

Review Article

Recent progress in carbon dioxide capture technologies: A review

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Abstract: The continuous increase in anthropogenic CO₂ emissions is widely acknowledged as one of the main reasons for global climate change. To address this issue, significant advancements have been made in developing CO₂ capture and utilization technologies that offer new solutions for mitigating carbon emissions and promoting a carbon economy. In this review, we summarize the recent research progress in CO₂ capture and separation technologies, including pre-combustion, post-combustion, oxy-fuel combustion, chemical looping combustion and calcium looping combustion. Among these technologies, post-combustion is seen as one of the most promising options for reducing CO₂ emissions from existing power plants, as it can be easily integrated into existing facilities without requiring major modifications. Therefore, the second section of this article focuses on the various post-combustion processes and technologies, such as physical absorption, amine scrubbing, dual-alkali absorption, chilled ammonia, membrane separation, and solid adsorption, with a particular emphasis on most recent research reports. As amine-based chemical absorption is the most leading post-combustion CO₂ capture technique, the third section summarizes the recent development in amine-based absorption technology by covering conventional and emerging types of absorbents such as single amine, blended amine, biphasic amine, and non-aqueous amine processes. The different liquid absorption-based process is compared in terms of regeneration energy consumption, CO₂ intake capacity, and optimal operating conditions, and the comparison data is summarized in tables. A critical literature review and comparison of various techniques show that non-aqueous amine absorbents can be promising alternatives to the conventional monoethanolamine (MEA) process. The goal of this review is to provide strategies and perspectives for accelerating the further study and development of CCS technologies.

Keywords: post-combustion technology; amine capture process

1. Introduction

The fast development of modern society has resulted in an increase in CO₂ emissions from 1.95 billion metric tonnes in 1900 to 34.81 billion metric tonnes in 2020. Each year, more than 30 billion tonnes of CO₂ is further emitted into the atmosphere, aggravating the climate change issue^[1]. With CO₂ emissions increasing every year, the efforts Cesare Marchetti, an Italian physicist, proposed a method for controlling CO₂ levels in the air in the 1970s, in which the CO₂ is collected at appropriate concentrated emission points and transferred to the deep sea or underground caverns for permanent storage^[2]. In 2005, IPCC Working Group III introduced the concept of carbon capture and storage (CCS) in a special report and addressed the relevant technologies of CCS^[3]. The purpose of the IPCC report was to alert the policy-makers, engineers, and researchers about global warming due to CO₂ emissions and the need to develop practical solutions to deal with this problem^[4]. Since then, CCS has been widely recognised as an effective technology for reducing atmospheric CO₂ levels and is increasingly being used in industrial carbon capture^[5-7]. In 2020, 26 commercial CCS plants were in operation around the globe, with many in early development or under construction. Of these 26 operational plants, the vast majority were used for natural gas processing, while others were used in power plants, fertilizers, ethanol

production, hydrogen (H₂) and other industries. The estimated capacity of these plants to capture and permanently store the CO₂ is around 40 million tonnes of CO₂ per year.

CO₂ is used in the beverage industry, food preservation, urea manufacture, water purification, enhanced oil recovery, cement production, and polymer synthesis, making the worldwide CO₂ utilisation around 232 million tonnes per year^[7,8]. However, only under 1% of the CO₂ that is released into the atmosphere at this time is used as a raw material in the aforementioned industries^[8-11], clearly indicating that a rapid growth in the efforts and scale of CO₂ capture technology is required. An important pillar of CO₂ abatement efforts is the concept of circular economy, where captured CO₂ can be used to make valuable commodities like petroleum products and high-value chemicals. The carbon in CO₂ molecules is thermodynamically stable because it is at its highest oxidation state (+4), its chemical conversion to target chemicals is difficult, and therefore, energy is required activate and convert CO₂ through a redox reaction, where the CO₂ is reduced (accepts electrons)^[12-14]. Shifting the focus to CO₂ capture involving conversion, the oxidation state reveals the existence of eight distinct reduction levels, each yielding its unique product results and potential for synthesis. The redox reaction highlights two essential aspects within the reduction procedure: the introduction of hydrogen and the elimination of oxygen^[15,16]. The redox reaction can undergo through photochemical, thermochemical, electrochemical, and biological methods, each of which have distinct advantages^[17]. The use of CO₂ in resource recovery in chemical and oil industry (Enhanced Coal-bed Methane Recovery, Enhanced Oil Recovery (EOR)) has the highest potential for non-captive demand^[11]. The amount of CO₂ utilised globally is below 200 Mt per year, while the global anthropogenic CO₂ emission is over 32,000 Mt per year^[18]. The development of CO₂ capture helps to accelerate the deployment of carbon capture utilization and storage (CCUS), which pays attention to not only the storage of CO₂ but also the use in industrial applications^[19]. CCUS makes it possible to allow the continued use of fossil fuels while maintaining stable concentrations of greenhouse gases in the atmosphere. Every element within the CCUS value-chain, as illustrated in **Figure 1**, plays a vital role in ensuring the economic and technical feasibility of the CCUS process.

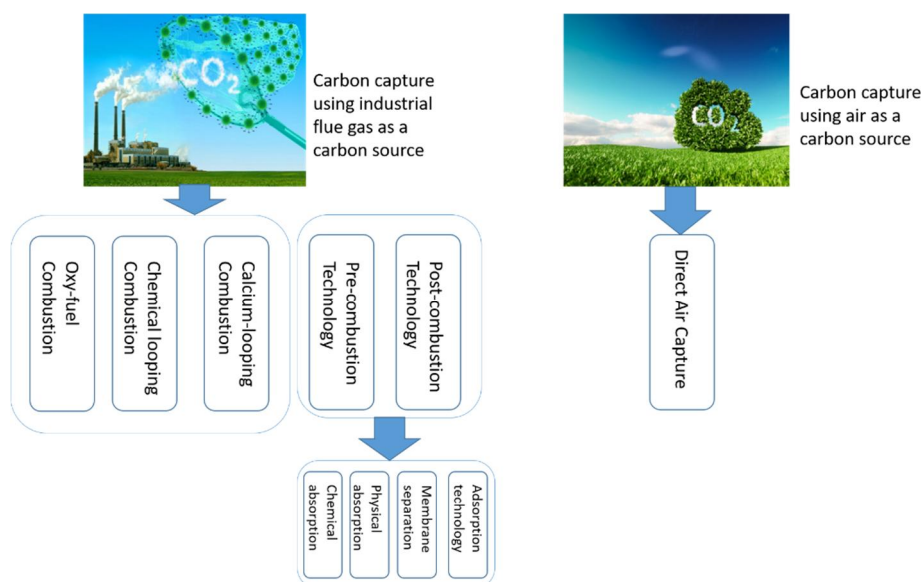


Figure 1. Pathways of current technologies of CO₂ production, capture and separation.

Currently, a significant reduction in CO₂ emissions is required to align with the COP21 agreement. The primary hindrance in implementing carbon capture and storage (CCS) is the massive economic penalty of a CO₂ capture unit that can ultimately increase the price of electricity by 33%. Currently, the estimated cost of capturing CO₂ using existing technology is ~\$60 per metric tonnes of CO₂^[20] and a significant reduction in the

economic penalty is required to make CCS a profitable option and to attract investors from government and private sectors. To overcome this challenge, the scientific community around the globe is putting their efforts to reduce the cost of carbon capture to around \$20 per metric tonnes of captured CO₂^[21].

Nevertheless, numerous technical hurdles confront the possible widespread integration of Capture in power plants. **Figure 1** outlines the streamlined routes of present CO₂ production, capture, and separation technologies. The current technologies of CO₂ capture includes pre-combustion technology, post-combustion technology, oxy-fuel combustion technology and chemical looping technology^[22]. Direct air capture (DAC) is a specific type of carbon capture that involves capturing carbon dioxide directly from the air using specialized equipment, as opposed to capturing it from industrial sources or power plants^[23–25]. DAC technology uses chemical reactions to capture CO₂ and remove it from the atmosphere. The key difference between DAC and other carbon capture technologies is that DAC captures CO₂ from the air, whereas other carbon capture technologies capture CO₂ from industrial or power generation processes. This means that DAC has the potential to capture CO₂ from a wide variety of sources, including sources that are difficult to capture using other technologies, such as transportation or agriculture^[26,27].

In this review article, we thoroughly review and analyse the recent innovations and advancement in the carbon capture and storage (CCS) technologies. Section 1 focuses on the principles and recent research advancements of the four major CCS technologies, i.e., pre-combustion CO₂ capture, post-combustion CO₂ capture, oxy-fuel combustion, and chemical looping combustion. Section 2 provides an overview of various post-combustion processes, including process configurations and principles. Section 3 delves into advancement in the absorption media by discussing and reviewing the novel amine absorbents, blended amine, biphasic solvent, and non-aqueous absorbents. In Section 4, as an important part of CCUS, the CO₂ utilization is summarized. In Section 5, we summarize this paper and comparing and analysing the key benefits and challenges of each technology. With an aim of analysing the recent research, the scope of this paper is to summarize and analyse the research efforts and innovation made in the field of carbon capture technology after 2014.

2. CCUS technologies

CCUS technology includes technologies for CO₂ capture, transport and storage, and CO₂ utilization. The CO₂ capture alone accounts for more than 70% of all operating expenses of CCS^[28]. Three main technologies in practice for CO₂ capture are pre-combustion CO₂ capture, post-combustion CO₂ capture, and oxy-fuel combustion^[29]. Chemical looping combustion is a non-conventional combustion method with an inherent CO₂ capture capability. In the next section, we shall thoroughly summarize the developments and current status of these technologies.

2.1. Pre-combustion CO₂ capture technology

Pre-combustion carbon capture technology removes CO₂ from the streams of fossil fuels or biomass prior to combustion^[30]. The conventional pre-combustion carbon capture technique layout is shown in **Figure 2**. In the pre-combustion CO₂ capture, fossil fuels first undergo a fuel conversion process where gasification takes place. In the gasification process, fossil fuels are partially oxidized in steam and oxygen to produce syngas (CO + H₂), as described in Equation (1). The syngas is further transformed into CO₂ and additional H₂ by using a catalytic reactor (also called a converter) (Equations (2) and (3)). The resulting hydrogen-rich syngas can be used for power generation after the CO₂ has been separated out. The pre-combustion capture approach is primarily utilized in conjunction with either integrated gasification combined cycle (IGCC) or natural gas gasification combined cycle (NGCC). **Figure 3** displays the layout of the IGCC combination with pre-combustion equipment.

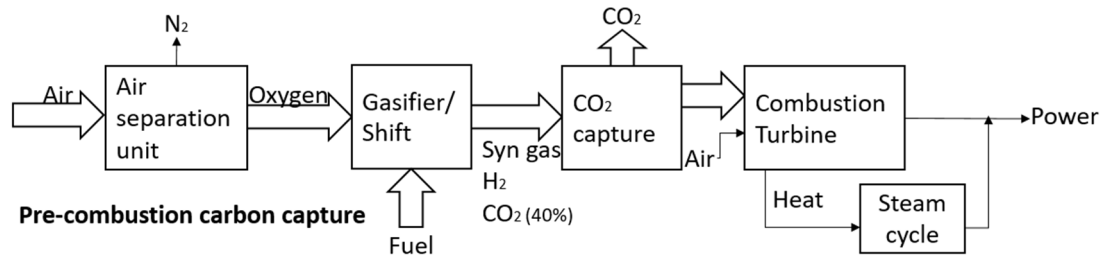


Figure 2. The process flowsheet of pre-combustion carbon capture.

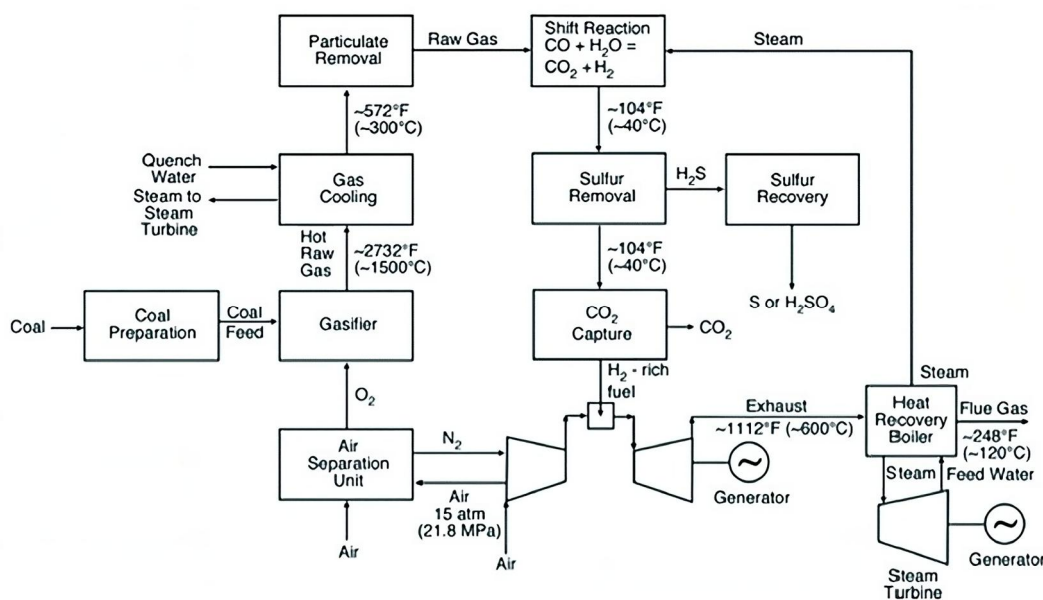
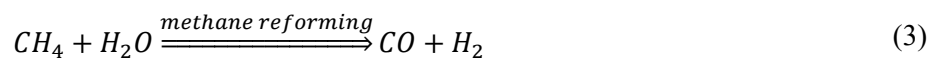
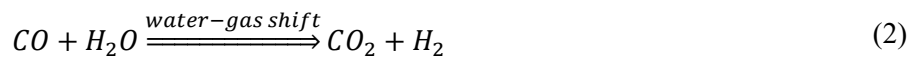


Figure 3. A schematic layout of an IGCC power plant using pre-combustion carbon capture. Reproduced with permission from Sifat and Haseli^[21].

In general, pre-combustion CO₂ capture is environmentally friendly and energy efficient. It transfers energy from carbon fuels to hydrogen fuels by gasification process^[31]. The combustion product of hydrogen is water, instead of CO₂, and no other pollutants such as SO_x are produced in this way as conventionally burning the carbon fuels do. Although this process is complex and expensive than other CO₂ capture technologies, the high pressure (2–7 MPa) and a high concentration of CO₂ (15%–60%) in the gas stream requires less energy for CO₂ separation and CO₂ compression than other CO₂ capture technologies^[20]. Most recent research on the pre-combustion CO₂ capture technology is summarized in **Table 1**. Mainly, research efforts are focused on reducing the thermal and economical penalties of pre-combustion capture technique. Park et al.^[32] investigated several physical absorbents in the gas separation process, and found the Selexol process the most energy-efficient. Other advanced gas separation technologies include membrane separation, hydrate based gas separation and ionic liquid separation^[33].

Table 1. Recent research progress of pre-combustion technologies.

Ref	Year	Separation techniques	Key findings
[32]	2015	Selexol physical absorption	Utilized three physical absorbents, in terms of energy consumption, Selexol was discovered to be the most effective pre-combustion technique
[33]	2015	Amine-TiO ₂ adsorption	Mesoporous amine-TiO ₂ was employed. This low-cost sorbent was stable and readily regenerable without capacity or selectivity loss.
[34]	2016	Membrane separation	Under high pressure and temperature, the separation performance of ionic-liquid based membrane was tested, the separation effectiveness is decreased in high pressure.
[35]	2016	Hydrate based gas separation	The optimal concentration of tetrahydrofuran (THF) at 282.2 K and 6 MPa was 5.56 mol%.
[35]	2016	Hydrate based gas separation	Hydrate-based carbon capture was found to be most suitable with the combination of 5% TBF and 10% TBAB.
[36]	2018	Membrane contact separation	Investigating the cost of CCS by using membrane contactor with PSA process, which was not suitable for commercial usage.
[37]	2018	Ionic liquid physical absorption	They demonstrated that utilizing ionic liquid for carbon absorption provides comparable results to Selexol method.

2.2. Post-combustion technology

Post-burning capture (PCC), often known as the “end-of-pipe” CO₂ separation technology, removes CO₂ from flue gases after the combustion of fossil fuels or biomass. The left panel of **Figure 4** provides a flow chart of post-combustion CO₂ capture. PCC technology commonly collects CO₂-contained flue gas from conventional oil, coal, and natural gas power plants’ flue emissions. Typically, low CO₂ concentration flue gas is released from the power plants at atmospheric pressure. The CO₂ is selectively captured and then pressurized through a compression unit before transporting it, while the CO₂-free flue gas is released to the atmosphere. PCC is currently the most widely used capture method because compared to the other carbon capture technologies, it is easy to retrofit to existing power plants, can handle large gas volumes, and can achieve good CO₂ separation rate.

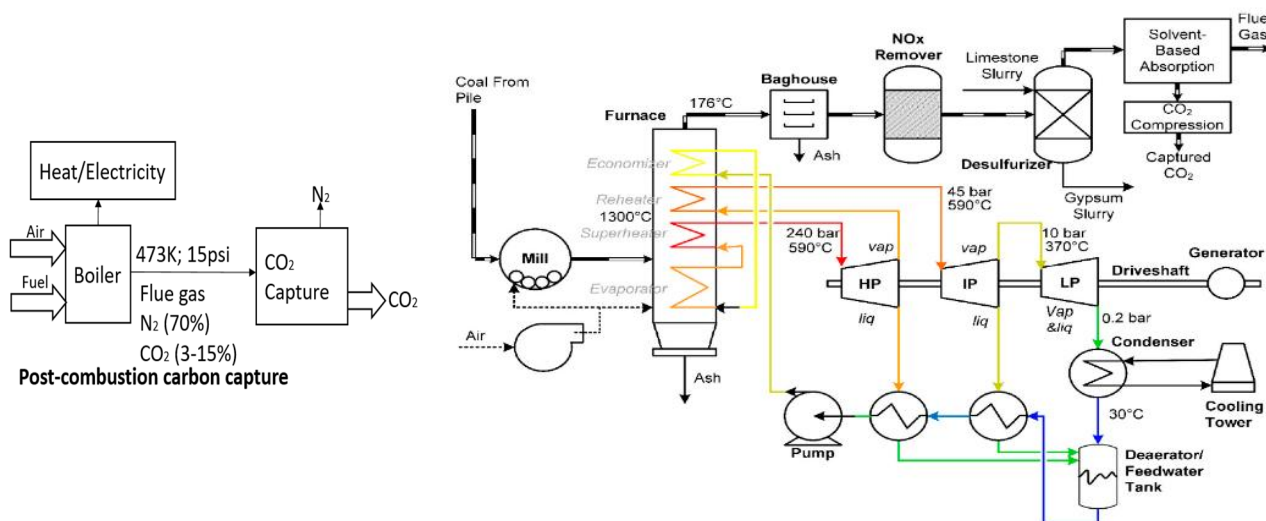


Figure 4. Left: process flowsheet of post-combustion carbon capture. Right: post combustion carbon capture power plant operating with natural gas as the fuel. Reproduced with permission from Sifat and Haseli^[21].

Nonetheless, there are several challenges to this post-combustion technique including high flue gas temperature and significant parasitic load stems from the low CO₂ concentration in combustion flue gas, leading to associated expenses in operating the capture unit to enhance CO₂ concentration (beyond 95.5%).

This elevated concentration is necessary for effective transport and storage^[38–40]. Large amounts of flue gas containing low CO₂ concentrations (typically 4%–14%) need to be treated, which requires a vast volume of the separation unit and high capital investment as well. In addition, the flue gas also contains fly ash, NO_x, and SO_x which need to be removed before the PCC, increasing the operation cost in the existing separation process. Mainly, chemical absorption method is employed for post-combustion CO₂ capture using alkanolamines as absorbents.

Right panel of **Figure 4** depicts the configuration of a natural gas power plant integrated with PCC. MEA, a primary amine, is generally employed to scrub CO₂. The burning of natural gas produces heat, which is subsequently used to create steam. Then steam is transformed into electricity by steam turbines. In the absorber column, MEA removes CO₂ from exhaust flue gas, and the CO₂-loaded MEA is regenerated in the stripper column by heating up to 120–150 °C, where high-purity CO₂ is collected from the top of the stripper column. Refreshed MEA is then recycled to the absorber column for cyclic use. Thermal degradation of amine absorbent and high energy penalty for solvent regeneration are the main challenge of the PCC process. In particular, the thermal energy required for amine regeneration accounts for up to 70% of the total operational cost^[41].

In efforts to enhance the PCC (post-combustion capture) process performance, innovative designs for amine processes and absorbents have been proposed. Ahn et al.^[42] have explored nine distinct process configurations, each aiming to curtail the steam demand in the amine capture process. This reduction would mitigate the extent of modifications needed in existing steam cycles when retrofitting a carbon capture unit to a power plant. The study revealed that, in comparison to the conventional configuration, the integration of absorber intercooling, condensate evaporation, and lean amine flash could bring about a 14.1% decrease in total energy cost. Surprisingly, when taking stripper overhead compression configuration, the reboiler heat duty decreased from 3.52 GJ/ton CO₂ to 2.41 GJ/ton CO₂. The stripper overhead compression configuration reduced the energy consumption by maximising heat recovery at the heat exchanger. Non-aqueous MEA has also been researched by Bougie et al.^[43, 48]. Compared to 30 wt% aqueous MEA, the energy consumption of 20 wt% MEA in DEGMEE decreased by 78%. The primary factor contributing to decreased energy consumption during absorbent regeneration is the low specific heat capacity of DEGMEE. **Table 2** contains more details of current research on post-combustion carbon capture processes.

Table 2. Recent research progress of post-combustion technologies.

Ref	Year	Separation techniques	Abstract of techniques
[42]	2013	Chemical absorption	Investigated 9 different amine process configurations and evaluating their total energy consumption.
[44]	2016	Membrane absorption	A mathematical model was proposed to identify the optimal operating parameters for CO ₂ absorption in the hollow fibre membrane.
[45]	2017	Chemical absorption	Investigated the carbon capture performance of more than 30 amine solutions. 2-ethylaminoethanol was deemed superior due to its excellent CO ₂ absorption capacity and low regeneration energy.
[46]	2017	Chemical absorption	A two-stage stripping process was developed, where the secondary stripper utilizes the wasted heat from the primary stripper, leading to a reduction in overall heat and energy consumption.
[47]	2018	Membrane absorption	A 2D model of piperazine membrane absorption system was proposed. For ideal performance, the optimal gas velocity, CO ₂ concentration, and solvent are investigated.
[48]	2019	Chemical absorption	Non-aqueous MEA process was proposed. MEA/DEGMEE absorbent could decrease the energy consumption by 78%.

2.3. Oxy-fuel combustion technology

Oxy-fuel combustion is basically a modified post-combustion technology. **Figure 5** provides a flow chart of oxy-fuel combustion CO₂ capture. In this technique, fuel is burnt in the presence a high-purity oxygen stream (>90%) and thus major components of the flue gas stream are CO₂ and water^[49]. Air separation units, typically cryogenic separation, are used to separate and concentrate the oxygen from the ambient air for combustion. Another critical unit of this process is the boiler, also called the combustion chamber, which is a key unit determining the overall thermal and economical penalty of oxyfuel combustion. Modern boilers can significantly decrease SO_x and NO_x emissions and increases the fuel combustibility^[21]. Since the flame temperature in the boiler becomes too high when the fuel is burned in pure oxygen, recycling a portion of CO₂-rich flue gas into the boiler to decrease the burning temperature is generally required.

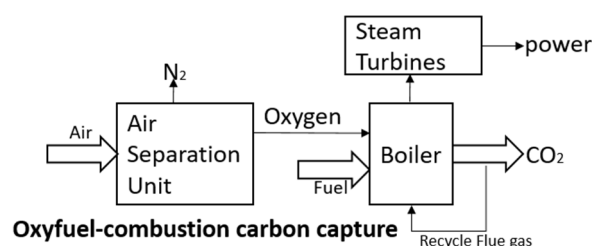


Figure 5. The process flowsheet of oxy-fuel combustion carbon capture.

Due to the absence of N₂, the oxy-fuel combustion process can be more cost-effective than other techniques for CO₂ capture because N₂ consumes a huge amount of energy during fuel combustion. Another significant benefit of oxy-fuel combustion is that the flue gas contains a high concentration of CO₂ (65%–80%), in contrast to the flue gas of a conventional power plants where CO₂ concentration is generally low (12 to 16%). Therefore, the final CO₂ separation is achieved by condensing and knocking out the liquid water to produce a high-purity stream of CO₂. However, the researchers have discovered that oxy-fuel combustion demonstrated 1%–5% less efficiency than other capture technologies^[50]. Other drawbacks of oxy-fuel combustion are high operating expense on high purity O₂ production, the large amount of electricity consumed in this process, and unavailability of a low-cost method to produce pure O₂. Moreover, the concentrated high-purity O₂ collected in the combustion chamber of oxy-fuel technology leads to several problems, such as corrosion, fouling, high maintenance costs, and safety issue^[30,31].

Lately, research efforts are focused on designing novel boilers and energy-efficient O₂ separation methods, and evaluating the influence of recycled water vapour on flame temperature. Vellini and Gambini^[51] analysed and integrated the membrane separation process in an oxy-fuel combustion process. Their results have shown promising performance, and the cost of CO₂ decreased from €40 per tonne to €16 per tonne in IGCC. Further membrane configuration to oxy-fuel combustion was studied by Falkenstein-Smith et al.^[52], where a high CO₂ selectivity is achieved (87.5%) through a novel oxygen transport membrane. Instead of flue gas, supercritical steam is employed as the recycled media in Clean Energy Systems (CES)^[53]. The fuel is combusted in the boiler with supercritical steam, and then mixed gas-contained steam is transported to turbines for power generation. This CES configuration is considered an option for application in the oxy-combustion of natural gas. Latest research on oxy-fuel combustion is summarized in **Table 3**.

Table 3. Recent research progress of Oxy-fuel combustion technologies.

Ref	Year	Abstract of techniques
[51]	2015	An examination was conducted on a revolutionary power plant utilizing a supercritical steam cycle, combined with CO ₂ collection and the utilization of oxy-fuel combustion.
[52]	2016	An evaluation was performed on the CO ₂ selectivity and O ₂ permeability of a ceramic membrane catalytic reactor.
[54]	2017	Super critical CO ₂ cycles was investigated in energy generating.
[55]	2017	An investigation was conducted on the impact of recuperator performance on a semi-closed oxygen combustion mixed cycle.
[56]	2018	The thermal effect of CO ₂ concentration in oxy-combustion process, the non-linear temperature drops when CO ₂ was added.

2.4. Chemical looping combustion technology

Chemical looping combustion (CLC) technology is used to realize fuel combustion in a nitrogen-free environment. Richter and Knoeke^[57] first proposed it in 1983 to reduce the energy loss of fossil fuel combustion. IPCC has considered the CLC process as one of the cheapest carbon capture technologies^[58]; hence, it attracts much interest from researchers.

There are two main reactors employed in the CLC process; one carrying air, called air reactors, while the other containing fuels, called fuel reactors. The left panel of **Figure 6** displays a schematic diagram of the CLC process. In the air reactor, the reduced metal particles are moved to be oxidized by oxygen. The exit gas from the air reactor mostly consists of nitrogen with a trace quantity of oxygen, and it is possible to direct purge into the atmosphere without further purification^[21]. After oxidation, the solid oxygen carrier flows to the fuel reactor. In the fuel reactor, the fossil fuel is oxidized to CO₂ and H₂O while the metal oxides react with the fuel, then the metal oxides are reduced to solid metal particles. These solid metal particles are also called metal oxygen carriers (MOC) and are recycled in the air reactor.

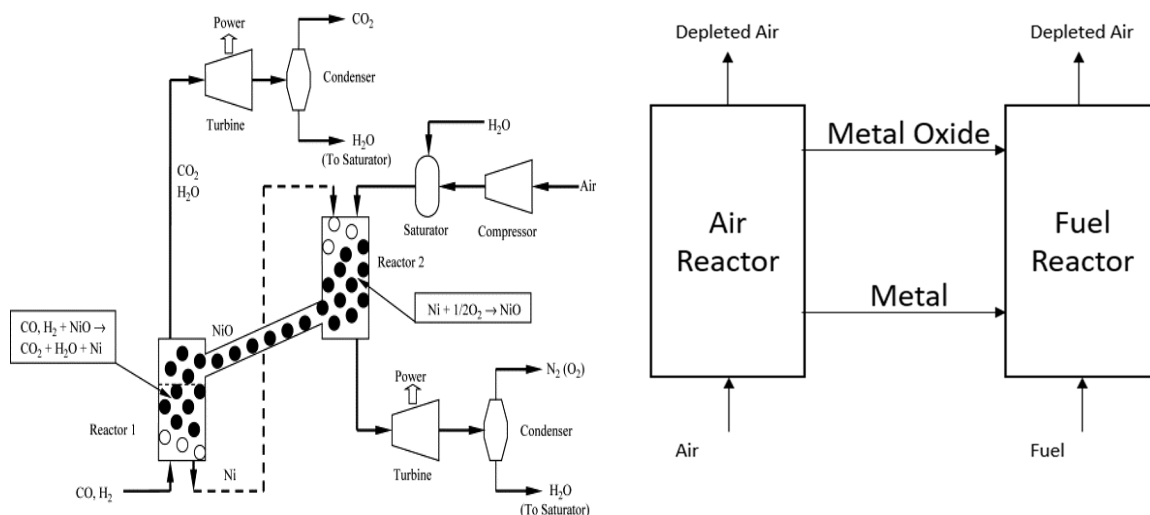


Figure 6. Left: a CLC reactor with two fluidized beds. Reproduced with permission from Jin and Ishida^[63]. Right: process flowsheet of chemical looping combustion carbon capture.

Chemical looping techniques were initially designed for fluidized bed systems. **Figure 6** displays a conventional fluidized bed configuration of the chemical looping combustion process. The fossil fuels are fed to the fluidized bed system through a screw or hopper. After interacting with the fuel, the reduced oxygen carrier is sent back to the air reactor through a loop seal. In the CLC process, all forms of fuel are acceptable;

be it a gas fuel (syngas, natural gas, and propane), liquid fuel (diesel, asphalt, and heavy oil), or solid fuel (coal, biomass and coke)^[59–61].

The CLC process could achieve higher thermal efficiency than other carbon capture technologies, with corresponding operating temperatures and pressures of 1200 °C and 13 bar in the air reactor. It was discovered that the thermal efficiency of IGCC-CLC achieved 52%–53%, 2.8% higher than PCC-IGCC process in carbon separation^[59]. Also, the CLC process achieves 3%–5% higher carbon capture efficiency than other techniques^[62]; and 100% carbon removal efficiency can be achieved, while the chemical absorption is generally limited to 95% removal efficiency^[62].

Finding an appropriate oxygen carrier with a high fuel conversion ratio, excellent stability, and a high oxygen transport capacity is a key component of CLC research^[59]. Iron, copper, manganese, and nickel are some of the most probable elements to act as oxygen carriers. More than 290 oxygen carriers have been evaluated for the CLC process, and the nickel-based metal oxide is shown to perform better in a 10 kW prototype reactor^[64]. The recent research states of the CLC process and CLC oxygen carriers are summarized in **Table 4**.

Table 4. Recent research progress of chemical looping combustion technologies.

Ref	Year	Research focus	Abstract of techniques
[65]	2015	CLC reactor	A 1000 MW _{th} boiler was designed for CLC process, the total cost of CO ₂ capture could as low as €20/ton CO ₂ .
[66]	2015	CLC process	A 100 MW _{th} CLC unit was designed and 95% CO ₂ capture efficiency was achieved.
[67]	2018	CLC process	A 0.5 KW _{th} biomass-CLC process was performed. Almost 100% CO ₂ capture can be attained during CLC fueled by biomass without the requirement of stripping.
[68]	2016	CLC process	1 MW _{th} CLC process with hard coal was operated. The converted hard coal in the boiler decrease the CO ₂ removal efficiency, carbon stripper is needed for hard coal-CLC process.
[69]	2019	CLC process	1 MW _{th} CLC process with natural gas was operated. The conversion efficiency of natural gas achieved to 80%.
[70]	2020	CLC process	Improved oxygen carrier was performed in CLC unit, the O ₂ demand was decreased from 9.6% to 4.1%.
[71]	2017	CLC carriers	The iron-based, copper-based and calcium-based oxygen carrier was performed in CLC process. Natural ores showed better performance than purified metal oxides.
[72]	2018	CLC carriers	Cu-Mn mixed oxide was taken as oxygen carrier in biomass-CLC process. This novel Cu-Mn oxygen carrier improve the CO ₂ efficiency to 98%.
[73]	2022	CLC carries	Highly reactive NiFe ₂ O ₄ oxygen carrier was studied for CLC process, the reaction rate of NiFe ₂ O ₄ is two times faster than conventional Fe ₂ O ₃ oxygen carrier.

2.5. Calcium looping technology and integrated CO₂ conversion

2.5.1. Calcium looping capture

The concept of Calcium Looping technology (CaL) was initially introduced by Shimizu in 1999^[74]. **Figure 7** illustrates the schematic diagram depicting the application of CaL for post-combustion CO₂ capture. In this method, CO₂ engages in a direct reaction with CaO to generate solid calcium carbonate, which can be conveniently separated from other gases. The fundamental reversible reaction underlying this process is the carbonation reaction, which releases heat (exothermic), whereas the inverse reaction, referred to as the calcination reaction, absorbs heat (endothermic). The reaction is presented below^[75]:



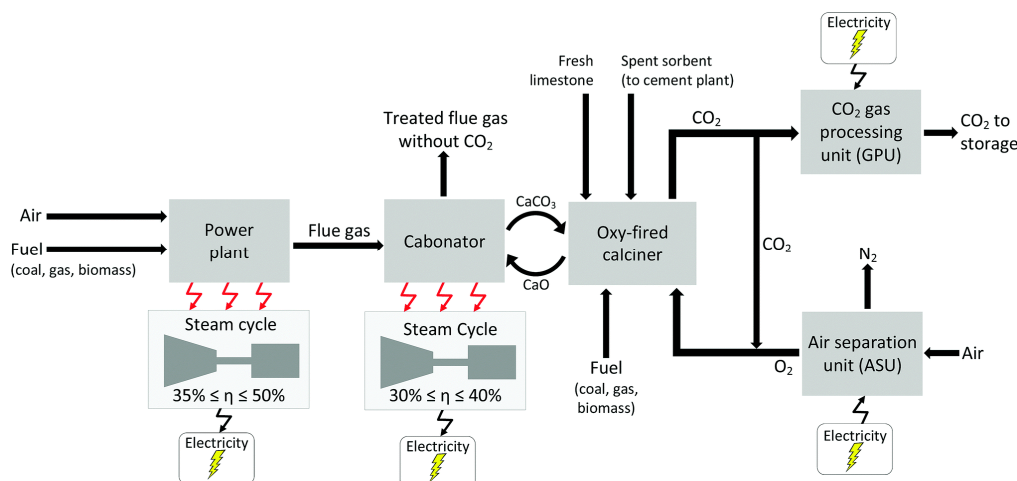


Figure 7. Calcium looping within a post-combustion capture process. Reproduced with permission from Bui et al.^[76].

While the carbonation reaction displays an initial rapid pace, it gradually decelerates over time^[77]. The calcination reactor necessitates a substantial input of heat, often achieved through oxy combustion of coal or natural gas at elevated temperatures^[78]. Following retrieval from the calcination reactor, the CO₂ is compressed and stored. This process finds applicability in both pre-combustion and post-combustion approaches, where the pivotal reaction in the gasifier for pre-combustion carbon capture is as follows^[75]:



The primary utilization of this process centers around post-combustion carbon capture, where limestone is employed to capture CO₂ from the exhaust flue gases of a power plant through a circulating fluidized bed carbonator^[76]. Subsequently, the sorbent is directed to a higher-temperature calciner for regeneration and then cycled back to the carbonator. In the calciner, coal or natural gas is burned within an oxy-fuel environment to produce the necessary heat. The overall reaction for solid carbonate formation is exothermic, and the high-grade heat generated during carbonation can be used for a steam cycle to generate additional power. This helps mitigate the energy penalty associated with traditional post-combustion capture^[79]. The limestone (CaCO₃) used in this method is non-hazardous, readily available, and more cost-effective compared to amines typically used for scrubbing in post-combustion carbon capture. Furthermore, spent sorbents can be repurposed for secondary applications. While the sorbent is recycled and reused for CO₂ capture, it's important to note that the reversibility of the core reaction diminishes with each cycle, resulting in a reduction in the sorbent's overall capacity^[80]. The main cause of this receptivity decay is sintering and attrition. The capacity of the sorbent is reduced by 15%–35% after the first cycle, depending on favourable and unfavourable conditions^[77], but this loss of capacity decreases in each cycle. Other natural materials such as dolomite (CaMg(CO₃)₂), oyster shells, egg shells are also tested^[81]. It was found that utilizing these materials in CaL cycles is economically feasible. However, it is unlikely that the required quantities of these residues can be produced for the commercial implementation of CaL. A significant amount of makeup sorbent is required for this process. The recent research states of the CaL process are summarized at **Table 5**.

Table 5. Recent research progress of chemical looping combustion technologies.

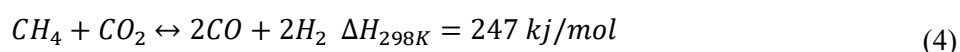
Ref	Year	Research focus	Abstract of techniques
[82]	2015	CaL sorbents	An analysis was conducted to compare the performances of dolomite and limestone. Dolomite have better performance.
[83]	2016	CaL sorbents	Egg shell based CaO materials were developed, with being >55% conversion after 40 cycles.

Table 5. (Continued).

Ref	Year	Research focus	Abstract of techniques
[84]	2016	CaL sorbents	Compared to unmodified limestone, the CO ₂ absorption after 13 cycles was observed to increase by up to three times for limestone doped with HBr.
[85]	2019	CaL sorbents	The core-shell structured CaO-CuO/MgO sorbent was developed, this material is suitable for CaL-CLC process.
[86]	2016	CaL process	The CaL-CLC method had a greater process efficiency than CaL alone, and generates more power output. (136 vs 110 MW).
[79]	2017	CaL process	The CO ₂ cost of CaL process was calculated and estimated to €10.0/ton CO ₂ and €33.9/ton CO ₂ , depends on carbon source.
[87]	2018	CaL process	The impact of impurities in flue gas were proposed through experiments under CaL process. The NO _x emission is also investigated.
[88]	2020	CaL process	Coal-fired power plants was integrated with CaL process, the CO ₂ capture cost decreased to \$19/ton CO ₂ . It proves the application potential of CaL process.
[89]	2020	CaL process	Integration of supercritical CO ₂ cycle with CaL and to evaluate their benefits by Aspen Plus tm . The electricity price was 26% higher than reference unit.

2.5.2. CaO coupled with the metal-based catalysts for CO₂ reforming

In recent years, significant attention has been devoted to high-temperature CO₂ capture and in situ utilization methods, which employ CaO along with commonly used catalysts like Ni, Fe-based, or small amounts of noble metal-based materials. The use of inexpensive CaO at elevated temperatures allows for swift and effective carbon capture. Furthermore, well-established catalysts such as Ni, Fe, or Cu-based ones can facilitate industrially viable CO₂ hydrogenation^[83,90-92]. It's noteworthy that the warming power of CH₄ exceeds that of CO₂ by a factor of twenty-two^[93,94]. Presently, CH₄ finds extensive use in generating H₂ through chemical looping reforming or steam methane reforming. A promising avenue involves the dry reforming of methane (DRM) as outlined in Equation 4, wherein both major greenhouse gases are utilized. This integrated approach, not only offers potential for tapping into low-carbon alkanes but also contributes to the mitigation of CO₂ emissions. Exploiting the catalysts for the DRM process to synthesize liquid fuels or high-value hydrocarbons using Fischer-Tropsch approach presents a pragmatic pathway for the enhancement of alkanes^[95,96].



The DRM procedure encompasses two primary phases: initial CO₂ capture utilizing alkali metal oxides and the subsequent dry reforming of methane facilitated by a catalyst. Among adsorbents, CaO-based materials are widely favoured due to their alignment with the thermodynamic prerequisites of DRM. However, a notable challenge within this process is the tendency of CaO to undergo sintering, a phenomenon of particle coalescence. Furthermore, the efficacy of adsorbents in the DRM process is influenced by the presence of catalysts^[97].

The DRM process frequently employs catalysts such as Ni, Ru, Mo, or Co-based ones, which effectively lower the thermodynamic barrier and consequently reduce the necessary reaction temperature^[95]. The interplay between metals and adsorbents holds a pivotal role in the DRM process. Tian et al.^[98] scrutinized two forms of NiO within CaO-Ni bifunctional sorbent-catalysts. The proportion of interacting NiO expanded from 64.0 to 80.7 atomic % with an increase in the Ca/Ni ratio. This heightened presence of interacting NiO was linked to an enhancement in the DRM process. The authors also suggested that catalyst sintering could be averted by reinforcing the interaction between the metal and the support, and/or by leveraging the confinement effect of the support within the material matrix. Another study presented by Xu et al.^[99] involved the synthesis of a

three-dimensional Ni/CaO network through a precipitation-combustion method. The remarkable outcomes demonstrated that this intricate network architecture, featuring both mesopores and macropores, effectively restrained the growth and coalescence of CaO particles. In a separated avenue, Zhu et al.^[100] proposed the oxygen vacancy strategy for enhancing CO₂ methanation in nickel-based catalysts. They prepared a Y₂O₃-promoted NiO-CeO₂ catalyst with exceptional methanation activity, which is three times greater than NiO-CeO₂ and six times greater than NiO-Y₂O₃, particularly at mild reaction temperatures (<300 °C).

Fe-based catalysts have also demonstrated favourable performance in the DRM process, offering cost-effective alternatives. For instance, Zhao et al.^[101] introduced a Ca-Fe chemical looping reforming method for DRM. The study revealed a sequence of reactions involving CH₄, CaCO₃, and Fe₂O₃. Initially, a swift and complete CH₄ oxidation reaction took place, leading to the conversion of all Fe₂O₃ into Fe₃O₄ without generating CO. Subsequently, the interaction between Fe-based oxygen storage materials and CO₂ adsorbents, coupled with the reforming of CaCO₃, facilitated the production of pure syngas. During this stage, Fe₃O₄ gradually transformed into Fe and FeAl₂O₄, with concurrent changes in grain size. A recent investigation introduced an innovative ICCU process utilizing environmentally friendly and cost-efficient CaCO₃-derived CaO, serving as both an effective adsorbent and a highly efficient catalyst for producing high-purity syngas^[102]. The findings indicated that the improved DRM process yielded a lower cost of \$292/ton for producing CO, in contrast to the reference scenario's cost of \$447/ton.

In the context of DRM, elevated temperatures (>500 °C) are imperative to drive reactions. This makes both CaO and Ni suitable and economically viable. The reaction duration plays a critical role in controlling coke formation during DFMs and optimizing the H₂/CO ratio of syngas in DRM process. The challenge of sintering, leading to a decline in catalytic activity due to site coverage and metal agglomeration, is significant at high temperatures. Additionally, the generation of environmentally undesirable CO from coke in DFM during the adsorption step merits attention.

2.6. Direct air capture technologies

Direct air capture (DAC) aims to extract carbon dioxide from the atmosphere and generate a concentrated stream of the gas, with the ultimate objective of enabling scalable CO₂ storage as a means of positive climate intervention. Given the broad definition of DAC, numerous promising and evolving methods for accomplishing this goal are currently being explored^[5,25,26].

Regarding development, the liquid solvent and solid sorbent direct air capture (DAC) processes have made significant progress and will receive more comprehensive discussion in the subsequent section^[25]. Nevertheless, there exist several alternative pathways to DAC that have not advanced as extensively in their development. Cryogenic DAC involves utilizing the sublimation point of CO₂ to generate solid CO₂ from ambient air, which can then be stored or resublimed to yield high-purity gaseous CO₂^[103]. Moisture or humidity swing adsorption leverages anionic exchange resins to capture and release CO₂, offering the potential to reduce energy demands but possibly increasing water consumption^[104]. Voskian and Hatton^[105] propose an electro-swing process where a composite of polyanthraquinone and carbon nanotubes binds to CO₂ upon charging and releases it during discharge, creating a high-purity CO₂ stream without the need for thermal energy. Other strategies involve intentionally produced alkaline feedstock like caustic calcined magnesia (MgO) to capture CO₂ from the atmosphere^[106], as well as using an aqueous amino acid solution to absorb CO₂ and regenerate it through crystallization of an insoluble carbonate salt with a guanidine compound^[107]. While each of these techniques presents distinctive avenues for innovation in DAC, the solid sorbent and liquid solvent approaches stand out as the most advanced and promising in terms of scalability^[27].

2.6.1. Liquid sorbent in existing DAC technology

Carbon engineering is committed to the development of liquid-based DAC absorbents. **Figure 8** shows that DAC demonstrations of carbon engineering, which have utilized aqueous solutions of alkali hydroxides. This liquid base DAC technology comprises of two loops, the contactor loop and the calciner loop^[108]. The contactor loop involves forcing air horizontally through a series of long air contactor units, the first stage involves the reaction of CO₂ with an alkali hydroxide solution in an air contactor, resulting in the formation of a solution containing alkali carbonate species. Subsequently, this solution is introduced to Ca(OH)₂ within pellet reactors, initiating the creation of a carbonate precipitate. These generated CaCO₃ pellets undergo drying and are subsequently introduced into the calciner. In this chamber, they are subjected to a decomposition reaction at 900 °C, yielding CaO, water, and CO₂. Currently, the desired temperature in the calciner is achieved through the use of natural gas and oxygen, resulting in a gaseous mixture mainly composed of CO₂ and water. The CaO is further hydrated in a slaking unit to form Ca(OH)₂, which is then reintroduced into the pellet reactors for the anionic exchange process^[27].

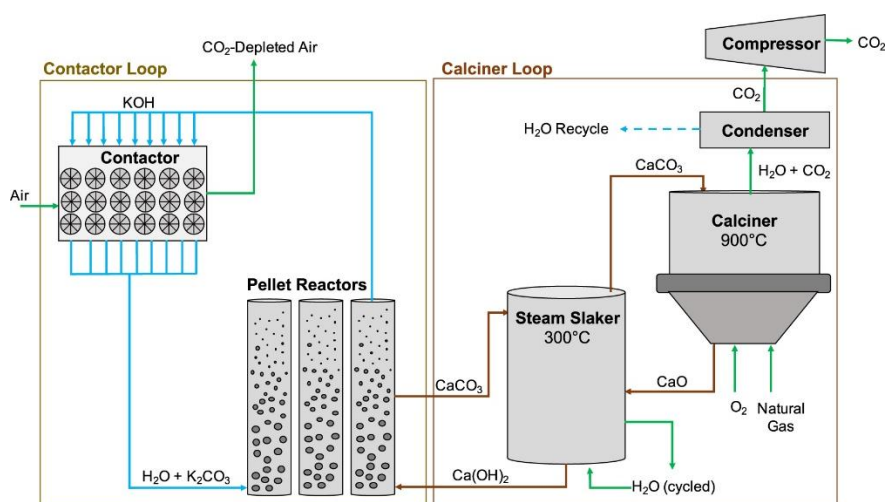


Figure 8. DAC process diagram for the solvent process. Reproduced with permission from Bui et al.^[76].

In order to address the issue of toxic emissions from amine solutions, researchers have explored the use of aqueous amino acids for direct air capture (DAC) due to their non-volatile and environmentally benign nature. This technique utilizing amino acids revolves around the crystallization of a guanidinium carbonate salt characterized by low aqueous solubility. This process involves the regeneration of the amino acid sorbent (guanidine) and the subsequent release of CO₂ upon heating. Given the endothermic nature of this phase, concentrated solar power has been employed as an energy source, with the aim of bolstering the process's sustainability^[106,107].

2.6.2. Solid sorbent in existing DAC technology

Climeworks have developed a series of solid sorbents and they are widely employed in their DAC plants^[27]. These solid sorbents are amine-grafted mesoporous silica. Much of this prior work has focused on the use of poly(ethylenimine) (PEI) on mesoporous silica, owing to PEI's high amine content and widespread commercial availability. Replacing PEI with poly(propylenimine) (PPI) on mesoporous silica has been found to enhance capacity and improve resistance to oxidative degradation^[103].

The tuneable chemistry of metal-organic frameworks (MOFs), both in terms of their framework and post-synthetic modification, makes them attractive for gas separation applications. However, in DAC process, they must exhibit moisture durability, which is not a typical characteristic of MOFs, and be amenable to amine

functionalization. One kind of MOF that has been extensively studied in this context is MIL-101(Cr), which is known for its water stability and multiple options for amine functionalization^[109]. Nevertheless, a balance must be struck between low CO₂ uptake with low amine loading and high CO₂ uptake with poor kinetics resulting from pore blockage or loss of amines at high-amine loading^[110]. Recently, a novel core-shell structure MOFs have been proposed to use in DAC. MOFs-UIO-66 and MOFs-UIO-67 are proven effective DAC solid sorbents^[111].

2.6.3. Economic assessments for DAC technology

At present, DAC technology has begun to be put into practical application. According to previous report^[110], the 19 DAC plants currently operational are able to capture almost 10,000 tonnes CO₂ annually. These DAC facilities are increasing their carbon capture capacity and expanding their operations globally. Providing a specific cost for DAC technology is difficult due to its early stages, resulting in high costs being a significant challenge. Specifically, it has been observed that the sorbent DAC process has heat energy needs close to 6 GJ/ton CO₂ and electricity requirements close to 1.5 GJ/ton CO₂^[27,112].

Comparatively, other carbon capture technologies have varying costs, depending on the limiting factors. For instance, BECCS has a price range of \$20–100/ton CO₂, which is lower than DAC's current cost, always above \$100/ton CO₂^[110]. However, DAC has more promise due to its limiting factors being related to high costs, minimal fundamental understanding, and issues for scaling. DAC's commercial companies, such as Climeworks and Carbon Engineering, report capture costs of \$600/ton CO₂ and \$94–232/ton CO₂, respectively, which are considered high due to the technology being new^[27,110]. Experts have projected a hopeful capture cost of \$100–200/ton CO₂, and possibly below \$60/ton CO₂ by 2040 or 2050, assuming the technology continues to scale^[113]. Fluctuations in costs can be attributed to several factors, including capital costs, operating costs, and the choice of sorbent used in the system, which can affect the required land area and energy needed. **Table 6** presents a list of significant DAC plants that are currently operational.

Table 6. The working statuses of current DAC plants.

Company	Plant type	Location	Sorbent type	CO ₂ removal ability	Operational date
Carbon Engineering ^[110]	Under construction	Texas (USA)	Liquid absorbent	1million tons/year	2022–2023
	Under construction	California (USA)	Liquid absorbent	1500 tons/year	2022
Climeworks ^[5,110]	Operational	Iceland	Solid absorbent	4000 tons/year	2021
	Operational	Switzerland	Solid absorbent	900 tons/year	2017
	Operational	All Europe	Solid absorbent	2000 tons/year	2015–2020
Infinitree ^[89]	Operational	New York(USA)	Ion exchange material	100 tons/year	2014–2018
Global Thermostat ^[89]	Under construction	Oklahoma (USA)	Solid absorbent	2000 tons/year	2023
	Planning	Chile	-	0.25 tons/h	2023–2024

2.7. Comparison of various carbon capture techniques

In this section, we reviewed the progress of CO₂ capture technologies from 2015 to 2022. In addition to CO₂ capture using industrial flue gas as a carbon source, DAC technology using air as a carbon source has also been reviewed. There are other CO₂ capture technologies, such as bioenergy with carbon capture and storage (BECCS), clathrate hydrate process, and cryogenic carbon capture that have not been thoroughly summarized

and reviewed in detail. This is partly because they are still in the early stages of development and also due to limitations in space^[67,114].

To conclude this section, even though pre-combustion, oxygen-fuel combustion and chemical cycle combustion each have their own benefits, it is unlikely that these methods will replace post-combustion capture in the near future. This is based on the fact that post-combustion capture offers the clear benefit of allowing current combustion technology to be utilized without the need for significant modifications, making it simpler to implement in plants that are already in operation^[21]. There are also large-scale CCS facilities in operation by post-combustion methods. The pre-combustion technique is mainly combined with integrated gasification combined cycle technology (IGCC), but it needs a substantial auxiliary system for optimal functioning. Therefore, this system's capital costs are high in comparison to other techniques used for this purpose. Regarding the oxy-fuel combustion and CLC process, although these technologies have the benefits of reducing equipment size, compatibility with a variety of fuel types, and low energy penalty, their research is still at the beginning stages and has not yet been applied to the industrial scale. In 2017, the 50 MW pilot scale power plant was constructed by Net Power in Texas by using oxy-fuel combustion process^[115], which demonstrates a net zero emission in the concept of carbon capture. Techno-economic assessment of these processes was performed by Zhu et al.^[116], have found that the CLC process displayed a higher energy efficiency of 39.78% compared to physical absorption (36.21%) and calcium looping (37.72%). The estimated payback period for these three capture processes was 13.45 years for CLC, 13.21 years for physical absorption, and 17.25 years for calcium looping.

The benefits and drawbacks of CO₂ capture expenses across various technologies are outlined in **Table 7**. It's crucial to acknowledge that the cost of CO₂ capture is contingent on several factors, including the origin of CO₂ emissions and the extent of the capture initiative. Typically, the cost of CO₂ capture constitutes only a portion of the comprehensive expenses associated with carbon capture and storage (CCS), encompassing the costs of transporting and storing the captured CO₂. The overall expense of CCS can significantly fluctuate based on the unique nature of the project and the regulatory context.

Table 7. The advantages and disadvantages of various CO₂ capture technologies.

Combustion technology	Advantages	Disadvantages
Pre-combustion	<ol style="list-style-type: none"> 1. Can produce useful and clean hydrogen fuel. 2. High CO₂ concentration contributes to the separation efficiency. 	<ol style="list-style-type: none"> 1. High efficiency drops and energy penalty in water-gas shift section. 2. Insufficient experience due to few gasification plants in actual application.
Oxy-fuel combustion	<ol style="list-style-type: none"> 1. High concentration at the flue gas exit for simple separation. 2. Significant reduction in NO_x emissions from the combustion process. 3. There are advanced air separation technologies. 4. Lower equipment and operating cost are needed, and there is less flue gas that has to be treated. 	<ol style="list-style-type: none"> 1. Cryogenic O₂ production is costly and energy intensive. 2. Corrosion problems maybe arise. 3. The high concentrations of oxygen used are prone to be dangerous.
Post-combustion	<ol style="list-style-type: none"> 1. More mature technology and enrich industrial experience. 2. Easier to retrofit existing plants. 	<ol style="list-style-type: none"> 1. Low-concentration and pressure of the CO₂ in the outlet flue gas, which is not beneficial for absorption.
Chemical looping	<ol style="list-style-type: none"> 1. The combustion products mainly consist of water and CO₂, so it is easy to separate CO₂ using simple separation device. 2. Reaction takes place at medium temperature and remains unmixed with N₂, so no toxic gases such as NO_x will be produced. 	<ol style="list-style-type: none"> 1. Insufficient experience since no large-scale operation experience.

Table 7. (Continued).

Combustion technology	Advantages	Disadvantages
Calcium looping technology	<ol style="list-style-type: none"> 1. CaL can achieve high capture efficiencies of up to 90% or more. 2. CaL requires relatively low energy input compared to other carbon capture technologies. 3. CaL can utilize low-grade and waste heat sources to regenerate the calcium oxide, which could reduce the overall energy. 	<ol style="list-style-type: none"> 1. The repeated cycles of calcination and carbonation that occur during calcium looping can cause the calcium oxide to decay or degrade over time. 2. CaL require significant amounts of land to accommodate the large equipment and infrastructure required for the process.

3. Post-combustion: Process and technologies

As mentioned in Section 2.5., currently, the most significant technology to upgrade conventional fossil fuel power plants is the post-combustion capture (PCC), which can be retrofitted to existing power plants with minor modification. However, PCC technology requires a substantial investment in terms of reactive solvents and other equipment, which may raise the cost of power generation by around 70%^[117]. Therefore, scientist has devoted their research efforts on finding superior solvents that are less energy-intensive and inexpensive. In this section, the current progress of PCC technologies in terms of advanced solvent formulations, process configuration, and superior solvents is comprehensively summarized and reviewed.

Various CO₂ separation technologies are available for post-combustion capture, such as (a) physical absorption; (b) chemical absorption; (c) adsorption; (d) cryogenics; and (e) membrane separation (**Figure 9**). Other methods, such as biochemical methods involving the biological fixation and microbial immobilization are less practiced to date, and not considered in this present review. The selection of the appropriate technology is determined by the characteristics of the flue gas stream, such as temperature, pressure, and CO₂ concentration and some other factors, such as purity of the target CO₂ product, sensitivity to impurities, and the environmental impacts.

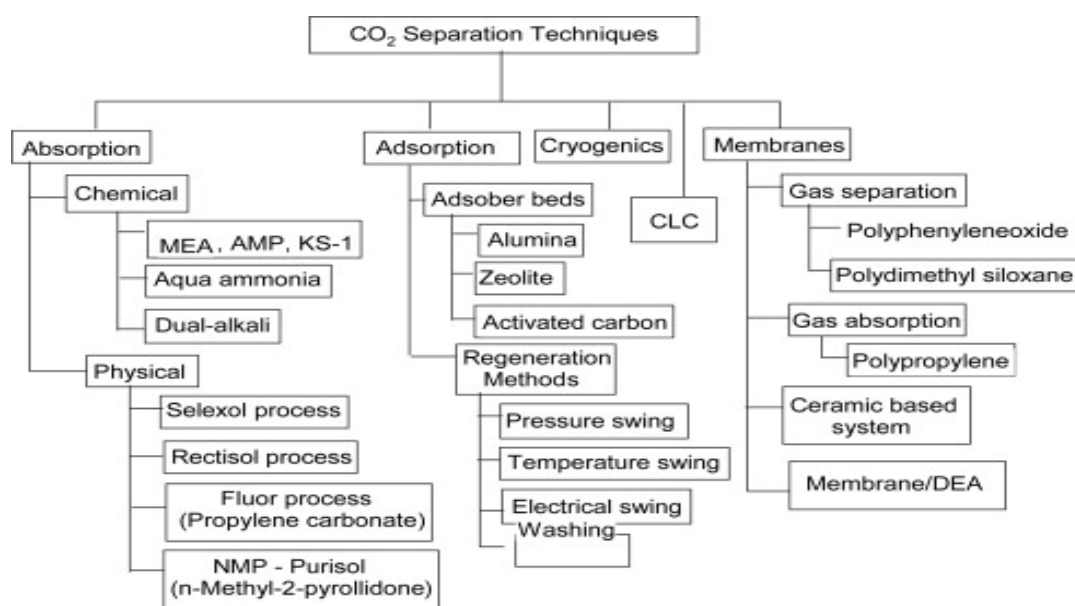


Figure 9. Technology options for CO₂ separation. Reproduced with permission from Olajire et al.^[61].

Among these, absorption of CO₂ by liquid solvents is the most advanced technique, due to it is been thoroughly tested, has significant processing capacity, and extensive industrial operating data is available. It is advantageous to deal with significant large combustion emissions, and it has useful applications in a variety of sectors, including flue gas purification, biogas upgradation, and processing of natural gases^[118]. Physical absorption and chemical absorption are the two subcategories of liquid absorption. When the absorption

process solely involves the mass transfer of gas molecules between the gas and liquid phases, physical absorption is contingent on the gas's solubility and the operating circumstances. Chemical absorption happens when a reaction occurs between the gas being absorbed and the existing solute in the solution. Chemical absorption enhances selectivity and separation efficiency compared to physical absorption^[119].

3.1. Physical absorption

Physical absorption uses organic solvents to physically dissolve the acidic gas instead of performing a chemical reaction. The driving force for CO₂ absorption by physical absorbents is solubility, which varies in different solvents, and the solubility also heavily relies on the partial pressure and temperature of CO₂. Henry's law states that a lower temperature and higher partial pressure make CO₂ easier to dissolve in organic solvents^[61].

The advantage of using the physical absorption method is that the association bond between the physical absorbent and CO₂ is weaker than in chemical absorption process. It reduces the amount of energy needed for regeneration and simplifies the regeneration process which consists of only a gas-liquid contactor and several flash drums (**Figure 10**). As the physical solvent is a non-corrosive absorbent, expensive alloy steel is not required for piping and plants, thus reducing the capital investment^[120]. However, physical absorption relies on the pressure of CO₂ and generally taken into account when the partial pressure of CO₂ is more than 3.5 bar^[1]. Moreover, it is not economical to apply physical absorption in flue gases where the partial pressure of CO₂ is less than 0.15 bar, since high energy is required to pressurize the flue gas^[10].

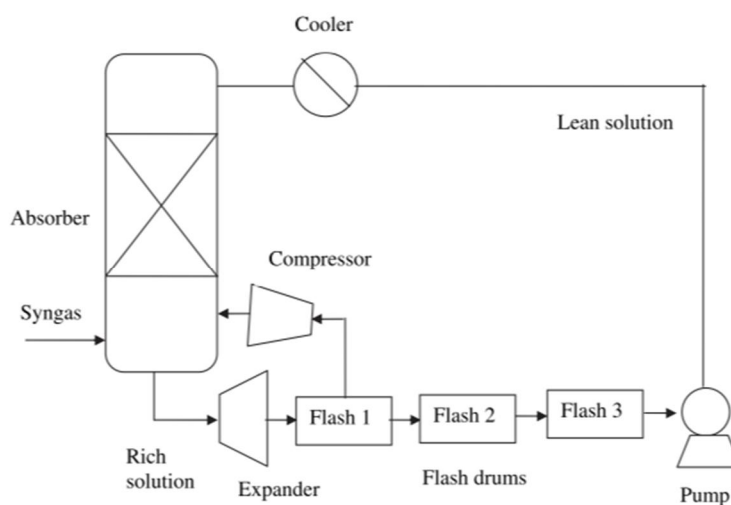


Figure 10. Process flowsheet of physical absorption process. Reproduced with permission from Olajire et al.^[61].

There are several existing industrial methods for physical liquid absorption, such as Fluor (Propylene carbonate), Rectisol (Methanol), Estasolvan (Tributyl phosphate), Purisol (Normal methyl pyrrolidone or NMP), and Selexol (Dimethyl ether of polyethylene glycol)^[43,61]. Among these, Selexol (Dimethyl ether of polyethylene glycol) and Rectisol (Methanol) are the most common and already used on a commercial scale. Kapetaki et al.^[121] investigated a dual-stage Selexol process for higher degree of CO₂ removal and found that, for 95% carbon capture, the Selexol process requires 65% more energy than in the 90% capture case. Reducing the size of equipment and energy penalty have been the primary goals of research in physical absorption technique. Therefore, latest research on physical absorption includes reducing energy demands by developing new solvents, refining the process configuration design, and developing mathematical models of mass transfer

rates, to optimize the thermal and economical aspects of this process^[122]. **Table 8** summarizes the latest research on physical absorbents and details the benefits and drawbacks of a variety of physical solvents.

Table 8. Recent research progress of physical-absorption technologies.

Ref	Solvents	Abstract of techniques
[123]	DEPG	A two stage Selexol process simulation was deeply investigated, the energy needed to capture 95% of CO ₂ is 65% more than the energy required to capture 90% of CO ₂ .
[124]		Dual-stage Selexol process was simulated in the IGCC system for eliminating CO ₂ as well as H ₂ S. The authors demonstrate that by modifying the operating parameters, a typical, integrated dual-stage Selexol device may achieve 95% CO ₂ collection.
[125]		The economic feasibility of the Selexol process was improved by incorporating dimethyl carbonate (DMC), diethylcarbonate (DEC), and triacetin (TAT) into the DEPG solution.
[126]	Methanol	The single-stage and two-stage Rectisol procedures were both evaluated, taking into account factors such as the efficiency of gas removal, heat recovery, equipment needs, energy consumption, and costs.
[127]		Simultaneous optimization of the energy penalty and CO ₂ capture rate in the Rectisol process was performed to determine the optimal operating parameters.
[128]		Predicting the thermodynamics behavior of Rectisol process by using SAFT EOS.
[129]	Glycerol	The performance of CO ₂ capture increased with temperature and pressure increased.
[37]	Ionic liquid [hmim] [Tf2N]	The physical absorption of ionic liquid [hmim] [Tf2N] showed a similar energy consumption as Selexol process.

3.2. Chemical absorption

Chemical absorption is most widely used method for CO₂ capture because of a higher CO₂ selectivity and faster absorption kinetics. Unlike physical absorption, chemical absorption is favourable even when the CO₂ partial pressure is low. Since CO₂ is an acidic gas, removing it from a gaseous stream using chemical absorption is based on acid-base neutralisation reactions using an alkaline solution. This process is also known as the electrophilic reaction of CO₂, which is determined by its molecular structure. As the oxygen atom is more electronegative than the carbon atom, it causes the electrons on the carbon atom to be shifted away, thus making the carbon atom on CO₂ electron deficient. The electron-deficient CO₂ is easily attacked by the electron-rich group of an amine that contains nitrogen and oxygen atoms, ultimately creating a chemical bond^[130].

The intermediate compounds are formed by a weak bond between absorbent and CO₂, and these bonds are then broken by providing thermal energy to obtain pure stream of CO₂. However, this approach also has a number of drawbacks, including high corrosivity, high energy consumption during solvent regeneration, a rapid rate of solvent degradation, and evaporation of solvents. These drawbacks are the main obstacles to the wide application of chemical absorption in large industrial emission sources.

To address these challenges, many types of chemical absorbents have been developed, such as alkanolamine solutions, carbonate solutions, water ammonia solutions, double alkali absorbents, and cold ammonia absorbents^[61]. Among these, CO₂ absorption by alkanolamine solutions gained unmatched interest due to their strong CO₂ affinity.

A representative configuration of the chemical absorption method is depicted in **Figure 11**. Within the absorber column, flue gas is introduced from the bottom, coming into contact with the absorbent descending from the top. The solvent assimilates the CO₂ and exits the absorber through its lower section. This CO₂-enriched solvent is conveyed to a stripper column, where thermal energy is supplied to regenerate the amine. This thermal treatment disrupts the chemical bonds between CO₂ and the absorbent. The CO₂ liberated during this process enters the condenser, which serves to separate the vaporized absorbent and water from the CO₂. The resultant high-purity CO₂ is then pressurized and conveyed for the subsequent phase. Subsequently, the

regenerated solvent undergoes cooling and is cycled back to the absorber column for the ensuing absorption cycle. The operational parameters governing the absorber and stripper, such as temperature and pressure, typically fluctuate based on the chosen chemical absorbent.

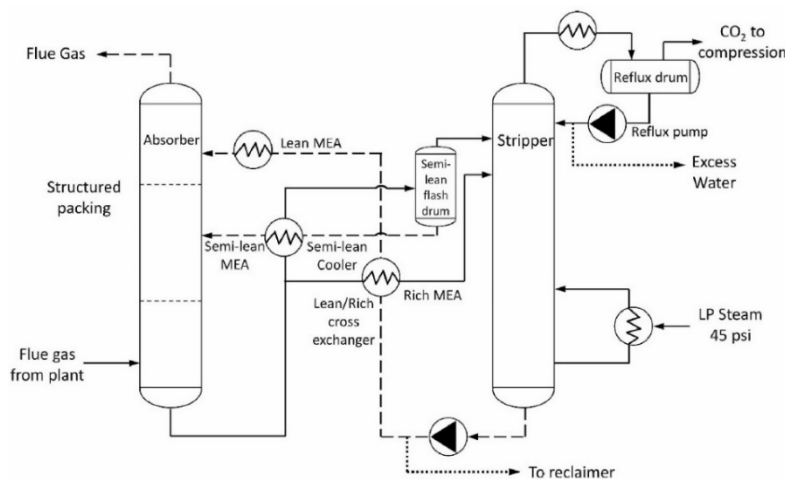


Figure 11. Typical configuration for CO₂ chemical absorption. Reproduced with permission from Chao et al.^[22].

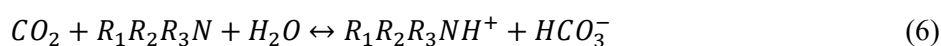
3.2.1. Amine-based chemical absorption

Aqueous amine solutions have been used in industry for decades as the most common method of chemically CO₂ scrubbing because the amine reacts to CO₂ quickly, with high selectivity, and weak bonds are formed during absorption reaction. The weak bond can be destroyed by heating, leading to regeneration of the amine absorbent. Amines usually contain amino groups and hydroxyl groups. The presence of the amino group enhances the alkalinity of the aqueous solution, enabling the effective absorption of acidic gas components. The hydroxyl group reduces the compound's vapor pressure and enhances its water solubility.

Alkanolamines can be classified as straight-chain and cyclic organic amines based on their molecular structure. Straight-chain organic amines are categorized as primary, secondary, or tertiary based on how many hydrogen atoms are linked to the amino nitrogen atom. For both primary and secondary amines, the nitrogen atom on the amino group attacks the carbon atom of the CO₂ molecule to produce zwitterion. It is a charge-separated resonant form of isomeric carbamic acid. The carbamic acid that is formed is structurally unstable. Thus, it readily loses its proton to another molecule of free amine, leading to the formation of the more stable ammonium carbamate^[130]. The stoichiometric coefficient for reaction (Equation (5)) indicates that two moles of amine and one mole of CO₂ will react, resulting in a theoretical maximum CO₂ loading of primary and secondary amine of 0.5 mole CO₂ per mole amine.



Tertiary amines lack hydrogen atoms linked to their nitrogen atoms. Hence, the generated zwitterions cannot be converted to carbamic acid by intramolecular proton transfer, nor can they undergo the deprotonation process. Therefore, they cannot produce stable ammonium carbamates with CO₂^[130]. Instead, the tertiary amine can react with CO₂ indirectly through a base-catalysed hydration reaction (Equation (6)) involving water to produce bicarbonates. According to the chemical reaction formula, each mole of tertiary amine can react with one mole of CO₂. Compared to primary and secondary amines, tertiary amines have a theoretical maximum loading of 1^[131].



Typically, the reaction rate for reaction (4) is faster than that of reaction (5). However, the rate of reaction also depends on the extent to which the reaction proceeds and the solution's viscosity. Several types of amines have been subject to investigation by researchers, including primary monoethanolamine (MEA), secondary diethanolamine (DEA), tertiary N-methyldiethanolamine (MDEA), cyclic piperazine (PZ), and the sterically hindered 2-amino-2-methyl-2-propanol (AMP). CO₂ absorption using amine solutions such as monoethanolamine (MEA) is a technology that has been applied commercially to the field of natural gas industry for 60 years^[61]. The 30 wt% aqueous MEA is always seen as the benchmark amine absorbent. MEA is especially suitable for applications with low partial pressures of CO₂. However, the main drawback of aqueous MEA process is the high energy penalty during amine regeneration, which accordingly reduces the power plant efficiency. The estimated efficiency are in the range of 36%–42% for retrofitting an amine based CO₂ capture unit to existing plants and between 25%–28% for application to new plants^[132]. Research efforts to reduce energy consumption include improving the operating temperature of the stripper column^[133], using catalyst-assisted regeneration, and using novel energy-efficient absorbents. In addition, the aqueous MEA solution itself is highly corrosive to the reaction equipment and transport pipelines^[134].

The absorbent plays a crucial role in the chemical absorption process. An ideal absorbent for CO₂ capture should possess several key attributes, such as a fast absorption rate, ample absorption and desorption capacity, low energy consumption during regeneration, thermal stability, nontoxicity, low corrosiveness to equipment, and economical feasibility^[135]. In this regard, substantial work has gone into the development of absorbents. The amine-based absorbents are by far the most common materials in the CCS industry. The amine absorbents explored to date can be broadly divided into four categories: single amine absorbents, blended amine absorbents, bi-phasic absorbents, and non-aqueous absorbents^[136].

Single amine absorbent

Single amines have been the most thoroughly investigated solvents in chemical absorption for CO₂ capture. Main categories of single amines are primary amines, secondary amines, tertiary amines, cyclic amines, and sterically-hindered amines^[43]. The most commonly used representative from each category of single amine absorbents is thoroughly discussed below.

Monoethanolamine (MEA) is a primary amine first used by Bottoms in 1930 to separate acidic gases^[137]. It has been regarded as the benchmark of the CO₂ separation process due to its high water solubility, low viscosity, cheap price and high reactivity with CO₂^[137]. However, the major drawbacks of the aqueous MEA absorber are the high corrosion rate and the high regeneration energy of approximately 3.3–4.4 GJ/ton CO₂^[138].

Diethanolamine (DEA) is a secondary amine which has similar structure as MEA. Compared to conventional MEA process, the DEA process have around 4.5% energy saving under same CO₂ capture condition^[139]. Generally, DEA is always used as an activator or additive to make blended amine absorbents, such as DEA/AEEA absorbent, MDEA/DEA absorbent and DEA/MEA absorbent^[140–142].

Methyl-diethanolamine (MDEA) is a typical tertiary amine and has been widely used in gas purification since 1980^[143]. Because of the lack of active hydrogen atoms on the amino nitrogen atom, the stability of MDEA cause less susceptible to solvent degradation and less foamy and corrosive than MEA. The absorption capacity of CO₂ in the MDEA-H₂O-CO₂ system was studied at temperatures ranging from 313 K to 393 K, with MDEA concentrations as high as 50 wt%, and CO₂ loadings reaching up to 1.32^[144]. However, the disadvantage is that MDEA can only react with CO₂ in aqueous solutions under a low reaction rate.

Due to their unique cyclic diamine structure, cyclic amines such as piperazine and its derivatives have fast reaction rates with CO₂ and high absorption capacity. The presence of two amine groups increases the reaction site with CO₂ and the proton acceptance probability, resulting in the formation of carbamates and

catalysing the formation of bicarbonates. The CO₂ uptake rate and capacity of 40 wt% PZ are twice as high as that of the 30 wt% monoethanolamine (MEA) reference solvent. Therefore, piperazine (PZ) has been proposed as a second-generation amine absorbent after MEA washing^[145].

Sterically-hindered amines (e.g., 2-Amino-2-methyl-1-propanol (AMP) and its derivatives) were proposed by Sartori and Savage^[146]. AMP is a primary amine with a similar molecular structure to MEA but with two additional methyl groups attached to the amine group's carbon atoms, providing a steric hindrance effect and reducing the reaction product's stability. This effect allows for easier regeneration of the amine. The formation of bicarbonate in sterically-hindered amine aqueous solution gives a larger theoretical absorption capacity of 1 mol-CO₂/mol-amine loading, which is twice that of the unhindered primary amine. Sun et al.^[147] analyzed and simulated the AMP process and found that, compared to conventional MEA process, the energy consumption of AMP process is 19% less, while the CO₂ removal efficiency was also increased from 88% to 93%. Moreover, pilot-scale experiments showed that the regeneration of AMP was 41.7% less energy intensive than MEA. Chakraborty et al.^[148] explained this phenomenon based on molecular orbital justification. They claimed that the negative charge of the amine nitrogen atom of the AMP molecule is reduced by 3.4% compared to that of the MEA molecule because of the dimethyl α -substituent. This leads to weaker basicity of AMP and weakens the stability of AMP's binding bonds to CO₂.

Blended amine absorbents

Using single-amine solutions have hampered their further application as CO₂ absorbents. Aiming to compensate for the disadvantages of single amine solutions and exploit their respective advantages, Chakravarty et al.^[148] first introduced the concept of mixing amine solutions of different properties to prepare blended amine solutions. These blended amine absorbents display great absorption efficiency and require less energy for regeneration.

Generally, the amine mixtures consist of a primary or secondary amine with a tertiary or sterically hindered amine. These amine mixtures combine the high reactivity of primary and secondary amines with the high absorption capacity of tertiary and sterically hindered amines^[149]. In addition, PZ is often used as it has been reported to be used as a substitute for MEA and DEA to substantially increase the absorption rate of mixed amine solutions^[147]. Typically, there are two ways of mixing blended amine absorbents. One is to use a primary or secondary amine with fast reaction kinetics as the mainstay and gradually add tertiary or sterically hindered amines to decrease energy consumption. The other way is to add an activator (primary amines or cyclic amines) to the tertiary or sterically hindered amines to improve the absorption rate. Both ways require the selection of the appropriate amine and optimization of the concentration of each amine (i.e., the mixing ratio).

The blended amine absorbents could accelerate the reaction of CO₂ with amine molecules. Because the interaction between primary and tertiary amine molecules takes place via a termolecular reaction mechanism^[150]. Chen et al.^[151] investigated that tertiary amines could react as bases with equimolar molecules of MEA and CO₂ via termolecular reaction mechanism. In other words, the tertiary amine molecule could restore the protonated MEA to a free molecule. A large number of free MEA molecules in solution increased the CO₂ absorption rate.

Adding the activator PZ to MDEA or AMP absorbents not only increases the amine solution's absorption rate but also addresses the precipitation of PZ solids^[152]. The mixture of PZ and AMP is a well-known novel blended amine absorbent. Seo et al.^[153] first investigated the mixing of PZ as a reaction activator into an aqueous AMP solution. Their experimental results showed that the addition of PZ greatly increased the reaction rate. Later, Yang et al.^[154] found that the mixed amine solution of PZ and AMP had a fast absorption rate and

high absorption capacity. Moreover, the regeneration energy consumption was about 80% of the conventional MEA absorbents. In contrast to the precipitation problems associated with employing PZ as an activator, MEA does not form precipitates. Recent studies have shown that MDEA absorbents activated with MEA have mass transfer rates close to those of aqueous MEA solutions and have higher absorption than MDEA at lower partial pressures of CO₂^[155]. The regeneration energy is reduced by 6%–12% compared to the conventional MEA aqueous solution^[41]. Improved MDEA/PZ blended absorbents was demonstrated for a 650 MW power plant by Zhao et al.^[156]. The reboiler duty in this process was 2.24 GJ/ton, which is 42% lower than the conventional MEA process.

Additionally, blended absorbents consisting of more than two different amines have also received attention recently. Zhang et al.^[157] investigated the carbon capture energy consumption of MEA/MDEA/PZ amine absorbents with different composition ratios. They discovered that energy penalty can be decreased by 15.22%–49.22% depending on the mixing ratio. Nwaoha et al.^[158] compared a ternary amine absorbent consisting of AMP/MDEA/DETA with an MEA absorbent and found that the cyclic loading and cyclic capacity of the ternary amine absorbent increased by more than 100% compared to the MEA absorbent, while the regeneration energy consumption was reduced by more than 50%. They also investigated the performance of AMP-PZ-MEA amine sorbents in blends. They found that this ternary solvent absorbent had a greater recyclability and lower regeneration energy consumption (around 50%) than the 5 molar MEA solution^[149]. MEA/MDEA absorbents and MEA/MDEA/AMP absorbents were evaluated by Liu et al.^[159], and it was found that, compared to the conventional MEA process, the regeneration efficiency of MEA/MDEA/AMP absorbents increased from 24% to 51% in twenty minutes desorption stage. A summary of recent research on single and blended absorbents is presented in **Table 9**.

Table 9. Recent research of CO₂ absorption performance of aqueous amine absorbents.

Ref	Device	Temperature	CO ₂ loading	Concentration	Energy consumption	Absorbents
[160]	Bench-scale unit	313 K	0.429 mol/mol	5 M/2 M	-	MEA/MDEA/Al ₂ O ₃
[160]	Bench-scale unit	313 K	0.432 mol/mol	5 M/2 M	-	MEA/MDEA/H-ZSM-5
[161]	Stirred reactor	318 K	0.885 mol/mol	10 wt%/5 wt%/0.05 wt%	-	MDEA/PZ/nMWCNT
[161]	Stirred reactor	318 K	0.738 mol/mol	10 wt%/5 wt%/0.05 wt%	-	MDEA/MEA/nMWCNT
[162]	Stirred reactor	298 K	0.54 mol/mol	20 wt%/2 wt%	Around 3.2 GJ/ton	MEA/TiO(OH) ₂ /H ₂ O
[163]	Jacket reactor	308 K	0.7 mol/mol	4.5 wt%/0.5 wt%	-	MDEA/PZ/H ₂ O
[164]	Stirred reactor	308 K	98.76%	30 wt%	-	AMP/PZ/H ₂ O
[165]	Stirred reactor	293–323 K	0.5 mol/mol	30 wt%	2573 GJ/ton	MEA/H ₂ O
[165]	Stirred reactor	293–323 K	0.91 mol/mol	30 wt%	1823 GJ/ton	MEA/EG/H ₂ O
[166]	Stirred reactor	298–313K	0.49–0.67 mol/mol	23.5 wt%	-	MDEA/H ₂ O
[166]	Stirred reactor	298–313 K	0.25–0.38 mol/mol	28.7 wt%	-	TEA/H ₂ O
[166]	Stirred reactor	298–313 K	0.79–0.85 mol/mol	23.6 wt%	-	DEEA/H ₂ O
[167]	Bench-scale unit	313 K	0.536 mol/mol	3.35 mol/L	3.74 GJ/ton	AMP/H ₂ O
[167]	Bench-scale unit	313 K	0.533 mol/mol	3.03 mol/L	3.76 GJ/ton	DEA/H ₂ O
[167]	Bench-scale unit	313 K	0.487 mol/mol	5 mol/L	4.01 GJ/ton	MEA/H ₂ O

Table 9. (Continued).

Ref	Device	Temperature	CO ₂ loading	Concentration	Energy consumption	Absorbents
[168]	Stirred reactor	313 K	0.41 mol/mol	30 wt%	2.13 GJ/ton	MDEA/H ₂ O
[45]	Parallel glass reactors	313.15 K	1.35 mol/mol	30 wt%	-98.39 Kj/mol *	Hexamethylenediamine/H ₂ O
[45]	Parallel glass reactors	313.15 K	0.83 mol/mol	30 wt%	-87.17 Kj/mol *	Diethylamine/H ₂ O
[45]	Parallel glass reactors	313.15 K	1.03 mol/mol	30 wt%	-97.23 Kj/mol *	1,3-diaminopropane/H ₂ O
[169]	Stirred reactor	303–323 K	0.2–1.2 mol/mol	20 wt%/10 wt%	-	AEP/MDEA/H ₂ O
[170]	Stirred reactor	313 K	0.73 mol/mol	3 M/1.5 M	-60.97 Kj/mol *	DEEA/MAPA
[170]	Stirred reactor	313 K	0.87 mol/mol	3 M/2 M	-54.35 Kj/mol *	DEEA/MAPA
[170]	Stirred reactor	313 K	0.84 mol/mol	3 M/3 M	-57.55 Kj/mol *	DEEA/MAPA
[170]	Stirred reactor	313 K	0.81 mol/mol	3 M/3.5 M	-61.97 Kj/mol *	DEEA/MAPA

* Reaction heat of absorbents with CO₂.

Biphasic amine absorbents

The biphasic absorbent is referred to as a phase-split absorbent or phase-separation absorbent. Because the amine solution starts as a single phase and after absorption of CO₂ in the absorber, two immiscible phases formed (liquid-liquid or liquid-solid) due to a change in the polarity of the reaction products^[171]. Usually, the upper liquid layer is the CO₂ depleted phase and is separated out before being transported to the stripping column. Therefore, only the CO₂-rich phase is separated and regenerated in the stripper column. Moreover, the higher content of CO₂ in the CO₂-rich phase leads to an increase in regeneration efficiency, which allows for less pump work.

The aqueous biphasic absorbents usually consist of an absorption promoter, a phase separating agent, and water. Zhang et al.^[172] investigated a biphasic mixture containing MEA, 1-propanol, and H₂O. They found that the CO₂-enriched solution was within 33% of the total solution, which significantly reduced the volume of liquid to be regenerated. Another MEA-based biphasic absorbent was studied by Wang et al.^[173], and they found that the regeneration heat consumption of MEA-sulfolane-H₂O system was 2.67 GJ/ton CO₂, which is 31% lower than the conventional MEA process. The biphasic solvents can reduce regeneration energy consumption by 30%–50% compared to the conventional MEA process. However, the water content in biphasic absorbent is an important influencing factor on CO₂ capture performance. Water has a high specific heat capacity and enthalpy of vaporization, which requires a high amount of energy in regeneration. Moreover, the presence of water also accelerates the corrosion of the equipment^[135].

Non-aqueous biphasic absorbents, known as water-lean solvents, find application through various solvents such as sulfolane for the creation of biphasic absorbents^[174–176]. In the context of TETA/DEEA, sulfolane is employed to modulate phase separation behaviour, resulting in simultaneous volume ratio reduction and heightened CO₂ loading within the rich phase. A comparison between TETA/DEEA/H₂O and TETA/DEEA/Sulfolane showcases a decline in the volume ratio of the rich phase from 83% to 39% and an increase in CO₂ loading within the rich phase from 3.10 to 4.92 mol/L^[174,177]. This approach reduces regeneration heat to 1.81 GJ/ton CO₂, indicating a 26.4% reduction compared to DEEA-TETA and a 54.6% decrease compared to the 30 wt% MEA solution. Furthermore, novel solvents have been introduced to the phase change absorption technique, employing long-chain alcohols such as 1-Heptanol, 1-octanol, and iso-octanol. In this approach, MEA/alcohols and DEA/alcohols show lower CO₂ loadings compared to

MEA/water and DEA/water. During absorption, alcohols (forming the CO₂-lean phase) are present in the upper phase, while amine carbamate (constituting the CO₂-rich phase) is situated in the lower phase^[178].

Recently, a multi-components non-aqueous biphasic solvent was proposed by Li et al.^[179] that consists of MEA, AMP, dimethylsulfoxide (DMSO) and N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA). The experimental results showed a relative high CO₂ capacity of biphasic absorbents, which is 0.88 mol/mol. Biphasic absorbents are advantageous in terms of absorption capacity, cycle capacity, and regeneration energy. However, the high viscosity of CO₂-enriched fluids is a significant barrier to its application, as it reduces the efficiency of mass and heat transfer^[135,172,180]. The details of recent research on biphasic absorbents are summarized in **Table 10**.

Table 10. Recent research of CO₂ absorption performance of biphasic amine absorbents.

Ref	Device	Temperature	CO ₂ loading	Concentration	Energy consumption	Absorbents
[181]	Stirred cell reactor	303 K	2.51 mol/kg	30 wt%	2.4 MJ/kg	MEA/1-propanol (phase-changed)
[182]	Stirred cell reactor	298 K	1.48	30 wt%	2.12 MJ/kg	DETA/1-propanol (phase-changed)
[173]	Stirred cell reactor	318 K	3.88 mol/L	4 M/5 M	2.67 MJ/kg	MEA/Sulfolane (phase-changed)
[180]	Stirred cell reactor	313 K	0.98	4 M	1.83 MJ/kg	TETA/TMBDA/DEGMEEb (phase-changed)
[180]	Stirred cell reactor	303 K	4.92 mol/L	n _{DEEA} :n _{TETA} = 4:1	1.81 MJ/kg	DEEA/TETA/Sulfolane (phase-changed)
[180]	Stirred cell reactor	303 K	3.1 mol/L	n _{DEEA} :n _{TETA} = 4:1	2.3 MJ/kg	DEEA/TETA/H ₂ O (phase-changed)
[183]	Stirred cell reactor	333 K	1.78	N _{AEEA} :N _{DMSO} = 4:6	1.76 MJ/kg CO ₂	AEEA/PMDETA/DMSO (phase-changed)
[183]	Stirred cell reactor	333 K	1.77	N _{AEEA} :N _{DMSO} = 5:5	1.69 MJ/kg CO ₂	AEEA/PMDETA/DMSO (phase-changed)
[184]	Stirred cell reactor	293 K	0.82	0.2 mol/L	-	PZ/DMF (phase-changed)
[185]	Stirred cell reactor	323 K	0.85	N _{AMP} :n _{TETA} = 2:1 V _{NMF} = 70%	-	TETA/AMP/NMF (phase-changed)

Non-aqueous amine absorbents

As mentioned earlier, massive energy penalty of amine regeneration is one of the major drawbacks of absorption-based CO₂ capture. The energy consumed for absorbent regeneration can be divided into three parts: (i) the sensible heat (Q_{sen}) that is the heat consumed to raise the temperature of amine solution; (ii) the desorption reaction heat (Q_{des}) which is the energy to break the chemical bond between the CO₂ and the amine; and (iii) the heat of vaporization (Q_{latent}) that is the heat consumed to vaporize water^[186,187]. Among these, the desorption reaction heat (Q_{des}) depends on amine types, while the sensible heat and latent heat mainly depend on the water content in the solvent as water is used as a co-solvent in aqueous amine solutions. Due to water's high specific heat capacity and vaporization enthalpy, in conventional aqueous amine absorbents, around half of the total provided energy is wasted to heat and vaporize water. Regeneration at high temperatures can increase the degradation rate of the amine solution and the corrosion of the equipment. As a result, more researchers are now interested in developing non-aqueous solvents, which they believe will avoid many of the problems mentioned earlier. So far, most non-aqueous absorbents based on amines have been tested with organic solvents or room-temperature ionic liquids.

Alcohols, ethers, and glycols are common co-solvents in the non-aqueous absorbents. These solvents offer a significant advantage in reducing equipment corrosion and amine degradation. Among alcohols, methanol and ethanol are the most investigated co-solvents. Chen et al.^[188] compared EMEA/ethanol with EMEA/water and found that the absorption of non-aqueous absorbents was less than that of aqueous solutions. However, the regeneration efficiency was 50% higher than that of the aqueous solution. Liu et al.^[189] investigated TETA and AMP mixed amine absorbents using ethanol as a co-solvent. It was found that this non-aqueous absorbent exhibited a high absorption capacity (3.71 mol kg^{-1}) and regeneration efficiency (95.4%). Other non-volatile alcohols such as 1-hexanol and 1-propanol are also thoroughly investigated. The CO_2 absorption performance of MEA/MDEA/1-Hexanal was examined by Ulus et al.^[190]. The additive tertiary amine increased absorption capacity from 0.39 to 0.67 mol CO_2 per mol amine with a reasonable absorption rate. Barbarossa et al.^[191] devised a series of AMP-based solutions for chemical CO_2 capture. From their results, the AMP/MMEA/1-propanol mixture had an equilibrium absorption efficiency of 95.9% at 333 K. All AMP-based blended absorbents had more than 90% equilibrium absorption efficiency at regeneration temperature of 363 K.

Glycols are also commonly used non-aqueous solvents, including ethylene glycol (EG), triethylene glycol (TEG), and polyethylene glycol (PEG). The mixture composed of 2-PE and EG showed high CO_2 loading ($0.97 \text{ mol-CO}_2/\text{mol-amine}$), and 2-PE/EG absorbent could be fully regenerated under low temperature (323.15 K)^[192]. Zheng et al.^[193] studied CO_2 solubility in AMP/TEG non-aqueous absorbents, and found that the AMP/TEG absorbents could consume less energy than the MEA/TEG absorbents. Li et al.^[194] investigated MEA/PEG, DEA/PEG and DGA/PEG absorbents. In particular, a solution of 3 mol/L DGA/PEG exhibited a high cycling loading of $0.438 \text{ mol-CO}_2/\text{mol-amine}$ with regeneration efficiency up to 94.6%. Another research about AMP/Glycols absorbent was investigated by Barbarossa et al.^[191]. In their study, AMP anhydrous absorbents were mixed with various alcohol mixtures (EG/Ethanol; EG/1-Propanol). A regeneration efficiency of 90% was achieved at 80 °C. The energy consumption of glycol-based non-aqueous absorbents was investigated by Tian et al.^[195]. The regeneration energy of 30 wt% MEA/PEG₂₀₀ was found to be 2.55 MJ/kg, which is 33% lower than the conventional aqueous MEA process.

Glycol ethers, due to their low viscosity, are frequently used in the formation of non-aqueous absorbents. Guo et al.^[196] examined the efficacy of MEA in 2-ME and 2-EE glycol ethers. They discovered that the ability of 30 wt% MEA to absorb in these solvents was comparable to its absorbency in water, and it had a higher efficiency of regeneration and required approximately 45% less energy than in water. Barzagli et al.^[197] evaluated DEGMME as a solvent for non-aqueous amine absorbents and found that a mixture of DGA and DEGMME was a viable alternative to aqueous MEA solutions, offering a faster absorption rate and a lower heat of absorption. Bougie et al.^[43] investigated the desorption performance of MEA in DEGMEE by microwave regeneration. Their results showed that the DEGMEE solution could reduce energy consumption by 78% compared to the conventional 30 wt% aqueous MEA process. Barzagli et al.^[198] tested the continuous absorption and desorption performance of AMP and AMP-amine mixtures in anhydrous solvents, such as EG/1-PrOH mixtures or DEGMME. Results showed CO_2 removal ranging from 87%–95% at desorption temperatures of 90–95 °C.

Room temperature ionic liquids (RTILs) can also be classified as novel non-aqueous solvents. These solvents are known for their low evaporation pressure, high heat stability, and adjustable physical characteristics, making them more environmentally friendly than traditional solvents. Research conducted by Xu et al.^[145] showed that the addition of RTILs [C2OHmim][DCA] and [bmim][DCA] to a 30 wt% MEA aqueous solution could lower energy consumption by 27%. Khan et al.^[199] experimentally analysed the physicochemical properties of another ionic liquid addition CO_2 absorbent. The addition of ionic liquids

([bmim][OTf] and [bmim][AC]) to 30 wt% MDEA/3wt% PZ showed a significant increase in the CO₂ absorption capacity. At 10 wt% ionic liquid content, the CO₂ loading increased from 1.32 to 1.77 for the [bmim][OTf] solvent and to 1.84 for the [bmim][AC], but these ionic liquids also increased the viscosity of the absorbent. Yang et al.^[200] found that the addition of the hydrophilic ionic liquid [bmim][BF₄] to the aqueous MEA solution can significantly reduce the loss of MEA in the carbon capture process and the regeneration energy consumption. The regeneration energy consumption of 50% [bmim][BF₄] + 30% MEA + 20% water was found to be 2.38 GJ/ton CO₂, which is 33.8% lower compared to the conventional MEA process. Xiao et al.^[201] demonstrated that an ionic liquid solution composed of [bmim][BF₄], MEA, and MDEA exhibits superior regeneration performance and reduced energy consumption compared to aqueous solutions.

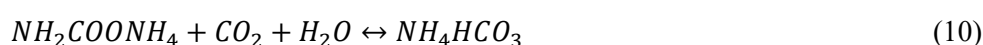
For CO₂ separation from flue gas, non-aqueous solvents include alcohols such as methanol, ethanol, and propanol, glycols like EG, DEG, and TEG, and ionic liquids. However, using high-volatility alcohols with high saturated vapour pressures leads to significant solvent losses and can have negative environmental impacts. However, the use of glycols as solvents is hindered by their non-linear viscosity increase, which slows down mass transfer and reduces absorption rate. The high complexity, expensive fabrication materials, and unknown toxicity of ionic liquids pose additional challenges to their widespread commercial use. The details of recent research on non-aqueous amine absorbents are summarized in **Table 11**.

Table 11. Recent research of CO₂ absorption performance of non-aqueous amine absorbents.

Ref	Device	Temperature	CO ₂ loading	Concentration	Energy consumption	Absorbents
[43]	Stirred cell reactor	298 K	0.47	30 wt%	1700 KJ/mol CO ₂	MEA/EG/PrOH
[43]	Stirred cell reactor	298 K	0.50	30 wt%	3630 KJ/mol CO ₂	MEA/Water
[43]	Stirred cell reactor	298 K	0.49	30 wt%	-	MEA/NMF
[43]	Stirred cell reactor	298 K	0.48	30 wt%	929 KJ/mol CO ₂	MEA/DEGMEE
[195]	Stirred cell reactor	313 K	0.483	5 mol/L	2547 KJ/g CO ₂	MEA/PEG200
[196]	Stirred cell reactor	313 K	2.1 mol/kg	30 wt%	5.1 MJ/kg	MEA/2-ME
[196]	Stirred cell reactor	313 K	2.045 mol/kg	30 wt%	5.0 MJ/kg	MEA/2-EE
[196]	Stirred cell reactor	313 K	1.662 mol/kg	30 wt%	-	DEA/2-ME
[196]	Stirred cell reactor	313 K	2.198 mol/kg	30 wt%	10.8 MJ/kg	MEA/H ₂ O
[202]	Stirred cell reactor	333 K	1.74	2 mol/L	39 MJ/kg	TETA/EG
[202]	Stirred cell reactor	333 K	1.72	2 mol/L	41 MJ/kg	TETA/DEG
[202]	Stirred cell reactor	333 K	1.86	2 mol/L	25 MJ/kg	TETA/PEG200
[203]	Stirred cell reactor	303 K	1.82	30 wt%	84 MJ/kg	TETA/PEG200
[203]	Stirred cell reactor	303 K	1.75	30 wt%	92 MJ/kg	TETA/BDO
[192]	Stirred cell reactor	298 K	0.97	1:6	-	2-PE/EG
[204]	Rotating packed bed	323 K	-	40 wt%	33.6 KJ/mol	PZ/DEG
[205]	Stirred cell reactor	293 K	0.23–0.5	10 wt%–90 wt%	25.49 KJ/mol	DMEA/EG
[150]	Stopped-flow reactor	298–313 K	-	0.2 M MEA 0.3 M DMEA	12.19 KJ/mol	MEA/DMEA/Ethanol
[150]	Stopped-flow reactor	298–313 K	-	0.2 M MEA 0.3 M DEEA	14.19 KJ/mol	MEA/DEEA/Ethanol
[198]	Stirred cell reactor	293 K	89.1%	3 M AMP	-	AMP/IPMEA/ EG/PrOH
[198]	Stirred cell reactor	293 K	89.1%	3 M AMP	-	AMP/EG/PrOH
[206]	Stirred cell reactor	298 K	1.65 mol/kg	2.5 M AMP 0.5 M AEEA	2.09 MJ/kg	AMP/AEEA/NMP

3.2.2. Chilled ammonia absorbent

Ammonia uptake is a possible alternative to traditional amine-based solutions. During the CO₂ absorption procedure, CO₂ is physically absorbed into the liquid phase first before reacting with the ammonia in the solution. The chemical reactions for the reaction of ammonia with CO₂ are shown in Equations (7)–(10)^[131]. The CO₂-rich solution is heated from 27 to 92 °C in a vapour extraction tower, where the ammonium bicarbonate is broken down to produce CO₂^[22]. Ammonia solutions have many benefits, such as superior CO₂ capture capacity, low thermal and oxidative degradation, negligible corrosiveness, low cost, less regeneration energy consumption, and the ability to remove a variety of contaminants from flue gas (SO₂, NO_x, HF, etc.)^[61].



However, the high volatility of ammonia leads to its escape which is a significant obstacle to its broader application. In the CO₂ capture process, ammonia evaporates from the liquid phase into the gas phase, escaping from the top of the absorption and stripping columns. A conceptual diagram of the ammonia escape during absorption and desorption processes is shown in **Figure 12**. The escaped ammonia can react with CO₂ in the gas phase to form ammonium salt solids, which could lead to the blockage of equipment such as pipes and valves and a reduction in the heat transfer efficiency of the heat exchanger. Additionally, if not appropriately handled, ammonia can leak into the air, resulting in significant secondary atmosphere contamination. Some effective methods are developed to contain ammonia leaks or to reduce the chances of ammonia escape. Generally, ammonia based process needs to be operated at temperatures below 25 °C and purging devices are needed at the CO₂ absorber outlet to prevent excessive ammonia evaporation.

For solving the issue of high volatility of ammonia, researchers developed the chilled ammonia process (CAP) in 2006. In CAP, the ammonia absorption is carried out at 0–10 °C, limiting the NH₃ evaporation to 6% of the solvent, while traditional aqueous ammonia processes often result in losses of NH₃ up to 9%. As for the regeneration step, the CO₂-rich stream is compressed and heated to around 100 °C to release CO₂, and it has been stated that the energy consumption of the CAP process is just half of the standard MEA process^[207]. Nevertheless, the CAP process requires additional cooling devices and multiple columns, increasing capital costs. In addition, low-temperature conditions reduce the gas-liquid mass transfer rate and lead to the formation of solids, which affects the absorption efficiency.

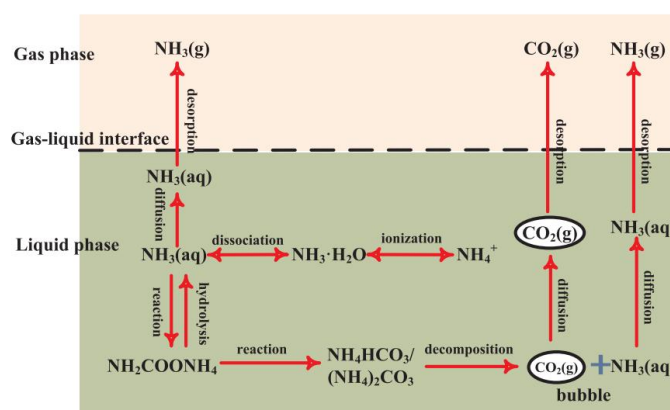


Figure 12. Schematic of ammonia escape in the absorption and desorption process. Reproduced with permission from Wang et al.^[208].

3.2.3. Carbonate absorbent

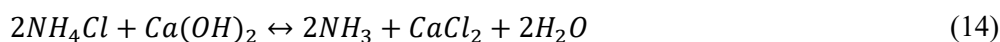
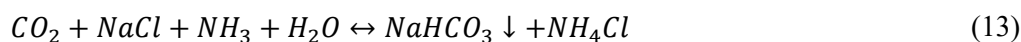
As early as 1904, German patents explored the absorption of CO₂ using carbonates at high temperatures^[209]. Subsequently, Benson et al.^[210] created the Benfield technique, which reduces the expense of the carbon capture process by using potassium carbonate as the CO₂ absorbent under high temperatures and pressure. Following that, the ability to absorb CO₂ has often been studied using carbonate solutions such as potassium carbonate and sodium carbonate^[209–212]. The chemical reactions of these process are given below. In carbonate solutions, CO₂ is hydrated to bicarbonate HCO₃⁻ as shown in Equation (11). The rate limiting step is shown in Equation (12).



Chemical absorption using carbonate solutions offers the following benefits: (1) inexpensive raw materials, (2) low regeneration costs, (3) high absorption capacity, (4) low degradation and corrosion rates, and (5) low toxicity^[213]. However, the main challenge of carbonate solutions is the poor absorption rate. High pressure (30–60 bar) absorption can be employed to solve this problem^[214–216]. It also has been found that high-temperature absorption is beneficial to increase absorption capacity^[217]. High temperature absorption also provides the benefit of not removing the hydrocarbons from the gas stream prior to absorption, as the hydrocarbons condense at low temperatures. The high-pressure conditions of the absorption tower allow the absorption solution to operating at temperatures close to the atmospheric boiling point of the potassium solution (100–140 °C) without significant evaporation of the solution. Several activators, such as amines, salts, and enzymes have also been employed to speed up the absorption rate^[131]. Valluri and Kawatra^[218] proposed that stirring usage also could aid the uptake of CO₂ in the dilute slurry of sodium carbonate, leading to a significant increase in capture efficiency.

3.2.4. Dual-alkali absorbents

The dual-alkali process is also called the Solvay process. Ammonia, the first alkali used in the Solvay process, acts as a catalyst to speed up the reaction between CO₂ and sodium chloride (NaCl) to produce sodium bicarbonate (NaHCO₃). Calcination of sodium bicarbonate produces high-purity CO₂ for storage and commercial-grade sodium carbonate (NaCO₃). Calcium hydroxide (Ca(OH)₂), the secondary alkali, reacts with ammonium chloride, allowing ammonia to be recovered. The reaction equations for CO₂ absorption and ammonia regeneration are listed below:



However, the process needs to calcine large quantities of limestone to regenerate the primary alkali, which consumes a high amount of energy and produces extra CO₂. According to Equations (13) and (14), the calcination of the limestone releases one mole of CO₂ for every two moles that are collected.

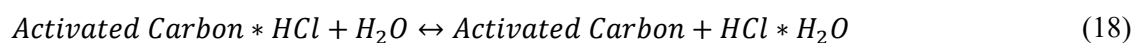
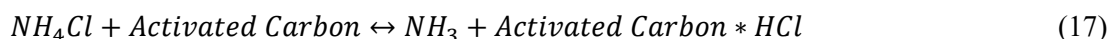


Overall reaction equation:



In order to overcome the disadvantages of the Solvay process, a modified method was proposed by Huang et al.^[219]. Methylaminoethanol (MAE) was used as the main base for CO₂ absorption instead of ammonia in their study. The second step of the dual-alkali process is to use the secondary base to regenerate the primary

base. It regenerates ammonia by using activated carbon (AC) instead of limestone. Due to the alkalinity of the AC, the Hydrochloric acid (HCl) is chemisorbed by the AC. The ammonia is recovered in this reaction.



Before dual-alkali absorption, the gas stream must be treated in a denitrification/desulphurization step. Because acidic impurities (SO_x and NO_x) and ash in the flue gas will interact with the MAE to create thermally stable salts, which heavily decreased absorption rate^[219]. A summary of the advantages and disadvantages of chemical absorption is concluded in **Table 12**.

Table 12. The advantages and disadvantages of chemical absorption using different solutions.

Absorbent	Advantages	Disadvantages
Amine solution	<ol style="list-style-type: none"> 1. Fast absorption rate and high absorption capacity. 2. Proven technology with many practical applications. 	<ol style="list-style-type: none"> 1. Solution regeneration consumes a lot of energy. 2. Highly corrosive to equipment. 3. Susceptible to oxidation and degradation.
Ammonia solution	<ol style="list-style-type: none"> 1. High absorption loading. 2. Not easily corroded and degraded. 3. Regeneration is relatively easy. 	<ol style="list-style-type: none"> 1. Ammonia gas is highly volatile and easily escapes. 2. Causes pollution and equipment damage.
Carbonate solution	<ol style="list-style-type: none"> 1. Low solvent cost. 2. Low corrosion and degradation rates. 3. Low toxicity. 	<ol style="list-style-type: none"> 1. Slow reaction rate. 2. Strong corrosive.
Dual-alkali solution	<ol style="list-style-type: none"> 1. Low corrosion and degradation rates. 2. Low toxicity. 	<ol style="list-style-type: none"> 1. Gas stream must be treated in a denitrification/desulphurization step. 2. The calcination of limestone causes high energy penalty.

3.3. Membrane separation process

Membrane separation is relatively a new method for selectively removing a component from a mixture. Membranes are semi-permeable barriers that are separated mainly by four mechanisms: Knudsen diffusion, surface diffusion, molecular sieving, and configurational diffusion^[61]. The main mechanism of membrane gas separation is molecular sieving. The advantages of membrane separation technology include simplicity of installation, simple operation, low energy consumption, and minimal environmental effect. However, the high cost of the module, the large footprint, and the relatively weak durability of the membrane material are the main challenges which limit the wider application of membrane-based separation^[118].

Membranes are the critical factor of the separation process, and the membrane materials usually determine the separation efficiency. Membrane materials are generally classified as inorganic (ceramics, zeolites, metal oxides), organic (acetate membranes, polysulfone, polyamides), and mixed matrices^[61].

As displayed in the right panel of **Figure 13**, the membrane technology can be separated into two categories: membranes for gas separation and membranes for gas absorption. Lately, the membrane gas separation technology has attracted massive attention as it is a simple operation and does not involve regeneration and chemical reactions^[221]. In membrane gas separation process, CO_2 -containing gas is pumped into a membrane separator in the membrane system for gas separation at high-pressure conditions^[21]. CO_2 travels through the membrane preferentially and is collected at reduced pressure on the other side. Permeability and selectivity of membrane materials are two main characteristics that affect membrane separation performance. Pressure, temperature, and the concentration of a specific gas are additional factors that influence the separation performance. The rate at which a specific gas flows across a particular membrane surface area

is known as permeability (transport coefficient). The gas flow may be calculated if the membrane's permeability, size, and trans-membrane driving force are known. Typically, the pressure differential between the feed side and the permeate side acts as the trans-membrane driving force for an ideal gas. Based on this, most studies use the assumption that the feed gas is compressed to a greater pressure and the permeability is fixed at atmospheric pressure. Selectivity (separation coefficient) refers to the preference of gas passage through the membrane, based on the high or low permeability of different gas types. In recent years, more emphasis has been placed on gas flux rather than permeability, as membranes can increase the gas flux through the membrane without losing selectivity^[222]. Since the permeability of a membrane is inversely proportional to the separation area required, using a membrane with a high permeability may minimise costs. However, permeability and selectivity often trade-off, with high permeability membranes typically being less selective and vice versa. Reaching this limit is a key goal in membrane research in order to attain high permeability and high selectivity. According to the research of Robeson, this trade-off effect may be represented as the top limit of membrane performance^[35].

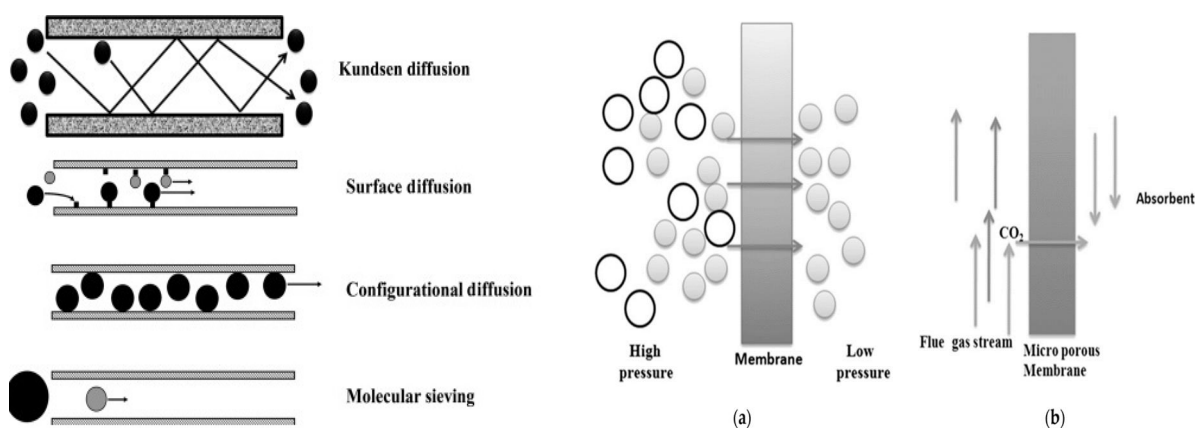


Figure 13. Left: transport mechanism of gas separation membrane. Reproduced with permission from Vaezi et al.^[220]. Right: principle of (a) gas separation membrane and (b) gas absorption membrane. Reproduced with permission from Chao et al.^[222].

The gas absorption system employs a solid microporous membrane to extract CO₂ from a gas stream. This system achieves a high CO₂ removal rate by avoiding issues like flooding, foaming, channelling, and entrainment. Notably, the required equipment is more compact compared to membrane separator setups^[223].

Despite these advantages, the majority of membrane technology applications are still in the developmental phase. Additionally, effective membrane separation necessitates significantly high flue gas pressures and CO₂ concentrations of 20% or higher. This becomes challenging when dealing with the low CO₂ partial pressure commonly found in post-combustion flue gas, where the CO₂ content is typically only around 4%. In such scenarios, the use of multistage membrane systems could present a viable solution^[222]. Favre et al.^[224] discovered that in comparing membrane separation with basic amine absorption, it's evident that the energy consumption of membrane separation significantly exceeds that of a basic amine system when dealing with CO₂ streams containing CO₂ concentrations of 10% or less.

3.4. Adsorption process

Adsorption is an important alternative method to absorption in post-combustion capture due to its potential to reduce energy penalty for regeneration^[225]. The adsorption process also holds the merits of requiring simple and easy-to-operate equipment, and being more sustainable. However, it too suffers from poor separation efficiency when dealing with large gas streams^[118].

Chemical adsorption generates covalent bonds between the gas molecules and the adsorbent surface, while physical adsorption depends on weak van der Waals forces^[225]. The adsorption process generally consists of two columns filled with adsorbents; while one is adsorbing, the other is desorbing simultaneously. Flue gases rich in CO₂ are always passed to the already regenerated column for adsorption. For this reason, these techniques are called swing adsorption^[226]. Depending on the desorption method, swing adsorption methods can be classified as pressure swing adsorption (PSA), vacuum swing adsorption (VSA), temperature swing adsorption (TSA), electro swing adsorption (ESA) and some composite techniques such as temperature-vacuum swing adsorption (TVSA), pressure-vacuum swing adsorption (PVSA)^[22].

The PSA technique uses high-pressure adsorption and low-pressure desorption (around atmospheric pressure) while maintaining a constant working temperature. The TSA technology is based on low-temperature adsorption in the adsorber column and high-temperature desorption in the regenerator, while the pressure is almost constant for both columns. In addition, composite techniques such as pressure/vacuum swing adsorption (PVSA) are often studied due to their low energy demands and high regeneration efficiency^[22].

CO₂ adsorption materials can be categorized based on their chemical composition, encompassing activated carbons, zeolites, metal organic frameworks (MOFs), amine-functionalized adsorbents, alkali-doped metal oxides, and other compounds. These materials have demonstrated a notable capacity for CO₂ adsorption, even when subjected to higher CO₂ pressures, outperforming the typical applications of VSA or TSA methods^[227]. The effectiveness of the adsorption process in capturing CO₂ is significantly influenced by the characteristics of the adsorbents. Extensive investigations have been conducted to evaluate the potential of various porous materials for CO₂ adsorption^[228–230]. Two primary mechanisms are considered: physical adsorption, which relies on van der Waals forces between CO₂ and the adsorbent, and chemical adsorption, where CO₂ forms a chemical bond with the surface of the adsorbent. Specific criteria have been established to gauge the suitability and efficiency of CO₂ adsorbents, encompassing aspects like capacity, selectivity, rates of adsorption and desorption, required temperature conditions, thermal and mechanical stability, regenerability, manufacturing and regeneration costs, and the influence of impurities (such as H₂O, SO₂, and NO_x) present in flue gas^[22]. Environmental considerations are also taken into account. In practical applications, it's vital to comprehensively assess the pros and cons of an adsorbent material within the context of its real-world implementation, factoring in cost considerations^[231].

Several prerequisites of adsorbents are necessary to achieve effective CO₂ adsorption: (i) high tolerance for common impurities like SO_x, which can adhere to the adsorbent surface and resist regeneration; (ii) a significant total exposed surface area providing numerous adsorption sites; (iii) rapid rates of adsorption and desorption to minimize the time the gas spends in the column; (iv) an optimal distribution of pore sizes enabling efficient gas diffusion within particles; (v) strong selectivity for CO₂ and weak selectivity for other impurities in flue gas; and (vi) the application of gentle desorption conditions, such as maintaining a minimal temperature difference between adsorption and desorption.

Therefore, the performance of adsorption is based on (i) the difference in size and shape of the component molecules in the gas stream, (ii) the influence of thermodynamic equilibrium effects, and (iii) the different diffusion rates of the gas stream components^[225].

3.5. Comparison of various post-combustion techniques

Table 13 summarises the benefits and drawbacks of the different post-combustion CO₂ capture systems. Although the fact that each technique has its advantages, none of them is sufficient to economically manage the significant quantities of post-combustion flue gas from power plants or other industrial sectors. The following factors usually constrain these technologies:

- 1) CO₂ partial pressure/concentration: Technologies such as physical absorption, adsorption, membrane, and cryogenic, usually need high CO₂ partial pressure/concentration in the flue gas since all of them work by physical mechanism. Especially a CO₂ concentration over 20% is required for membrane separation technology^[221].
- 2) Impurities in flue gas: The separation performance of adsorption and membrane can be influenced by the water and other gas (SO_x and NO_x) impurities. These impurities will reduce the selectivity and permeation of the adsorbents and membranes; it will cause dangerous operational problems such as clogging of piping heat exchangers and other equipment.
- 3) Processing capacity: The adsorption technique has poor separation performance when handling huge emission quantities.
- 4) Energy consumption: In the chemical absorption process, high energy is consumed to heat the CO₂-riched absorbents for regeneration.
- 5) Separation efficiency: The bulk removal of CO₂ from flue gas mainly involves physical absorption and membranes. Multiple stages of recycling are needed for the membrane technology to achieve high degrees of separation.

Table 13. The advantages and disadvantages of different post-combustion CO₂ capture technologies.

Capture technologies	Benefits	Drawbacks
Absorption	<ol style="list-style-type: none"> 1. High absorption rate and efficiency (>90%) 2. Could be used at low partial pressures of CO₂. 3. The most widely used technology in practice. 	<ol style="list-style-type: none"> 1. Considerable energy consumption for solvent regeneration. 2. Environmental impact caused by absorbent degradation or evaporation. 3. Equipment corrosion.
Adsorption	<ol style="list-style-type: none"> 1. The adsorbent has little environmental pollution and can be recycled. 2. The adsorption efficiency is relatively high (>85%). 	<ol style="list-style-type: none"> 1. The cool-down and dehydration treatment required for the flue gas prior to adsorption. 2. Impurity gases can have an irreversible effect on the adsorbent.
Membrane	<ol style="list-style-type: none"> 1. Low environmental pollution. 2. Direct separation of CO₂ without energy penalty. 3. Simple and modular designs. 	<ol style="list-style-type: none"> 1. Gas needs to be compressed prior to separation. 2. Gas impurities can have an irreversible effect on the membrane. 3. Limited separation purity. 4. Large footprint required.

Among all available options discussed above, amine-based chemical absorption is one of the most promising separation methods. The amine absorption process has higher capture efficiency (>90%) and larger processing capacity; Furthermore, it exhibits efficacy at low CO₂ partial pressures and demonstrates the capability to capture multiple acid gases (including CO₂, NO_x, and SO_x) from flue gases while generating valuable by-products^[232]. The key drawbacks are high energy consumption for regenerating the absorbents and potential environmental impacts related to absorbent degradation. However, advanced absorbents have been developed to overcome these problems by lowering the regeneration temperature and energy consumption. In the next section, we shall summarize the advancements in solvent formulations made in the recent past to overcome the issue of high thermal penalty and solvent degradation.

It should be noticed that both of physical absorption and adsorption relies on physical driving force to capture the CO₂, but there are significant differences between these two techniques. For physical absorption, the CO₂ is dissolved in the liquid phase without changing its chemical structure, and for CO₂ adsorption, which generally occurs between the gas phase and the liquid phase^[233]. In physical absorption, the solvent capacity increases nearly linearly with pressure following Henry's law, and the solvent is regenerated by reducing the pressure (flash). As for adsorption, CO₂ molecules are adhered to the surface of a solid material. This involves

weak van der Waals forces, electrostatic interactions, or other surface interactions^[234], these forces are relatively weaker compared to chemical bonds, resulting in adsorption that is generally more reversible than absorption. The adsorption is always occurred between gas phase and porous solid. Due to the adsorption is typically more reversible than physical absorption, CO₂ molecules can be released easily from the surface by altering conditions like temperature, pressure, or gas composition^[235-236]. However, for enhancing the CO₂ capture performance in adsorption, the modification strategy is always taken such as amine-impregnated^[237]. In this composite material, van der Waals forces and chemical absorption coexist. In summary, CO₂ capture by physical absorption involves the incorporation of CO₂ into a liquid with solubility, while CO₂ capture by adsorption involves attaching CO₂ to the surface of a solid material with weaker van der Waals forces.

4. CO₂ utilisation options

In addition to storage, carbon capture and utilisation (CCU) investigates various uses for CO₂. The procedure must be economically feasible, safe, and environmentally benign^[17]. In recent research, major areas of study for CO₂ utilisation including (i) chemicals and fuels conversion by using CO₂ as feedstock, (ii) CO₂ mineralization to solid carbonates, (iii) desalination by CO₂ for water production, and (iv) enhanced oil/gas recovery. There are still numerous basic and technical problems to be resolved in the development of these technologies to assure net CO₂ emissions. For instance, creating efficient thermal and (photo)electrochemical catalytic reaction pathways, comprehending the processes that lead to the creation of inorganic carbonate in minerals and industrial waste systems, or speeding up biological CO₂ conversion pathways, among other things^[8].

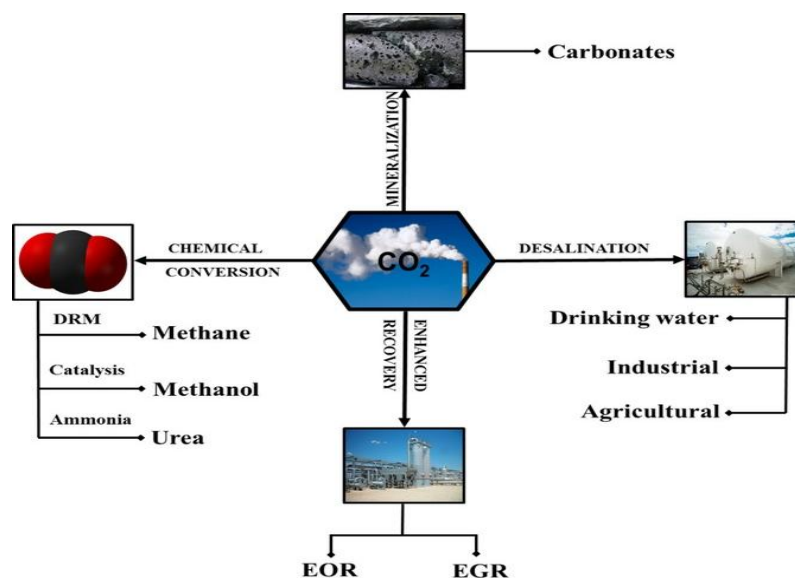


Figure 14. Various carbon-utilization pathways. Reproduced with permission from Al-Mamoori et al.^[8].

4.1. Enhanced oil/gas recovery

EOR/EGR is a kind of technique that involves injecting a chemical into the storage reservoir in order to repressurize a rock and extract any entrapped oil/gas^[238].

During CO₂-EOR, the injected CO₂ interacts with the oil, releasing it from its often difficult-to-recover rock structure. This stream is then driven to the surface, where CO₂ is extracted from the oil and injected into the cycle to continue the cycle. Typically, this technology yields more barrels per reservoir than conventional oil recovery techniques. CO₂ flooding is one of the most common and successful EOR procedures because, by inflating the oil, it makes it lighter and easier to extract^[239]. Recent research has focused on extracting CO₂

from potentially hazardous gas streams, such as flue gas and other industrial gas effluents, as opposed to using naturally occurring CO₂. Since 1972, when CO₂-EOR operations began in the world's most desirable CO₂-EOR location, the Permian Basin in Texas, CO₂-EOR has been a financially successful endeavour in the United States. It has generated over 30 billion barrels of oil, of which 1.3 billion barrels were produced using CO₂ as the recovered medium.

EOR technologies are challenged by a number of difficulties. Fluid properties and capillary pressure reduce the efficacy of CO₂ flooding as a consequence of the varying geological formations across wells. In addition, a multitude of parameters, such as fluid production rates, the corrected neutron log (CNL), and the production log, are required for efficient execution^[240]. In spite of these difficulties, CO₂ EOR/EGR has gained a considerable lot of interest and is anticipated to increase rapidly in the near future despite these challenges. Overall, CO₂ EOR/EGR is a promising approach applicable to the great majority of reservoir types for enhanced oil/gas recovery. Despite this, EOR provides just 3% of CO₂ usage as now. Although the price of CO₂ has slowed progress in this sector, its usage is continuously increasing and various facilities have adopted this technique in their reservoirs^[239–242].

4.2. Chemicals and fuels conversion by using CO₂ as feedstock

Conversion CO₂ to valuable chemicals or fuels is considered as the most potential method in CO₂ utilization. Furthermore, it validates CO₂ extraction and may partly replace fossil fuels as the primary energy source. It may provide novel methods for creating environmentally friendly technology to augment traditional fossil fuels^[17].

4.2.1. Chemical production

CO₂ is a useful feedstock for the production of several high-quality compounds. Urea (160 Mt/year), inorganic carbonates (60 Mt/year), polyurethane (18 Mt/year), acrylic acid (10 Mt/year), polycarbonates (4 Mt/year), and some alkylene carbonates (Kt/year) are the most major usage^[9]. The greatest market for CO₂ usage is in producing urea, a significant fertiliser. It is also a key ingredient to produce fine chemicals and urea resins, as well as an initial feedstock for synthesising of polymers and pharmaceuticals^[13].

Given the demanding conditions of high temperature and pressure involved in the process, the use of heterogeneous catalysts with excellent performance and numerous active sites becomes essential. Achieving high-performance catalysts is imperative for the electrochemical reduction of CO₂ under mild conditions. In Aresta et al. study, various catalyst electrodes (Sn/Cu, BiSn/Cu, Bi₂Sn/Cu, Bi₃Sn/Cu, Bi₄Sn/Cu, and Bi/Cu) were fabricated through electrodeposition, and their effectiveness, stability, and selectivity in the reduction of CO₂ to formic acid were systematically assessed^[243].

4.2.2. Fuels production

The fuels that converted by CO₂ including methane, methanol, syngas, and alkanes. CO₂ is a thermodynamically stable molecule, therefore using it takes huge amount energy and catalyst to produce these chemical^[14]. The two most major processes for creating fuels from collected CO₂ are hydrogenation and dry reformation of methane (DRM). CO₂ hydrogenation has the ability to recycle CO₂, store H₂, create fuel, and solve the issue of electric energy storage, making it a very appealing strategy for CO₂ usage. The Fischer–Tropsch (FT) process uses the DRM as a significant route for the synthesis of methanol and a range of other liquid fuels^[244].

Many scientists are now investigating DRM as a means of producing syngas from CO₂, when compared to partial oxidation and steam reforming, the syngas produced by DRM is purer^[245]. Additionally, DRM may be used at distant natural gas sources to produce liquid fuels, which are more convenient to transport than

gaseous fuels, since the quantity of unreacted methane is just 2%, which is less than that in steam reforming. The DRM reaction has been widely tested using Ni, Ni-Co, Ru, and Rh supported on silica, alumina, and lanthanum oxide^[5,11]. High-activity, very stable catalysts for DRM have been developed, but finding a catalyst that can withstand the high temperatures required for this reaction is still difficult; High temperatures cause most catalysts to deactivate.

4.3. CO₂ mineralization

The process known as carbon mineralization involves the creation of solid carbonate minerals, including calcite, magnesite, dolomite, and various hydrated magnesium carbonate minerals like nesquehonite. This is achieved by the interaction of carbon dioxide (in its gas, liquid, dissolved in water, or supercritical form) with rocks rich in calcium or magnesium. The sources of magnesium and calcium are primarily mafic and ultramafic rocks (such as mantle peridotite, basaltic lava, and ultramafic plutons), mining tailings from these rock types, and industrial by-products like cement kiln dust, steel slag, and fly ash^[8].

The mineralization process is energy intensive with high pressure (10–15 MPa) and temperature (150–600 °C)^[246]. In addition, the carbonation reaction period is lengthy (6–24 h), and minerals must be extracted (37 m). Moreover, the exothermic character of the mineralization process and the geothermal gradient (up to 20 °C per kilometre) contribute to a decrease in energy usage^[247]. Furthermore, CO₂ purity is not necessary, and flue gas may be used without the removal of pollutants including SO_x and NO_x.

4.4. CO₂ desalination

The collected CO₂ might be employed to eliminate total dissolved solids (TDS) then convert brine to water^[8,13,248]. In CO₂ desalination process, firstly, the sea water is mixed with ammonia, when exposed to CO₂, weak bonds begin to form, resulting in the removal of ions from the water phase. The later NH₄Cl may be recycled by thermal processes using calcium oxide or employed as a raw material for the production of ammonia and chlorine^[248]. The cost of CO₂ desalination has been researched by 2013 DOE (US department of energy) report, which is estimated around \$0.83 per litre. Currently, whereas CO₂ remains an appealing desalination option, but this technique is unlikely marketable due to cost^[8].

5. Conclusion and outlook

This article discusses and summarises the recent developments in carbon capture process. In recent years, significant advancements have been made in the design and development of various CCU systems, with a few instances being implemented on a commercial scale. However, the majority of the available technologies are so far limited to lab scale.

Within the various carbon capture methods, the post-combustion process is the most promising in short term, as it can be easily installed into existing power plants. Amine absorption method is currently the most mature technology. Typically, a 30 wt% aqueous MEA solution is considered the benchmark for CO₂ capture solvent. However, the major problems it faces are the high energy consumption for regeneration, oxidative and thermal degradation of amines, and corrosion of equipment. Thus, developing advanced absorbents that can reduce energy penalty and maximize the CO₂ capture capacity are the primary research goals. Recently, a series of novel amine absorbents have been proposed and investigated that include blended amine absorbents, phase change absorbents and non-aqueous absorbents. Among them, blended amine absorbents combine the advantages of different amines to compensate for their disadvantages, phase change absorbents significantly reduce the volume of solution to be regenerated, and non-aqueous amine absorbents use organic solvents with low specific heat capacity and heat of vaporisation instead of water as a solvent to significantly reduce the energy requirement to regenerate the solution. However, the regeneration energy is still high as the blended

amine solution still uses an amine that produces a stable carbamate to enhance absorption rate. The CO₂-enriched phase of the phase change absorbent has a high viscosity which affects desorption efficiency and increases the capital and operating costs. Non-aqueous absorbents can directly replace conventional aqueous solutions for CO₂ capture without extra cost, but different non-aqueous solvents have their own drawbacks. For example, alcohols, such as methanol and ethanol, can lead to large amounts of solvent volatilisation, resulting in solvent loss and contamination; glycols and other polyhydroxy alcohols show non-linear increase in viscosities after absorption; ionic liquids have a complex and expensive synthesis process. These factors have been obstacles to further application and development of non-aqueous amine absorbents for CO₂ capture. An ideal absorbent should have low volatility, maintain a low viscosity, and energy-efficient regeneration. At the same time, it should also have a relatively good absorption performance, and cycling capacity.

Future research should focus on hybrid processes that integrate CO₂-capture and utilisation systems, since thermodynamic assessments have shown the energy and cost effectiveness of such systems (by decreasing both capital and operating expenses). To better assess the materials development, process operating needs, and process scalability, more research on hybrid process is required.

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Conflict of interest

The authors declare no conflict of interest.

Abbreviations

[bmim][AC]	1-butyl-3-methylimidazolium acetate
[bmim][BF₄]	1-butyl-3-methyl-imidazolium-tetrafluoroborate
[bmim][DCA]	1-n-butyl-3-methylimidazolium dicyanide
[bmim][OTf]	1-butyl-3-methylimidazolium trifluoromethanesulfonate
[C₂OHmim][DCA]	1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide
0EG	Ethylene glycol
2-EE	2-ethoxyethanol
2-ME	2-Methoxyethanol
2-PE	2-piperidineethanol
AEEA	Aminoethylethanolamine
AMP	2-amino-2-methyl-1-propanol
BECCS	Bioenergy with carbon capture and storage
CAP	Chilled ammonia process
CES	Clean energy system
CLC	Chemical looping combustion
DAC	Direct air capture
DEA	Diethanolamine
DEA	Diethanolamine
DEEA	Diethylethanolamine
DEG	Diethylene glycol
DEGMEE	Diethylene glycol monoethyl ether
DEPG	Dimethyl ether of polyethylene glycol
DETA	Diethylenetriamine
DGA	Diglycolamine
DMEA	Dimethylethanolamine
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
EG	Ethylene glycol
EMEA	EthylMonoethanolamine
IGCC	Integrated gasification combined cycle

MAE	Methylaminoethanol
MDEA	Methyldiethanolamine
MOF	Metal organic framework
MWCNT	Multi-walled carbon nanotubes
NGCC	Natural gas combined cycle
NMF	N-methylformamide
NMP	Normal methyl pyrrolidone
nMWCNT	Multi-walled carbon nanotubes
PCC	Post combustion capture
PMDETA	Pentamethyldiethylenetriamine
PrOH	1-propanol
PZ	Piperazine
TEA	Triethylamine
TEA	Triethylamine
TETA	Triethylenetetramine

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