentration of carbon dioxide in the resulting mixture of flue gases can reach 80–98%, depending on the fuel, the combustion process, the air in the leakage levels, the purity of O_2 and its excess. The rest of the chemical components are water vapor (condensed

Table 4
Post-combustion capture characterization.

Advantages/Opportunities	Reference
✓ Applicable to existing coal-fired power plants as well as new ones (existing technology).	[47,54]
✓ Extensive research is conducted to enhance sorbents and capturing apparatus.	[54]
✓ Retrofitting existing power-plant designs is a viable option.	[46]
✓ Higher thermal efficiency for conversion to electricity than pre-combustion method.	[12]
✓ Emission of CO_2 is quite low (80–95% CO_2 recovery by adsorption, 90–98% by absorption).	[53]
✓ Extra removal of NO_x and SO_x.	[47]
✓ Use of hybrid processes (membrane-pressure swing adsorption) to optimize CO_2 capture efficiency.	[53]
✓ Increasing the efficiency of pulverized coal systems in the future will result in lower CO_2 emissions and higher plant productivity.	[53]
Disadvantages/Challenges	Reference
➢ At ambient pressure, the concentration of CO_2 is low (typically 7–14%), which results in large process equipment sizes and high costs - a large volume of gas has to be handled.	[12,47,54]
➢ The relatively low CO_2 partial pressure and high temperature of the flue gases offers a design challenge.	[12,47]
➢ To capture CO_2 at low concentrations in absorption method, powerful chemical solvents must be utilized and regeneration of the solvents to release CO_2 will demand a significant amount of energy.	[12,47]
➢ The amine technologies in absorption method employed result in a nearly 30% drop in net power production and an 11% fall in efficiency.	[54]
➢ In the absorption method, the corrosivity of amines, the high energy footprint of regeneration, and degradation all contribute to solvent loss and evaporation.	[19,47,53]
➢ Absorption method based on MEA is related with expensive capital and operating costs. As a result, certain initiatives that relied on that technology have been shelved.	[65]
➢ Due to the low concentration of CO_2 in the flue gas, the additional cost of power production increases by approximately 60–70% for new infrastructure and by 220–250% for retrofitting.	[56]
➢ Greatly affected by trace impurities (NO_x, SO_x) in adsorption method.	[53]
➢ Steam extraction reduces the flow to the low-pressure turbine, lowering its efficiency and capacity.	[54]
➢ High pressure drop for adsorption separation process.	[53]
➢ For high capture levels, high performance, circulation volume, and water needs are required.	[54]

Table 5
Selected worldwide CCUS projects from 2013 to 2019 with post-combustion capture technology [58].

Project name	Country	Project start date	Overall status	Plant size	Amount of CO_2 capture/stored	Capture/ stored unit	Project cost	Currency
China Resources Power Integrated CCS Project	China	2019	Planned	–	2,740	Metric Tons Per Day	–	–
Large Pilot Testing of Linde	United States	2018	Active	10 MW	–	–	899,744	US Dollar
Large Pilot Testing of the MTR Membrane Post-Combustion CO_2 Capture	United States	2018	Active	–	–	–	1,196,388	US Dollar
UKy-CAER Heat-Integrated Transformative CO_2 Capture Process	United States	2018	Active	10 MW	–	–	1,177,550	US Dollar
CATO1 - Rotterdam ROAD project	Netherlands	2015	Terminated	250 MW	3,014	Metric Tons Per Day	330,000,000	Euros
Trailblazer Energy Center	United States	2015	Terminated	600 MW	15,755	Metric Tons Per Day	3,000,000,000	US Dollar
Boundary Dam Integrated CCS Project	Canada	2014	Active	115 MW	2,740	Metric Tons Per Day	1,300,000,000	Canadian Dollar
EW Brown Generating Station	United States	2014	Active	0.70 MW	–	–	21,425,289	US Dollar
PureGen Project	United States	2014	Terminated	500 MW	90	% Reduction	5,000,000,000	US Dollar
RWE nPower - Blyth Post-Combustion Project	United Kingdom	2014	Terminated	2400 MW	8,220	Metric Tons Per Day	2,000,000,000	British Pound
Aalborg - Northern Jutland Power Station Project	Denmark	2013	Hold	411 MW	4,932	Metric Tons Per Day	2,000 000 000	Danish Krone
Enecogen Cryogenic CO_2 Capture	Netherlands	2013	Active	850 MW	24.66	Metric Tons Per Day	37,000,000	Euros
Jamestown BPU	United States	2013	Potential	40 MW	98	% Reduction	145,000,000	US Dollar
RWE nPower - Tilbury Project	United Kingdom	2013	Terminated	1131 MW	90	% Reduction	1,000 000,000	British Pound
Veolia Environment CCS Project	France	2013	Active	23 MW	548	Metric Tons Per Day	1,900,000	Euros

Table 6
Oxy-fuel combustion characterization.

Advantages/Opportunities	Reference
✓ It may be used in existing or new power plants (existing technology)	[47]
✓ CO_2 recovery at the 90–98% level.	[53,54]
✓ Various sorts of fuels can be utilized (biomass/municipal solid waste), resulting in the development of a carbon neutrality - BECCS.	[72,74]
✓ The use of oxy-fuel combustion modification in order to reduce both economic and efficiency penalties.	[72,73]
✓ Produce steam cycles with excellent efficiency.	[54]
✓ NO_x formation is kept to a minimum due to a absence of nitrogen	[47]
✓ By using this method, NO_x emissions are decreased by 60–70% compared to air-fired combustion.	[12]
✓ Potential to be operated at high pressure, therefore, less CO_2 compression energy is required.	[12]
✓ Less expensive than other techniques of carbon capture because of the reduced flue gases volume and greater concentration of CO_2 (70–95%).	[12]
✓ There are no on-site chemical operations required and the system is simple to adapt into an existing power plant.	[54]
✓ Due to the absence of nitrogen, the volume of gases produced is low, resulting in a reduction in the size of the overall process.	[47]
Disadvantages/Challenges	Reference
➢ Combustion in pure oxygen is complicated – high temperature.	[47]
➢ Requires large amount of oxygen compared to pre-combustion, which is costly, both in terms of capital expenditure and energy consumption.	[47,53]
➢ High energy input for air separation unit, which has a significant influence on the overall efficiency of the power plant.	[12,47]
➢ Development of air separation unit methods other than cryogenic distillation.	[73]
➢ The cost of air separation and flue gas recirculation significantly reduces the economic benefit.	[12,53]
➢ It is necessary to develop building materials that can resist the high temperatures of the combustion gases, which are caused by the enormous oxygen content during fuel combustion.	[12,53]
➢ Technology needs to be proved for large scale operations.	[54]
➢ High risk of CO_2 leakage.	[54]

to ensure the highest concentration of CO_2) and in smaller amounts sulfur oxides (II), nitrogen oxides and solid particles, which must be removed, respectively [12,46,66]. This nature of the exhaust gas greatly facilitates the capture and separation of CO_2 as well as reduces the costs of its recovery, allowing direct transport and storagealong with achieving almost zero emissions into the atmosphere. Given that the process of capturing and separating CO_2 is relatively simple to carry out, the oxy-fuel combustion technique is by far the most attractive energy-efficient route in conjunction with two other approaches to primary technologies (pre-, post-combustion capture), with a low efficiency penalty of 4%, compared to 8–12% for the post-combustion capture [68].

Oxy-fuel combustion is a relatively young technology used for a combination of power generation and CO_2 capture. Until now, it has been examined in a variety of demonstration projects and pilot-scale facilities. The first pilot installation with a capacity of 30 MWth was launched in Germany in 2008 (Vattenfall's pilot plant) [67]; another was commissioned in Australia in 2012, called the Callide Oxyfuel Project [69]. Similarly, the OXYCFB300 Compostilla Carbon Capture and Storage Demonstration Project in Spain [70] and the Lacq pilot plant in France [71] have proven the practicality of oxy-combustion. Currently, a certain trend can be seen regarding the modification of this technology along with combining it with others to appeal in terms of commercialization to reduce both economic and efficiency penalties or accelerate decarbonization. These can be mentioned, among others: oxy-fuel combustion integrated with the supercritical carbon dioxide cycle (replace the conventional steam cycle) [72]; heat recovery from the air separation unit, CO_2 compression and purification unit [73]; or considering biomass as a replacement fuel for coal, as a synergistic method combining bioenergy with carbon capture and storage (BECCS) [72,74].

Unfortunately, apart from the above attempts of commercialization of oxy-fuel combustion, the separation processes (energy-intensive unit for the removal of nitrogen from air to obtain of high-purity oxygen – ASU) constitute a certain barrier to the possibility of wide implementation of this combustion technology on an industrial scale. It results in high operating costs and a higher electricity price of 7% compared to installation without CCS [46]. Nowadays, the only established method for creating a large volume of high-purity O_2 for wide-scale use is cryogenic distillation [73]. Therefore, it is very necessary to investigate new and innovative air separation approaches, for example: ion-

Table 7
Oxy-fuel combustion technology in selected worldwide CCUS projects from 2006 to 2020 [58].

Project name	Country	Project start date	Overall status	Plant size	Amount of CO_2 capture/stored	Capture/stored unit	Project cost	Currency
Datang Daqing CCS Project	China	2020	Hold	350 MW	2,740	Metric Tons Per Day	–	–
Shanxi International Energy Oxyfuel Project	China	2020	Potential	350 MW	6,850	Metric Tons Per Day	–	–
Hydrogen Energy International LLC	United States	2019	Terminated	400 MW	7,124	Metric Tons Per Day	4,028,136,691	US Dollar
White Rose CCS Project	United Kingdom	2014	Potential	450 MW	–	–	–	–
SaskPower	Canada	2012	Terminated	300 MW	8,000	Metric Tons Per Day	1,500,000,000	Canadian Dollar
Aviva Corp Coolimba Oxyfuel Project	Australia	2010	Terminated	400 MW	7,946	Metric Tons Per Day	1,000,000,000	Australian Dollar
FutureGen 2.0	United States	2010	Terminated	200 MW	2,740	Metric Tons Per Day	1,650,000,000	US Dollar
OXYCFB300 Compostilla Project	Spain	2009	Active	323 MW	100,000	Metric Tons Total	180,000,000	Euros
Petrom Zero Emissions Plant (ZEP)	Romania	2009	Potential	15 MW	–	–	–	–
South Korea CCS2	South Korea	2009	Active	300 MW	3,288	Metric Tons Per Day	–	–
Vattenfall CO_2-Free Oxyfuel Plant	Germany	2008	Terminated	30 W	216	Metric Tons Per Day	120,000,000	Euros
ZENG Worsham-Steed	United States	2007	Potential	70 MW	870	Metric Tons Per Day	–	–
CS Energy Callide Oxyfuels Project	Australia	2006	Completed	30 MW	82.20	Metric Tons Per Day	245,000,000	Australian Dollar

transport and oxygen-transport membranes [75–77] along with chemical looping combustion (CLC) [78–80].

The oxy-fuel combustion method has many research areas that are not fully understood. These are the following processes: degassing of volatile components; combustion of coke residues; ignition and stability of the dust-air flame; transformation of mineral substances; combustion and emission of gaseous pollutants (NO_2, SO_2) and their effective capture. The overall description of oxy-fuel combustion method is characterized in Table 6 and its application examples in CCUS projects between 2006 and 2020 are included in Table 7.

3.2. CO_2 separation technologies

In each of the CO_2 capture systems at different stages of its course, it is necessary to use appropriate CO_2 separation technologies. The choice of CO_2 separation depends on the conditions under which the process is to take place, considering the fuel used, the partial pressure of CO_2, and the composition of the gas to be treated. The CO_2 separation technologies vary from those used by industrial sectors for various gases (chemical absorption and membranes) to those that need more progressive ideas, such as cryogenics method or calcium looping. Depending on the capture system, there are few main methods for CO_2 separation, including chemical and physical absorption, membrane techniques, cryogenic method, chemical looping combustion (CLC), calcium looping (CaL), and adsorption process. Selected R&D projects that potentially can be commercialized for the above key CO_2 separation technologies covering absorption, membrane, and adsorption are also presented. Data on current R&D projects were collected from the National Energy Technology Laboratory (NETL) database of the United States Department of Energy.

3.2.1. Absorption

3.2.1.1. Chemical absorption. Chemical absorption is the most mature CO_2 separation technique that was developed in 1930 s and has been used in industrial applications for several decades. Today, it is projected that its combined CO_2 capture capacity in commercial facilities is approximately 860 $MtCO_2$/year [81]. The CO_2 separation process is based on the reaction of a solvent with CO_2, creating a new intermediate during a reversible or irreversible chemical transformation, as shown in Fig. 13 [82,83]. Commonly used solvents include mainly monoethanolamine (MEA), diethanolamine (DEA), *N*-methyl diethanolamine (MDEA), and di-2-propanolamine (DIPA) [83–85]. Regeneration occurs through an increase in temperature; therefore, the intermediate compound breaks down into the primary solvent and the CO_2 stream [82,83]. However, the recovery of CO_2 depends on the specific case and the nature of the chemical reaction. The advantage of the method, according to the current scientific literature, is that chemical absorption gives good results in terms of the efficiency of removing low-concentration CO_2 from the exhaust gas mixture at relatively low pressure. The disadvantages include the need to clean the flue gases, that is, remove SO_2, O_2, as well as dust and hydrocarbons, because the presence of these substances can interfere with the operation of the absorber column [86]. Additional disadvantages are the corrosiveness and high energy consumption of the process related to solvent regeneration.

The TRL assessment of chemical absorption is closely related to the post-combustion capture approaches, and its values depend primarily on the type of liquid solvents. Thus, chemical absorption based on traditional amine solvents is considered to have a TRL of 9 as the most mature technology (widely used in fertilizer, soda ash, natural gas processing plants, e.g., Sleipner, Snøhvit CO_2 storage and Boundary Dam 3 CCS Facility). The Benfield process also achieved commercial scale (fertiliser plants, e.g., Enid Fertilizer Plant) by using potassium carbonate (K_2CO_3) as an alkali absorption solvent. Other chemical absorption technologies exploit: sterically hindered amines, which have TRL 6–9 (depending on the technology suppliers, e.g. coal-fired power plants - Petra Nova CCS); chilled ammonia (chilled ammonia process - CAP) to remove CO_2 especially from low-pressure flue gases - TRL 6–7; water-lean solvent (coupling of physical and chemical absorption, e.g. Gerald Gentleman Station and Jinjie Power Plant) - TRL 4–7; phase change solvents (e.g.

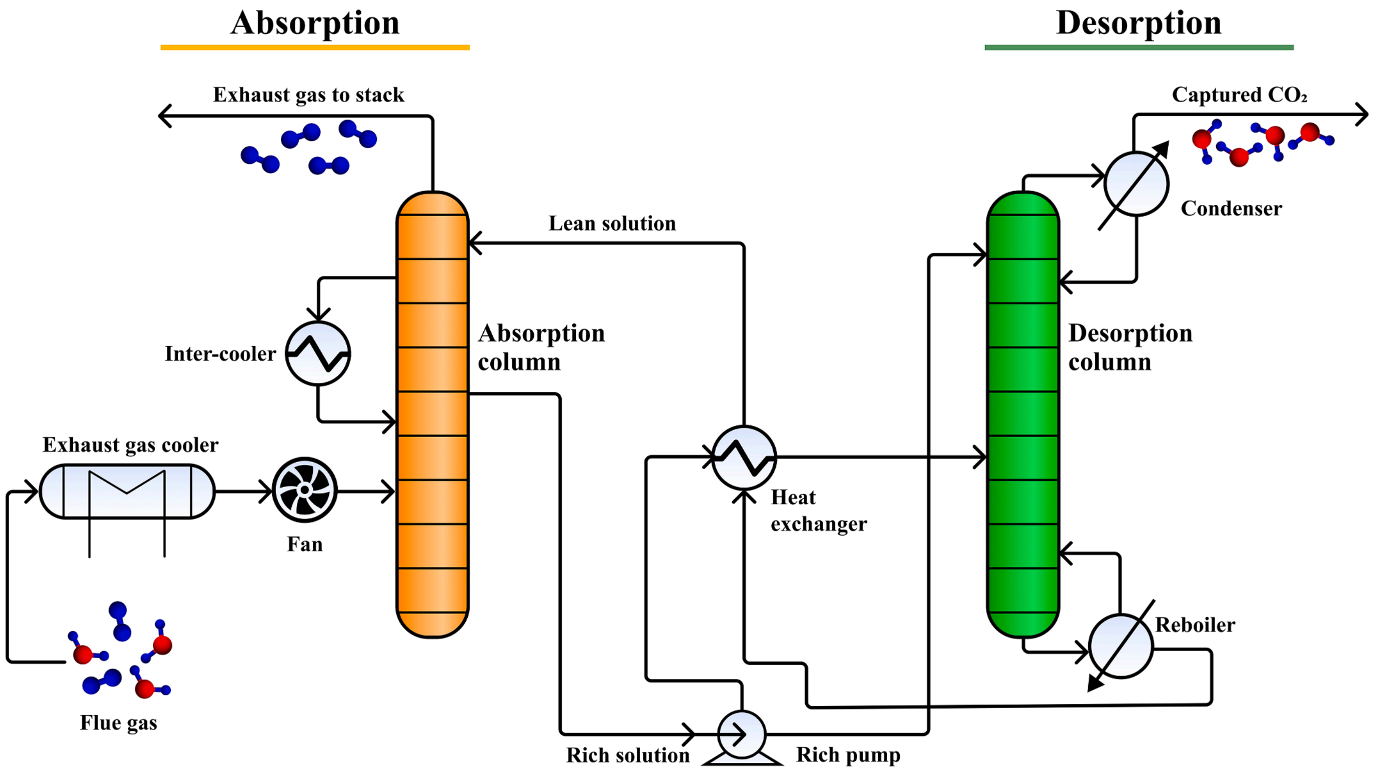


Fig. 13. Simplified process flow diagram of chemical absorption for CO_2 capture.

DMX Demonstration in Dunkirk) - TRL5–6; amino acid-based solvent - TRL 4–5; encapsulated solvents - TRL 2–3; and ionic liquids that has TRL 2–3 [166].

In the case of chemical absorption verification on the TRL scale for specific CO_2 capture sectors, it is mainly chemical production: ammonia (TRL 9), methanol (TRL 9), high-value chemical (7–8). There are also other industries, such as iron and steel: direct reduced iron (TRL9), blast furnace - process gas hydrogen enrichment (5–6); cement sector (TRL 7–8); power generation - coal (TRL 9) and biomass (TRL 7–8) [81].

3.2.1.2. Physical absorption. Physical absorption consists of the fact that the absorbed carbon dioxide is dissolved in a solvent that does not react with CO_2 (it is chemically inert). The process itself is based on Henry's law; according to him, the concentration of gas dissolved in the absorption liquid is proportional to the partial pressure of the gas above the liquid [82,86]. Typical substances that act as a solvent in physical absorption include Rectisol (cold methanol) and Selexol (polyethylene glycol dimethyl ethers) [52], which both have TRL 9 [166]. They are often employed in natural gas processing (Fig. 14) and coal gasification facilities, e.g., Shute Creek Gas Processing Plant, Century Plant, Coffeyville Gasification Plant, or Great Plains Synfuels and Weyburn-Midale Plant. When considering specific industrial applications same as for chemical absorption, physical adsorption is widely applied in ammonia production (TRL 9), methanol synthesis (TRL 7–8), and high-value chemicals development (TRL 7–8).

This type of absorption has a better efficiency than chemical absorption at a higher partial pressure of CO_2, such as those found in an IGCC [87]. Therefore, it must be carried out for a flue gas mixture where the partial pressure of CO_2 is not lower than 15% by volume, otherwise it would be economically unprofitable, which is a drawback [82,86]. Regeneration of sorbents takes place through desorption of the absorbed component by means of high temperature, pressure reduction, or both process parameters. The advantages of using physical absorption include the low consumption of energy needed to regenerate the absorbent (weak energy interaction between the absorbent-absorbate complex) and a lower temperature required for its occurrence compared to chemical methods [88]. Moreover, the solvents have low corrosivity. The equilibrium CO_2 loading, operating conditions cost of CO_2 capture and many others essential parameters on different chemical and physical solvents in latest R&D projects are compared in Table 8.

3.2.2. Membranes

Membrane techniques are an innovative concept for the separation of CO_2 from the flue gas mixture [12]. Membrane separation is based on the use of a membrane, which is a thin layer of semipermeable barrier material that separates a given gaseous medium when a driving force is applied, e.g., pressure difference, temperature, or electric potential on both sides of the membrane. The membrane divides the gas stream (feed) into a permeate gas stream and a retained stream (retentate) [90,91].

The classification of membranes used for CO_2 separation can be based on three general criteria: origin, morphology, and structure [90]. The industry mainly uses organic membranes, which show a great variety in terms of physical structure and the materials from which they are made. They are resistant to hostile process conditions, i.e. high temperature and pressure or the reactive chemical properties of the exhaust gas mixture. In view of this, polymeric membranes and their hybrid system were acknowledged as an effective method of CO_2 separation, due to their excellent permeability, selectivity performance, and simplicity in regulating membrane pore size throughout the formation process. As a single technique, polymeric membranes have reached a TRL 7 (Front-End Engineering Design (FEED) studies for large pilot installations). On the contrary, their combinations with other separation methods achieved lower scaling steps, that is, the polymeric membranes/cryogenic separation hybrid in the pilot phase (TRL 6), and the polymeric membranes/solvent hybrid, which has a TRL of 4 (conceptual studies) [166]. In the case of inorganic membranes, the most promising are carbons, zeolites, ceramics, and metals [12]. A wide variety of membrane materials have been studied recently in R&D project between 2022 and 2023 and their selectivity toward CO_2, operating conditions, cost of membrane material with technology maturity are compared in Table 9.

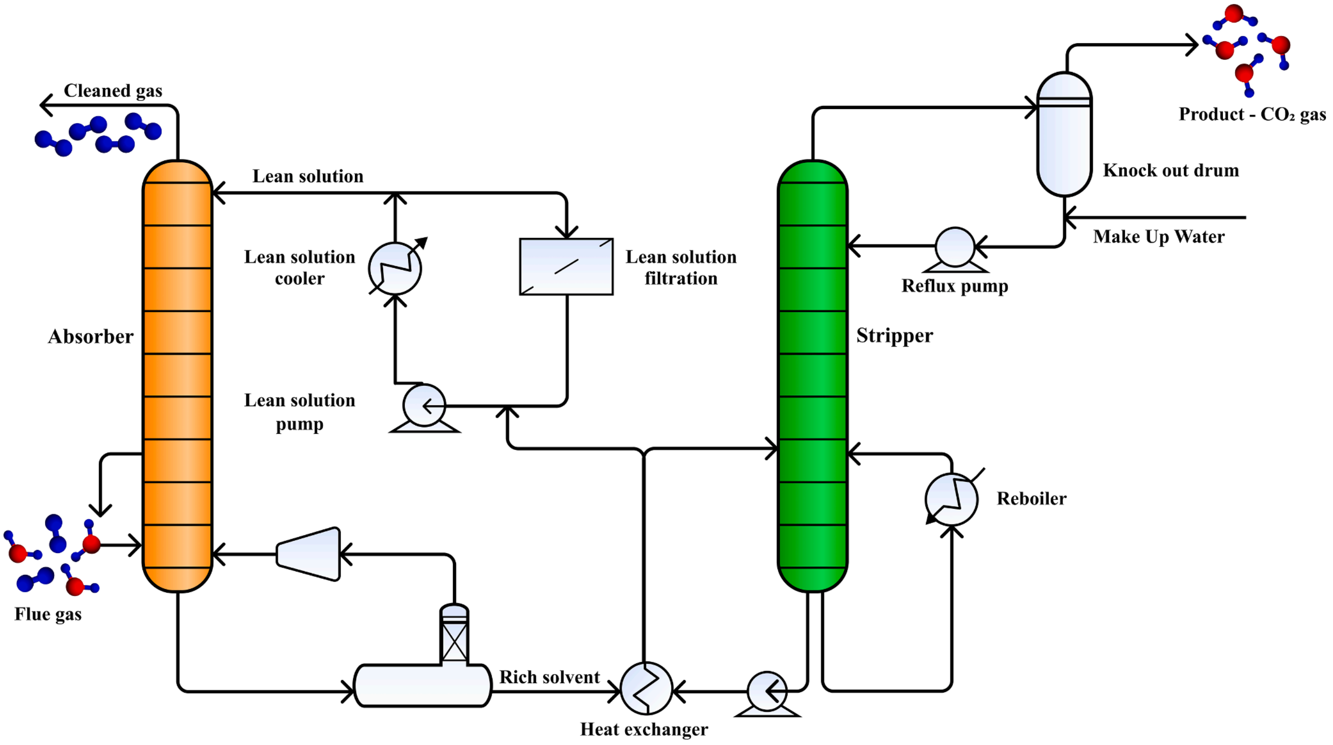


Fig. 14. Physical absorption (Selexol process) for CO_2 capture from a natural gas stream.

Table 8
Selected R&D projects completed in 2020–2022 on absorption process in post-combustion CO_2 capture technology [89].

Type of solvent	Project focus	Prime performer	Project duration	Equilibrium CO_2 loading [mol/mol]	Operating pressure [bar]	Operating temperature [°C]	Manufacturing cost for solvent [$/kg]	Estimated cost of CO_2 capture [$/t$CO_2$]	CO_2 recovery [% vol.]	CO_2 purity [%]	Technology maturity	TRL
Amine-based solvent	Retrofit the NGCC plant	Bechtel National, Inc.	2019–2022	0.4–0.49	1.089	53.5	1–2	114.50	80–90	>99	FEED	5–7
Water-lean amine solvent	Develop a novel amine-based solvent for CO_2 capture	ION Engineering, LLC	2019–2022	0.5–1.0	1	40	–	39–45 (550 MW coal-fired power plan)	–	–	Pilot-scale (0.6 MWe)	6
Amine-based solvent	Amine-based technology retrofit to NGCC	Southern Company Services, Inc.	2019–2022	–	0.9–1.1	30–60	–	–	90	99.9	FEED	5–7
Hindered amine-based solvent	Advanced KM CDR process retrofit	University of Illinois	2019–2022	–	–	–	–	43.42	95	–	FEED (816 MWe)	5–7
Water-lean solvent	Water-Lean solvent emissions Mitigation	Research Triangle Institute	2018–2022	2.04–2.22	0.133	34–45	30	–	–	–	Bench-scale (6 kWe)	4
Amine-based solvent	Integrated advanced solvent process	University of Kentucky	2018–2022	0.5	1.01	40	14.74	23.97	90	95	Large bench scale (0.1 MWth)	5–6
Water-lean amine solvent	Novel additives for amines	Liquid Ion Solutions, LLC	2018–2022	0.48	1.01	40	2	3.8	80	10	Laboratory-scale	3
Ammonium and potassium salt solvent	Developing mixed-salt solvent process	SRI International	2018–2022	1.5–3.5	1	20–40	–	30 (target)	90	95	Laboratory-scale	3
Solvents	Flue gas pretreatment to minimize solvent losses	Linde, LLC	2018–2021	–	–	–	–	55.89–62.15	–	–	Pilot-scale	6
Water-lean solvent	Molecular refinement of water-lean solvents	Pacific Northwest National Laboratory	2018–2021	0.29	1	40	13	–	90	95	Laboratory-scale	3
Amine-based solvent (MEA)	Transformative process using advanced solvents	University of Kentucky Research Foundation	2018–2021	0.42	1	40	4–6	41.4	90	99.9	Large pilot-scale (10 MWe)	6
Water-lean solvent	Water-lean solvent technology retrofit	ION Engineering	2018–2019	0.4–1.0	1.0–1.15	20–50	–	37.15	89–91	–	FEED	5–7
Hindered amine-based solvent	KM-CDR™ process retrofit	University of North Dakota	2018–2019	–	1	40	–	53.8	95	99.9	Commercial-scale design	5–7
Amine-based solvent	Electrochemical regeneration of amine solvents	Massachusetts Institute of Technology	2017–2020	1	1	50	<50	45–65	90	99	Laboratory-scale	3

Based on their structure, membranes can be divided into four groups: porous, homogeneous solid, and solid carrying electric charges, liquid or solid containing selective carriers. Moreover, the structure of the membranes may be symmetrical, the structure is identical throughout the entire cross-section of the membrane, or asymmetric when the structure changes in the cross-section [90,91]. In the spectrum of the mentioned membrane structures, only a few technologies are currently considered to reduce CO_2 emissions, they are: electrochemical membranes integrated with MCFCs (Molten Carbonate Fuel Cells) with a TRL 7 – large pilots installation at Plant Barry, and room temperature ionic liquid (RTIL) membranes at the formulation of the application phase (TRL 2) [166].

This separation method has the benefit of not causing weeping, entrainment, foaming, or flooding, all of which are typical concerns when using a packed column. Along with that, membranes feature a larger surface area and improved control over gas flow rates [92]. The most significant drawback of membranes is that their efficiency is reduced at lower CO_2 concentrations. When the concentration of CO_2 in the gas stream is <20%, the membrane exhibits limited flexibility and becomes impractical (additional stages and the recycling of one of the streams are required) [93]. The other problems are related to the functioning at high temperatures, sensitivity to corrosive gases, and the maintenance of adequate efficiency for long-term operation.

Regarding the CO_2 capture process and the emerging transport mechanism through the membrane structure, membrane separation can be divided into two methods: gas separation membrane and gas absorption membrane, illustrated in Fig. 15 [94]. Between these two types of mechanisms based on significantly different forms of CO_2 separation by membrane structure, only gas separation membranes in natural gas processing are at commercial phase operations (TRL 9) that has been

Table 9
Selected completed and ongoing R&D projects in 2022–2023 on membrane-based techniques in CO_2 capture technology [89].

Type of membrane	Project focus	Prime performer	Project duration	CO_2 selectivity [-]	CO_2 pressure normalized flux [GPU]	Operating temperature [°C]	Manufacturing cost for membrane material [$/m^2]	Module cost of manufacturing and installation	Cost of CO_2 capture [$/t$CO_2$]	CO_2 Recovery [% vol.]	CO_2 purity [%]	Technology maturity	TRL
Pre-combustion CO_2 capture													
Carbon molecular sieve hollow fiber membranes	Capture CO_2 from coal-derived syngas	State University of New York	2018–2022	0.5 (H_2O) 2 (H_2S) 0.025 (H_2)	200	150	20	~1000 $/kg/h	–	90	95	Laboratory-scale	3
Polymeric membranes	CO_2 capture in IGCC power plant	Membrane Technology and Research, Inc.	2018–2022	0.50 (H_2)	225	200	500	15 $/kg/h	84	90	99.5	Bench-scale	4
Amine-containing polymeric membranes	CO_2 capture from coal-derived syngas	Ohio State University	2018–2022	0.1 (H_2O) 3 (H_2S) 139 (H_2)	327	107	~54	97 $/m^2	–	90	95	Laboratory-scale	3
Polybenzimidazole polymer hollow-fiber membrane	CO_2 capture from a syngas stream	SRI International	2018–2022	40 (H_2) (dense layer thickness of >1 μm)	80–120	200–250	30–80	–	–	–	–	Bench-scale	4
WGSR catalytic membrane reactor	Integration of WGSR, H_2 separation, and CO_2 enrichment	Bettergy Corporation	2018–2022	>75 (H_2)	150	350–550	1200	–	–	80	>95	Laboratory-scale	3
Ceramic-carbonate dual-phase membrane reactor	Integration of WGSR, H_2 separation, and CO_2 enrichment	Arizona State University	2018–2022	>500 (H_2O) >500 (H_2S) >500 (H_2)	300–600	700–900	1000	~1000 $/kg/h	–	99	90	Laboratory-scale	3
Post-combustion CO_2 capture													
Polymeric mermbrane	Large pilot polymer membrane system	Membrane Technology and Research, Inc.	2018–2026	0.3 (H_2O) 50 (N_2) 0.5 (SO_2)	1000	30	–	50–100 $/m^2	–	70–75	99	Large pilot-scale	6
Mixed matrix membranes (rubbery polymers and metal–organic polyhedral)	Achieve high carbon dioxide permeance	State University of New York	2019–2023	0.3 (H_2O) 50 (N_2) 0.5 (SO_2)	1500–2000	60	–	–	30 (target)	–	95 (target)	Bench-scale	4
Polymeric composite membrane	CO_2 capture from flue gas	The Ohio State University	2019–2023	1 (H_2O) 170 (N_2)	3500	57–77	20	40 $/m^2	40.0-41.5	>60–90	>95	Bench-scale	4
Polymeric mermbrane	Retrofit process of polymeric membrane CO_2 capture system	Membrane Technology and Research, Inc.	2019–2022	0.3 (H_2O) 30 (N_2) 0.5 (SO_2)	1000	30	10	50 $/m^2	57.64	90	>96	FEED	5–7
Polymeric membrane	CO_2 capture from coal flue gas	Membrane Technology and Research, Inc.	2018–2022	0.3 (H_2O) 50 (N_2) 0.5 (SO_2)	1700	30	50	–	–	75	>85	Engineering-scale	5
Molten hydroxide dual phase mamebrane	Membrane support materials (metal oxides)	Luna Innovations	2017–2022	999 (N_2)	800	300	300	–	–	99	>96	Bench-scale	4
Amine carriers as the membrane matrix/ nanoporous polyethersulfone polymer support	Selective membranes for < 1% CO_2 sources	Ohio State University	2016–2020	0.3 (H_2O) 50 (N_2) 0.5 (SO_2)	2299	57–67	10	32 $/m^2	246	90	>95	Pilot-scale	6
Polyimide-based membrane	Combine with cryogenic separation to reduce	American Air Liquide, Inc.	2015–2020	<0.2 (H_2O) >50 (N_2) 0.3 (SO_2)	–	−30 to −45	–	100 $/kg/h	–	80-90	>58	Bench-scale	4

(continued on next page)

Table 9 (*continued*)

Type of membrane	Project focus	Prime performer	Project duration	CO_2 selectivity [-]	CO_2 pressure normalized flux [GPU]	Operating temperature [°C]	Manufacturing cost for membrane material [$/m^2]	Module cost of manufacturing and installation	Cost of CO_2 capture [$/t$CO_2$]	CO_2 Recovery [% vol.]	CO_2 purity [%]	Technology maturity	TRL
	the cost of CO_2 capture												
Graphene oxide-based membrane	Retrofit high-selectivity membranes in a pulverized coal or natural gas power plant	Gas Technology Institute (GTI)	2013–2022	1/10 (H_2O) 680 (N_2)	1020	80	–	–	≤40 (2025 goal)	70–90	>95	Bench-scale	4
Graphene oxide-based membrane	Retrofit the high-flux membranes in a pulverized coal or natural gas power plant	Gas Technology Institute (GTI)	2013–2022	>30 (N_2)	2500	70	–	–	≤40 (2025 goal)	70–90	>95	Bench-scale	4

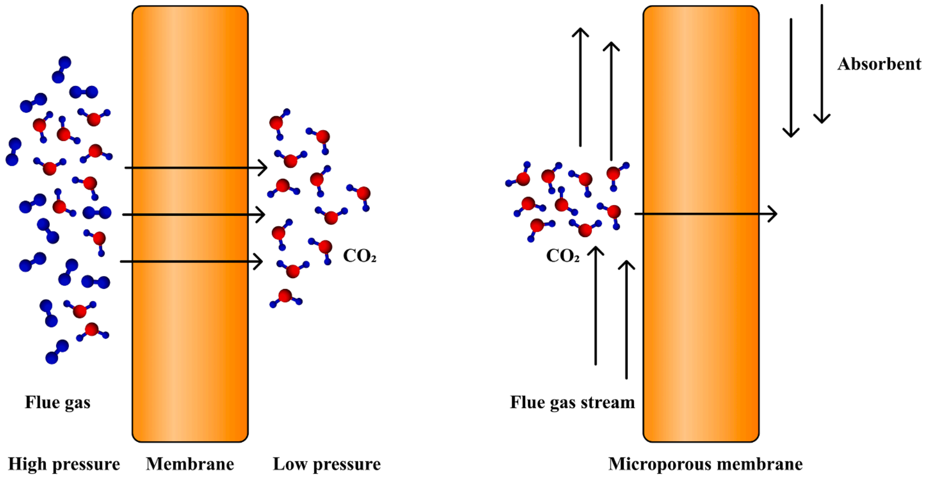


Fig. 15. Scheme of CO_2 separation membrane (from the left) and gas absorption membrane methods [97].

utilized in Petrobras Santos Basin Pre-Salt Oil Field CCS [166]. In Fig. 16 is given schematic flow diagram of membrane process for CO_2 capture from a coal-fired power plant [95].

3.2.2.1. Gas separation membrane. For gas separation membranes (homogeneous solids), the gas transport mechanism is based on dissolution and diffusion. Separated CO_2 dissolves in the membrane material and then diffuses through it depending on the form of mass transport (passive, facilitated or active transport). The components of the exhaust gases are separated due to differences in their solubility in the membrane material and discrepancies in the rates at which they pass through it [12,94].

3.2.2.2. Gas absorption membrane. In the case of gas-absorbing membranes, which are microporous solids, the transport mechanism is the transfer of carbon dioxide through the pores of the membrane to the other side of the membrane into the liquid that absorbs it. The mechanism of this type of separation depends on the pore size of the membrane and the type of absorbing liquid used, the affinity for the separation of a specific component of the flue gas stream. In this way, the membrane enables the separation of waste gases into CO_2 rich and low streams [12,94,96].

3.2.3. Cryogenic method

Cryogenic carbon capture (CCC) methods consist of compressing the flue gas mixture and cooling it to the appropriate temperature at high pressure in several stages to separate CO_2 based on the dew point or sublimation for a specific component, inducing phase changes only of carbon dioxide, as shown in Fig. 17 [98]. This method can obtain higher CO_2 recovery (99.99%) and purity (99.99%) than other separation technologies [94]. Furthermore, they are used mainly for the separation of gaseous streams with high concentrations of CO_2, usually >50% [99]. In the case of low concentrations of CO_2 (corresponding to boiler exhaust gas), the use of this technology is unprofitable due to the too large amount of energy needed for the compression and cooling processes [100]. Thus, cryogenic methods are currently mainly studied to advance the low-TRL cryogenic capture process and scale-up in association with other CO_2 capture processes, for example polymeric membrane techniques (TRL 6) [166]. Other existing cryogenic based hybrid CO_2 capture systems in addition to membrane, involving hydrate [101], adsorption (zeolites 4A and 13X) [102] and absorption (chilled ammonia process) [103]. However, their TRL is mostly assigned to a

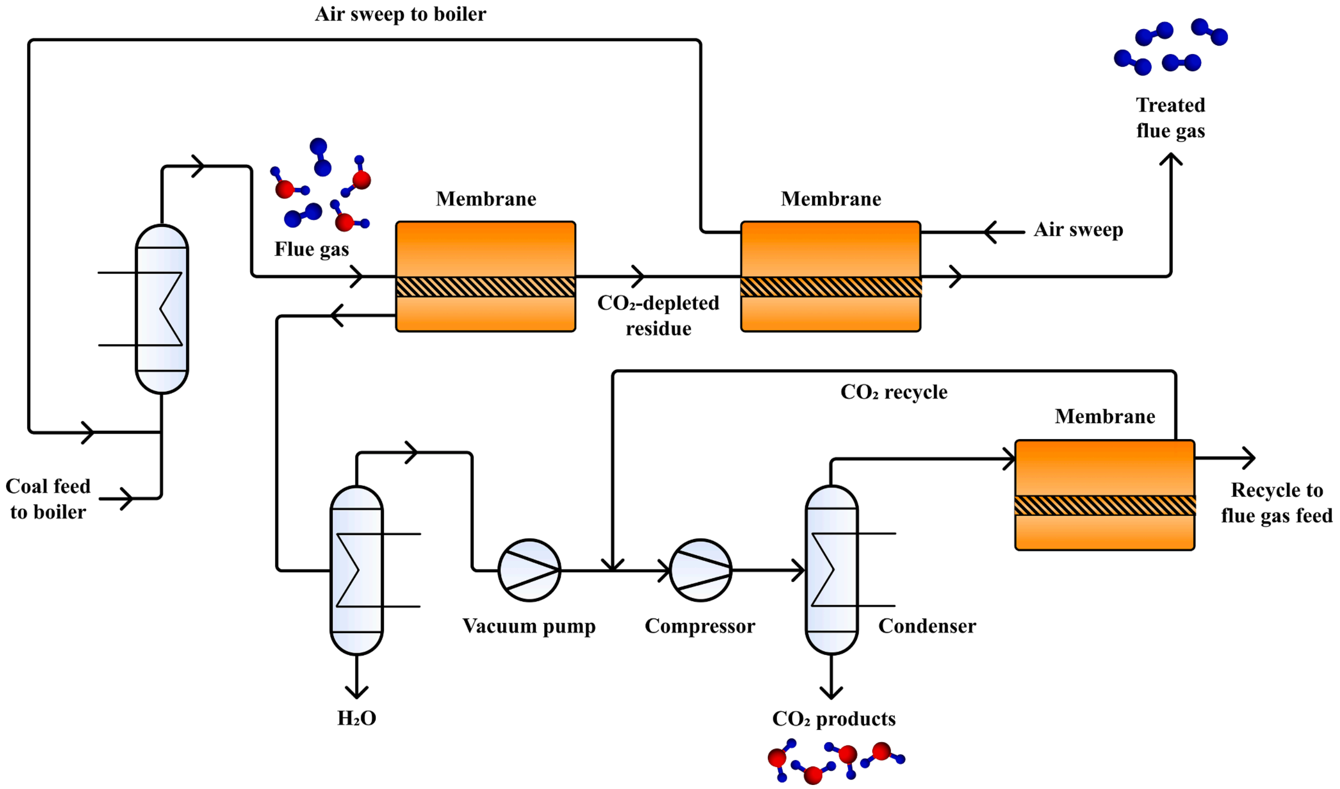


Fig. 16. Simplified scheme of membrane technology for post-combustion capture from power station flue gas.

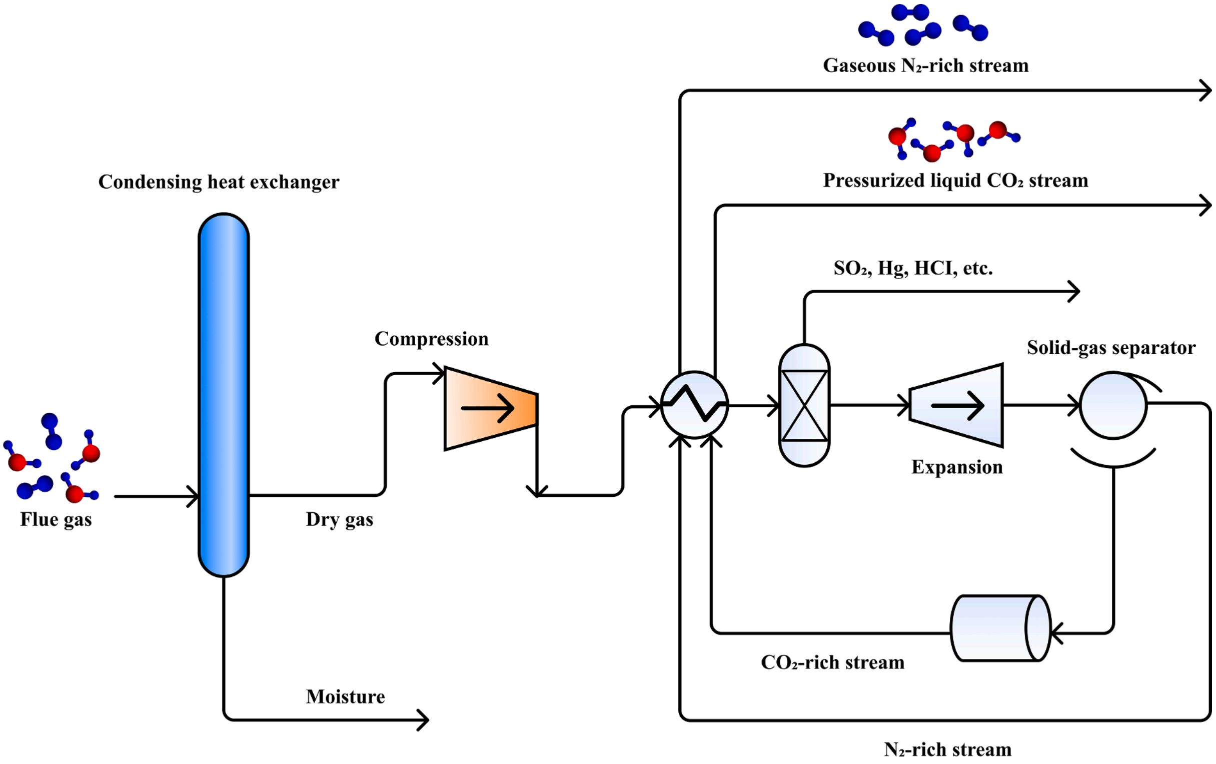


Fig. 17. Schematic diagram of CO_2 separation by cryogenic carbon capture (CCC) process [108].

laboratory scale (TRL 3).

If mentioned the current R&D projects, they focus mainly on using CCC in the cement production sector. One of the prime performers is Sustainable Energy Solutions (2022–2025), LLC wishing to advance CCC to engineering scale (30 tonnes of CO_2 captured/day – TRL 5) at Central Plains Cement Plant in Sugar Creek, Missouri. Another project led by the University of Illinois (2022–2023) concerns a pressure swing adsorption (PSA) unit combined with a cryogenic unit to produce a high-purity CO_2

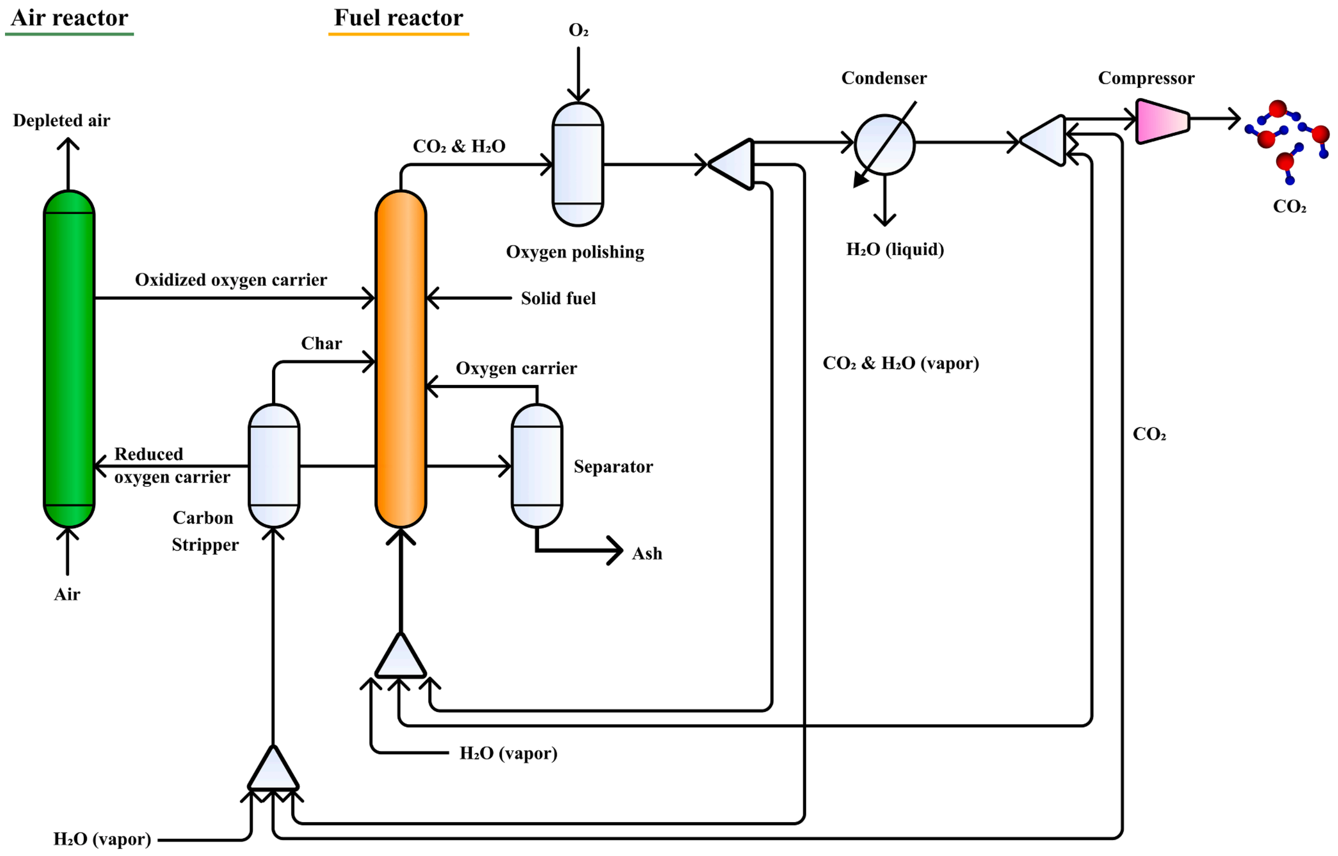


Fig. 18. Schematic representation of chemical-looping combustion process (CLC) [98].

product stream at Holcim Ste. Genevieve cement plant in Missouri. The goal is to complete a FEED study (TRL 5–7), for a commercial-scale carbon capture system that can separate 95% of the total CO_2 emissions [89].

This separation process entails numerous phases of compression and cooling of gas mixtures to produce phase changes in CO_2 in flue gases and, typically, other components in the mixture [12]. The separated carbon dioxide in the liquid phase or in the form of a solid (dry ice) is removed directly. The selectivity of the cryogenic method results primarily from different values of dew/sublimation points for individual components of the exhaust gases subject to separation, they may be: CO, SO_2, NO_x, H_2O, CH_4, and NH_3. They significantly impair cooling and result in corrosion, fouling, and plugging [100].

The greatest advantages of this method of CO_2 separation are no need to use chemical reagents, and ease of transport of CO_2, which is obtained directly in the liquid phase [12,104]. On the other hand, the main disadvantage is the energy consumption of the installation due to additional processes that must be carried out to minimize the water content in the flue gas stream that supplies the cryogenic equipment (preventing ice formation and blocking the process equipment with it and limiting the achievement of values of unacceptably high pressure drop) [12,105]. Therefore, one of the research areas is the assessment of CO_2 frosting characteristics [106,107].

3.2.4. *Chemical looping combustion (CLC)*

To reduce CO_2 emissions, an option that has been proposed by Ritcher and Knoche is the use of fossil fuels in a process known as chemical looping combustion (CLC) [109]. This approach compartmentalizes combustion into intermediate oxidation and reduction processes that are carried out independently, with a solid oxygen carrier moving between the two separated units. The CLC technology is based on two reactors that are internally connected, one of which is an air reactor (also known as a “oxidizer”) and the other of which is a fuel reactor (“reducer”), as shown in Fig. 18. Oxygen for fuel combustion is obtained from the reduction of transition metal oxides (those of copper, cobalt, iron, manganese, and nickel), which are the bed material circulating between the two reactors - oxygen carriers (OC) [110,111]. All of these chemical individuals have been recognized as potential candidates for oxygen carriers, where the most influential properties of OC to increase the efficiency of CLC are high oxygen capacity, high reactivity, high reoxidation rate, excellent stability during CLC cycles, high mechanical strength to resist the stress associated with circulation, high resistance to agglomeration, minimal environmental effect, and low price [98,112]. In the next step of CLC, the reduced metal oxides are sent to an air reactor, where they are oxidized by oxygen. After oxidization, OCs are transported to the fuel reactor, where they are reduced and used as a source of oxygen by the fuel, and then oxidize to CO_2 and H_2O.

Currently, most CLC systems have been evaluated in TRL 5–6, which correspond to pilot tests. Compared to another native technology of solid looping (comprising high-temperature looping cycles), i.e. calcium looping (CaL), CLC is less advanced in implementation on the commercial scale [166].

The primary advantages of the CLC method are the absence of harmful compounds in the air reactor exhaust gases (which are primarily composed of nitrogen) and the ease with which CO_2 can be separated from the exhaust gas stream from the fuel reactor via a condenser, thus reducing energy consumption and separation costs [47,113]. This approach has certain disadvantages, including poor stability of the oxygen carrier and slow redox kinetics [114].

3.2.5. *Calcium looping (CaL)*

Calcium looping (CaL) is an is a novel way of separation method that is becoming extremely prevalent in post-/oxy-combustion CO_2 capture

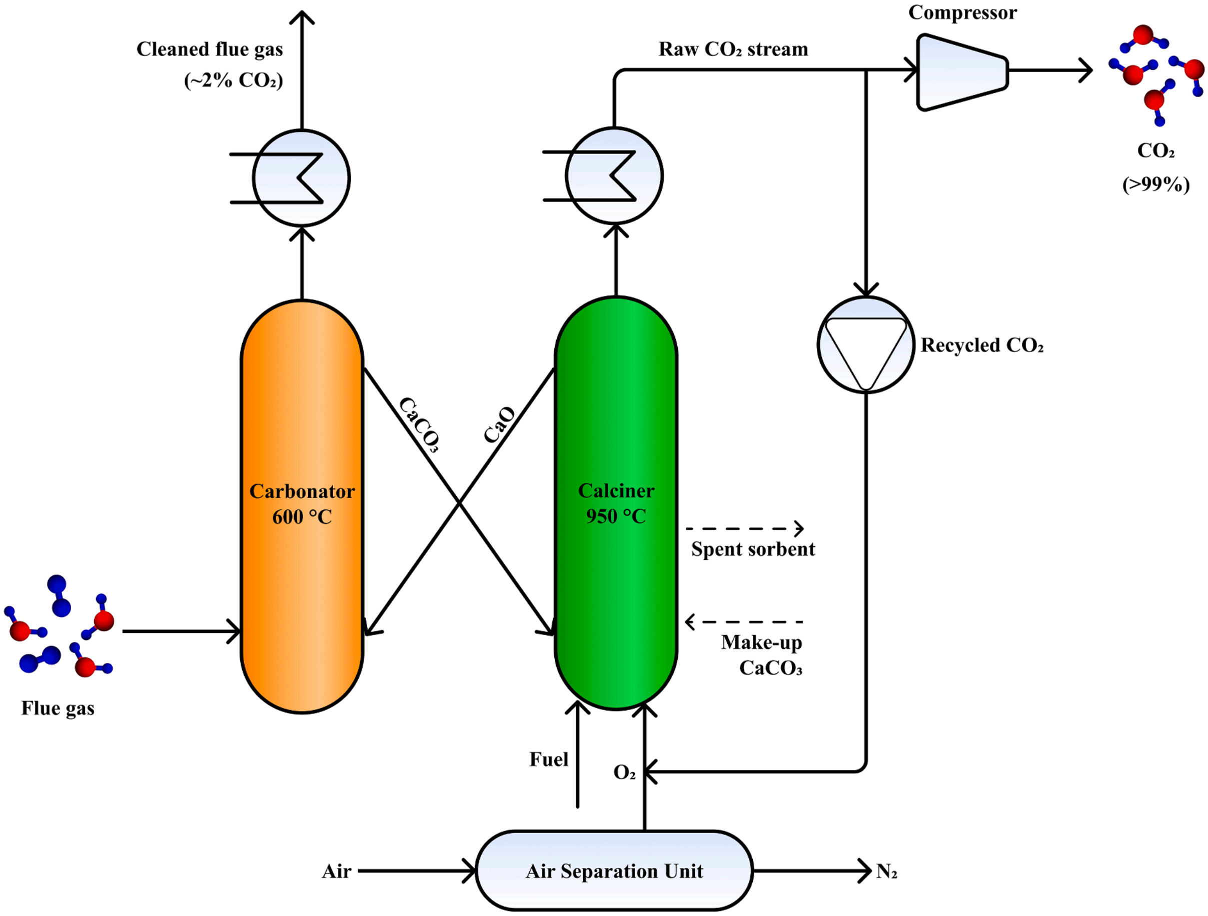


Fig. 19. CO_2 capture from flue gas by calcium looping process (CaL).

technologies from coal power plants [115], greenfield capture-ready biomass-fired plants [116], electricity generation sector, and other carbon-intensive sectors (such as cement, lime, and steel), which uses CaO-based sorbents [117]. The CO_2 capture mechanism occurs through reversible reactions between CaO and CO_2, commonly referred to as carbonation and calcination, respectively, for each stage [118]. Fig. 19 shows typical configuration for calcium looping. CaL was first suggested in the 1990 s, but has only been shown to be successfully demonstrated in recent years in actual settings at a pilot scale. Currently, this technique is in the stage of feasibility and cost studies on a commercial scale (TRL 6–7) [166]. CaL, in general, has been a particularly promising subject of research for the retrofit of pulverized coal-fired power plants, but it has also been suggested for standalone biomass power plants (BECCS) [116,118]. Although there are some CAL concepts related to the retrofit of sorption-enhanced hydrogen production processes [119].

As CaO-based sorbents, which are covered in the section on adsorption (a fundamental phenomenon in the cycles of chemical looping) in terms of the current scope of recent related studies, CaL will not be considered in detail here. In general, CaL provides several benefits that cannot be found in other CO_2 separation technologies, including a decrease in power plant efficiency that is only marginally noticeable and the possibility of this decrease being further reduced [120]. Unfortunately, this approach has a number of drawbacks, one of the most significant being that calcium sorbents deactivate during the cyclic operation of adsorption and regeneration in many successions. This phenomenon is the result of sintering, which causes modifications in the porosity and crystal structure of the sorbent, deterioration of the reactivity of the sorbents, and a rapid decline in CO_2 capture performance [118,121]. As a direct consequence of this, it is necessary to regularly remove part of the sorbent and replace it with a new one. This leads to an increase in the cost of the procedure, and the wasted sorbent also has to be removed from the premises. When these barriers are considered, they remain a pressing concern and must be solved before the CaL method achieves TRL 9.

3.2.6. *Adsorption*

In the last decade, intensive research has been carried out on adsorption as a potential method of separating CO_2 from the flue gas, owing to its quite high capacity at low temperature and high pressure, obtaining the final product with high purity, the possibility of complete automation of its process, and the reduction of many unnecessary steps. Nowadays the most significant challenges of adsorption deployment on an industrial scale are four fundamental aspects: cost-effective production on a large scale of adsorbents, reduction of CO_2 uptake due to the negative impact of impurities in flue gas mixture, controlling and regulating temperature of flue gas to a proper level, and costs associated with frequent adsorbent replacement. Table 10 shows the performance of the CO_2 capture and its cost, operating conditions, and manufacturing cost of an adsorbent material for selected adsorption R&D projects in 2013–2023.

The adsorption process is cyclical and consists of two separate processes: the adsorption and desorption of CO_2 (Fig. 20). It takes place as a result of the uneven sorption capacity of the adsorbent and the speed of the adsorption kinetics of selected gaseous agents from the separated

Table 10
Selected completed and ongoing R&D projects in 2014–2023 on adsorption in CO_2 capture technology [89].

Type of adsorbent material	Project focus	Prime performer	Project duration	Equilibrium loading [mg or mmol CO_2/kg]	Operating pressure [bar]	Operating temperature [℃]	Manufacturing cost for adsorbent [$/kg]	Cost of manufacturing and installation [$/kg]	Cost of CO_2 capture [$/t$CO_2$]	CO_2 recovery [% vol.]	CO_2 purity [%]	Technology maturity	TRL
						Post-combustion CO_2 capture							
Alkyl-amine coated MOF	Novel adsorbents for CO_2 capture (TSA)	Lawrence Berkeley National Laboratory	2017–2021	2.5	0.13	50	<75	–	–	90	90	Bench-scale	4
Alkalized alumina (Al_2O_3) adsorbent	0.5 MWe CO_2 capture process using TSA	TDA Research, Inc.	2014–2022	1.0	1.12	140	6.5	–	37	90	95	Pilot-scale	6
Microporous adsorbent	Reduce the cost of CO_2 capture (TSA)	InnoSepra, LLC	2019–2022	3.25	1.15	25–32	4.0	336	31	90	99	Laboratory-scale	3
Ion exchange amine polymeric resin	Develop novel adsorbent material to CO_2 capture using TSA	TDA Research, Inc.	2018–2022	0.72	1.1	60	<20	–	29.7	90	95	Bench-scale	4
Bi-layer laminated structured sorbents (MOFs)	Optimization of novel adsorbent materials	Electricore, Inc.	2019–2022	1.5–2.5	1–1.1	40–50	100–200	–	–	90	90	Bench-scale	4
TiO_2/Al_2O_3 on Zeolite 13X	Reduction in CO_2 capture cost and energy penalties (PSA)	Rensselaer Polytechnic Institute	2019–2023	0.965–1.2	0.15	20	3.6 (target)	–	~30	90	95	Bench-scale	4
Low-temperature physical adsorbent	Develop membrane-adsorbent hybrid system	TDA Research, Inc	2018–2023	0.5	1.0	30	3.75	–	38.89	–	–	Pilot-scale	6
MOF on microlith in adsorption modules	Develop novel adsorbent to CO_2 capture using TSA	Precision Combustion, Inc.	2017–2023	–	–	30	–	–	30 (target)	–	–	Bench-scale	4
SIFSIX-2-Cu-I MOF	CO_2 capture using VCSA	TDA Research, Inc.	2019–2023	2.3	1.0	30	30 (target)	–	30.7–36.4	90	95	Laboratory-scale	3
Carbon pellets sorbent	Novel low-cost carbon adsorbent	SRI International	2013–2018	4	1	20	–	–	45	90	95	Bench-scale	4
Amine functionalized aerogel adsorbent	Improving the performance of CO_2 capture	Aspen Aerogels, Inc.	2013–2016	100–200	0.8	40	7–10 (target)	–	–	–	–	Bench-scale	4
						Pre-combustion CO_2 capture							
Functionalized carbon sorbent	High-capacity regenerable adsorbent	TDA Research, Inc.	2013–2022	1.04	33.8	198	3.88	212.8	28–40	90	96	Pilot-scale	6

mixture. During adsorption, a experimental apparatus is filled with the adsorbent. After that, the flue gas containing CO_2 is transported through it. Further, the gas mixture is led to the surface of the solid sorbent material, which adsorbs CO_2 molecules and passes other gases through its structure. After adsorption, CO_2 is removed from the adsorbent layer (desorption process) - regeneration of the adsorbent for reuse and then desorbed CO_2 is transported, conditioned and compressed [122].

Theoretically, the capture of CO_2 by adsorbent material is mainly conditioned by two factors: the degree of development of its porous structure (the degree of expansion of micropores/mesopores, and the size of the specific surface area of the adsorbent) and its chemical properties. The first factor determines the space available for gas adsorption, and the second affects the interaction forces between the CO_2 molecules and the solid surface, which determine the adsorption properties [123]. The effectiveness depends on a variety of other factors that strongly influence the practical utilization of CO_2 adsorbent on an industrial scale: process parameters, the composition of the flue gas mixture, the specific branch of industry for application, physicochemical parameters, environmental criteria, etc. The choice of a particular adsorbent is related in part to the type of CO_2 capture, where temperature plays an important role. For post-combustion capture, the flue gas temperature is relatively low; for coal-fired flue gas it is approximately 60–150 °C, and for natural gas-fired flue gas around 100 °C, in that case most types of adsorbent can be used. On the other hand, CO_2 capture before the combustion process, where the gas resulting after gasification or the post-water–gas shift reaction of the fuel has a much higher temperature, 500–1800 °C and 250–550 °C, respectively [124–126]. The temperatures of the oxy-fuel combustion reach similar or even higher

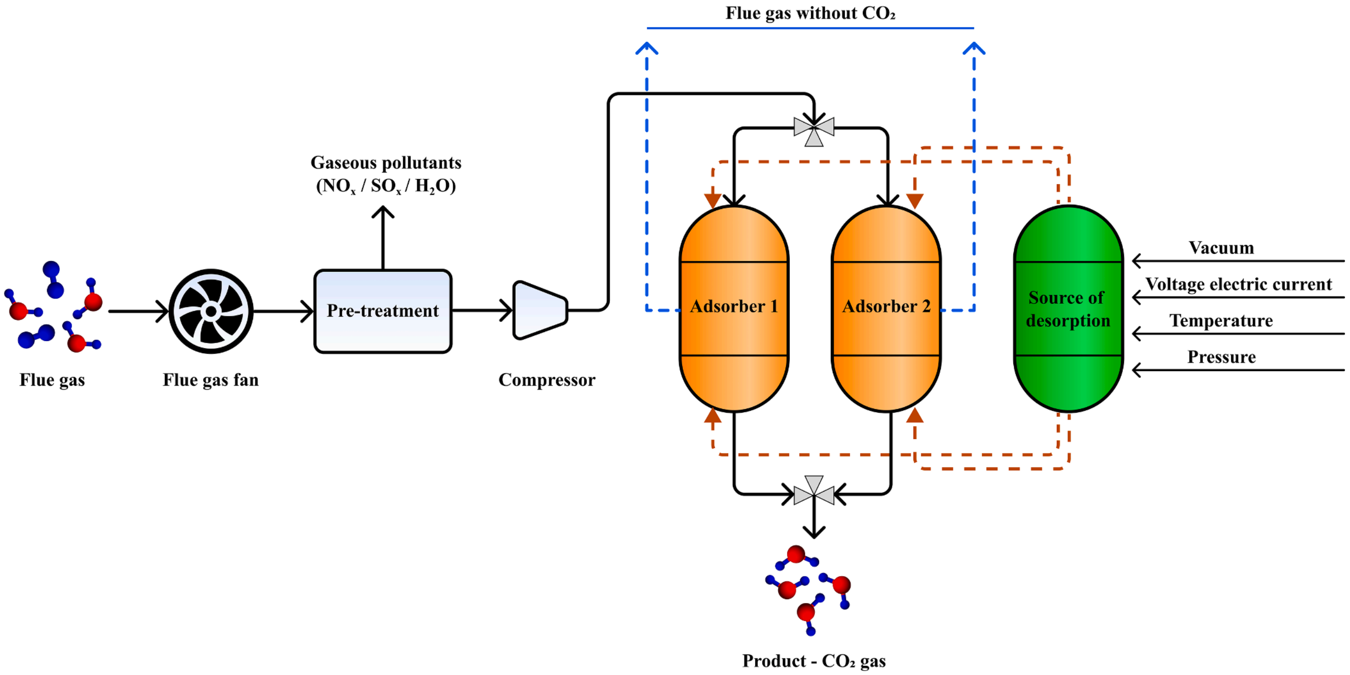


Fig. 20. Schematic diagram of the CO_2 adsorption process.

values [12]. This results in the application of adsorbents that are more resistant to high temperatures to avoid degradation of their material structure.

In view of adsorption progress in the market, the two major types of adsorption, as key factors, may interchangeably be referred to as phases in the advancement of technology. Physical adsorption (e.g. activated carbon, silica, alumina, MOFs, or zeolites) is now used most often in cement industry (TRL 5–6); chemical industry i.e. ammonia (TRL 5–6), methanol (TRL 7–8) production; and iron and steel sector i.e. direct reduction process (TRL 5–6), smelting reduction process (TR 7–8) [81]. In contrast, chemical adsorption is in a much earlier technology stage, substantially in the research and development phase (amine-based adsorbents, metal oxides, metal salts, hydrotalcites). Apart from the choice of materials, adsorption also has other segments that interact with each other, which should be considered in the spectrum of conducting experimental research. They are contactors (adsorbent beds) and solid sorbent technologies (mainly a method of adsorbent regeneration). In other words, the selection of the contactor and the regeneration method must be tightly connected with the advancement of the adsorbent material in the CO_2 capture. Specific gas–solid contacting systems are a vital aspect in the efficient use and development of each type of adsorbent material to obtain the maximum potential from them, as they influence not only the overall outcome of the process, but also the operational/capital costs (CO_2 capture costs) [127] and the acceleration of the commercial implementation of adsorption technologies [128].

When assessing the adsorbent beds itself through TRL, it is difficult to define them because of the close connection with the regeneration method and the examined adsorbent material, or because of the lack of specific information in the literature of larger-scale projects. Therefore, it is not advisable to verify them in terms of the TRL. Until now, contactors were reported with various modifications, mainly in coal sector, etc. on the laboratory scale (TRL 3) - multistage fluidized/VTSA/PEI + SiO_2 [129], fixed bed + membrane hybrid/VSA/zeolite 13x molecular sieve [130], sound assisted fluidized bed/fine activated carbon [131]; bench scale (TRL 4) - multistage fluidized/TSA-N_2/PEI + SiO_2 [132]; and pilot scale (TRL 5–6) - fluidized bed/TSA/dry sorbent (K or Na) [133], moving bed/TSA/amine functionalized sorbent [134], fixed bed/VPSA/zeolite 13x and activated carbon [135], moving bed/TSA/advanced carbon sorbent [136], fluidized bed/TSA/PEI-based adsorbent (cement sector) [137], and fixed-bed/VSA-light product pressurization (LPP)/zeolite 13x [138].

In relation to the way regeneration modes until now, various types are used in different scale. The most recognized and mature method in industry is pressure swing adsorption (PSA), achieving TRL 9 [166]. The other PSA modifications mainly concern the way of CO_2 desorption, which is conditioned by a combination of the following various parameters: increase in temperature, reduction in partial pressure, or CO_2 concentration in the volume of the flue gases, flushing out with an inert fluid, change of chemical conditions or electric field application. Consequently, the main classification was divided into several characteristic variations, i.e., pressure swing adsorption with the use of vacuum in the desorption process (vacuum pressure swing adsorption (VPSA)), vacuum swing adsorption (VSA), temperature swing adsorption (TSA), combined temperature and pressure swing adsorption (temperature–pressure swing adsorption (TPSA)), and adsorption with the use of low-voltage electric current passed through the bed during the desorption stage (electric swing adsorption (ESA)). Of the above PSA modifications, only VSA also managed to achieve industrial scale implementations (TRL 9, Air Products Port Arthur SMR CCS) [166]. Other methods of regeneration are found at various technology advancement, VPSA and TPSA reached TRL 6 [139], TSA has a TRL of 5–7 (large pilot tests to FEED studies for commercial plants) [166], ESA is between a TRL of 3–4 [140]. For PTSA, no specific values are given in the literature, so it can be suspected that it is at very early stage of technology. In addition, the scientific literature reports unconventional adsorption technologies that do not fit into the scope outlined above conventional regeneration method, these are: enzyme catalyzed adsorption (TRL 6), sorbent-enhanced water gas shift (TRL 5), and electrochemically mediated adsorption (TRL 1) [166].

Characteristics of all investigated CO_2 separation technologies are summarized in Table 11, and current technology readiness levels are presented in Fig. 21 and Fig. 22.

4. CO_2 transport

Carbon capture and storage technologies are heavily dependent on CO_2 transit. After capture and separation, carbon dioxide must be transported in the appropriate phase state. This can be done in several

Table 11
General advantages and disadvantages of CO_2 separation technologies [12,42,47,55,98,141,142].

Method	Advantages	Disadvantages/Challenges
Physical absorption	✓ >90% CO_2 separation efficiency. ✓ Low energy consumption for sorbent regeneration. ✓ Temperature required for the process is lower than for chemical methods. ✓ Low corrosivity and toxicity. ✓ More economical at a higher partial pressure of CO_2.	➢ Low effectiveness of CO_2 capture. ➢ Low selectivity towards CO_2. ➢ Limitation on operating temperature (the capacity of solvents is best at low temperatures). ➢ High capital and operational costs. ➢ Economically unprofitable if CO_2 partial pressure <15% vol.
Chemical absorption	✓ Most mature technology. ✓ Simplicity and the possibility of using it with a low partial pressure of CO_2. ✓ Suitable for retrofit. ✓ High absorption capacities. ✓ Product purity >99% vol.	➢ Need to clean the exhaust gases (water, SO_x, NO_x). ➢ Corrosivity of proces apparatus. ➢ High energy demand for regenerating the solvent. ➢ Solvent toxicity and loss ➢ Large absorber volume. ➢ Environmental impacts due to solvent degradation.
Membranes	✓ >80% CO_2 separation efficiency. ✓ Uncomplicated process. ✓ No regeneration energy is required. ✓ Simple modular system. ✓ No waste streams. ✓ Higher separation energy efficiency compared to absorption and adsorption. ✓ No additional chemicals in separation process.	➢ Strength problems at high pressures. ➢ Strict temperature requirements. ➢ Plugging by impurities in gas stream. ➢ Sensitivity to corrosive gases. ➢ Need for gas compression. ➢ Difficult to maintain performance over long-term operation. ➢ Preventing wetting is a major challenge. ➢ Permeation and selectivity issues.
Calcium looping (CaL)	✓ Cheap raw materials for sorbents synthesis. ✓ Optimal method for retrofit of pulverized coal-fired power plants, sorption-enhanced hydrogen production process or BECCS.	➢ Reduced CO_2 uptake due to sintering of sorbents in many cycles. ➢ Additional expenses regarding fast rapid degradation of sorbent. ➢ Waste management of sorbents.
Cryogenic method	✓ High CO_2 purity. ✓ High separation efficiency(up to 99.9% vol. CO_2). ✓ Production of ready to transport, pure liquid CO_2. ✓ No need of chemical reagents. ✓ Suitable for high pressure gas stream with high concentration(>50% vol.). ✓ Easy scaled-up to industrial application.	➢ Significant energy penalty due to refrigeration (low temperature, high pressure condition). ➢ The energy consumption to minimize the moisture level in the flue gas stream (preventing ice formation and blocking the process. equipment). ➢ High capital costs.
Chemical looping combustion (CLC)	✓ Simplicity and the possibility of using it with a low partial pressure of CO_2. ✓ The exhaust gas from the air reactor is mainly N_2. ✓ The exhaust gas stream from the fuel reactor is composed of CO_2 and H_2O (CO_2 can be easily separated by a condenser). ✓ Avoids huge energy penalty and thus less operational cost.	➢ Insufficient stability of the oxygen carrier. ➢ Slow redox kinetics. ➢ Process is still under development and not implemented in industry scale.
Adsorption	✓ >85% CO_2 separation efficiency. ✓ Ease of use and maintainability of the installation. ✓ Since adsorbents can be reused, low waste generation. ✓ Reversible process (physical adsorption). ✓ Large selection of materials with high CO_2 uptake. ✓ Low energy requirement to regenerate a adsorbent material. ✓ Wide operability range. ✓ Possibility to use waste biomass or industrial resides as raw materials do adsorbent synthesis.	➢ Low CO_2 selectivity. ➢ Lower CO_2 uptake compared to other separation technologies, such as absorption or cryogenics. ➢ Lack of expertise. ➢ Scalability. ➢ Problem with the resistance to high temperature. ➢ Continuous, low-cost manufacture on a widespread scale of a adsorbent. ➢ Sensitivity to sulfur/nitrogen oxide and moisture. ➢ Poor durability of adsorbents (additional cost of material replacement).

ways, e.g. in the gaseous phase. However, the distribution of CO_2 as a gas is not an economically viable option, similar to the situation with a two-phase flow, which can result in high pressure losses [143]. Generally, there is a consensus that significant amounts of CO_2 should be transported as liquid or preferred in the supercritical state (above the critical temperature and pressure), and as a dense phase fluid (above the critical pressure but below the critical temperature) [144]. The dense phase offers the greatest number of advantages as the most energy-efficient conditions, due to its viscosity being comparable to that of a gas and its density being closer to that of a liquid [143]. In addition to the phase characteristic, there are also other existing studies of the effects of CO_2 property on the transport process, such as density, viscosity, heat capacity, and thermal conductivity. And their impact is determined on transport cost, pressure drop/loss, and temperature drop [145].

The CO_2 transmission process itself is well established and can be divided into offshore and onshore transport, which are two distinct subsets of the overall transport system. Onshore transport options include highways, railroads, and pipelines, while offshore shipping options include pipelines and ships, the choice is particularly based primarily on the distance to the CO_2 storage site [146]. The advantages and disadvantages of these transport methods are given in Fig. 23. The two most technically mature advanced transport research methods are onshore & offshore pipelines and transport ships. CO_2 can also be transported by road and rail tanker as well, but it is not the preferred mode of transportation for a large CCS project. However, China still relies heavily on highway cryogenic storage tanks for its offshore CO_2 transit, as a pioneer in this field of research [145]. Therefore, all transport technologies reached a TRL 9 stage, since they are now being used on a commercial scale.

4.1. Pipeline transport

Pipelines are today considered a mature market technology. They are reviewed as safe transmission technology, because CO_2 is not toxic or flammable, and generally the possibility of pipeline leakage is low [145]. From 2014, >6.500 km of CO_2 pipelines were spread around the

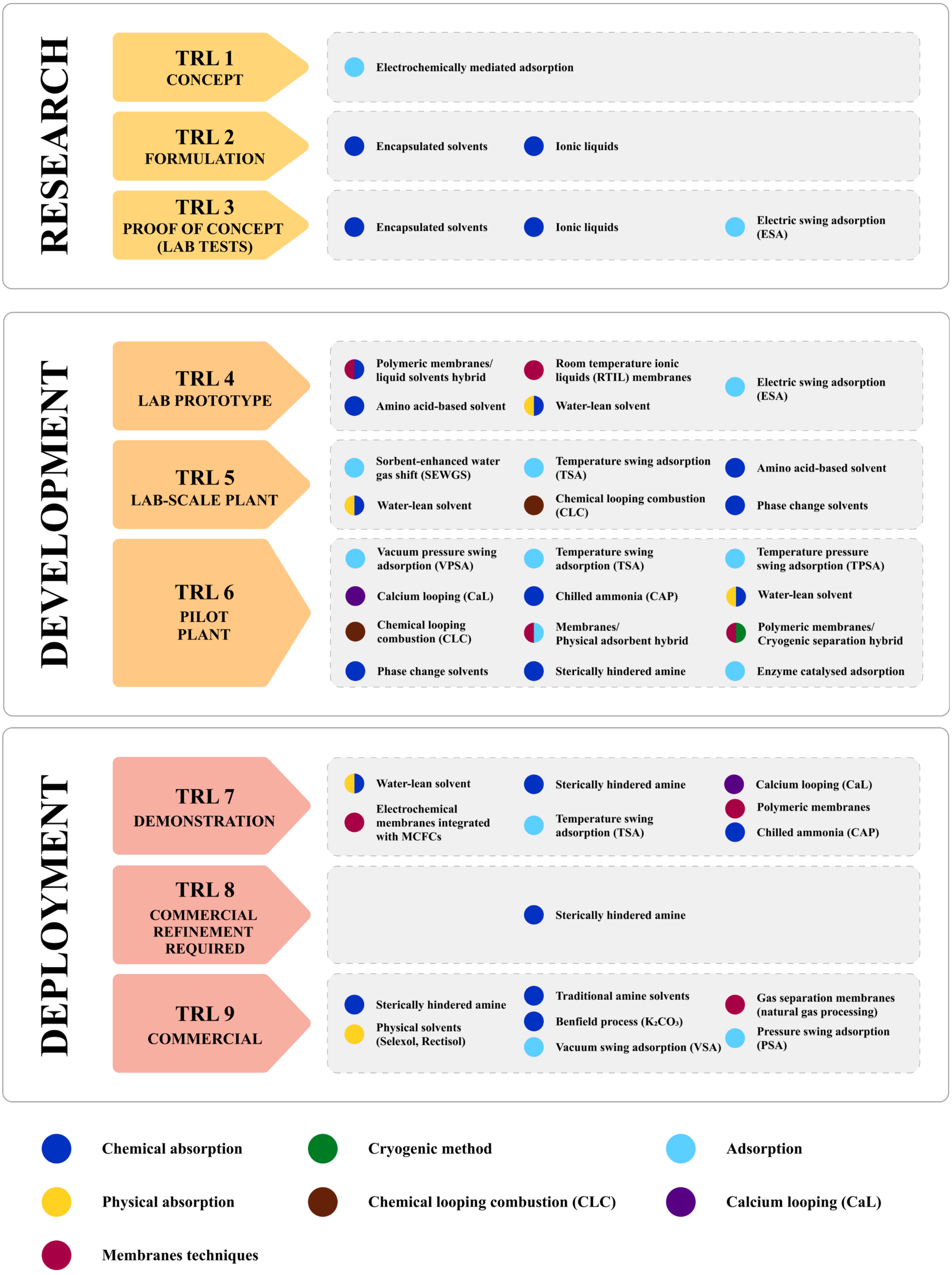


Fig. 21. TRL of CO_2 separation methods (the following scheme is not meant to be all-inclusive).

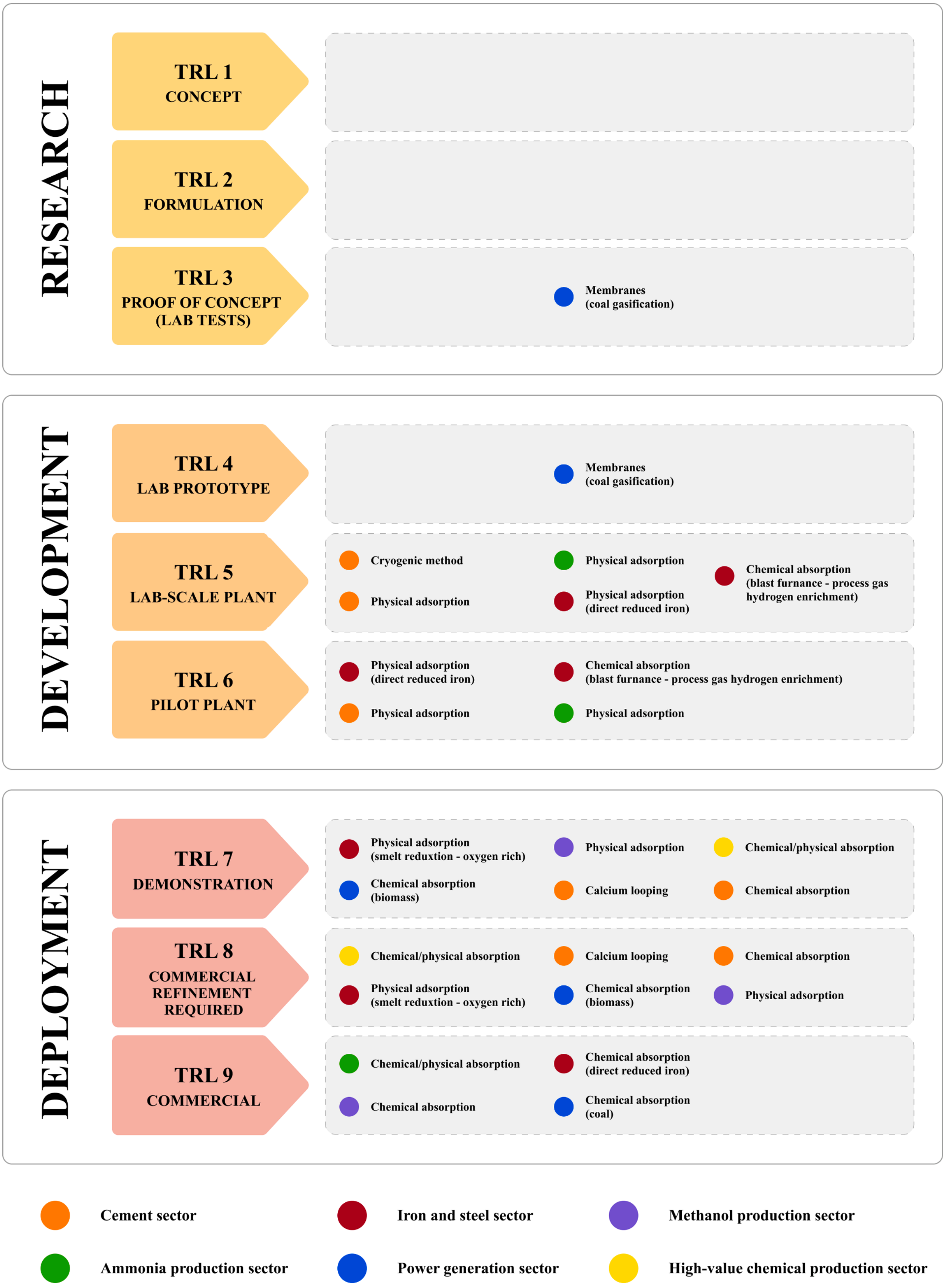
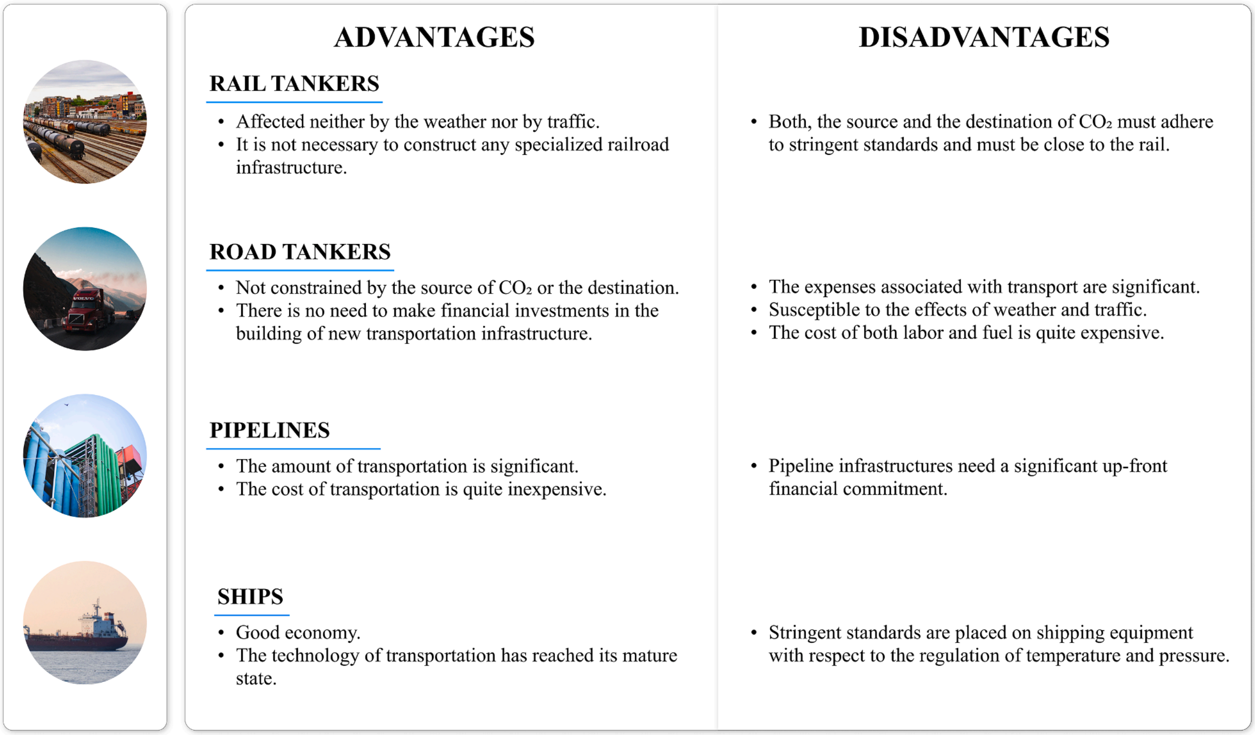


Fig. 22. TRL of CO_2 separation technologies by economic sector (the following scheme is not meant to be all-inclusive).



	ADVANTAGES	DISADVANTAGES
RAIL TANKERS	• Affected neither by the weather nor by traffic. • It is not necessary to construct any specialized railroad infrastructure.	• Both, the source and the destination of CO₂ must adhere to stringent standards and must be close to the rail.
ROAD TANKERS	• Not constrained by the source of CO₂ or the destination. • There is no need to make financial investments in the building of new transportation infrastructure.	• The expenses associated with transport are significant. • Susceptible to the effects of weather and traffic. • The cost of both labor and fuel is quite expensive.
PIPELINES	• The amount of transportation is significant. • The cost of transportation is quite inexpensive.	• Pipeline infrastructures need a significant up-front financial commitment.
SHIPS	• Good economy. • The technology of transportation has reached its mature state.	• Stringent standards are placed on shipping equipment with respect to the regulation of temperature and pressure.

Fig. 23. Evaluation of the merits and disadvantages of CO_2 transport techniques [145].

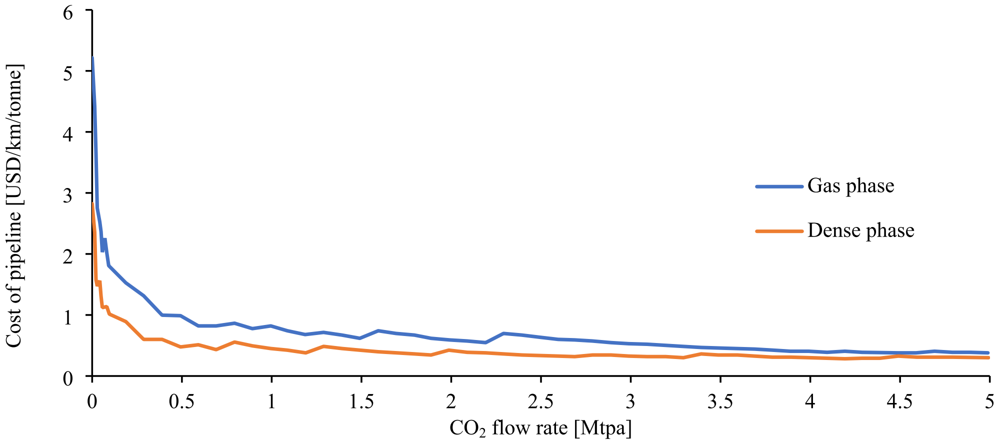


Fig. 24. Indicative costs of CO_2 pipelines influenced by CO_2 flowrate [31].

world, which operated particularly in enhanced oil recovery (EOR) projects in the United States [147]. According to the latest available data, the total length of the global CO_2 pipeline exceeded 8000 km in 2015, with the United States accounting for the highest proportion (>7,200 km) [145]. In 2013, Europe had only about 500 km of CO_2 pipelines, so the difference is enormous [148]. In the case of future trends that depend on the level of industrialization development, estimates by IEA professionals showed that the length required for CO_2 pipeline networks in 2030 will be approximately 100.000 km, and the length required in 2050 will range between 200.000 and 550.000 km [149]. The carbon dioxide stream transported by the pipelines is compressed to a pressure of 10–20 MPa, higher than the critical one (~7.38 MPa) to avoid multiphase flow regimes, making it less difficult and more affordable to transport [150].

The transport capacity of CO_2 pipelines is a function of the diameter of the pipeline; therefore, it should be correctly dimensioned according to the appropriate source of CO_2 emissions [151], also in terms of technological evaluation, as the diameter strongly influences the amount invested capital. In most cases, the amount of money invested will be proportional to the diameter of the pipe [145]. As a result, the most practical pipe diameter would be as small as possible while still meeting the CO_2 transmission requirements [152]. In the design of a pipe diameter, in addition to the diameter itself, pressure, flow rate, and fluid flow should be taken into account [153,154]. The influence of one those process parameters is clearly seen in Fig. 24, where the flow rates of transported CO_2 correlate significantly with capital and operational expenditure of the pipeline, and the advantage of the dense phase over the gas phase is noticeable.

Today, research on CO_2 pipelines is focused on their design (e.g. impact of impurities - H_2S, O_2 H_2O, N_2 on phase equilibrium), utilized materials, safety and maintenance (e.g. corrosion processes in pipelines), and management as challenging factors. Additionally, the development of innovative construction and detection methods is also essential [145].

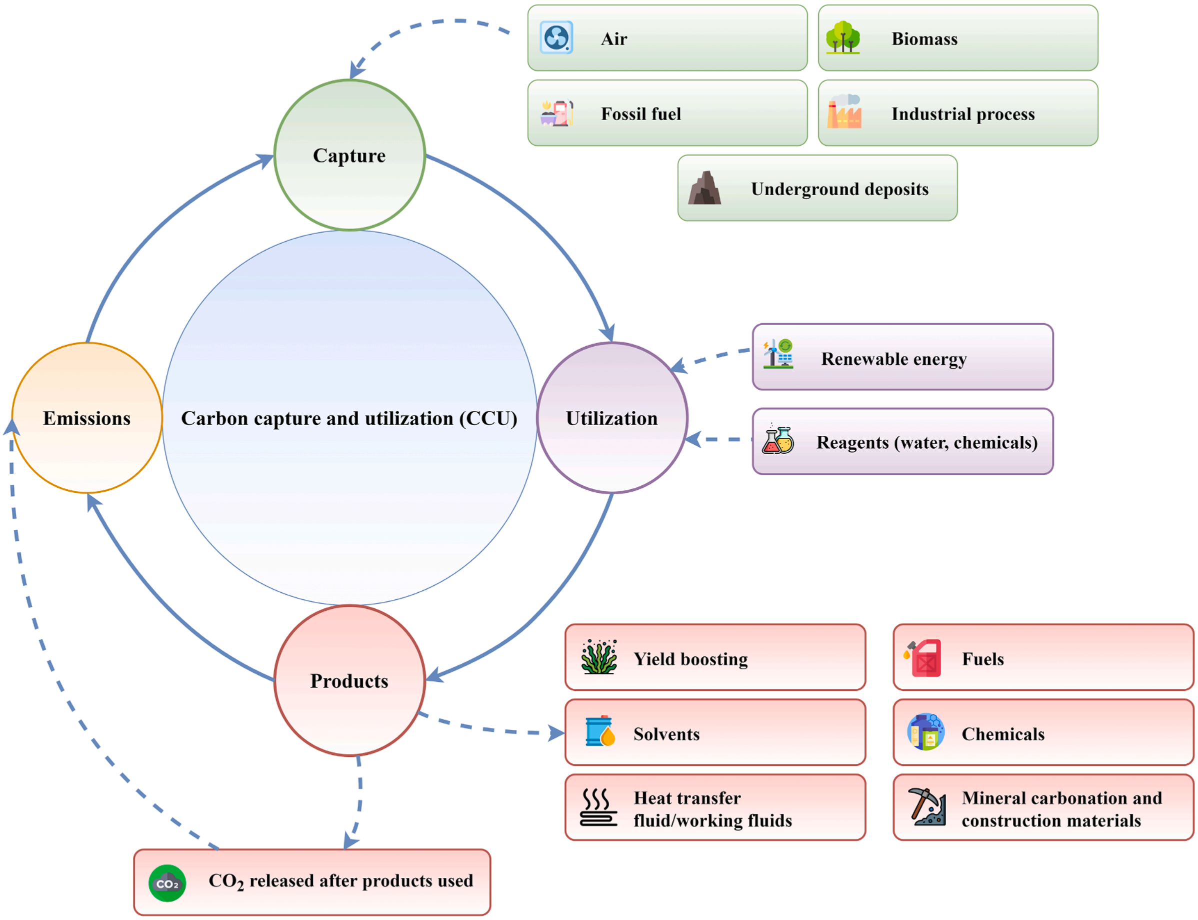


Fig. 25. Scheme of CCU process flow.

4.2. Ship transport

For the last 30 years, CO_2 has been transported by ships, in any way connected to food or industrial industries, with a working pressure of 15–20 bar and a temperature of –30 °C, as the optimal cryo-compressed conditions of their operation [155]. In certain cases, particularly over longer distances, shipping through a ship rather than a pipeline may be the most cost-effective option, as ships are more adaptable [42] and have good economy [145]. Ship transport requires the use of certain pieces of machinery, such as an intermediate storage tank, loading and unloading facilities, and CO_2 carrier/cargo tanks. In general, carrier tanks may be classified into three distinct categories: pressurized, completely refrigerated, and semi-refrigerated. These categories are considered the target designed characteristic and are determined by three obligatory factors to be considered throughout the design procedure, the two most important such as: the boiling temperature (determining element in the selection of the tank), and the internal pressure (conceived on the vapor pressure and the liquid pressure) and the third one - cargo density, which is essential for the choice of scuttling of the tanks and its assistance [151]. Therefore, the greatest challenge of this method of transport are the strict requirements for the control of temperature and pressure in specific range of values in the CO_2 transport equipment, taking into account possible mechanical damage to the tanks, leakage or different atmospheric conditions.

5. CO_2 utilization and storage

5.1. Carbon capture and utilization (CCU)

In 2000, global CO_2 consumption was around 150 Mt/year, and the demand for CO_2 grew steadily over the previous years. In 2015, it increased rapidly to 230 $MtCO_2$, and in 2020, the level was expected to reach 250 $MtCO_2$ [156]. The trend of increasing demand is willing to remain constant due to the economic development of three major CO_2 market, which are the USA (33%), China (22%), together with Europe (16%), and in 2025 its predicted value seems to rocket to approximately 272 $MtCO_2$. For 2015 data, the largest industrial consumers were primarily the fertilizer industry (responsible for around 57% – 130 $MtCO_2$ for urea production), and the oil sector (34%), including the use of 70–80 $MtCO_2$ in CO_2-EOR. Other areas of the economy where CO_2 is used are the production of food (3%) and beverages (3%), the fabrication of metals (2%) and other applications (4%) [156]. In light of this, CCU technology combines the potential for mutual benefit, both for the net-zero strategy and for many branches of industry, which attract governments and the community of investors to support its development. Throughout the last decade, total private financing for CO_2 utilization start-ups across the world reached nearly 1 billion dollars.

The carbon capture and utilization (CCU) process consists of the CO_2 capture from flue gases and its subsequent disposal. It is a competing technique for the CCS approach, which is required to get to the point where large-scale CO_2 emissions can be minimized as rapidly as feasible. However, in contrast to that, CCU technology, as a vital feature of the long-term strategy, aims to recycle CO_2 that has been captured and convert it into a variety of other chemicals, solvents, raw materials in the manufacture of fuels, carbonates, polymers, or as a recovery agent in techniques such as enhanced oil/gas recovery (CO_2-EOR/EGR), and enhanced coal bed methane (CO_2-ECBM) [157] - CO_2, which is stored simultaneously, is treated as a means of its utilization while obtaining valuable new products. Therefore, these methods are classified as both CCS and CCU. The same is the case with CCMC technology, where CO_2

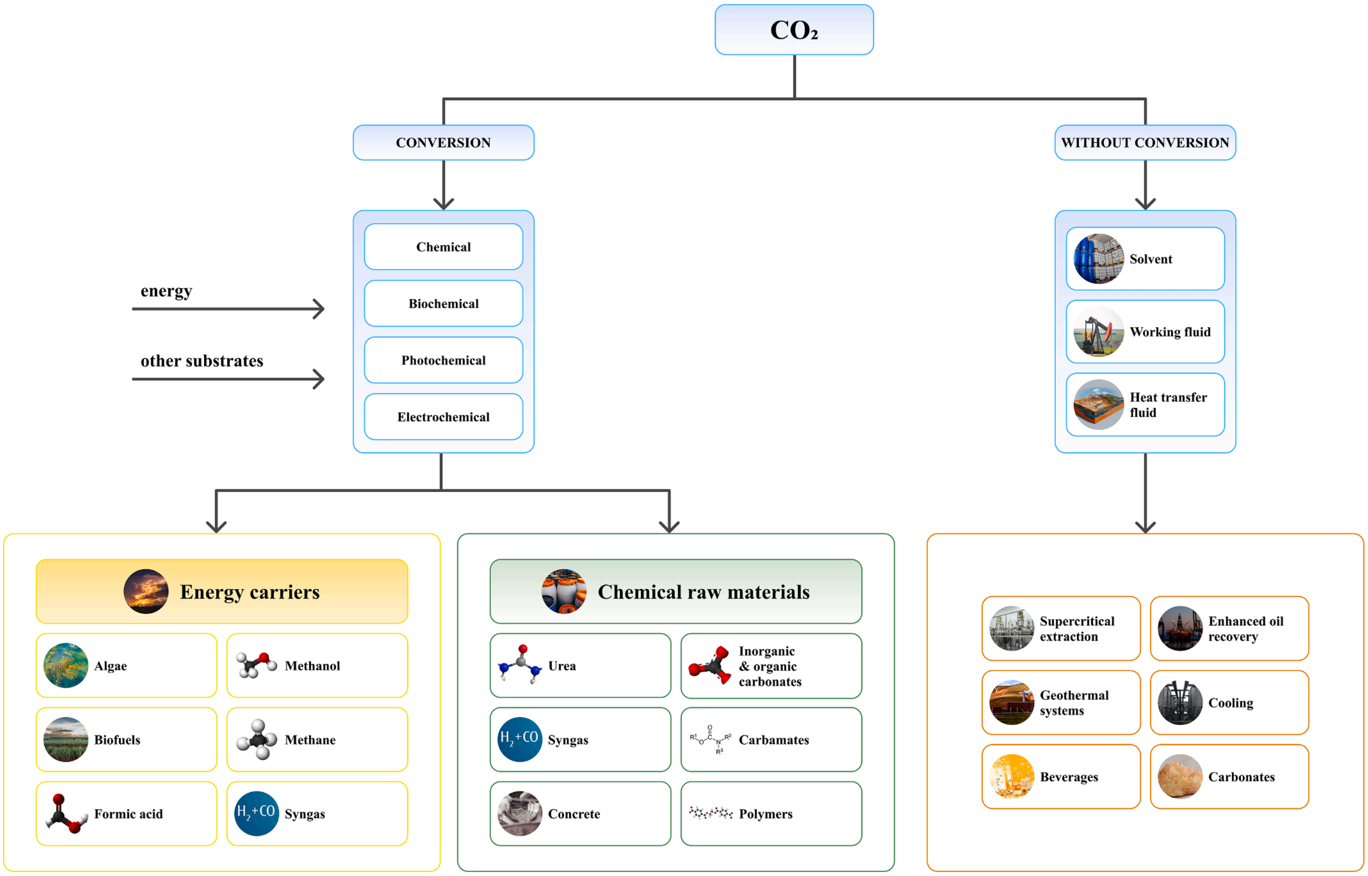


Fig. 26. The ways of utilization and re-use of CO_2 in CCU technology (the following scheme is not meant to be all-inclusive).

can be reused in the form of carbonates in industry. Generally, new pathways to reuse CO_2 has crucial implications for the current problems of many economy sectors and ecology, causing positive effects on them. It especially includes its contribution to the goal of reaching global climate goals; providing various substitutes for carbon feedstock, which is essential for growing societies; enabling the development of the circular carbon economy, and waste management; facilitating transmission and distribution of power derived from renewable sources [158,159].

The CCU process itself can be divided into characteristic stages that repeat cyclically: emission, capture, utilization, and obtaining products (Fig. 25) Therefore, the goal of highly developed economies is to identify and develop technologies that allow the creation of useful and valuable substances or products from recovered CO_2, which can have a significant impact in many industrial sectors. Complete incorporation of CCU into value-added goods provides an opportunity to reduce unavoidable process emissions and mitigate process costs. An exhaustive examination of the viability of the process is necessary to achieve the successful construction of a CCU process; however, it is not immediately clear which of the available solutions is best suited for this. To determine which CCU solutions have the greatest potential, the set of criteria can be used to reflect various aspects of the utilized process, such as: the specific mass of CO_2 in the product; CO_2 utilization potential (CUP), robust life-cycle assessment; technology readiness level (TRL); the resources used; the requirements for CO_2 quality and health, safety, and environment (HSE) issues; they are all important factors [160].

According to current trends, captured carbon dioxide can be reused in CCU in two ways: by conversion (additional energy and other substrates are required) or without conversion (Fig. 26). In the first method, 4 subgroups can be distinguished: chemical, biochemical, photochemical, and electrochemical. As a result, energy carriers (methane, syngas, methanol, gas hydrates, biomass fuels) and chemical raw materials (organic and inorganic carbonates, carboxylic acids, carbamic acids, and biodegradable polymers) are created [161]. On the other hand, the second method usually produces solvents (hydroformylation/hydrogenation/oxidation/biocatalysts/polymers synthesis in CO_2) [157], working fluid in a power cycle, and heat transfer fluid [161]. They are used primarily in cooling and geothermal systems, in supercritical extraction, or CO_2-EOR/CO_2-EGR/CO_2-ECBM.

In the case of the CCU, the determination of TRL is still fraught with some degree of doubt, when it comes to non-CO_2-EOR (CO_2-EOR only has achieved truly TRL 9) [44]. CCU is representative of a diverse set of technologies, most of which have their conceptual viability established in the pilot commercial project and the need to transform CO_2 into products that cannot yet be made available on the market due to the need for more research and/or modifications to the existing regulatory structure [162]. Therefore, it can generally be assumed that mainly all CO_2 utilization methodologies have TRL 6 [44]. However, considering the mature state, there are possibilities to identify specific CO_2-based products on the TRL scale [163]. Only the group of CO_2-based chemicals, fuels, and durable minerals reached TRL 9, as follows: methanol, CO_2-based polycarbonates, polyols, polyurethanes, salicylic acids, and urea. The rest of the technologies in this group are between TRL 1 (malates), and TRL 8 (cyclic carbonates, dimethyl carbonates, and methane). In the case of mineral carbonation and construction materials, it is TRL 4 (magnesium carbonates) to TRL 8 (sodium bicarbonates, concrete curing). A biological algae cultivation and enzymatic conversion oscillates between TRL 3 (CO_2-based enzymatic and microbial products) and TRL 8 (dry algae powders) [163]. Fig. 27. presents more details of development approaches to CO_2 utilization in the CCU.

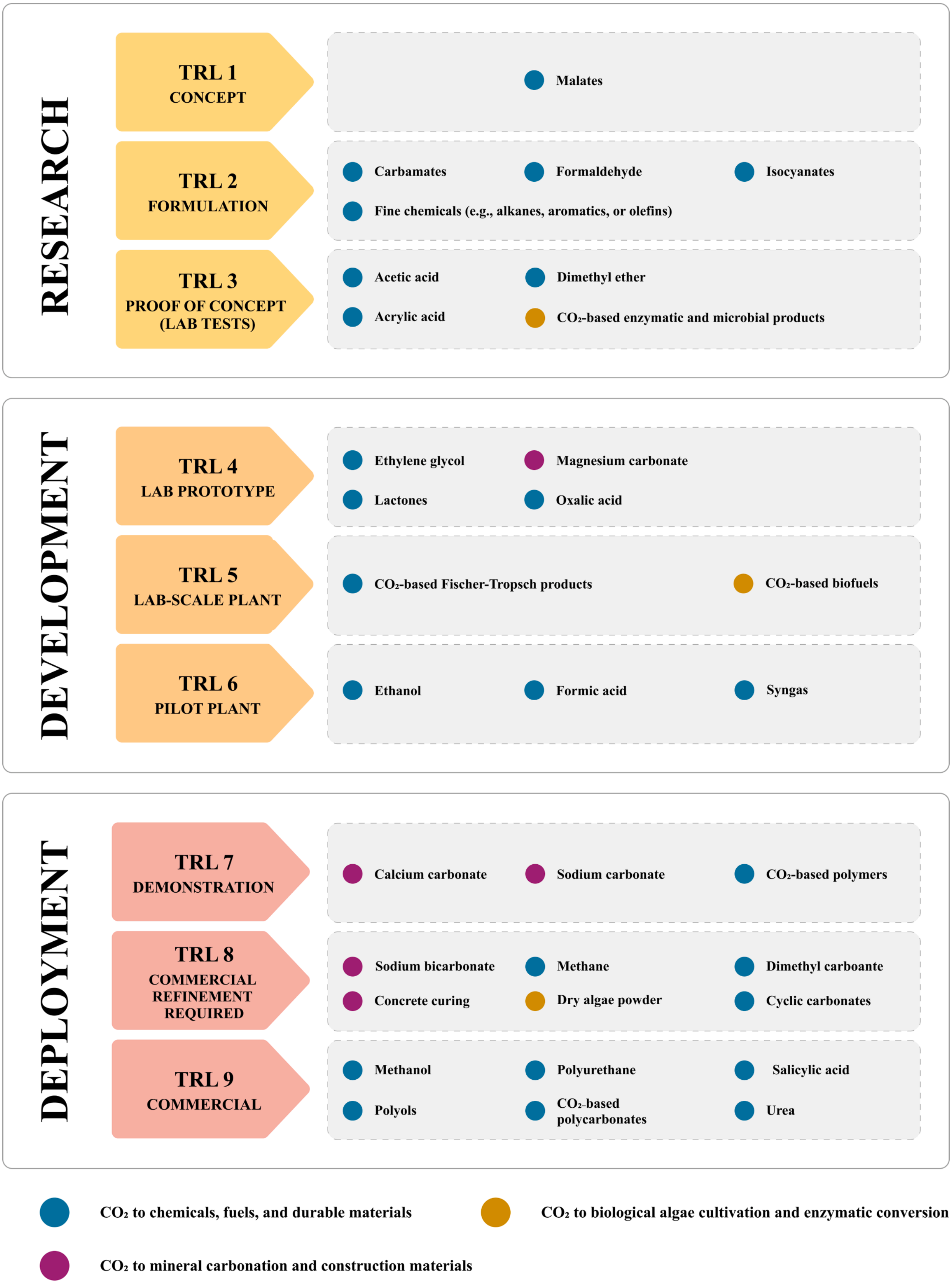
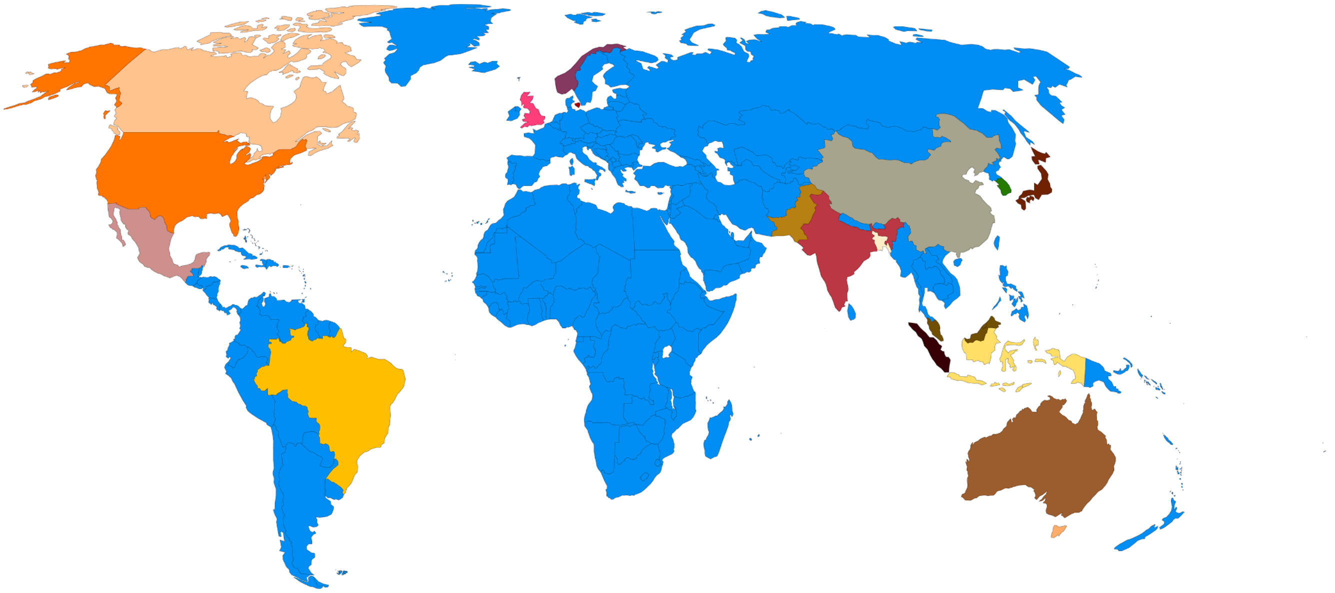


Fig. 27. TRLs for main ways of CO_2 utilization (non-EOR) [163].



●	**United States**	**62.205%**	**(8,061.812 GtCO$_2$)**
●	**China**	**23.746%**	**(3,077.431 GtCO$_2$)**
●	**Australia**	**3.877%**	**(502.43 GtCO$_2$)**
●	**Canada**	**3.117%**	**(403.971 GtCO$_2$)**
●	**South Korea**	**1.569%**	**(203.362 GtCO$_2$)**
●	**Japan**	**1.175%**	**(152.266 GtCO$_2$)**
●	**Malysia**	**1.154%**	**(149.573 GtCO$_2$)**
●	**Mexico**	**0.778%**	**(100.8 GtCO$_2$)**
●	**Norway**	**0.722%**	**(93.626 GtCO$_2$)**
●	**United Kingdom**	**0.599%**	**(93.626 GtCO$_2$)**
●	**India**	**0.495%**	**(64.135 GtCO$_2$)**
●	**Pakistan**	**0.245%**	**(31.702 GtCO$_2$)**
●	**Bangladesh**	**0.163%**	**(21.133 GtCO$_2$)**
●	**Indonesia**	**0.122%**	**(15.855 GtCO$_2$)**
●	**Brazil**	**0.019%**	**(2.47 GtCO$_2$)**
●	**Denmark**	**0.013%**	**(1.629 GtCO$_2$)**

Fig. 28. Worldwide total storage resources by country in late 2021 [31].

5.2. CO_2 storage

CO_2 transported to a specific storage location can finally be sequestrated, which is the most difficult challenge in CCS technology. The last storage step may be divided into three categories: geological, oceanic, and mineral storage. In 2021, according to the CO_2 Storage Resource Catalog, the theoretical capacity of CO_2 total storage resources is approximately around 13,000 Gt across the globe and their abundant availability can achieve Paris Agreement climate targets (1.5 °C scenarios) [5]. The highest geological storage capacity of CO_2 is available primarily in the United States, which represents 62.2% of total storage resources (8,061.812 Gt). The second largest score has China with 23.75% (3,077.431 Gt) and the third, Australia with the result of 3.88% (502.430 Gt). The rest of the countries include the following: Canada (3.11%), South Korea (1.60%), Japan (1.17%), Malaysia (1.154%) and others (2.38%) [31]. The illustrative share of countries in CO_2 total storage resources is given in Fig. 28.

The most proven method is to store carbon dioxide underground by injecting it into an appropriate geological environment or a given geological reservoir/stratum with a specific depth. There are typically few distinct types of geological formations that are examined for CO_2 storage: depleted reservoirs of oil and natural gas; nearly depleted, or unexploited reservoirs of oil and natural gas (CO_2-EOR/CO_2-EGR); deep unmineable coal deposits or coal seams - enhanced coal bed methane (CO_2-ECBM), deep saline aquifer [42]. Only some of the above geological storage options have achieved a TRL of 7 or higher. As a result of the huge capacity for CO_2 storage, CO_2-EOR (enhanced oil recovery) [164], as well as saline formations [165], are widely used in CCS. In 2021, 22 of 27 CCS facilities and projects operating on a commercial scale exploited CO_2-EOR [31], so it has reached the TRL 9. Similarly, 5 of commercial-scale CO_2 storage projects have used saline deposits (TRL 9), which are Sleipner CO_2 Storage, Snøhvit CO_2 Storage, Quest CCS, Illinois Industrial CSS, Gorgon CO_2 Injection [31]. The CO_2-enhanced gas recovery (CO_2-EGR), the depleted oil and gas reservoir, they are still in the demonstration phase (TRL 5–8 [166], or TRL 7 [44]), and CO_2-ECBM is between TRL 2–3 [166].

The waters of the oceans make up the most extensive natural habitat on Earth and also contain the greatest quantity of elemental carbon. In the past, given the amount of carbon dioxide the oceans could absorb by injecting it into the deep ocean to form liquid CO_2 lakes, sequestration in this ecosystem was proposed. Over time, this procedure was declared illegal because of the possibility of leakage, which could cause volatilization into the atmosphere, threatening human life. More importantly, the release of CO_2 into the ocean would first and foremost result in the acidification of seawater and, as a consequence, the destruction of entire marine ecosystems. As it has never been possible to conduct a controlled experiment in which significant quantities of relatively pure CO_2 were injected into the deep ocean [42], any findings on the potential for environmental damage are based on the formulation of technological concepts (TRL 2) [44].

The geological process of mineral storage, also known as mineral carbonation, occurs when CO_2 reacts with alkaline earth metals such as calcium or magnesium from rock formation minerals made up of silicate groups to form carbonate minerals ($CaCO_3$/$MgCO_3$) [167]. These storage methods aim to simulate the process of weathering rocks, which can be observed in nature and that phenomenon. The storage potential of mineral carbonation has been estimated to be 100,000–250,000 GtCO_2. This statistic accounts for all basaltic rocks, a prevalent form of rock, which comprise 70% of ocean basins and 5% of continents on the Earth [16]. Thus, there is a large possibility of CO_2 storage through mineral carbonation on a commercial scale; however, currently the TRL ranges from 2 to 6 [166]. This is related to the need to develop monitoring

Table 12
Comparison of CO_2 storage methods [17,166].

Storage method	Current status	TRL
Saline formations	➢ CO_2 rapid injection at a significant rate (1Mtpa). ➢ Injected CO_2 can be monitored, and storage is permanent. ➢ The tools required to identify, appraise are well established. ➢ Low economic costs.	9
CO_2-EOR	➢ Proven storage locations. ➢ Maximize oil recovery. ➢ More specific monitoring is needed to make sure that the CO_2 injected is being stored permanently.	9
CO_2-EGR	➢ Proven storage locations. ➢ Maximize natural gas and gas condensate recovery. ➢ Tight and low-permeability reservoirs.	7
Depleted oil and natural gas field	➢ Technically mature. ➢ Airtight structures. ➢ Limited capacity. ➢ They have only been applied in demonstration projects.	7
Mineral carbonation (basaltic rocks, ultramafic rocks)	➢ High storage potential. ➢ Storage is safe and durable. ➢ Permeability of rocks is difficult to predict. ➢ Majority of tools for conventional CCS cannot be applied to monitor a CO_2 plume in a basalt.	2–6
CO_2-ECBM	➢ Viable technology and can increase methane production. ➢ The produced methane provides revenue to the operation. ➢ Injection of CO_2 significantly reduces the permeability of coal -additional costs and increasing operational complexity. ➢ ECBM applies only to coal seams which will never be mined.	2–3
Ocean storage	➢ Currently, this method is prohibited by law. ➢ A very risky with unpredictable results. ➢ Itis at stage of formulation of technological concepts.	2

methods for the verification and measurement of CO_2 plumes in basaltic formations. Later in this review, a comprehensive explanation of this approach (CCMC) will be provided. The current status of underground CO_2 storage technology is presented in Table 12.

5.3. Carbon capture and mineral carbonation (CCMC)

CCMC technology (carbon capture and mineral carbonation) is one of the methods of preventing the emission of CO_2, consisting in the reaction of CO_2 with raw materials, including minerals found in nature or alkaline industrial waste, which is particularly worth emphasizing in the context of CO_2 utilization. CCMC provides the possibility to produce construction materials as well as the opportunity to recover valuable ones [168]. Accordingly, CCMC is partially classified as CCS and CCU technology range considering the stage of storage and the possibility of utilization, and may also be considered a waste-to-product valorization sector. That is why its TRL strictly depends on whether the CCMC technology is considered in terms of the storage process itself (TRL 2-6) or the additional utilization of the CO_2-based product (TRL 4 – magnesium carbonates, TRL 7 – calcium carbonates, and sodium carbonates, TRL 8 – sodium bicarbonates, concrete curing), as discussed earlier.

The result of CCMC is the formation of stable and persistent carbonate compounds, commonly found in nature, which are environmentally neutral. This is one of the significant advantages of the CCMC, in addition to reducing CO_2 emissions and waste management. The formed carbonates ensure safe and long-term storage of CO_2 (stable storage conditions over a long period of time with a monitoring-free solution) [169]. The main steps of the CCMC process are shown in Fig. 29, and the possibilities to reuse the final carbonated products on an industrial scale are given in Fig. 30.

In most cases, the CCMC uses natural ores, such as serpentine ($Mg_3Si_2O_5(OH)_4$), talc ($Mg_3Si_4O_{10}(OH)_2$), forsterite (Mg_2SiO_4) and wollastonite ($CaSiO_3$) [168,170] from deposits of basalt rocks. Because they are generally available, there is no need to make additional investments in raw materials. On the other hand, the extraction step of natural minerals itself is a process that consumes a lot of energy (huge reactors) and has negative effects on the surrounding ecosystem (required milling and activation stages usually performed under high temperatures and pressures) [171]. Along with naturally low rates of carbonation, the technology in question presents a great deal of difficulty and expense. An exemplary reaction for wollastonite is presented below [172]:

$$CaSiO_3 + 2CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^{\ -} + SiO_2 \tag{7}$$

Where then:

$$CaSiO_3 + CO_2 + H_2O \rightarrow CaCO_3 + SiO_3 \tag{8}$$

In the case of worldwide alkaline industrial waste for CO_2 mineralization, they include in particular iron/steel slags, pulp/paper industry

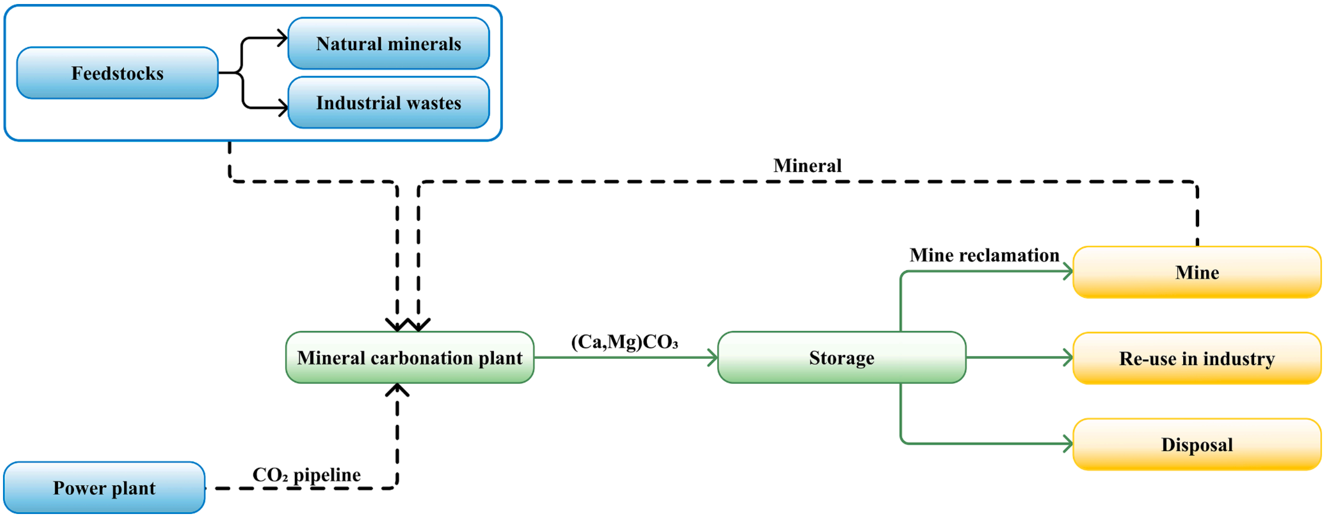


Fig. 29. Illustration of CCMC technology steps.

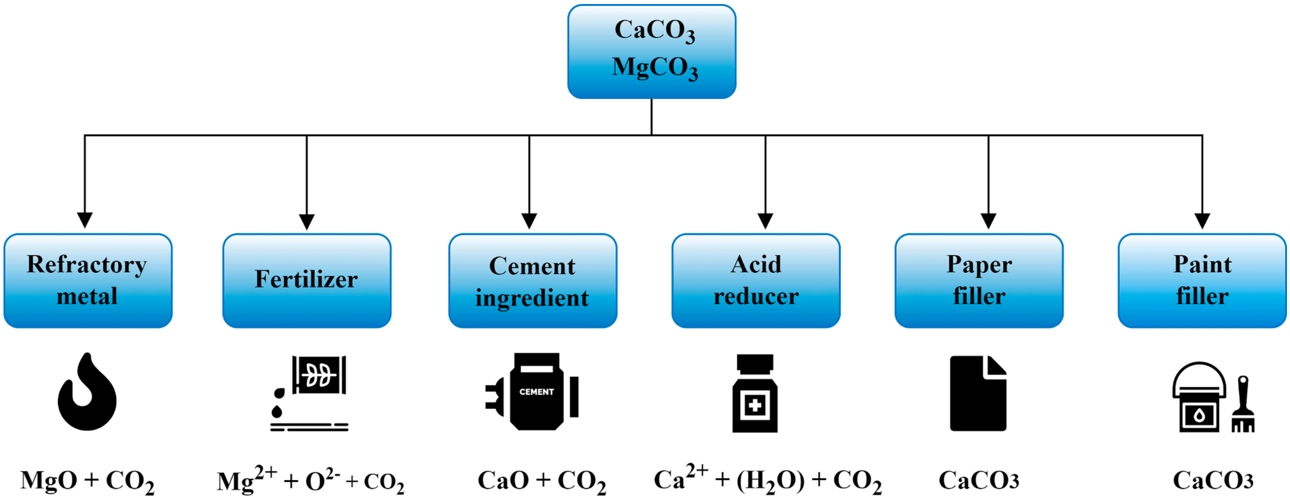


Fig. 30. Possibilities of reusing mineral carbonation products in industry [174].

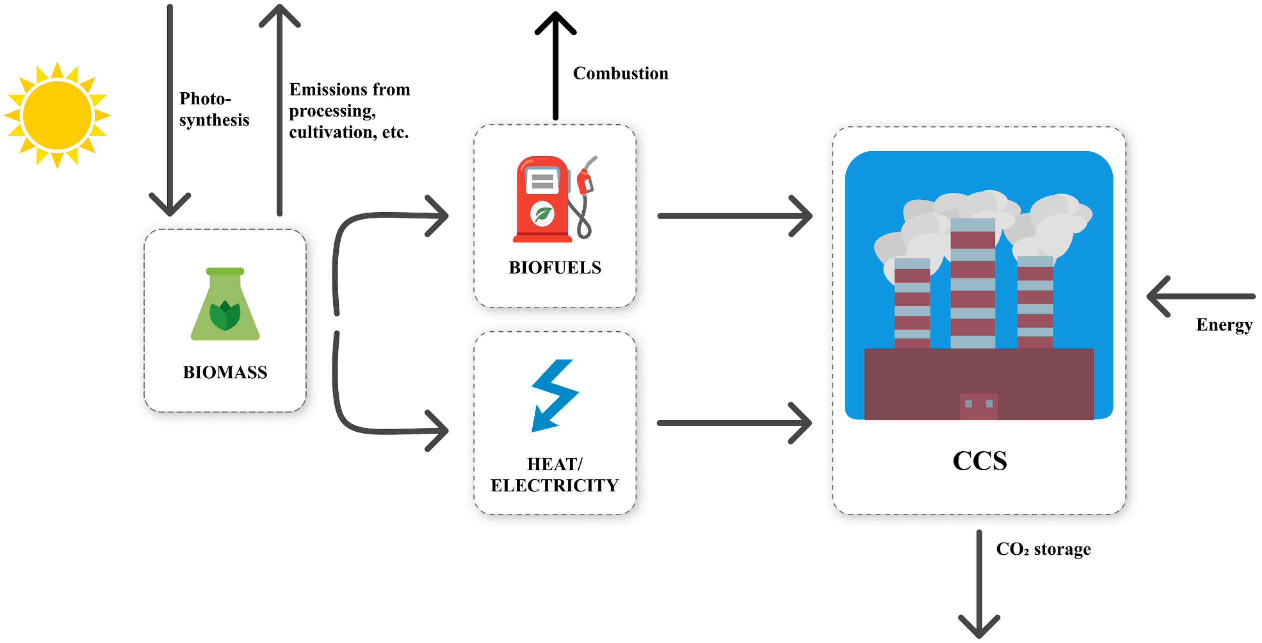


Fig. 31. BECCS technology diagram.

wastes, mining/mineral processing wastes, cement/concrete waste, incinerator residues (blast furnace slags) and wastewaters [171,173]. Furthermore, the commonly waste used in the CCMC technology is also coal fly ash, which is one of the coal-fired, or fuel combustion product. Within the context of the mineral carbonation process, it is considered a great option for use alone or in combination with mineral silicates to sequester CO_2 [170]. Because of solid wastes substantially greater reactivity and inherent alkalinity, they are much more suited for the process of CO_2 mineralization and are readily available in close proximity to industrial locations. The most recent findings from this line of study indicated that roughly 310 $MtCO_2$ should be credited to the direct reduction by mile-on of alkaline solid wastes over the globe [171]. According to this estimation, mineralization with iron and steel slags was responsible for 43.5% of the total amount of direct CO_2 reduction, the use of cement wastes for 16.3%, mining wastes were for 13.5%, and the use of coal combustion ashes was for 12.3%. Compared to the indirect CO_2 reduction by utilization of carbonated products, the difference is very clear. This path of CCMC reached 3.7 $GtCO_2$, where the largest share has cement/concrete wastes (55.7%), subsequently coal combustion wastes (17.4%), iron and steel slags (13.6 %) and mining wastes (8.0%) [171].

6. Bioenergy with carbon capture and storage (BECCS)

When discussing the potential to reverse the effects of climate change, the terms biomass, bioenergy, and biofuels are becoming an increasingly common topic of discussion as alternative energy sources that are carbon neutral compared to fossil fuels. The bioenergy with carbon capture and storage technology involves not only the generation of energy from biomass (forestry residues, energy crops or agricultural residues, and biodegradable waste products), but also the combined effect of photosynthesis with the subsequent capture of CO_2 and its geological storage [175]. Hence, bioenergy production coupled with carbon capture and storage (CCS) is referred as BECCS and has reached TRL 7 in industry sector, or TRL 4 in power sector (Fig. 31) [44,176]. BECCS has the potential to contribute a large amount to achieve the required severe reduction in CO_2 emissions, whether used individually or as part of a cost-effective unified strategy in an effort to achieve negative emissions and a net reduction in atmospheric CO_2 emissions [177]. The magnitude of the impacts of BECCS varies on the scale of deployment, the location of biomass cultivation (includes emissions associated with earlier land use and indirect change in land use change), initial land use, type of land, type of bioenergy feedstock, initial carbon stocks, climatic region or management regime and the final energy carrier generated [18,178].

Furthermore, the evaluation period of BEECS is unimaginably significant and closely influences the amount of GHG emissions per unit of bioenergy produced (emission factors - EFs), due to the reality that they contribute to emissions caused by changes in land use, as well as foregone sequestration. Numerous regions have been reported to generate power with negative EFs, resulting in a substantial global power supply and potential connection with CCS [178]. Across a range of representative concentration pathways by 2030, 2050 and 2100 presented by IPCC (scenarios that include timeseries of emissions and concentrations of the full suite of GHGs) for several climate change mitigation strategies, the options with largest potential for carbon dioxide removal is delivered by BECCS, achieving the maximum value for the most optimistic forecast of 0.1, 6.8 and 14.9 $GtCO_2$ per year, respectively [18]. Although the overall potential of BECCS may seem substantial, it is hard to realize owing to the limited land resources of mankind. Even when sustainability concerns are considered, the BECCS potential falls to a maximum of 5 $GtCO_2$ per year in 2050 [5]. Furthermore, experts' confidence in the precise potential of BECCS is poor due to widely varied assumptions, including: the amount of energy crops produced, incomplete estimates of processes occurring in ecosystems, and emissions associated with native vegetation clearance for energy crops growth and subsequent processing [5,18].

The applicability of BECCS is not universal, and certain nations and localities will be much more suited to the large-scale deployment of BECCS considering biomass availability than others [177]. The challenges facing BECCS also emerge in terms of the consequences on: land use competing with food production, food consumption, and thus food security; environmental impacts (water scarcity, the constraints on negative emission potential imposed by collateral emissions, and change in land use change); comparatively poor energy efficiency compared to fossil fuels; cost penalties (retrofitting or integrating CCS technologies in bioenergy systems); and the repercussions on biodiversity resulting from the heavy use of land, water, and nutrients [18,175,178]. Another crucial drawback of BECCS is an apparent overreliance on it in models and frameworks for developing policies to mitigate the effects of climate change, where uncertainties appear for scaling up to the commercial scale [175].

The problem mentioned above can be solved by specific actions; therefore, targeted economic and social activities are recommended [18,175,176]:

- favoring agricultural, forestry, municipal waste, and algae as biomass sources;
- it is necessary to conduct in-depth research on the topic of the effect of collateral emissions and the real negative emission potential of the energy, transportation, and processing sectors;
- integration of bioenergy into sustainably managed agricultural landscapes;
- strong routes to public and governmental backing, which will be essential for wide-scale adoption and successful deployment of BECCS;
- utilize the co-firing of coal-biomass with CCS;
- continue advanced studies of the effects of the technological advancement of BECCS for biofuel production as an option to reduce costs and improve energy efficiency;
- in order to account for the unknowns posed by BECCS, future models will need to make necessary adjustments and adaptations and anticipate the worst-case scenarios for large-scale implementation;
- development and formulation of plans for the incorporation of BECCS into global environmental programs.

7. Conclusion

One of the methods of limiting global warming to meet the long-term climate targets of the Paris Agreement, or European Green Deal, and consequently reaching net zero emissions by 2050 is the CCUS. Until the share of new energy carriers in the world total energy supply (nuclear energy, RES, hydrogen, or methane) increases to a certain point, carbon capture utilization and storage is essential in terms of its role in the energy transition. Over the past few decades, it has become a proven successful climate mitigation tool in all ways, with 135 global facilities so far and a total CO_2 capture capacity of 149.3 Mtpa. In view of above, this review covers and discusses a wide variety of technologies utilized at different scales in the CCUS system related to CO_2 capture, separation, transport, storage, and utilization, as well as critically assesses their technical merits in the sense of the technology readiness level (TRL). Consequently, TRLs provided consistent and universal evaluations of technical maturity each of them, based on a scale of 1 to 9, and enabled to illustrate scaling up by research, development, and deployment stage. Furthermore, we highlight significant disadvantages of specific technologies that have to be resolved, as well as difficulties that need to be addressed further in regards to the CCUS R&D projects.

Based on our investigation there is the significant apparent inconsistency between strict goals for decarbonization and the delayed implementation of CCUS on industrial scale. In regard to this situation, the findings and future CCUS research paths would be highlighted and proposed for consideration as follows:

- Many vital elements of CCUS system have different technological maturity that hinder it complete commercialization in the major industrial sectors, considered the largest emitters of CO_2 (power, chemical, cement, iron, and steel). Especially, where CO_2 capture and storage in geological formations, or utilization is connected with other technologies.
- By the specific steps of CCUS, today's maturity of CO_2 capture is mainly influenced by the plant application, technological configurations, separation technology and the type of fuel used in industrial facilities.
- Of the three main capture configurations, only post-combustion capture (power generation/aqueous amines) and pre-combustion capture (natural gas processing) are widely used commercially (TRL 9). Ox-fuel combustion is investigated between lab prototype and demonstration stage with TRL ranging from 4 to 7.
- To enhance the overall performance of CO_2 separation methods, thus increasing the TRL at the same time, is to create separation hybrid systems (polymeric membranes with physical adsorbents (TRL 6), cryogenic method (TRL 6), or liquid solvents (TRL 4)). This enables to overcome the barriers of a single technique and accumulate benefits from both processes, resulting in greater efficiency and lower costs.
- CO_2 transport is strictly based on ships, shore and offshore pipelines, which are currently used worldwide (TRL 9). In the case of rail and road tankers, their intensive development is recommended in specific regions of the world.
- The most examined geological formations for CO_2 storage are saline formations and unexploited reservoirs of oil with TRL 9. Other storage methods require more commitment to criteria for evaluating storage sites, CO_2 behavior in reservoirs, and techniques for assessing CO_2 storage capacity.
- CO_2 conversion to large-scale production, e.g., plastic, fuels, or synthetic gas, possess a much greater impact on the overall reduction of CO_2 emissions and higher TRL than its direct application as solvent, working or heat transfer fluid.

In summary, determining the current TRL for each element of the past and present large-scale CCUS projects and their established scientific contribution is crucial. It represents the progress path and the guide to maximize their commercial implementation in the industry, resulting in a larger and more favorable influence within the context of the economics of carbon management. Therefore, it is highly advised to create global databases of current research in different phases from concept to commercial use, both for capture, transport, storage and utilization, making it possible to share information. That activity will be a great fundamental theoretical source and indicator for currently low-TRL R&D projects and potential investor participation, which will ultimately directly affect a reduction of the negative impact of CO_2 emissions on the environment and achieve the goals of an increasingly stringent set of policy initiatives.

CRediT authorship contribution statement

Bartosz Dziejarski: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Visualization, Project administration, Writing – original draft, Writing – review & editing. **Renata Krzyżyńska:** Conceptualization, Investigation, Writing – review & editing, Supervision. **Klas Andersson:** Conceptualization, Investigation, Writing – review & editing, Supervision.

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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