Chapter 1

Introduction

1.1 CO_2 Emissions, consequences and its solution

In this modern era, the world's population is increasing drastically, such that carbon dioxide (CO_2) emissions are also increasing in the environment due to various human activities [1,2]. This anthropogenic CO_2 released during the combustion of conventional fossil fuels is mainly responsible for severe environmental issues like global warming and climate change [3,4]. If it is not adequately checked, CO_2 emissions will rise to 37.2 gigatons by 2035 [5]. This scenario would result in rising sea levels, droughts, flooding, storms, severe heat waves, and other natural calamities. To fulfill the basic needs and requirements, various industries like food processing industries [6], cement industries [7], aluminum industries [8], iron and steel industries [9], petrochemical industries [10], thermal power plants [11], and numerous other chemical-based industries [12,13] are the primary sectors that are responsible for the large CO_2 emissions.

Due to a lack of technologies, coal-fired thermal power plants emit a high percentage of CO_2 in the form of flue gas in order to meet the rapidly growing demand for electricity by the rapidly growing population and manufacturing industries [14-18]. The CO_2 emissions by thermal power plants contribute to one-third of the overall CO_2 emissions worldwide [7]. Approximately 85 % of electricity production relies mainly upon the combustion of fossil fuel commodities [2,19]. To imagine life without electricity is impossible, so it is essential to generate it effectively without imposing a hazardous burden on environmental conditions. So, researchers are targeting alternatives of conventional energy resources.

However, in this present scenario, installing power plants that utilize a clean energy medium (fuel) to produce no CO_2 is impossible soon [2]. The serious issue of global warming can be restricted by using the carbon capture and storage (CCS) technique [20,21]. The Worldwide CCS technique is very promising and has been operating for the past few decades [22,23]. The main techniques used for CCS are pre-combustion, post-combustion, and oxy-combustion [24-27]. In this series, the post-combustion technique is regarded as the most reliable and developed [28]. Its easy retrofit, flexible operation, low energy demand, and low operational costs are some of its advantages [14,29-31]. Figure 1.1 shows the flow diagram for the CCS technique and its implementation.

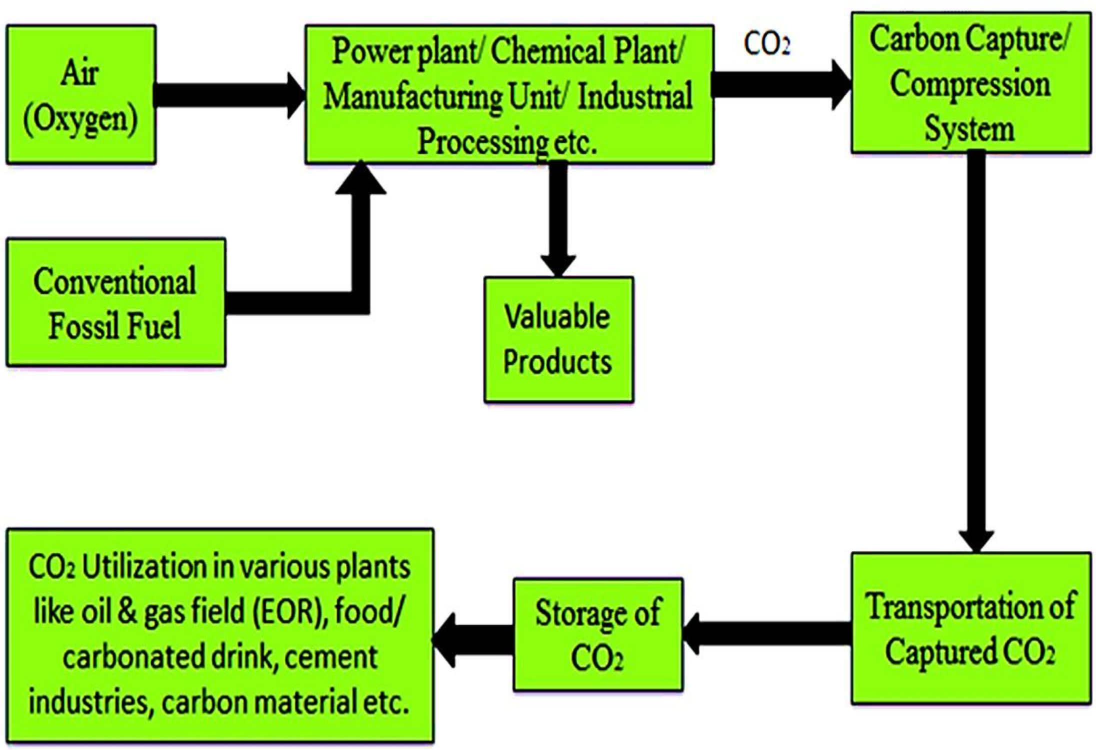


Figure 1.1 Flow diagram for CCS technique and its implementation [2,28,31].

Absorption, adsorption, cryogenic separation, membrane technology, chemical looping combustion, and microalgae are the methodologies available for CO_2 capture [5,28,31-35].

However, for thermal power plants, chemical absorption with amine solvent is regarded as the most versatile, cheap, and flexible method [36]. Many traditional amine solvents are used to capture CO_2, including Monoethanolamine (MEA), Methyldiethanolamine (MDEA), Diethanolamine (DEA), 2-Amino-2-methyl-1-propanol (AMP), and Piperazine (PZ) [7,17,30,37]. MEA (30 wt%) due to higher reactivity towards CO_2 is regarded as the benchmark by various researchers [38,39]. The solvent regeneration method regenerated these alkanolamines at 120–150 ℃, so their regeneration cost is 70–80 % of the overall operational cost [40]. They have disadvantages of solvent degradation, corrosion, high energy demand, etc. [16]. Many decades ago, a single aqueous alkanolamine played a critical role in CO_2 capture. Still, a few challenges of limited CO_2 loading and high regeneration cost forced the researchers to work upon their various amine blends. Various amine blends are prepared by mixing primary/secondary amine (activators) with tertiary or sterically hindered amines (promoters), and they have fast reaction kinetics [41]. Some of them show biphasic behavior, and the solution is split up into two phases, i.e., CO_2 rich (approximately 90 % CO_2 loaded) and CO_2 lean after CO_2 absorption [3]. Further, this CO_2-rich phase is sent to the regeneration column for further operation [22,39,40]. Shen et al. [3], in their investigation of 40 various amine blends, revealed that the CO_2-absorption capacity with respect to an increase in amine alkalinity (pKa value) is mainly affected by the tertiary amines rather than the primary/secondary amines blended with all the tested tertiary amines in a biphasic system. Biphasic solvents have the potential for low energy penalty (lower than 2.1 GJ/tCO_2) for solvent regeneration [42]. Utilizing biphasic solvents is a much better option than using conventional MEA (3.80 GJ/tCO_2), but their solvent screening is a very rigorous task.

In the earlier stage, solvent screening was performed on some lipophilic amines and different blends of N,N-Dimethylcyclohexylamine (DMCA), AMP, and N-Methylcyclohexylamine (MCA) showed biphasic characteristics with 3.34 mol of CO_2/L of the solvent of CO_2 cyclic loading [14,16,43]. CO_2 loading, reaction rate, reaction kinetics, absorption heat, phase-separation temperature, cyclic capacity, heat duty, and thermodynamic behavior are some major parameters studied by most of the researchers on biphasic solvents during the years 2011 to 2020. Presently, many liquid-liquid phase-splitting solvents, such as 1,4-Butadieamine (BDA) + 2-(Diethylamino)ethanol (DEEA) blend [44], DMCA+MCA amine blend [41], MEA + 1-Heptanol blend [40], DEEA + N-Methyl-1,3-diaminopropane (MAPA) blend [22], Triethylenetetramine (TETA) + DEEA blend [38], Diethylenetriamine (DETA) + N, N, N', N'', N'''–Pentamethyldiethylenetriamine (PMDETA) blend [45], 2-(Ethylamino)ethanol (EAE) + Diethylene glycol diethyl ether (DEGDEE) blend [46], TETA + N, N, N', N'-Tetramethyl-1,3-propanediamine (TMPDA) blend [3], DEEA + 2-((2-Aminoethyl)amino) ethanol (AEEA) blend [42], TETA+DMCA blend [47] have been reported for CO_2 capture. Some solvents on CO_2 loading split up into two layers consisting of solid and liquid, collectively known as solid-liquid phase-changing solvents. Amine-alcohol solvents, amino acid-alcohol solvents, and room-temperature ionic liquid-amine blends are classified under non-aqueous phase-changing solvents. The solid products so formed in reaction with CO_2, when removed from the solution in the form of precipitation, may shift the equilibrium in the direction of the formation of carbamate or bicarbonate [45]. ^{13}C nuclear magnetic resonance (NMR) analysis and X-ray diffraction (XRD) analysis revealed the species present in the solid products.

1.2 Sources of CO_2

The major sources of CO_2 emissions are mainly responsible for establishing of CO_2-capturing systems. The sources of CO_2 emissions are mainly classified as combustion emissions and process emissions. Burning of conventional fossil fuels like coal, natural gas, and oil liberates enormous amounts of CO_2 and are known as combustion emissions. At the same time, all other CO_2 emissions rather than combustion processes are classified under process emissions. The conversion of limestone to lime, iron ore to iron metal, and the reduction of water shift reactions emit CO_2 into the atmosphere because of chemical reactions; all are examples of process emissions. Combustion and process emissions sometimes occur simultaneously within the same industrial unit and are mixed before being treated for high-purity CO_2 [10].

Coal-fired thermal power plants are assumed to be the largest source of CO_2 emissions and discharge many billion tons of CO_2 annually [26]. This emission contributes to one-third of overall CO_2 emissions across the world [28]. There are some industries, like ammonia (NH_3) production, hydrogen (H_2) production (during oil refining), and the fermentation process, which capture CO_2 by themselves [31]. Table B1 of Appendix – B shows statistics of United States (US) CO_2 released in 2020 by some major industrial sectors. Fossil fuel combustion, petroleum processing, and electricity-generating power plants are the US's top three largest CO_2-emitting industries.

1.3 Various carbon-capturing techniques

The various industrial units take up fuel, mainly including coal, oil, and natural gas, as a feed for combustion purposes. These naturally available biomasses have been used as a conventional fuel for many years. Various gases like CO_2, carbon monoxide (CO), nitrogen (N_2), nitrogen oxides (NO_X), sulfur oxides (SO_X), and many other harmful pollutants are emitted into the atmosphere on initial combustion. These gases are mainly responsible for the global warming of the earth. Some industries are the major sources of CO_2 emissions, and these industries, along with CO_2 composition, are listed in Table B2 of Appendix – B.

The sizeable CO_2 gas from the different industries in the form of flue gas can be effectively captured, compressed, and stored via pipeline. CO_2 gas compression changes its state from gas to liquid, making its transportation convenient [2]. The unfavorable effects of global warming on the climate can be checked and minimized by this method. This captured CO_2 can be used in the food industry, cement industry, petroleum industry, ammonia industry, pulp & paper industry, and iron-steel [48].

There are three main types of CCS technologies available nowadays. These technologies are pre-combustion, post-combustion, and oxy-combustion, which are mainly adopted by many industries [24,26]. Among these methods, the oxy-combustion technique is in the development stage, and commercially, it has yet to be accepted by the processing plant. The plant configuration handles the adaptation of any of the technologies by the industries [49]. The CO_2 capturing technology can be implemented within the already working coal-fired thermal power plants, as they are a tremendous source of CO_2 emissions. The plant modification by these techniques is compact and retrofits easily. The methods used in different technologies are absorption (physical or chemical), adsorption, membrane separation, chemical looping combustion (CLC), cryogenic separation (expensive method), and microalgae process to perform desired CO_2 separation [32]. Figure 1.2 indicates the various classifications of CO_2 capture methodology in various industries.

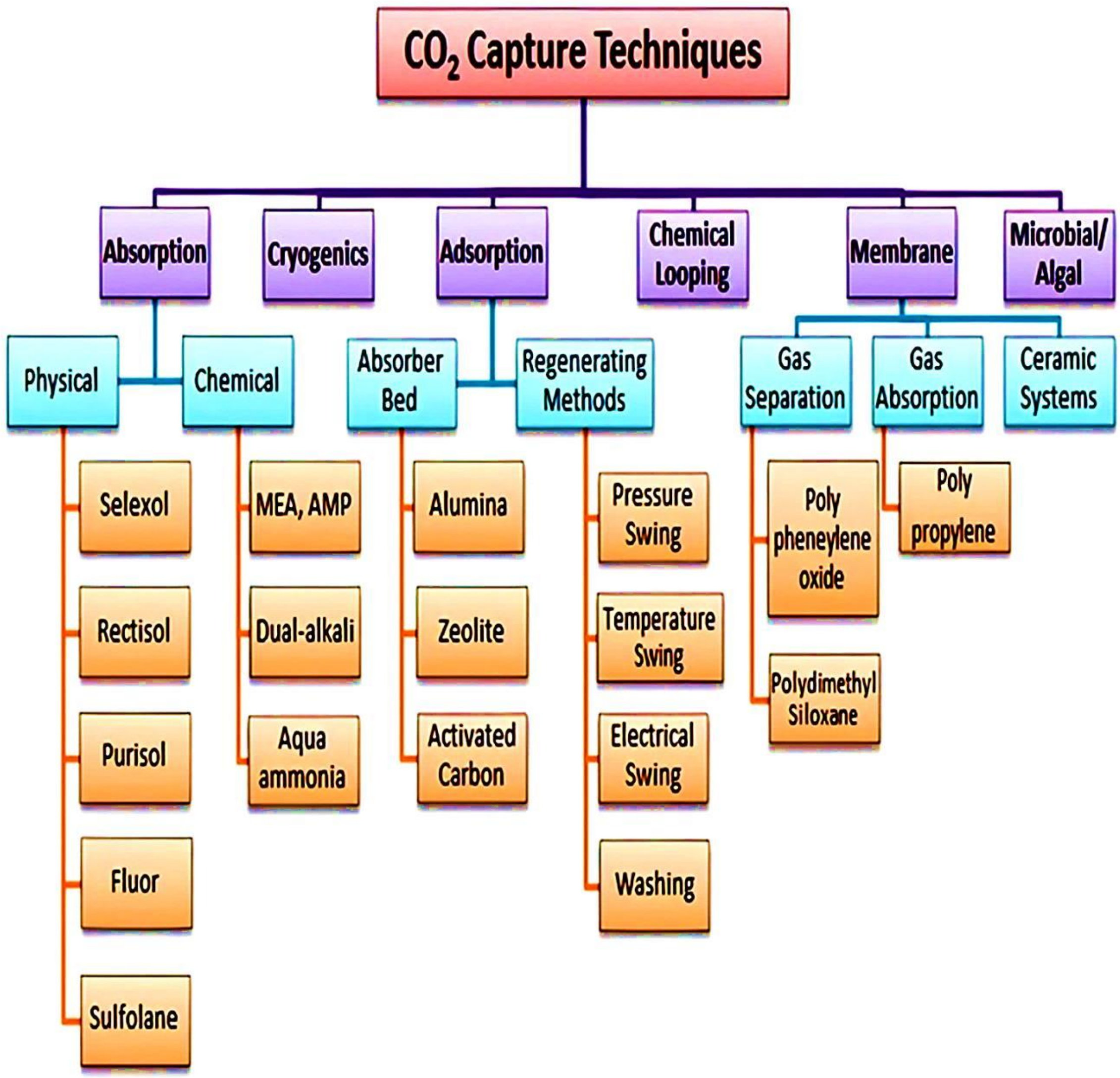


Figure 1.2 Various CO_2 capture techniques available for industrial purposes [2,28].

1.3.1 Pre-combustion technique

The pre-combustion technology eliminates CO_2 from fossil fuels before the complete combustion of these carbonaceous commodities takes place [21,23,50,51]. This process is extremely energy efficient, with a high CO_2 absorption rate. The captured CO_2 has a high concentration level [24], around 15–60 % by volume, a high-pressure range (i.e., 2–7 MPa), and an elevated temperature in the range of 200–400 ℃ [23].

The combustion of fossil fuels occurs either with oxygen (from the air) or with steam. The combustion through oxygen is a highly exothermic reaction known as partial oxidation (Eq. 1.1). Another phenomenon is governed by steam combustion, which is endothermic, called steam reforming (Eq. 1.2). Both these combustion reactions liberate carbon monoxide and hydrogen gas as a product. The mixture of these gases is known as synthesis gas, and the whole procedure is called the gasification of fossil fuels [2,23]. Although CO_2 capture efficiency is low and due to the higher processing capacity of fuels, partial oxidation is preferred over steam reforming by modern industries.

Partial Oxidation: $C_XH_Y + \frac{X}{2}O_2 \leftrightarrow xCO + \frac{Y}{2}H_2$ (1.1)

Steam Reforming: $C_XH_Y + xH_2O \leftrightarrow xCO + (x + \frac{Y}{2})H_2$ (1.2)

Pure H_2 gas is achieved after complete separation and storage of CO_2 takes place. The production of H_2 gas by the pre-combustion technique is highly economical as compared with conventional renewable energy resources. However, higher capital investment is required for the transportation of H_2 gas to the desired production site. Therefore, the transportation cost of H_2 gas can be minimized by installing the pre-combustion unit nearby a plant that requires H_2 gas. This pure H_2 gas is utilized in the fuel cell industry, furnaces, the petroleum industry, boilers, and the pharmaceutical industry. The schematic representation of pre-combustion technology is shown in Figure A1 of Appendix – A.

The coal-fired thermal power plant is the major source of CO_2 emissions; therefore, this pre-combustion technique is suitable for these power plants. The complete representation of the pre-combustion technique used in the thermal power plant is shown in Figure A2 of

Appendix – A. Some coal-fired thermal electricity plants were initially installed with an air separation unit (ASU). Whenever a gaseous air mixture passes through these ASUs, its various components, like oxygen (O_2), N_2, water (H_2O), carbonyl sulfide (COS), CO, CO_2, and hydrogen sulfide (H_2S), are separated. Only separated O_2 gas is passed to the gasifier unit for further oxidation purposes. Coal, pet coke, air residue, and industrial wastes are some of the major lower-grade feedstock suitable for combustion purposes. This feedstock combusts with O_2 gas inside the gasifier unit, and its operating pressure is very high, i.e., 30–70 atm. [49]. The gasifier unit partially oxidizes these carbonaceous fuels, leading to synthesis gas conversion. The combustion inside the gasifier unit produces syngas ($CO+H_2$) and impurities. The impurities must be separated while the syngas further cooled and pass to the cyclone separator [23]. Impurities left over from the gasification process are removed from the cyclone separator in the form of ash particles. A shift reactor with one or two stages containing a packed bed of catalyst (mainly iron-chromium and copper) is installed next to the cyclone separator [52]. The packed-bed reactor converts CO to CO_2 (15–20 % by volume on a dry basis) at a reduced temperature. This conversion reaction is exothermic and is called a water gas shift (WGS) reaction (Eq. 1.3) [28].

Water Gas Shift Reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$ (1.3)

Further, the desulphurization column (Claus unit) is used to remove sulfur impurities from the gas. The outlet stream from this desulfurizing column will act as feed for the CO_2 capturing system. The remaining gaseous mixture is physically absorbed, and CO_2 gets captured, compressed (at 150 atm.), and finally stored. The chemical solvent for industrial process i.e., selexol is widely used to capture CO_2 by the physical absorption method [2,53,54]. Ultimately, impure H_2 gas with the most negligible mixture content of methane

(CH_4) and CO/CO_2 is formed. The pressure swing adsorption method is highly beneficial for achieving high purity of H_2 gas. This pure H_2 gas combusts with air inside the turbine and finally produces electricity. The natural gas combustion-based power plant also uses pre-combustion technology. This pre-combustion technique is used in integrated gasification combined cycle (IGCC) power plants [28,55], and the treated gases coming out of such plants have a mixture of 40 % CO_2 and 60 % H_2 [50]. In these power plants, gaseous fuel combusts with oxygen inside the turbine and creates synthesis gas. This process requires costly fuels for combustion, and such combustion is termed as reforming of fuel [2]. The electricity production by these IGCC plants is highly expensive, and their commercialization is tough.

The pre-combustion technique produces a higher concentration of CO_2 gas, which is responsible for the smaller size of the equipment. Hence, it is cost-effective [48], less water consumption demand, regeneration cost is low [49], and production and utilization of H_2 gas as fuels are some of its advantages. The advancement of this technology is limited till now because it restricts its implementation in IGCC based power plants.

1.3.2 Post-combustion technique

The post-combustion carbon capture technology is used to capture CO_2 from its gaseous mixture, which is produced by directly burning carbonaceous materials like fossil fuels with air [54]. In trending coal-fired power plants, pulverized coal and air are used as feed, and their combustion takes place in the furnace or boiler. The combustion system generates steam, which is responsible for the turbine rotation and ultimately produces electricity. A complete representation of the post-combustion technique is shown in Figure 1.3.

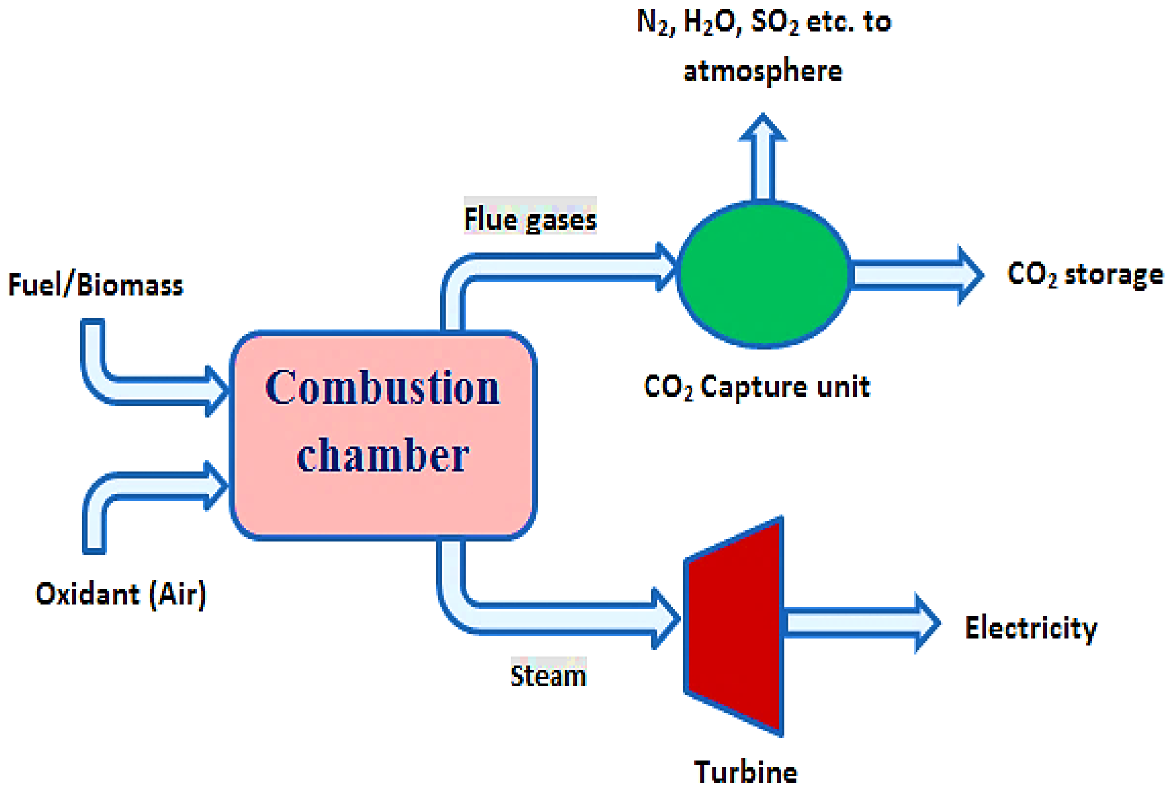


Figure 1.3 Schematic representation of the post-combustion technique [26,28,29].

At atmospheric pressure, a low concentration of CO_2 gas (around 15 %) is produced in the flue gas stream [26,49]. Instead of direct emission into the atmosphere, this CO_2-enriched flue gas is fed to equipment that separates CO_2 from its gaseous mixture. The separated CO_2 is compressed, stored, and ultimately transported in large storage vessels from one place to another. The impurities of coal on combustion produce air pollutants (SO_X and NO_X), toxic gases and trace impurities (mercury; Hg), particulate matter/dust particles (fly ash), and non-condensable gases (mainly O_2) [32,36,49,54]. To meet environmental emission standards, harmful entities must be removed before discharging them into the environment.

In this technique, CO_2 capturing is efficiently done by chemical absorption with an aqueous alkanolamine-based solvent (mainly aqueous amine solvent mixtures) [3,14,39,42]. Various approaches rather than absorption, i.e., adsorption, membrane separation, cryogenic separation, and microalgae process, are not efficient for CO_2 capture by this technique [56]. Initially, a proper chemical reaction (by chemical amine-based solvent) occurs in the absorber unit, so around 85 % to 90 % of CO_2 is captured [2,54]. This amine-CO_2 loaded solution is sent to the regeneration unit, and the absorbent is recycled back for further processing. This technique is the most established [23] and can be installed directly in the existing coal-fired based thermal power plant. As the partial pressure of CO_2 is low [51], so it requires a high volume of gas for treatment, costly amine solvents for absorption, high regeneration energy (i.e., 80 % of the entire procedure), large equipment size, and higher capital cost are some of its disadvantages [23,57-58].

1.3.3 Oxy-combustion technique

The oxy-combustion technology is the latest approach in the field of carbon-capturing, in which air is replaced by pure oxygen for combustion [57]. This purpose is fulfilled by separating oxygen from the air through ASU. Oxygen can be separated through membrane separation, adsorption, chemical looping, and cryogenic distillation methods. This technology was developed as an alternative to the post-combustion technique, and it does not require a costly CO_2-capturing system [54]. The combustion of fuel with purified oxygen generates a very high temperature (around 3500 ℃), which is not suitable for the material of construction for the existing power plant [49]. The high-temperature flue gas concentrated with CO_2 is recycled back [28] to the combustion unit for waste heat recovery. In the present power generation scenario, this temperature is restricted up to 1300–1400 ℃

for the gas turbine cycle and 1900 ℃ for the coal-fired boiler [59]. The combustion with oxygen restricts the large nitrogen content, and only their traces stay in the flue gas stream [51]. Fly ash, as particulate matter, is present in the flue gas stream that should be initially removed. Water vapor, CO_2 with the least sulfur dioxide (SO_2), and NO_X are finally left in the flue gas [32]. Further condensation of water vapor and removal of air pollutants generates a highly concentrated CO_2 stream [49] that can be directly transported via pipeline in a supercritical state [26,32,51]. The existence of inert gas in the concentrated CO_2 gas develops two-phase flow conditions in the pipeline while filling the storage tank. Therefore, it is crucial to remove inert gas initially during the transportation of CO_2 in the pipeline. The purification of CO_2 in this method is easier than the post-combustion technique, and NO_X content is also low in oxy-combustion [56,60]. A complete schematic representation of the oxy-combustion technique used in the thermal power plant is shown in Figure 1.4.

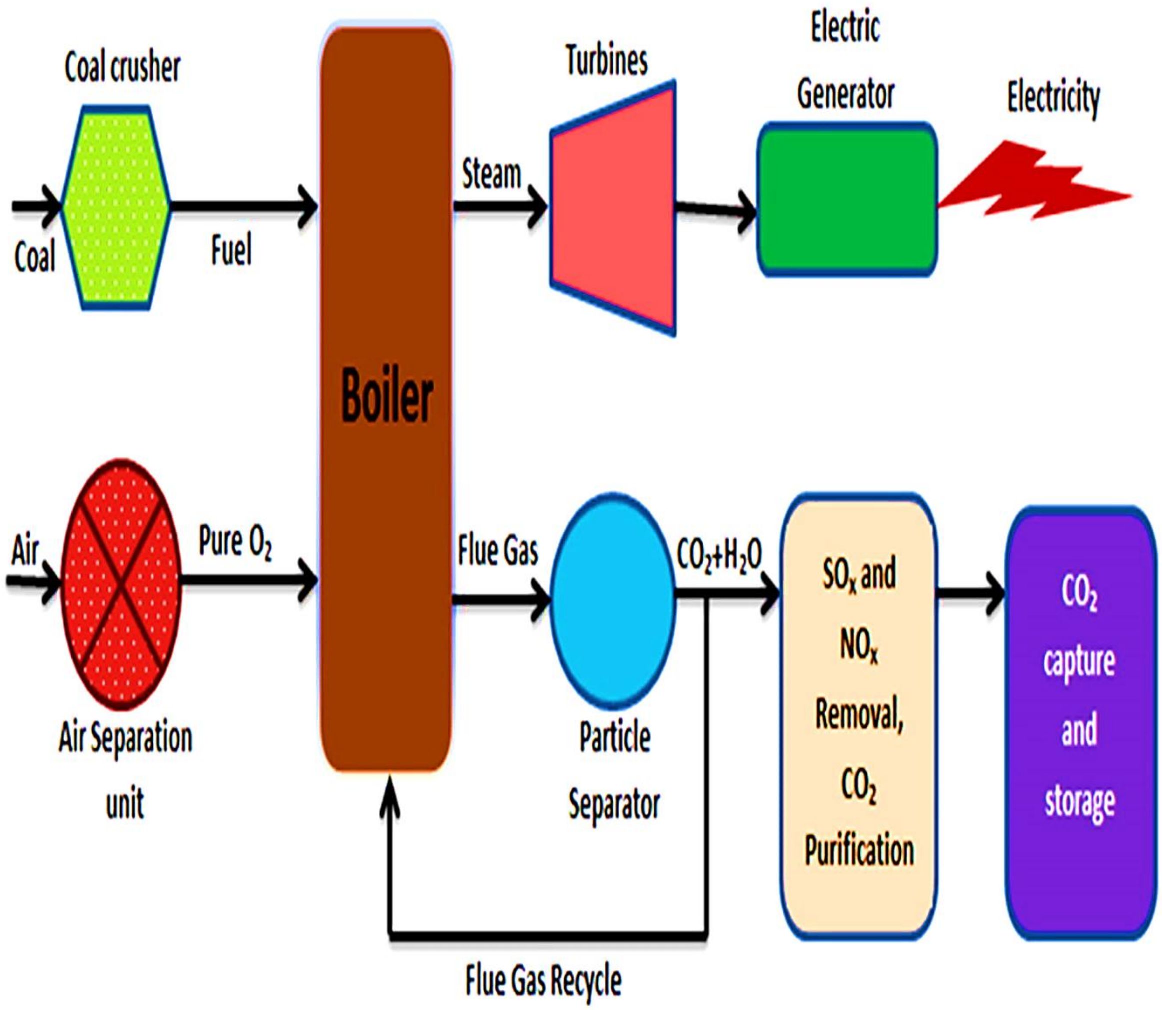


Figure 1.4 A schematic representation of oxy-combustion technique for thermal power plant [2,32,49,51,54].

Numerous research experiments have been performed at the laboratory and also at the pilot plant scale. A pilot thermal power plant with a capacity of 30 megawatt (MW) is being used to establish this oxy-combustion technique [2,54]. To make it fit for commercial use, many designs with different configurations and demonstrations have been proposed. Compared with other capture technologies, this technique is gaining more attention in CO_2 capture process due to its higher CO_2 purity (capture efficiency of around 100 %) and its economical operation. Their disadvantages are that they require a large volume of oxygen gas, is a risky operation, is highly expensive, and their commercialization has not been possible till now.

1.3.4 Comparison in between various CO_2 capture technologies for CCS

CCS technology is suitable for industrial and production divisions, as they are the major sources of CO_2 emissions. This technology is highly recommended to be installed in such plants. They mainly use fossil fuels for combustion purposes, and these plants are the most significant source of high CO_2 emissions. The various flue gas compositions present in CO_2 capture technologies are listed in Table 1.1.

Table 1.1 Flue gas composition (in volume %) obtained from various CO_2 capture techniques [26,29].

Flue gases	Pre-combustion	Post-combustion	Oxy-fuel combustion
CO_2	37.7%	10-15%	85.0%
CO	1.7%	20 ppm	50 ppm
H_2O	0.14%	5-10%	100 ppm
NO_X	-	< 800 ppm	100 ppm
SO_X	-	< 500 ppm	50 ppm
N_2	3.9%	70-75%	5.8%
H_2	55.5%	-	-
O_2	-	3-4%	4.7%
H_2S	0.4%	-	-

The CO_2 emissions enhanced from 32.27 to 36.02 billion tonnes from 2006 to 2024 [2,131]. Following the previous year's data for CO_2 emissions, it can be anticipated that CO_2 emissions can extend up to 43.22 billion tonnes by 2040 [2]. Wilberforce et al. [2] and Theo et al. [23], in their investigation, reported that the commercialization of post-combustion CO_2 capture facilities has increased from 2006 to 2019 as compared with pre-combustion facilities across the globe. In recent years, many countries have begun to acknowledge the issue of CO_2 emissions seriously and have increased their investment and research facilities in this area. According to the latest report published by Global CCS Institute [132], 26 CCS facilities are under construction, 121 are in the advanced development stage, and 204 CCS facilities are in the early stage of development as of 2023. A total of 41 CCS facilities with a CO_2 capture capacity of 49 million tonnes per annum (Mtpa) have started their commercialization in 2023. The list of all 41 commercialized CCS facilities has been incorporated in Table 1.9. Considering all stages of CCS facilities, 392 facilities have been pipelined that can establish a CO_2 capture capacity of 361 Mtpa if they start operating together. The capacity of carbon capture facilities from 2012 to 2023 has been shown in Fig. 1.5. According to recent trends, a significant increase in the total capacity of CCS facilities has been observed from 2020 (65 facilities) to 2023 (392 facilities). There were a total of 65 CCS facilities available in 2020, out of which 26 were commercialized, 13 were in the advanced development stage, 21 were in the early development stage, 3 were under construction, and 2 operations were suspended [133]. 26 commercialized CCS facilities yielded around 40 Mtpa CO_2 capture capacity in 2023. Therefore, as per the recent trend, the number of well-established commercialized CCS facilities increased from 26 to 41 in 2020 and 2023; this is an excellent achievement.

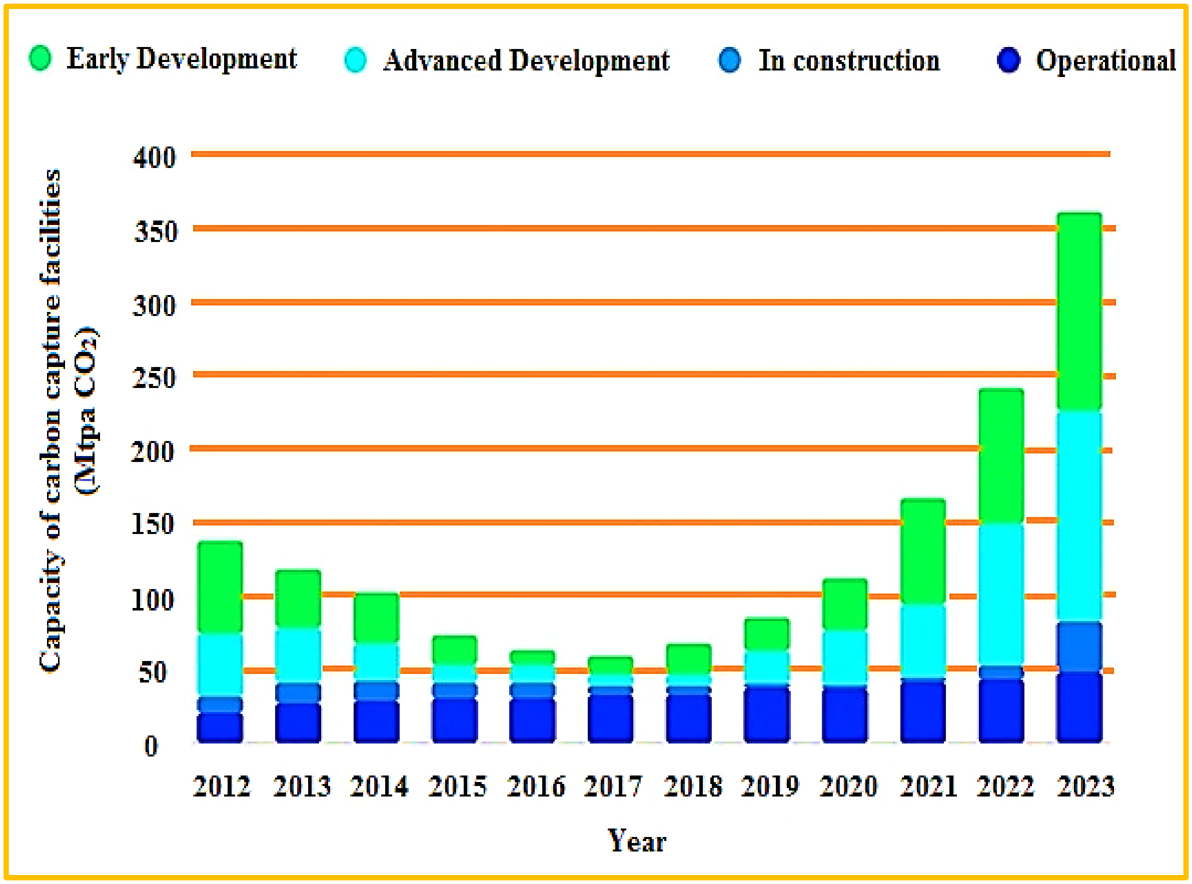


Figure 1.5 Commercialized statistics of CO_2 capture techniques across the globe [2,23,132,133].

Most countries are focusing and started working on this very serious issue of climate change. Because of this, 33.40 million tons of CO_2 is captured per year across the world [2]. This CO_2-capture data analysis is only 0.09 % of the overall yearly CO_2 emissions. For proper protection of climate change, it is vital to develop and expand CCS technology. Comparisons between three available CCS technologies- pre-combustion, post-combustion, and oxy-combustion are shown in Table 1.2, and their main operating conditions with performances are listed in Table 1.3. It was discovered that oxy-fuel combustion has drawbacks such as corrosion, a high energy penalty during air separation (in ASU), a lower net output power, and so on.

Table 1.2 Comparison in between various available CO_2 capture technologies [2,23,24,26,28,54].

Technical Aspects	Pre-combustion	Post-combustion	Oxy-combustion
Maturity level	Effective in process industries that remove acid gases through water shift reactions. Full scale CCS plants are under progress.	Highly matured technology and is utilized in many full-scale commercial production units.	There are currently no any full-scale oxy-combustion CCS plants working. Restricted to laboratories and pilot plants.
Advantages	Energy efficient process due to high concentration (~ 45 vol%) and pressure of CO_2 gas and low volume of gas is required while separating CO_2 gas. Consumption of water is less as compared with the post-combustion technique. Alternative fuel like hydrogen from synthesis gas is obtained. It has retrofitting possibilities with the existing plants in near future.	It retrofits easily with existing production units (like in coal-fired thermal power plant). It is highly developed process as compared with other techniques. Improved blends of chemical solvent enhance the overall efficiency.	CO_2 concentration is high (80–98%), resulting in higher absorption efficiency. Least emissions of pollutants, as large options are available for air separation. Smaller size of boiler and other equipment are required (cost-effective process). There is no need of chemical operations. It is a robust, simple and easy to reconstruct technique.
Disadvantages	Typical operating conditions (15–20 bars and 190–210 °C). High solvent regeneration energy is required. Costly auxiliary equipment is	Low CO_2 concentration (5–15 vol%) affects overall capture efficiency. Sorbent technologies are not robust for high performance.	High energy penalty for air separation (ASU) operation. Net output power is less. Cryogenic O_2 production is expensive.

	required for IGCC plants. Least efficient with hydrogen fuel gas turbine operation.	Water consumption is high.	In order to avoid air leakage, an air-tight instrument is required. Corrosion problems may occur.
Economic aspects	IGCC plants are more expensive than coal-fired thermal power plants.	Very expensive technology due to large equipment size.	Air separation cost is high.
Application area	Coal-gasification plants	Coal-fired and gas-fired plants	Coal-fired and gas-fired plants

Table 1.3 The operating conditions along with the performance of carbon-capturing techniques [26,29,31,57,59].

Carbon capture techniques	Operating conditions	Performance
1. Pre-combustion	Operating temperature = 190–210 ℃; pressure = 15–20 bar; reforming temperature = 700–850 ℃; shift reactor temperature = 400–550 ℃; solvent regeneration energy for biphasic solvent = 2.18 GJ/tCO_2.	High absorption rate and pressure (i.e., 2–7 MPa) of separated CO_2 is achieved; elevated temperature = 200–400 ℃; approximately 15–60 % by volume of CO_2 is obtained.
2. Post-combustion	Absorption temperature = 40–75 ℃; stripping temperature = 100–140 ℃; operating pressure = 1 bar; Energy requirement by MEA vary from 3.0–4.5 MJ/kg CO_2.	Low CO_2 concentration is obtained i.e., 5–15 vol %; it has retrofitting property; amine blends improve the capture efficiency.
3. Oxy-combustion	Absorption temperature & pressure = 50 ℃ and 1 bar respectively; stripping temperature & pressure = 116–120 ℃ and 2 bars respectively; Electrical power = 750 W.	Concentrated CO_2 is achieved (80–98 %); marvelous performance without any chemical requirement; can be installed in coal and natural gas fuel-fired thermal power plant; operational and production cost is low; least pollutant emissions.

1.4 Various available CO_2 capture methodologies

In this section, different methodologies for performing CO_2 capture for various available techniques of pre-combustion, post-combustion, and oxy-combustion are presented. These methods involve either physical or chemical absorption, adsorption, separation through the membrane, cryogenic separation, and microalgae process. The main operating conditions with the performance of different CO_2 capture methodologies are listed in Table 1.4. All these methods depend upon various separation principles, and the selection of any method depends upon the emission source to achieve the desired concentration of the component that is to be separated. The separated CO_2 can be utilized in various industrial units (i.e., the urea industry, fertilizer industry, dry ice manufacturing, food industries, etc.).

Table 1.4 The operating conditions with the performance of various CO_2 capture methodology [26,48,49,59].

CO_2 capture methodology	**Operating conditions**	**Performance**
1. **Absorption**		
i) Physical absorption	High pressure and low temperature for absorption and vice-versa for desorption occur; Operating conditions mainly depend upon the type of commercial process adopted, i.e., selexol, rectisol, purisol, fluor, sulfolane, etc. These processes, along with their operating conditions, have been reported in Table 5.	Low inert gases and high CO_2 content is obtained; CO_2 separation yield = 90–98 %; high absorption efficiency (more than 90 %); it is applied to many industrial processes; selexol process finds good performance in IGCC plants; rectisol process is favored when exhaustive gases contain sulfur; fluor process is suitable for gas streams with the partial pressure of CO_2 higher than 60 psig.
ii) Chemical absorption	Absorption temperature = 40–60 ℃; Stripping temperature = 100–140 ℃; Operating pressure = less than 1.5 Mpa; Partial pressure of CO_2 = 3–15 kPa; regeneration energy = 4–6 MJ/kg CO_2.	Highly matured method; CO_2 recovery = 80–95 %; CO_2 capture by amine blend is a highly energy-intensive process; it is least sensitive to acid gases; mass transfer rate is high.
2. Adsorption	PSA (T = 20–200 ℃ & P = 0.15 bar); TSA (T = 50–100 ℃ & P = 1.3 bar); Activated carbon = 2.5 ℃ & 3 MPa; Zeolite = 120–200 ℃ & 0.72 MPa; carbon	PSA (CO_2 recovery = 89 % & CO_2 purity = 16 %); TSA (CO_2 recovery = 81 % & CO_2 purity = 95 %); PSA has good performance for the removal of pure H_2 from the

	molecular sieve = 5–35 ℃ & 0.1 MPa; mesoporous silica = 25 ℃ & 1–3 MPa; calcium oxide = 650–950 ℃ & 1–42 bar.	syngas purification; good results at low temperatures; high moisture tolerance; more than 85 % absorption capacity.
3. Membrane technology	Operating temperature should be less than 100 ℃ to avoid membrane distortion; operating pressure depends upon the type of membrane used and it is mostly greater than 100 bars.	High separation efficiency (more than 80 %); no regeneration energy is not required; commercially readily available; low flux rate and fouling are still challenging tasks.
4. Cryogenic separation	Operating temperature and pressure = 298 K & 1 atm. respectively; energy requirement is 6–10 MJ/kgCO_2; separated CO_2 is achieved at a reduced temperature of -73.3 ℃.	Approximately 99.99 % of high purity and recovery of separated CO_2 can be achieved; CO_2 obtained can be directly used in industries as an energy source; low operating flexibility.
5. Microalgae process	pH range = 7.0–8.4; CO_2 absorption temperature = 15–30 ℃.	High capacity to absorb CO_2; it directly uses solar energy; catalytic framework coated with g-C_3N_4/TiO_2 nanoparticles gave good results in terms of CO_2 recovery.

1.4.1 Absorption

Absorption of the desired component from the flue gas stream is achieved either by non-reacting physical solvents (physical absorption) or by reacting chemical solvents (chemical absorption). This method for CO_2 capture is highly mature and has been used for many decades [61]. An absorption & stripping configuration is used to perform this separation task. Amine solution, ammonia solution, salt solutions, and different amine blends are classified under chemical solvents, while selexol, rectisol, purisol, morphysorb, sulfolane, and fluor are well-known industrial processes used to capture CO_2 [62-69]. CO_2 recovery is very high (> 90 %), solvents are highly reactive, flexible operation, a highly mature method, and moderate operational cost are some of their advantages. Researchers are mainly targeting solvent degradation, high energy penalty, and corrosion problems to overcome these challenges in the near future.

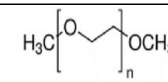
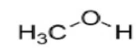
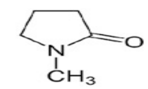
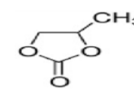
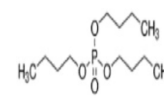
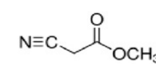
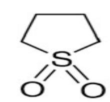
1.4.1.1 Physical absorption

Physical absorption is a method that is used to capture CO_2 by physical means. This method is mainly used to remove CO_2 from the mixture of H_2 and CO_2 emitted by the shift reactor during the pre-combustion of carbonaceous fuel [54]. A non-reacting liquid solvent known as an absorbent (either organic or inorganic) is helpful for performing this task. It is a bulk phenomenon in which the CO_2 absorption rate is a linear function of the partial pressure of the flue gas stream [23]. This method is a good option for attaining a lower concentration of inert gas and a higher concentration of CO_2 gas from the flue gas stream. This method mainly uses the absorption and desorption processes [2,23] to perform the entire CCS operation.

The absorption rate is governed by Henry's law [70] such that the physical properties of CO_2 and the working solvent remain unaffected. The flue gas stream initially contacts with physical absorbent in the absorption column in a counter-current manner. As the flue gas temperature is high, the absorption rate increases with the increase in pressure and decreases in temperature [19,57]. The factors affecting the absorption rate are the temperature of the system (gas and solvent mixture), operating pressure, the nature and concentration of flue gas, and the type of solvent used. The saturated solution is sent to the regeneration column at low temperature [48] and high pressure [54], and the solvent is regenerated and recycled back to the absorption column. Due to less interaction force between the molecules of saturated solutions, they require less energy for regeneration than the chemical absorption method [28].

The selection of a solvent is a rigorous task. A physical solvent with properties like low vapor pressure, high reactivity or absorptivity, easily regenerating, high thermal and mechanical tolerance, less corrosive, and least environmental impact is suitable for this method [26,54]. These solvents are thermally very stable, reducing the risk of solvent loss and contamination while regenerating at an elevated temperature. Selexol, rectisol, purisol, morphysorb, sulfolane, and fluor solvent are commercially available physical processes for CCS [2,23]. The process, characteristics, molecular structure, and various other properties of physical solvents are listed in Table 1.5. Among all the processes, selexol (liquid glycol solvent) has been widely used in CO_2-capturing for decades. It is advantageous over other physical solvents because of its lower vapor pressure, non-corrosive nature, lower heat requirement, and non-reactivity towards a few gases.

Table 1.5 Common physical solvents, along with their general properties, are used to capture CO_2 in pre-combustion technology [19,23,28,59].

Commercial Process	Physical solvent	Formula	CAS No.	MW (g/mol)	ρ (g/cm^3)	MP (℃)	BP (℃)	Operating condition	Structure	Vendor
Selexol	Dimethyl ether of polyethylene glycol (DMPEG)	$CH_3O(CH_2CH_2O)_nH_3$ n = 3-9	24991-55-7	250 (Avg.)	1.03	-23	> 245	3.59 MPa and 35 ℃		Union Carbide, USA
Rectisol	Methanol	CH_3OH	67-56-1	32.04	0.792	-97.6	64.7	3.6 MPa and -25 ℃		Lurgi and Linde, Germany
Purisol	N-methyl-2-pyrolidone (NMP)	C_5H_9NO	872-50-4	99.13	1.03	-24	202	-15 to 0 MPa and 6.8 ℃		Lurgi, Germany
Fluor	Propylene carbonate	$C_4H_6O_3$	108-32-7	102.09	1.204	-55	240	2.72–5.78 MPa and 25 ℃		Fluor Daniel, Inc.
Estasolvan	Tributylphosphate	$(CH_3(CH_2)_3O)_3PO$	126-73-8	266.31	0.979	-79	181	4.5 MPa and 30–90 ℃		Sigma Aldrich
Methyl cynoacetate	Methylcyanoacetate	$NC_2H_2CO_2CH_3$	105-34-0	99.09	1.123	-13	205	-		Sigma Aldrich
Sulfolane	Tetrahydrothiophenedioxide	$(CH_2)_4SO_2$	126-33-0	120.17	1.261	27.5	285	7.6 MPa and 25–130 ℃		Shell

1.4.1.2 Chemical absorption

CO_2 absorption is done with the help of a reacting liquid solvent along with chemical reactions. Either one or more reversible chemical reactions appear while reacting with the liquid solvent, leading to CO_2 separation. The chemical bonding between the CO_2 gas molecules and the liquid solvent creates a situation where the coupling reaction is mainly responsible for the CO_2 separation [48]. CO_2 is an acid in nature, so the primary solvent as a chemical is required for its complete separation by neutralization reactions. Complex compounds with weaker bonds are formed after such chemical reactions. These complexes are easily broken by applying heat and pure CO_2 with the original solvent is regenerated at the final stage. This method has been used for the separation of CO_2 from the flue gas mixture for many years.

Many chemical solvents, like amine, ammonia, salt solutions, and various amine blends, are classified as chemical absorbents [19]. Figure A3 of Appendix – A indicates the various classifications of chemical solvents for the CO_2 capturing technique. At an operating pressure of less than 1.5 mega Pascal (MPa), this method separates CO_2 from the mixture of synthesis gas during the pre-combustion technique [59]. Few coal-fired power plants and some chemical industries use this method to recover CO_2, and this pure CO_2-gas is utilized in the food industry and many other chemical industries [28].

In this modern era, numerous technologies for CO_2 capture are available for coal-fired thermal power plants. The absorption-desorption based chemical method is the most reliable and developed technology [52]. The flue gases emitted by industrial units mostly have a very high temperature. This flue gas initially passes through the gas cooler to reduce its temperature and make it suitable to feed the absorption column. In the absorption column, this flue gas meets up with the chemical solvent, and absorption of CO_2 occurs in the temperature range of 40–60 ℃. Wash water is used to recover the solvent vapor or its droplets before leaving the absorber. The chemical solvent is circulated between absorption-desorption columns for the effective working of the entire process [71]. Exhaust gases with the least CO_2 content are liberated at the top of the absorption column, while saturated solution (CO_2-enriched) is sent to the regeneration column. The CO_2-lean solution is recycled, and it is concentrated in the absorption column by the make-up of fresh amine solvent.

Heat is supplied from the reboiler to the desorption column continuously to raise the solvent regeneration situation. The solvent is regenerated at atmospheric pressure and temperature of around 100–140 ℃ [52]. Steam is removed by the condenser and recycled back to the stripper section. The absorption and desorption setup for CO_2 recovery by the chemical solvent is shown in Figure A4 of Appendix – A. Higher energy is required during the regeneration of CO_2 gas, and this is a major concern [72]. The whole absorption-desorption system requires 20–30 % of the overall energy produced by coal-fired thermal power plants [19]. Therefore, researchers focus on various configurations, designing, and optimization techniques to overcome this issue [71].

This technology is the least sensitive to acid gases (captures CO_2 up to ppm level), but the mass transfer coefficient is higher for absorption and desorption. Some disadvantages include limited CO_2 loading, large equipment size, high regeneration energy, poor selectivity towards acid gases, corrosive nature, and environmental effects.

1.4.1.2.1 Amine solvent chemistry

Alkanolamines-based solvents have been used in the field of CO_2 capture for many decades. Various studies on these amines have been performed on their chemistry, process modeling, and kinetic reactions. Amino (–NH_2, –NHR, and –NR_2) and hydroxyl (–OH) groups are present as functional groups in such amines. Amines are classified into primary, secondary, tertiary, hindered, and cyclic groups. Borhani et al. [19] selected a few crucial amines to treat the flue gas streams; these amines, along with their characteristics, are tabulated in Table 1.6. Liang et al. [36] concluded that CO_2 loading capacity increased with an increase in restrictions towards the amino group. The general trends in CO_2 loading capacity are directly related to the amine classification and follow diamines > 3° amines > 2° amines > hindered amines > 1° amines.

Table 1.6 Physical characteristics with important properties of some selected chemical solvents [19].

Amine classification	Amine used	Formula	CAS No.	MW (g/mol)	ρ (g/cm^3)	MP (℃)	BP (℃)	Solubility in water	Derivatives
Primary	Monoethanolamine (MEA)	C_2H_7NO	141-43-5	61.080	1.012	10.3	170	1000 (g/l at 25 ℃)	$MEAH^+MEACOO^-$
	Diglycolamine (DGA)	$C_4H_{11}NO_2$	929-06-6	105.140	1.056	-12.5	221	Miscible	$DGAH^+DGACOO^-$
Secondary	Diethanolamine (DEA)	$C_4H_{11}NO_2$	111-42-2	105.140	1.097	28	271.1	1000 (g/l at 20 ℃)	$DEAH^+DEACOO^-$
	Diisopropylamine (DIPA)	$C_6H_{15}N$	108-18-9	101.193	0.722	-61	84	Miscible	$DIPAH^+DIPACOO^-$
Tertiary	Triethanolamine (TEA)	$C_6H_{15}NO_3$	102-71-6	149.188	1.124	21.60	335.4	Miscible	$TEAH^+TEACOO^-$
	Methyl-diethanolamine (MDEA)	$C_{12}H_{17}NO_2$	105-59-9	119.163	1.038	-21	247	Miscible	$MDEAH^+$
Hindered	Aminomethyl-propanol (AMP)	$C_4H_{11}NO$	124-68-5	89.138	0.934	25	165.5	Miscible	$AMPH^+AMPCOO^-$
Cyclic	Morpholine	C_4H_9NO	110-91-8	87.120	0.996	-5	129	Miscible	$MORH^+MORCOO^-$
	Piperazine (PZ)	$C_4H_{10}N_2$	110-85-0	86.136	1.100	106	146	Miscible	$PZCOO^-$, PZH^+, PZH_2^{2+}, H^+PZCOO^-, $PZ(COO^-)_2$

1.4.1.2.1.1 The primary and secondary amines

For primary amines, one of the hydrogen atoms from ammonia is substituted either by one alkyl or one aromatic group. Similarly, two such substitutions by alkyl, aryl, or both are classified as secondary amines. MEA is a well-known primary amine, a highly matured method for capturing CO_2 in the post-combustion technique [42]. It has fine performance and high chemical reactivity towards CO_2 absorption, so it is used as a benchmark in the experimental analysis [14,43,73]. It is highly alkaline, suitable for gas streams having low CO_2 content, solution capacity is high, easy to produce [36], and cheap [74]. Although it has demerits of corrosive behavior, limited CO_2 loading capacity, oxidative and thermal instability [25], solvent degradation [16], limitations towards high-pressure gas streams [19], and demands high regeneration energy [3].

1.4.1.2.1.1.1 Hindered amine

In sterically hindered amines, the primary amine with an amino group is coupled with the tertiary carbon atom. For the secondary amine, this amino group is coupled with at least one secondary or tertiary carbon atom [7]. Hindered amines from CO_2 removal offer a high absorption rate, absorption capacity, and resistance to degradation as compared with conventional amines. These sterically hindered amines also have the potential to reduce the regeneration cost [75]. The overall reaction mechanism of sterically hindered amines in the presence of H_2O and CO_2 is given as:

$$\mathrm{RNH_2 + CO_2 + H_2O \rightarrow RNH_3^+ + HCO_3^-} \tag{1.4}$$

Bougie et al. [7] investigated various hindered amines like 2-Piperidineethanol (2-PE), 2-Piperidinemethanol (2-PM), 2-Amino-2-phenyl propionic acid (APPA), Diisopropylamine (DIPA), 1,8-p-Methanediamine (MDA), Pipecolinic acid (PA), Tertbutylamine (TBA), and 2-(Ter-butylamino) ethanol (TBAE). They analyzed various properties like density, vapor pressure, viscosity, heat capacity, the heat of absorption, diffusivity, CO_2 absorption capacity, and kinetics to design absorption equipment. Idris et al. [76] worked on 2-Amino-2-ethyl-1,3-propanediol (AEPD), 2-Amino-2-hydroxymethyl-1,3-propanediol (AHPD), 2-Amino-2-methyl propionic acid (AMPA), 2-Amino-2-methyl-1,3-Propanediol (AMPD), and reported acid dissociation constant (pKa) and CO_2 absorption affinity.

1.4.1.2.1.2 Tertiary amine

Tertiary amines, in their structure, have three replaceable bonding sites attached to the nitrogen atom, and the reacting properties of tertiary amines are different from those of primary and secondary amines. These amines, in the presence of water, absorb CO_2 and form hydroxyl radicals [19]. They do not directly react with CO_2; therefore, H_2O must be present to precede the reaction.

1.4.1.2.1.3 Cyclic amine

The cyclic amine can be either secondary amine (2^o) or tertiary amine (3^o) with a closed ring-type structure. These amines, along with numerous other amines, are extensively used as an additive. One of the well-known cyclic amines is PZ, which is used in CO_2 capture. PZ is a polyamine with more than one active site available to react with CO_2 at a faster rate. It shows low volatility, high absorption rate, and high absorption capacity [36,57].

In their investigation, Freeman et al. [77] suggested that at a particular concentration, piperazine's solution volatility is similar to MEA, but aspects like reaction kinetics and absorption capacity are doubled. Oxidative and thermal degradation is least for cyclic amines, performing well at elevated temperatures [57]. The morphysorb process uses morpholine cyclic amine, which is commercially used to separate acid gases from syngas [19]. These morpholine cyclic amines are industrially used for decarbonization because of their high CO_2 loading ability, fast reaction rate, minimum temperature operation possible at 263 K, low solvent circulation rate, low vapor pressure, stability in terms of chemical and thermal aspects, eco-friendly and economical process [48].

1.4.1.2.1.4 Ammonia solution

The ammonia solution has been used to capture CO_2 and remove H_2S from the industrial gas stream for many years. Depending on operating temperature, the CO_2 capture process in this category can be defined into two classes: conventional ammonia process and chilled ammonia. In a traditional ammonia process, the operating temperature lies in the range of 25–40 ℃ (i.e., ambient temperature), and no any precipitation product is obtained. The operating temperature is low for the chilled ammonia process and lies in the range of 2–10 ℃. The regeneration of CO_2-loaded samples occurs at a temperature of around 100–150 ℃ and operating pressure ranging from 30–2000 psi [19,31]. In this process, ammonium carbonate, ammonium nitrate, and ammonium sulfate are formed as a precipitate in the absorber section and are used as fertilizer for crops [28,54]. This situation retards the free ammonia concentration and reduces vapor losses, but the CO_2 absorption rate also reduces proportionally [7]. The advantages of CO_2 capture utilizing ammonia solution are high CO_2 capture efficiency, low regeneration costs, high absorption capacity, non-corrosive, and the ability to remove SO_2, NO_X, and CO_2 simultaneously. However, ammonia slip, slow reaction rate, complex process, and high volatility of ammonia are some of the biggest challenges of this CO_2 capture technology [19,57].

1.4.1.2.1.5 Salt solution

When salt is mixed with water, an electrolyte is formed, which aids in CO_2 capture. Carbonate solutions like potassium and sodium have properties of economical operation, less toxicity, ease of regeneration, non-corrosive, least degradation, highly stable process, and CO_2 absorption capacity is high [19,28]. Carbonate/bicarbonate solution, hydroxide solution, and amino acid salt solution are the major categories in which the salt solutions are classified for the CO_2 capture process [57].

These carbonate solutions can efficiently capture CO_2 in two ways: conventional carbonate/bicarbonate system and precipitating carbonate solvent system. In the conventional system, the reaction between the aqueous potassium carbonate solution with CO_2 is exothermic. When the concentration of CO_2 is high in the flue gas stream, then hot potassium carbonate is more beneficial in CO_2 capture. This potassium carbonate solution shows a slow absorption rate therefore, many researchers add promoters (i.e., activators) to the solution to increase its efficiency [54]. The characteristics and properties of sodium carbonate and potassium carbonate are almost similar due to the production of a considerable amount of carbonate in the solution [31]. The concept of a precipitating carbonate system was proposed by Shell, which uses potassium carbonate with crystallization, and then the concentration step comes into the picture, and finally, CO_2 absorption occurs. This process benefitted in reducing the enormous amount of regeneration energy, and nitrosamine formation is less than CO_2 capture by amine. Sodium carbonate/bicarbonate solutions are used as precipitating solvents.

Various types of hydroxides like sodium, potassium, and calcium are used to capture CO_2 from different gas streams. Sodium hydroxide (NaOH) is a powerful alkaline compound, and on mixing with water, it deionizes into Na^+ and OH^-. The CO_2 gas mixes in the NaOH solution and transforms into aqueous CO_2. Now, this aqueous CO_2 reacts with $OH^-$and produces bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) [19].

In amino acids, amine ($-NH_2$) and carboxyl groups ($-COOH$) are present. The amino acid salts are produced by reacting amino acids with the inorganic base like potassium hydroxide (KOH) and NH_3. This amino acid salt solution so formed can be used to capture CO_2. The potassium salt of taurine, glycine, and sarcosine are prime examples of amino acid salts [19,36, 57].

1.4.1.2.1.6 Various amine blends

The primary and secondary amines are classified as activators ($\Delta H_{abs} \approx$ 80 kJ/mol CO_2), whereas tertiary or hindered amines are known as promoters ($\Delta H_{abs} \approx$ 60 kJ/mol CO_2). The amine blends are prepared by mixing high kinetic solvents (activators) with low kinetics solvents (promoters) [6]. Some advantages of amine blending are fast reaction kinetics, high absorption capacity, low regeneration energy demand, high thermal stability, and low solvent degradation. Therefore, due to their advantageous behavior, the researchers relied mainly on amine blends rather than single amines. Some amine blends show phase-splitting behavior on CO_2 loading and are referred to as biphasic amine solvents [14,22,44-46]. Their regeneration energy demand is very low, and their CO_2 capture performance is also outstanding [1,3,38].

Gautam and Mondal [6], in their investigation, prepared a novel aqueous amine blend of TETA and 2-Dimethylaminoethanol (DMAE) and performed the CO_2 absorption and desorption investigations. In this novel aqueous blend, TETA acted as an activator, while DMAE was a promoter. TETA shows a high absorption rate, reaction kinetics is fast, and its equilibrium CO_2 loading is high, etc. Similarly, DMAE exhibits low degradation behavior, regeneration energy demand is low and high CO_2 loading capacity. Therefore, the individual advantages of each amine are utilized in their aqueous amine blend. For absorption experiments, the temperature (T) varied from 298.15–333.15 K, mole fraction of TETA (m_{TETA}) ranged between 0.05–0.20, CO_2 partial pressure (P_{CO2}) varied from 10.13–25.33 kPa, and the entire solution concentration (C) varied from 1–3 mol/L. The maximum equilibrium CO_2 loading was found to be 0.92 mol CO_2/mol amine at T = 315.65 K, P_{CO2} = 17.73 kPa, m_{TETA} = 0.13, and C = 1 mol/L. The desorption was conducted at a constant temperature and partial pressure of 393.15 K and 17.73 kPa, respectively. The cyclic loading capacity of 3 mol/L of this novel aqueous amine blend was 55.03 % higher than conventional 30 wt% MEA. The heat of absorption of this novel amine blend was calculated to be -67.135 KJ/mol, and it was estimated with the help of the Gibbs-Helmholtz equation. It is crucial to judge the presence of species in the CO_2-unloaded and CO_2-amine blend; therefore, they adopted ^{13}C NMR analysis. Finally, they optimized their experimental results of equilibrium CO_2 loading with the help of response surface methodology (RSM) software. The software-based approach provided the optimum equilibrium CO_2 loading of 0.926207 mol CO_2/mol amine at T = 304.36 K, m_{TETA} = 0.14, P_{CO2} = 17.24 kPa, and C = 1 mol/L. DEEA+1, 6-Hexamethyldiamine (HMDA) [17], DEEA+AEEA [18], 2- (Methylamino)ethanol (MAE)+AEEA [61], DEEA+Ethylenediamine (EDA) [73], BDA+DEEA [44] are some of the various amine blends that showed best performance as reported by many researchers. A few investigations were also performed on tri-amine blends like AMP+PZ+MEA [20] and DMCA+MCA+AMP [16].

1.4.1.2.1.7 CO_2 absorption mechanism

To understand the CO_2 absorption rate, it is essential to know all about the reaction mechanism between CO_2 and the amine-based solvents used. Many researchers mainly suggested three mechanisms: the Zwitterion mechanism, the Ter-molecular reaction, and the base-catalyzed hydration mechanism [36,40,49,57,78].

1. Zwitterion mechanism: The concept of this mechanism was initially suggested by Caplow [79] but modified by Danckwerts later [80]. It was demonstrated that CO_2 and amine solvents form a zwitterion intermediate then, with the support of the base, get deprotonated and result in carbamate formation [52]. This mechanism applies to primary, secondary, and hindered amines.

CO_2-amine zwitterian step: $\mathrm{CO_2 + R_1R_2NH \leftrightarrow R_1R_2NH^+COO^-}$ (1.5)

Deprotonated step: $\mathrm{R_1R_2NH^+COO^- + B \leftrightarrow R_1R_2NCOO^- + BH^+}$ (1.6)

2. Termolecular mechanism: This mechanism was coined by Crooks and Donnellan [81]. They found that CO_2 bonding with amine (Zwitterian formation step) and proton transfer (Deprotonated step) occur simultaneously. This mechanism was further reviewed by Silva and Svendsen [82]. They accepted and worked upon the same mechanism that was given by Danckwerts [80].

Reaction step: $\mathrm{CO_2 + R_1R_2NH + B \leftrightarrow R_1R_2NCOO^- + BH^+}$ (1.7)

3. Base-catalyzed hydration mechanism: This reaction mechanism exists with the solution of tertiary alkanolamine-based solvents and CO_2, but CO_2 does not participate in the reaction directly. Amine is dissociated with the base-catalytic effect due to the hydration of CO_2.

Reaction step: $\mathrm{CO_2 + R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3NH^+ + HCO_3^-}$ (1.8)

For reaction, the deprotonated step in zwitterion will be rate-determining, and for this 'zwitterion mechanism' will be the same as the 'termolecular mechanism.'

1.4.2 Adsorption

Adsorption is the process of removing one or more components from the gaseous mixture with the help of a suitable solid particle, which has many active sites [26,49]. A packed bed is filled with spherical-size adsorbents, and CO_2 gets attracted and adheres on the surface when the mixture of flue gas (having CO_2 content) comes into its contact. As soon as the equilibrium is achieved, the pure form of CO_2 can be removed through desorption, and the regenerated adsorbent can be used for the other cyclic process.

Adsorption phenomena occur due to the combination of the physical and chemical mechanisms of CO_2 with the available active sites on the adsorbents [2]. Mainly, materials like activated carbon or molecular sieves are used for CO_2 adsorption, and it is quite a different task of carbon-capturing when compared with absorption. Temperature, partial pressure, concentration, pore size, pore volume, surface force, etc., are some factors on which adsorption and its kinetics mainly depend [59].

1.4.2.1 Classification of adsorption

1.4.2.1.1 Physical adsorption

In the case of physical adsorption, the CO_2 gas molecules get adsorbed upon the surface through Van der Waals forces without undergoing any chemical reaction on the surface [48]. The physical adsorption can be reversible when the adsorption and desorption of the gas molecules can be obtained under the impact of temperature and pressure. When CO_2 adsorption is performed at room temperature, physical adsorption is preferred, and the adsorption process is directly related to the adsorbent's texture [2,83]. Activated carbon, zeolites, and metal-organic frameworks (MOFs) are examples of physical adsorption. The physical adsorption process is more significant for high-pressure operations, the regeneration of adsorbent is easy with less regeneration energy demand, and the cost of adsorbent preparation is less, which are some of the advantages of physical adsorption. CO_2 adsorption is less at low pressure, the presence of moisture limits the adsorption capacity, and the CO_2 capture process is reduced at high temperature are some drawbacks of physical adsorption.

1.4.2.1.2 Chemical adsorption

Poor selectivity of CO_2 is the major limitation of physical adsorption; therefore, chemical coating or grafting can be introduced at the surface of the porous adsorbent. This is done by incorporating some primarily essential compounds that have basic groups present in their structures that are fruitful in capturing acidic CO_2 gas molecules [83]. Mainly, amine compounds are utilized for coating the surface of the adsorbent. The CO_2 molecules make chemical bonds with the active site of the adsorbent. Chemical adsorption mainly benefits CO_2 capture processes that operate at high temperatures [2,48]. Amine, potassium, sodium, and lithium-based sorbents are some examples of chemical adsorbents. This process has the advantages of high CO_2 absorption capacity at low CO_2 partial pressure, good performance even in the presence of moisture, high mechanical strength, etc. Apart from their advantages, this process also has some drawbacks of high regeneration energy demand, cyclic capacity is low because of amine degradation, vaporization of amine at high-temperature operation, corrosion due to regeneration, and high operational cost.

1.4.2.2 Regeneration strategies

Pressure swing adsorption (PSA) or temperature swing adsorption (TSA) is used to desorb the initially formed CO_2-saturated complex. The selection of either of the two processes depends upon the concentration of CO_2 and can be used independently. PSA is used for higher concentrations of CO_2, but TSA is recommended for lower concentrations [23,31,83]. PSA is widely used for CO_2 removal (high purity), and very little focus is given to TSA. The main reason for this situation is that a tremendous amount of cyclic time and higher heat is required to increase the temperature of the solid bed during sorbent regeneration [59]. PSA is beneficial for CO_2-capturing and other gas separation from the flue gas mixture. It can also be beneficial for the production of high-purity H_2 gas (refinery-off gases as feed) at an elevated pressure of 6 MPa [59]. Mathematical models and numerous available pilot plant data analyses show that it has a high probability of feasibility in the near future. However, this method is yet to be commercially accepted, and it has the drawback of the initial treatment of flue gas before passing it to the absorber. Commercially, it is complex, requires many adsorption vessels, purging, depressurization of counter and co-current flow, pressurization on a large scale, etc., are some of the barriers to its use [48]. Zeolite and solid amine sorbents can be classified under physical adsorbents.

1.4.2.2.1 Pressure swing adsorption (PSA)

In PSA, the gaseous mixture for sorption is passed through the adsorbent bed at high pressure and low temperature, and it is continued until equilibrium is reached at the exit condition. On achieving equilibrium, the passage of the gaseous mixture stops, and the adsorbent gets regenerated by reducing the system’s pressure. Further, it can be used for another cyclic process. PSA can also be used in vacuum conditions-this can be implemented during the desorption of CO_2 [48]. The cyclic time of regeneration in PSA is very short (in seconds), and this process is used for higher CO_2 concentrations. NH_3 can be directly synthesized by using steam reforming of CH_4 (through off-gases) by PSA [83].

1.4.2.2.2 Temperature swing adsorption (TSA)

In this process, temperature plays a vital role since the regeneration of the adsorbent takes place at an elevated temperature range upon the selective adsorbent until the equilibrium is achieved. The saturated adsorbent is heated in temperature swing adsorption (TSA), and the CO_2 is separated mainly due to the breaking of the physical and chemical bonds. This process is used where the concentration level of CO_2 is lower in the range [83].

As the temperature of the system rises, the trapped gases try to escape from the system. To enhance the system's temperature, we have to provide heat from an external source; therefore, this process is somehow uneconomical [49]. The cyclic time of regeneration is higher than the PSA, and it takes time in hours.

1.4.2.2.3 Electrical swing adsorption (ESA)

In this method, adsorption can be done by passing a low-voltage electric current through the adsorbent bed. Hybrid adsorbents like monolithic activated carbon and zeolite are used in ESA to capture CO_2 [83]. The ESA has the potential to reduce the overall processing cost of the plant; therefore, it is a highly energy-efficient technique for CO_2-capturing. Ultimately, it is a highly recommended process for CO_2 adsorption as compared with PSA and TSA [49]. Usually, gases have to be cooled and dried during the industrial process, which ultimately affects the overall effectiveness of the ESA process; therefore, it is recommended to develop a material that can absorb CO_2 completely.

1.4.3 Membrane technology

The separation of desired components from the gaseous mixture can be done with the help of a barrier called a membrane. This membrane restricts the flow of a few components and allows others. Figure A5 of Appendix – A shows the schematic representation of gas molecule separation through the porous selective membrane. These membranes are made up of different materials, like polymeric, metallic, ceramic, zeolite, etc., and are classified into various pore sizes [57,83]. Separation depends on the membrane pore and the size of gas molecules, and this phenomenon is usually governed by Knudsen diffusion. Membrane technology is used to recover CO_2 from natural gas processing [28], pre-combustion, post-combustion, and oxy-combustion techniques [84]. Membrane separation is an efficient high-energy technique, as compared with conventional physical or chemical absorption methods [70]. Flue gas after post-combustion, having CO_2 content when it passes through the membrane, then CO_2 dissolves at the surface, and diffusion is maintained for a partial pressure gradient [2]. The membrane separation is very economical when the CO_2 concentration in the natural gas is high. The idea of an advanced zero-emission power plant utilizing membrane technology was proposed by Theo et al. [23] and is shown in Figure 1.6. The overall efficiency of these zero-emission power plants is around 49–50 % lower heating value (LHV) [59].

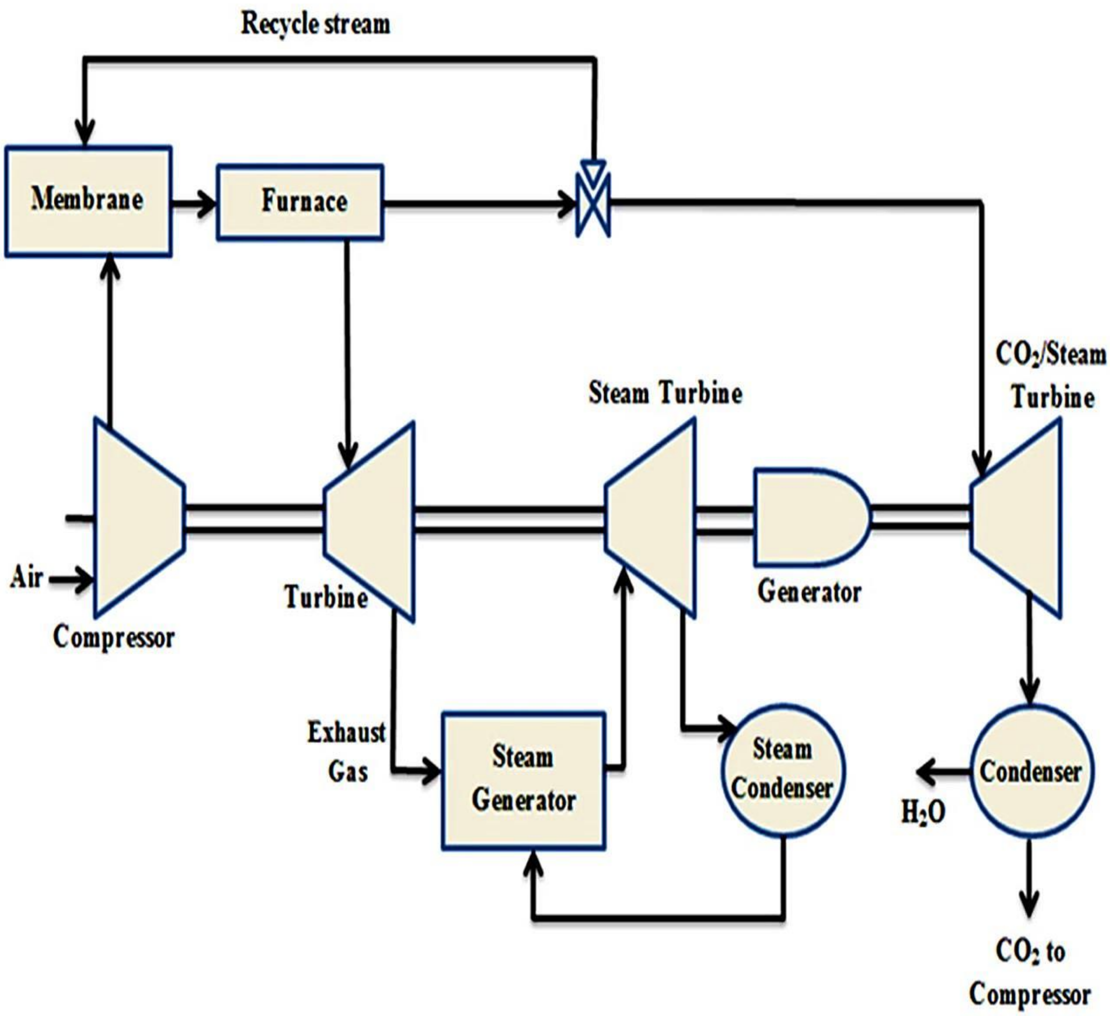


Figure 1.6 Proposed zero carbon emission power plant utilizing membrane technology [23,59].

1.4.3.1 Facilitated membrane separation

Researchers are developing and investigating various membrane separation techniques, and May-Britt et al. [85] recommended and patented the idea of newly developed facilitated transport membrane separation across the globe [49]. It is a membrane/solvent system that is highly compact so that overall equipment size and capital cost are reduced. It is widely used in the gas separation process; higher selectivity and a more significant flux rate make this technique popular.

It has a liquid carrier in the mobile phase, known as an agent (like cross-linked polyvinyl amine), added to the membrane, resulting in higher selectivity towards the gas molecule. Flue gas molecules contact the upstream side of the membrane, penetrate it, dissolve, and react inside with the agent, thus forming complex compounds. These formed complex transport through the membrane while permeate releases from the downstream side of the membrane. Recovery and back diffusion of the carrier agent occur simultaneously on the membrane. This technique can be implemented in numerous processing plants that emit CO_2 as a component of their gaseous feed mixture. Through this technique, separation and transportation of CO_2 can also be done by using carrier agents (amines, carbonates, and molten salt hydrates, etc.). These agents provide the moisture medium for CO_2 to form bicarbonate [23]. The carrier supports membrane permeability and CO_2 selectivity; therefore, this technique is efficient and eco-friendly [57]. The entire effectiveness of the process increases with an increase in CO_2 concentration.

1.4.3.2 Non-facilitated membrane separation

Non-facilitated membrane separation is widely used to eliminate CO_2 directly from natural gas, and this method of separation is also useful where CO_2 gas has a higher partial pressure [23]. The selectivity of the whole process is mainly reliant upon the permeability of the working membrane. During the carbon capture technique by this process, the CO_2 content is low in flue gas, and it requires a large amount of energy in the form of compression work to separate CO_2 from the gaseous mixture. Hence, the permeability of the membrane is a supreme factor. This membrane separation technique has a more negligible environmental effect, lower degradation, higher efficiency, ease of operation, lower energy demand, etc. However, it has the demerit of implementation in existing power plants.

1.4.3.3 Mixed-matrix membrane separation

The mixed-matrix membrane is another emerging technology for membrane separation, in which the membrane is embedded with an inorganic polymer filler. These inorganic fillers are zeolite, carbon molecular sieve, zeolitic imidazolate, titanosilicates, carbon nanotubes, and mesoporous silica [2,23]. Among all these fillers, zeolite is extensively used because of its uniform pore size and the higher porosity that allows selective permeation of CO_2. The slicoaluminophosphate (SAPO) zeolite is commonly used as a filler material. In SAPO, the molecular sieves with a pore diameter of 0.38 nm are interconnected and suitable for CO_2 permeation and its removal across the membrane [86]. The mixing of inorganic particles with the polymeric membrane creates interfacial defects that reduce contact of the gas molecules with the sieves/polymer interface, ultimately affecting gas selectivity [33]. Decantation and sonication techniques play a vital role in overcoming this defect [49].

1.4.3.4 Gas membrane contractor separation

The gas membrane contractor is another new approach to membrane separation known as the hybrid membrane/solvent system [55], which is independent of the Knudsen diffusion principle. The membrane serves as a contacting and absorbing medium for CO_2 gas molecules [23,36]. The absorbent is the heart of the membrane contractor, which comprises alkaline amine solution, amino acid salt, alkaline solution, ammonia solution, enzyme-promoted solution, and ionic liquids [70]. The advantages are compact in size, no flooding and foaming, large interfacial area, low capital cost, higher selectivity, linear scaling up or down, flexibility for various flows of gas and liquid, etc. [2,70,87]. High resistance and wetting of the membrane surface cause limited transport of CO_2 mass transfer; these are the major disadvantages [2].

1.4.4 Cryogenic separation

This separation technique is mostly used on a commercial scale to separate CO_2 from the gaseous mixture stream, and it requires many compression stages at atmospheric pressure and temperature. This technique utilizes the properties of condensation and de-sublimation of various components of its gaseous mixture to separate CO_2 in its concentrated form [26,42]. Due to the moisture content in the flue gas stream, there is always a very high risk of the formation of ice (in the cooling unit) that can block the pipeline during operation [2,26]. Therefore, some investment is required to remove all moisture content before using it in operation. Captured CO_2 has a physical state, either solid/liquid or slurry (CO_2), depending on the operating conditions [26]. The cryogenic separation technique gives recovery (99.99 %) and purity (99.99 %) of separated CO_2. Therefore, this technique is highly recommended when there is a high need for concentrated CO_2 [42,88]. More valuable chemical products can be made with the help of catalytic or biological reactions by using concentrated CO_2. It is economical to produce CO_2 in a liquid state since it can be easily transported to ships or through the pipeline as required [53]. This technique requires the least amount of water, uses cheap chemicals, is corrosion-resistant, operates in environmental conditions, handles large-scale gas volumes, and has the least environmental impact, etc. are some of their advantages.

1.4.5 Microalgae process

The microalgae system is another classification of CO_2 capture and utilization (CCU). It consists of microscopic organisms that grow up in the water without any special attention being required for them. They use the photosynthesis process to perform their basic task of CO_2 absorption [89]. The overall photosynthesis reaction to capture CO_2 can be written as:

$$6H_2O + 6CO_2 + \text{photon (presence of light)} \rightarrow C_6H_{12}O_6 + 6O_2 \tag{1.9}$$

Every cell in the microalgae system is photoautotrophic, which directly absorbs nutrients from sunlight. They take up CO_2 from the flue gases and convert it into the raw material that is utilized for the production of biofuels [90].

Past studies have revealed that the pH range of 7.0 to 8.4 is regarded as the best for the growth of microalgae species. It was found that inorganic carbon exists in the form of a bicarbonate ion (HCO_3^-) that is absorbed by microalgae. CO_2 capture exists mainly in three forms, i.e., active intake, direct uptake of HCO_3^-, active CO_2 transport mechanism, and utilization of carbonic hydration (CA) enzyme in the membrane [91]. These microalgae have a high capacity to absorb CO_2, so presently, they are majorly used to reduce the hazardous impacts of greenhouse gas emissions. Cultivation conditions like temperature, pH, presence of light, and nutrition availability are mainly responsible for the CO_2 capture process and the production of biomass as well.

Experimentally, CO_2 capture is performed inside a reactor in which photosynthesis reactions can be initiated on the entire surface of microalgae. It acts as a biocatalyst in which a series of chemical chain reactions occur at microalgae chloroplasts. After that, the conversion of CO_2 into a photosynthetic metabolic product takes place. CO_2 capture by the microalgae method has several advantages like it has a high photosynthesis rate, a high microbial growth rate, good environmental adaptability, and low operational cost.

Recently, microalgal biologically-mediated CCU (bio-CCU) has been gaining more attention and is a promising biotechnological way of reducing CO_2 emissions [91]. This method of CO_2 capturing is benefitted by the natural diffusion property of the microalgae, and it develops many carbon-concentrating mechanisms (CCMs). The simple operation and cost-effectiveness of this method drew researchers to work on it. CO_2 capture by this method is highly profitable, feasible, and sustainable and can be universally applicable.

Huang et al. [92] proposed a novel hybrid photocatalytic porous framework (i.e., photo-bioreactor) coated with g-C_3N_4/TiO_2 nanoparticles. This nanoparticle has stable physical and chemical properties, less toxicity, low cost, and is easy to prepare. Their purpose in selecting this hybrid setup was to eliminate the factors responsible for the inhibition of microbial growth due to the direct use of photocatalysts. The purpose of their experimental work was to capture CO_2 and produce electricity simultaneously. CO_2 inlet flow rate was provided at 0.8 % v/v using six photocatalytic frameworks (carbon source), and CO_2 sequestration through a capacity of 60 L was increased from 12 % to 22 %. Chemical oxygen demand (COD) in the phosphate buffer and algae suspension was 1.63 mg L^{-1} h^{-1} and 1.90 mg L^{-1} h^{-1}, respectively.

Monilo et al. [93] cultivated green microalgae, i.e., “Scenedesmus almeriensis,” to capture CO_2 and produce lutein. Their cultivation was done inside a vertical bubble column photo-bioreactor, and there was a continuous supply of a gaseous mixture composed of O_2, N_2, and CO_2 in the range of 0.0–3.0 % v/v. The liquid phase growth of S. almeriensis was finally optimized, and 129.24 mg L^{-1} d^{-1} of biomass production was obtained during the cultivation procedure. In continuation of this process, the lutein was also separated with the help of ethanol through the solvent extraction method. At a 3.0 % v/v concentration of CO_2, the lutein content was 8.54 mg g^{-1}.

1.5 Novel biphasic phase-changing solvents for CO_2 capture

On relying much more upon the conventional methods for CO_2 capture (by amine solvents), it was found that they adversely impacted the regeneration energy demand and capital cost [19,22,37,42,94-96]. Therefore, it was mandatory to resolve this serious issue; the researchers focused on the numerous amine blends with phase-splitting behavior. Developing such an organic solvent is not such an easy task, and it requires rigorous experimental work. Industrial regeneration (by conventional amines) is done around at a temperature of 120 ℃ but using these phase-changing solvents reduces this temperature up to 80 ℃ [14]. In recent times, phase-splitting solvents have gained attention in CO_2 capture to reduce the regeneration energy cost and the equipment cost [94,97-98]. Every solvent has its properties, and blending these solvents at variable composition positively impacts the solution so formed. Fast reaction, high absorption capacity, high CO_2 uptake, and lower regeneration energy are desirable parameters that can be obtained by mixing primary or secondary amines (activators) with tertiary or hindered amines (promoters) that have high loading capacity [3,19,22,47,94,99-106]. Tertiary amines require lower regeneration energy than primary and secondary amines; therefore, their amine blends positively impact the entire regeneration energy.

A homogeneous mixture of water, either with primary or secondary amines, has both kinds of proton donors and acceptors available that create self and cross-association hydrogen bonding in the aqueous amine blend. Due to the availability of multiple proton active sites (i.e., diamines and triamines), they are responsible for the growth of ionic strength during the CO_2 loading. In the case of tertiary amines, their aqueous amine mixture is only proton acceptors and ultimately forms only cross-association hydrogen bonding. At a low-temperature range, the formation of only cross-association hydrogen bonding leads to a homogeneous amine blend mixture at all compositions. As the temperature increases, the cross-association hydrogen interaction decreases, which puts more effect on a hydrophobic interaction [94], and thus mixture separates into two immiscible phases. The amines with high-temperature tolerance efficiency while operating at an elevated pressure range create the situation of higher CO_2 miscibility in the aqueous amine solvent. For the effectiveness of the process, the phase separation temperature can be changed by changing the total concentration of the amine blend solution. The optimum phase change temperature of the amine blend solution depends on the amine's effective selection and its mole ratio [107]. Such an amine solvent system is available in the homogeneous (single-phase system) state before CO_2 loading, but it changes to a heterogeneous state (two-phase system) on equilibrium CO_2 loading [1,22,36,42,108]. The homogeneous phase of the amine blend solution splits up into the CO_2-enriched phase (use for the regeneration step) and the CO_2-

lean phase. The CO_2-enriched phase exits in either a solid or liquid state, while the CO_2-lean phase exists only in a liquid state [39,94,98]. Only the CO_2-enriched phase is separated and used for regeneration [22], whereas the CO_2-lean phase combines with the regenerated stream and goes back to the absorber [36,39,95,109]. As a result, there is a tremendous decrease in demand of regeneration energy. The schematic representation of the initial solution preparation, CO_2 absorption, and the regeneration step for the biphasic solvent is shown in Figure 1.7.

The amine-water system undergoes a phase transition state at a particular temperature range, and in this, the concept of lower critical solution temperature (LCST) exists [14]. Hydrogen bonding interaction is mainly responsible for this type of phase separation. The LCST primarily depends on the type of amine and its aqueous blend concentration [110]. The idea of phase separation can easily be understood with the help of a phase behavior

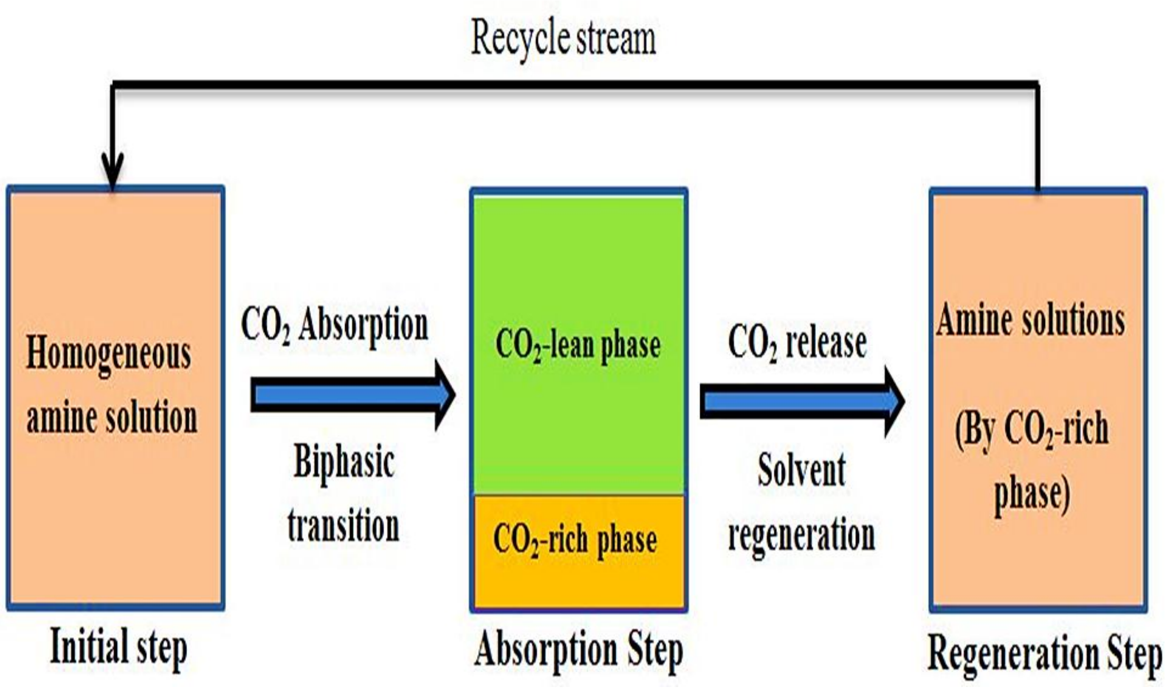


Figure 1.7 Phase splitting behavior of amine solution by CO_2 absorption [40,42,46].

diagram. In such a diagram, both lower critical solution temperature (LCST) and upper critical solution temperature (UCST) exist, and it is shown by Zhuang et al. [39].

Solid-liquid phase-changing solvents are prepared by dissolving amine in non-aqueous organic solvents. Amine + alcohol solvents, amino acid + alcohol solvents, and room-temperature ionic liquid + amine blends are the classifications of non-aqueous biphasic solvents for CO_2 capture [45,98,111]. These phase-changing solvents reduce stripping heat during regeneration and are industrially more convenient than liquid-liquid phase-changing solvents in terms of their application [112]. However, the processes involving CO_2 capture from liquid-liquid phase-changing solvents are easy to operate [3,45]. It was found that approximately 27 % of the total energy was required to regenerate conventional MEA [94]. Lower heat of vaporization of organic solvents as compared with water made this process cost-effective. Non-aqueous solvents overcome the disadvantages of aqueous solvents in terms of least amine degradation, less vaporization loss, less corrosion of equipment, and low heat duty requirement. Organic solvents having elevated boiling point, low heat capacity, low viscosity, and negligible foaming properties can be selected as organic solubilizers. The solvent polarity increases upon CO_2 loading in the non-aqueous solvent, resulting in the formation of carbamate. At saturation conditions, phase separation occurs when carbamate becomes insoluble in the organics solubilizer, showing solid-liquid phase-changing behavior. After CO_2 absorption, amine-carbamate is formed as a solid precipitate that is used for the regeneration step, resulting in a massive saving in regeneration energy costs [112-114].

Furthermore, the phase separation phenomenon of the absorber can easily be understood by considering the study performed by Xu et al. [102]. BDA + Diethylene glycol dimethyl ether (DGM) blend was used to study the phase separation behavior. After absorption of CO_2, the DGM went to the CO_2-enriched phase, whereas BDA transitioned to the CO_2-lean phase. After phase splitting, the concentration of BDA and DGM increases as their concentration increases in the CO_2-unloaded solution. Therefore, the CO_2 absorption capacity depends on the individual amine blend ratios. They reported that at a high BDA to DGM concentration ratio, the viscosity increased, resulting in low absorption. Viscosity is the detrimental effect of the CO_2-capture process, so there must be an optimized ratio of amines in their blend.

1.5.1 Advantages and disadvantages of biphasic solvents

Biphasic solvents are advantageous in reducing energy penalty in order to regenerate the CO_2-loaded solution by employing a low amount of regeneration heat. The operational cost of CO_2-capturing equipment associated with these biphasic solvents is less expensive [94]. Zhan et al. [100], in their investigation, prepared a novel biphasic solvent by dissolving dual-functionalized ionic liquid ([DETAH][Tz]) into a 1-Propanol-water solvent. This novel blend resolved the serious issue of high viscosity and challenging regeneration of the CO_2-enriched phase. Experimental results concluded that [DETAH][Tz] + 1-Propanol-water blend required 47.63 % lower heat duty than conventional MEA. High cyclic capacity and decreased absorption heat have also been identified as advantages of biphasic solvents, as reported in studies performed by researchers.

The most critical disadvantage of biphasic solvents is their rigorous experimental screening process. Ye et al. [38], Shen et al. [3], Zhang et al. [43], Liu et al. [42], and Zhang et al. [16] performed screening experiments on 50, 40, 32, 13, and 9 amine blends, respectively. To overcome this challenging task, solvent hydrophobicity (pKa value), phase separation behavior, CO_2 loading capacity, and efficiency of regeneration factors should be targeted [94]. The stability and volatility of biphasic solvents are a severe concern that may persist at the chosen operating conditions for absorption and regeneration.

1.5.2 Concept of lipophilic amine solvents

The solutions of partially miscible aqueous amine solvent are known as 'lipophilic amines' [109]; there exists a concept of 'lower consolute temperature' in such amines. It is the temperature at which various mixtures of the amines are miscible in every composition. It is a liquid-liquid phase separation (LLPS) temperature-induced method that takes place in the temperature range of 60–90 ℃ [19,38,95,107,115]. LLPS plays a significant role in determining two significant aspects: (a) whether the CO_2-loaded amine sample exhibits biphasic behavior or not and (b) liquid layer so formed must be at as low a temperature to reduce the regeneration energy demand. These lipophilic solvents are a highly energy-efficient technique used in the post-combustion CO_2 capture method [104]. Most lipophilic amines are classified under primary, secondary, and tertiary amines. Table 1.7 shows a few examples of lipophilic amines and their properties as chosen by the researchers. These lipophilic solvents have limited miscibility with CO_2, leading to a mixing gap while performing absorption, and this is a crucial step for phase separation [14,42]. One phase is CO_2 rich, while the other is CO_2 lean.

Table 1.7 Examples of some lipophilic amines [30,38,43].

Amine classification	**Amine selected**	**Abbreviation**	**CAS No.**	**Substitute**	**BP** (℃)	**MW (g/mol)**	**ρ (g/cm^3)**
Primary	Hexylamine	HxA	111-26-2	Linear	131	101.19	0.770
	Heptylamine	HpA	111-68-2	Linear	155	115.22	0.777
	Octylamine	OtA	111-86-4	Linear	176	129.24	0.782
	Cyclohexylamine	CHA	108-91-8	Cycloalkane	134	99.17	0.865
	Cycloheptylamine	CHpA	5452-35-7	Cycloalkane	54	113.2	0.889
	Cyclooctylamine	COA	5452-37-9	Cycloalkane	190	127.23	0.928
	Benzylamine	BzA	100-46-9	Benzyl group	185	107.15	0.981
Secondary	Di-n-propylamine	DPA	142-84-7	Linear	110.7	101.19	0.740
	N-Ethylbutylamine	EBA	13360-63-9	Linear	110	101.19	0.740
	Di-n-butylamine	DBA	111-92-2	Linear	159	129.24	0.767
	Diisopropylamine	DIPA	108-18-9	Branched	84	101.19	0.717
	Diisobutylamine	DIBA	110-96-3	Branched	137-139	129.24	0.740
	N-sec-butyl-n-propylamine	SBPA	39190-67-5	Branched	123	115.22	0.750
	N-Isopropyl cyclohexylamine	IPCA	1195-42-2	Cycloalkane	60-65	141.25	0.859
	Dicyclohexylamine	DCHA	101-83-7	Cycloalkane	255.8	181.32	0.912
	N-Methyl benzylamine	MBzA	103-67-3	Benzyl group	184-189	121.18	0.939
	N-Ethyl benzylamine	EBzA	14321-27-8	Benzyl group	191-194	135.21	0.909
	2,6-Dimethyl piperidine	2,6-DMPD	504-03-0	Piperidine group	113.2	113.20	0.840
	3,5-Dimethyl piperidine	3,5-DMPD	35794-11-7	Piperidine group	144	113.20	0.853
Tertiary	Triethylamine	TEA	121-44-8	Linear	89	101.19	0.726
	Tripropylamine	TPA	102-69-2	Linear	156	143.27	0.753
	Tributylamine	TBA	102-82-9	Linear	214	185.35	0.780
	N,N-Dimethyl butylamine	DMBtA	927-62-8	Linear	93	101.19	0.721
	N,N-Diisopropyl methylamine	DIMA	10342-97-9	Branched	114	115.22	0.754
	N,N-Diisopropyl ethylamine	DIEA	7087-68-5	Branched	127	129.25	0.742
	N,N-Dimethyl cyclohexylamine	DMCA	98-94-2	Cycloalkane	160	127.23	0.849
	N,N-Diethyl cyclohexylamine	DECA	91-65-6	Cycloalkane	193	155.28	0.840
	N,N-Dimethyl benzylamine	DMBzA	103-83-3	Benzyl group	180	135.21	0.910
	N-Ethyl piperidine	EPD	766-09-6	Piperidine group	131	113.20	0.824

Lipophilic amines and water systems are thermomorphic biphasic solvents (TBS) that exhibit the phase-splitting behavior of the CO_2-loaded aqueous amine blend solution [15,16,94]. The miscibility of TBS is the most crucial factor that finalizes whether the solution mixture will split up into layers or remain in a homogeneous phase [104]. TBS exhibits the auto extractive behavior that intensifies the desorption rate at a temperature much below that of the boiling point of the aqueous solution [14]. Four types of hydrogen bonding are seen in such a system, and they are arranged as: OH−O > OH−N > NH−H > NH−O (based on bond strength) [104].

1.5.3 DMX^{TM} process

The concept of DMX^{TM} solvents was initially proposed by Aleixo et al. [116], who targeted more than 300 different amines and performed CO_2 capture experiments at different temperatures (20–90 ℃), pressure (0–2 bar), and concentration (0 to 100 wt%) of the solution. Their results proved that the corrosion rates of DMX^{TM} solvents are very low, have high CO_2 absorption capacity, and have high thermal stability [117]. Particular unique properties (amine solvent) are responsible for evaluating novel DMX^{TM} solvents that form two immiscible liquid phases under particular CO_2 loading or temperature [40]. These solvents absorb CO_2 at 40 ℃, and after that, the CO_2-loaded sample is heated to 90 ℃ to obtain a liquid-liquid phase separation [94]. Density difference plays a significant role in separating two immiscible liquid phases after CO_2 absorption [98]. DMX^{TM} solvents, in comparison with other thermomorphic solvents, have higher LCST; therefore, their phase transition can be achieved at a higher temperature [94].

Raynal et al. [96] worked on DMX^{TM} solvents developed at IFP (French Institute of Petroleum) Energies Nouvelles, and they remarked that the concept of DMX^{TM} solvents for

CO_2 capture relies mainly on liquid/liquid and solid/liquid separation. However, they emphasized liquid/liquid solvents rather than solid/liquid solvents because handling liquid/liquid solvents is more accessible in industrial units. The solvents they used marked as DMX-1 (not disclosed) [38,118] have good CO_2 absorption capacity, are thermally stable, less corrosive, and have fast separation behavior. Initially, the "first-generation" solvent (MEA) was under trends for post-combustion CO_2 capture, but it required massive regeneration energy of 3.7 GJ/tCO_2 [116] at a solution concentration of 30 wt%. Due to this reason, the researchers targeted the "second-generation" solvents, i.e., various amine blends, and based on multiple available experimental data, it was found that regeneration energy demand can be reduced to 2.1 GJ/tCO_2 [30,42,46]. They utilized the particular properties of the different amine blends. The authors modified the setup used for the CO_2 capture done by the conventional MEA method. They added a decanter unit [40] after the amine/amine heat exchanger and before the desorption section. As the solvents split up into two immiscible phases, the denser phase is sent to the regeneration unit, and the rest stream is recycled to the absorption unit. Approximately 75 % of the CO_2 gets absorbed in the CO_2-rich phase, while the rest is available in the CO_2-lean phase [42]. IFP energies Nouvelles claimed that using their suggested DMX^{TM} solvents, the energy requirement for the CO_2 capture can be reduced up to $54/tonne [119].

1.5.4 Solvent screening and their selection

Gervasi et al. [1] focused upon a hybrid type of solvent (physical and chemical) for the post-combustion CO_2 capture by chemical absorption method. This hybrid solvent provided the best results in lower regeneration energy demand and high absorption capacity. Authors characterized, checked, and compared their own new hybrid solvent's regeneration energy requirement and absorption capacity. They prepared different amine blends of MEA, DEA, AMP with an acetal compound (act as physical solvent), i.e., 2,5,7,10-Tetraoxaundecane (TOU). Theoretically, it was discovered that using an amine blend composed of acetal compound as an essential entity in the overall solution can improve CO_2 absorption efficiency. Such marvelous properties of the acetal compound influenced the authors to select such amine blends. They concluded that the combination of amines with acetal compound is a promising alternative for post-combustion CO_2 capture compared with conventional solvents.

Shen et al. [3] focused on the solvent properties, absorption capacity, phase separation manner, reaction kinetics, and thermodynamics behavior for screening and selecting the biphasic solvent. Their experimental analysis proved that the tertiary amine’s alkalinity (pKa value) is the primary factor that determines the absorption capacity. According to their findings, tertiary amines with a pKa value of around 9.8 were found to have the highest absorption capacity in the biphasic amine blend. Primary amine’s hydrophobicity (log P value) is a crucial phase separation behavior. The phase separation is best suited to primary amines with lower log P values and tertiary amines with higher log P values.

Lee et al. [109] revealed that biphasic solvents could be classified into three classes mainly available for CO_2 capture: (1) an aqueous mixture of amine (aqueous amine + aqueous amine), (2) thermomorphic solvents (lipophilic amines + aqueous amine); (3) alkanolamine + ionic liquid. The authors targeted the feasibility and the cost of the process, and based on this, they selected an aqueous amine mixture for their study. They presented their system as A–B-H_2O (fully miscible), in which component A has at least one primary or secondary amino group while component B has a tertiary amino group in their structure.

Component ‘A’ acts as an absorption accelerator since it produces carbamate during the reaction with CO_2, while component ‘B’ acts as a regeneration promoter and forms bicarbonate. Moderate vapor pressure, either of the amines with a minimum loading capacity of 0.5 mol CO_2/mol amine, miscibility with water, high CO_2 distribution difference of the top and the bottom phase, etc., are essential factors for the selection of the amines.

Ye et al. [38] prepared a system A-B-H_2O in their solvent screening. Authors targeted upon boiling point (BP > 100 ℃), vapor pressure (VP < 10 mm Hg at 20 ℃), commercial availability, and the cost for component A. The solvents with high boiling point are thermally stable in nature. Hydrophobic DMCA (BP = 160 ℃ and VP = 3.6 mmHg) and hydrophilic DEEA (BP = 161 ℃ and VP = 1 mmHg) were chosen as component B.

1.6 Research progress of biphasic amine solvents

Researchers mainly target solvents that exhibit the proficiency of least regeneration energy demand as the best performance result. In this chain development of a phase-splitting agent and designing of multistage phase separation processes are in a running scenario in the field of CO_2 capture.

1.6.1 Development of phase splitting-agent

Adding a phase-splitting agent in the biphasic amine solvents provides the optimum phase separation and also reduces the heat duty in the biphasic amine system [120-122]. It is an inert organic compound that controls the water content and also does not participate in the chemical reaction on CO_2 loading [123,124]. They are CO_2-triggered solvents in which phase separation occurs due to a sharp increase of ionic strength of the CO_2-enriched phase because of the bicarbonate production after the CO_2-loading [125,126]. In non-aqueous solvents, organic solvents such as alcohols, polyethers, and different alcohol blends are predominantly utilized as phase-splitters [121]. The properties of the phase-splitting agent and the performance of the biphasic solvent should be targeted to select the effective phase-splitting agent.

Jiang et al. [124] selected 1,3-Dimethyl-2-imidazolidinone (DMI), N, N-Dimethylformamide (DMF), 1-Methyl-2-pyrrolidinone (NMP), and sulfolane as phase-splitting agents having different hydrophobicity. These selected agents have high chemical stability, and commercially they are readily available in a huge manner. The study was focused on TETA and DEEA biphasic amine blend as a reference because of their marvelous absorption performance. After adding phase-splitting agents, the kinetics and thermodynamics parameters of the chosen TETA+DEEA blend were investigated. They reported that the CO_2 absorption capacity decreases with the addition of phase-splitting agents due to a decrease in water content. With the increase in CO_2 loading, the volume of the CO_2-enriched phase (lower phase) increases, and the phase separation process is performed extensively with the addition of phase-splitting agents. The absorption rate depends on the absorption driving force and total liquid phase mass transfer. Furthermore, they concluded that a sharp decrease in heat duty was observed by adding a phase-splitting agent. ^{13}C NMR study revealed that these phase-splitting agents do not cause a chemical reaction with CO_2.

In their investigation, Zhou et al., 2022 [123] pointed out that biphasic solvents exhibit remarkable energy-saving potential. But, the high viscosity of the CO_2-enriched phase is the biggest issue in these biphasic solvents. They prepared a novel non-aqueous low viscous secondary amine blend that showed biphasic behavior. They selected 2-Methylethynolamine (MAE) due to its commendable properties in forming a biphasic solvent system. Dimethyl sulfoxide (DMSO) and PMDETA were chosen as organic solvents and phase-splitting agents, respectively. They reported that the amine blend system's phase-changing behavior was dependent on the proportion of PMDETA. Further, they concluded that varying the mass fraction of PMDETA will be helpful for the screening and selection of biphasic amine solvent. Switchable polarity is responsible for the phase separation of the amine blend. The formation of polar reaction products triggers the amine blend system into CO_2-enriched and CO_2-lean phases. The polarity depends on the dipole moment of various components; therefore, for the system, i.e., MAE+DMSO+PMDETA, dipole moment investigation was targeted for CO_2-unloaded and CO_2-loaded samples. Finally, they concluded that the biphasic solvent had 0.84 mol CO_2/mol amine of CO_2 loading. As the phase-splitting occurred, the CO_2-enriched phase acquired more than 90 % of absorbed CO_2 in 48 % of the entire volume. The overall aqueous system's viscosity was 8.87 millipascal second (mPa.s), which is lower than the majority of the biphasic amine solvents previously employed in most of the studies. Overall, the noteworthy features of these phase-splitting agents can be quite helpful in reducing excessive CO_2 emissions.

1.6.2 Designing of the multistage phase separation process

Biphasic solvents have remarkably higher absorption capacity, faster absorption rate, and lower heat duty requirement than conventional MEA. The CO_2-enriched phase shows a large viscosity, and it is approximately 40–200 times more viscous than water. The formation of carbamate and their linking of each other through hydrogen bonds and van der Waals forces are responsible for the high viscosity of the CO_2-enriched phase [94]. The solvent’s viscosity increases as the CO_2-loading increases but decreases with an increase in temperature for conventional phase separation methods. This rise in viscosity reduces the heat and mass transfer rate of the biphasic solvent and ultimately increases the CO_2 capture cost [127,128]. It is critical to develop such a process in which CO_2 absorption can be enhanced with reduced heat duty requirements. This can be possible only by using the modified operational unit, and in this chain, the multistage phase separation can be an effective and beneficial step.

Zhou et al. [129], in their investigation, selected a novel amine blend of TETA and DEEA, resulting in a biphasic solvent system after CO_2 absorption. They opted for a novel dual-stage phase separation process to address the critical challenge of viscosity. On CO_2 loading, the aqueous amine blend splits into two phases- CO_2-enriched and CO_2-lean phase leading to biphasic separation. The CO_2-enriched phase separates out, while the lean phase sends to the next stage to the absorption column in a continuous manner. The recovery of amine solvent leads to a reduction in the CO_2 loading of the remaining solvent. The CO_2-enriched phases from each separated stage are mixed and directly sent to the stripping section for regeneration. This regeneration step results in the decrease of concentration of carbamate, resulting in the reduction of the viscosity of the solvent. They concluded that by employing dual-stage phase separation at each stage, the cyclic capacity of the selected amine blend is lower than the standard single-stage separation method but still higher than the benchmark MEA. When compared to MEA, the proposed dual-stage approach enhanced the absorption rate at 50 °C by 49 % and reduced heat duty by 33 %. The thermodynamic assessment suggested that employing the dual-stage phase separation method can cut down energy consumption even more.

1.7 Investigations performed by various researchers on biphasic solvents

Zhang et al. [14] performed screening experiments on over 30 lipophilic amines and, from them, selected the best novel alkylamine (A1) but did not disclose it. For the absorption of CO_2, they used a 100 ml bubble column (2.5 cm in diameter and 145 cm in height). The CO_2 gas is initially absorbed in the amine solution at 30 ℃. A gas chromatography analyzer analyzed the outlet gas stream, and CO_2 loading was calculated by the $BaCl_2$ titration method. There are two phases formed after absorption: one is CO_2-enriched, and other is CO_2-lean. The composition of such rich and lean solvents is measured by volumetric Karl Fischer's (KF) method. Further, this CO_2-loaded solution was sent into the stripping section and desorbed by N_2 gas at 75–80 ℃. They calculated CO_2 loading with time, phase separation temperature, and percentage of regeneration. By using variable amine solution concentration, CO_2 loading initially rose with time and then became constant. Excellent performance regarding net CO_2 loading capacity was obtained for A1 (5M) and activated N, N-Dimethyl cyclohexylamine (a-DMCA), i.e., 3.34 mol/L at 30 ℃.

Zhang et al. [43] reviewed 32 novel lipophilic amine solvents to overcome the challenges of high regeneration energy demand in post-combustion carbon capture. They performed screening and investigated loading capacity, phase separation temperature, reaction kinetics, and regenerability. Absorption of CO_2 was done by test tube screening and bubble column experiments. The aqueous solubility of amine solution decreases with an increase in temperature, thus creating a biphasic situation.

- **Phase change behavior**

After screening all 32 lipophilic amines, phase-change behavior is only shown by Hexylamine (HxA), Cycloheptylamine (CHpA), A1-secondary alkylamine (Not disclosed), N-Methyl piperidine (MPD), and N-Ethyl piperidine (EPD).

- **Reaction rate**

Fast or slow reaction mainly depends upon the amine solubility. Primary and secondary amines, while reacting, form carbamates, and reactions are very fast. Researchers have reported that fast reactions were achieved by HxA, CHpA, A1-secondary alkylamine (Not disclosed), Di-n-propylamine (DPA), Diisopropylamine (DIPA), N-sec-Butyl-n-propylamine (SBPA), etc. were considered to be the activators for the CO_2 absorption. In the same manner, tertiary amines were used as regenerating promoters.

Carbamate reaction: $\mathrm{CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^-}$ (1.10)

- **Absorption capacity**

The CO_2 absorption capacity is affected mainly by the reaction mechanism, and tertiary amines are less reactive than primary or secondary amines. Tertiary amine takes up equal moles of CO_2 and H_2O to form bicarbonate (slow reaction and shows corrosive effect). CO_2 loading increases with an increase in carbamate generation and carbamate reversion. However, it is not an easy task because, during the reaction, steric hindrance, limited solubility, and salt formation restrict higher CO_2 loading. This CO_2 loading was reported to be higher for primary and secondary amines, i.e., CHpA, A1, DPA, 2,6-Dimethyl piperidine (2,6-DMPD), etc., and low CO_2 loading for tertiary amine solutions, i.e., with DIEA, Tripropylamine (TPA), and TBA. CO_2 loading was also significantly affected by the solution concentration.

Bicarbonate reaction: $\mathrm{CO_2 + RNH_2 + H_2O \leftrightarrow RNH_3^+ + HCO_3^-}$ (1.11)

Carbamate conversion reaction: $CO_2 + RNHCOO^- + 2H_2O \leftrightarrow RNH_3^- + 2HCO_3^-$ (1.12)

- **Regeneration effect**

The solvent regeneration at an elevated temperature is a major concern for alkanolamine-based CO_2 capture. B1-sterically hindered alkylamine (Not disclosed), DMCA, and EPD act as regeneration promoters and showed the best behavior to overcome the serious issue of high regeneration energy demand. DMOP and MPD also showed excellent behavior in terms of regenerability, but they have the drawback of slow absorption with high volatility. The most significant advantage of using lipophilic amines in CO_2 capture is that the regeneration of the solvent can be carried out at a modest temperature of approximately 80 ℃ or even lower. In their study, Zhang et al. [43] reported that the DMCA+A1 and A1+B1 blends showed phase-changing behavior with solvent regenerability at a lower temperature ($\approx$ 80 ℃) than conventional amine.

Zhicheng et al. [30] studied 12 amine solvents that have potential phase-change behavior. These solvents with variable concentrations were used for CO_2 absorption purposes in a semi-batch mode. The researchers calculated maximum CO_2 loading (by titration method), absorption capacity, and the reaction rate. The upper and lower phases in biphasic solvents so formed get titrated to calculate the CO_2 loading. They reported 1,4-Diaminobutane (DAB) (3 M) and 1,6-Hexanediamine (HAD) (3 M) performed regarding absorption capacity and absorption rate. N,N-Dimethylbutylamine (DMBA) (2 M) + DEEA (4 M) also has the potential of phase-separation and can be used further for the post-combustion carbon capture method.

Pinto et al. [22] selected tertiary amine (DEEA) and diamine (MAPA) and performed preliminary absorption. After absorption, the amine blend solution was separated into

MAPA (5 M) (CO_2 rich phase) and DEEA (2 M) (CO_2 lean phase). Phase separation was affected by the temperature, and they increased with temperature. The CO_2-rich phase was taken for desorption purposes, and at a high temperature (less than MEA), CO_2 was eliminated by the system. The researchers finally reported that this blend has a high cyclic capacity, lower heat of absorption, and lower regeneration temperature.

Ye et al. [38] performed screening upon 50 amine-based solvents and kept their overall amine concentration equal to 5 mol kg^{-1} in the fixed molar ratio for every blend. A bubble column reactor was used for CO_2 absorption at 30 ℃ for 90 min. Moreover, finally reported the CO_2-loading by the Chittick apparatus (Volumetric titration method). Every phase was analyzed by ^{13}C NMR spectroscopy at 100.575 MHz of spectral frequency. Desorption of CO_2-loaded solution was performed at 80 ℃ for 90 min. by the Parr reactor (model 4560, Parr Instrument Company). Polyamines, available in the solvent blends, act as an accelerator while absorbing CO_2 and are mainly responsible for the phase separations. Researchers reported that the TETA+DEEA blend has a low foaming tendency, low volatility, low viscosity, and low precipitating effects. This blend was considered to be the best among all the numerous solvents screened.

Luo et al. [106] investigated blends of DETA, sulfolane (non-volatile), and H_2O. A thermostatic VLE reactor was used to calculate the solubility. The researchers reported that high CO_2 loading was achieved during absorption by using blends of 20 % DETA + 40 % sulfolane + 40 % H_2O, and the blend showed phase-splitting properties due to limited solubility. The cyclic loading and cyclic capacities of CO_2 were calculated at different compositions of each species available in the blend. Cyclic loading of the blend was 35 % higher than that of MEA (30 wt%).

Machida et al. [46] worked on the hydrophobicity of 7 amine solvents with one ether solvent. They reported that three phases are possible, i.e., no phase-formation with CO_2, phase splitting with CO_2 loading, and initially immiscible phases. CO_2 solubility for each phase's biphasic solvents and mole fractions was measured at different temperatures (313 K to 353 K) and pressure (1 kPa to 100 kPa). EAE+DEGDEE+H_2O bled showed phase change characteristics with high-temperature dependency and reduced stripping cost, which was finally concluded by the researchers.

Shen et al. [3] selected 40 various blends by combining primary/secondary with tertiary amines. They performed absorption in a glass bubble column reactor (50 ml capacity) and took a 4 molar concentration of the overall solution. This bubble reactor was used to measure the CO_2 absorption capacity. In the same way, a double-stirred cell reactor (DSCR) was used to measure the CO_2 absorption rate. It was calculated by:

$$N = -\frac{\text{To (Qout} - \text{Qin)}}{\text{Vm,oTrA}} \tag{1.13}$$

Where N is CO_2 absorption rate (Kmol m^{-2} s^{-1}), Q_{out} and Q_{in} are the outlet and inlet gas flow rate (m^3 s^{-1}) respectively, To and Tr are the standard and room temperatures (℃) respectively, A is the interfacial area between the gas and liquid phase (m^2), $V_{m,o}$ is the molar volume of the gas at STP (m^3 $kmol^{-1}$). The researchers investigated absorption performance, kinetics, and thermodynamic behavior against biphasic solvents. They suggested that considering the hydrophobicity and alkalinity of the tertiary amines, so that selection of these solvents could be easier. They reported the heat duty of the selected amines by considering reaction heat (Q_{rxn}), sensible heat (Q_{sens}), and latent heat (Q_{latent}) and calculated by:

$$Q_{rxn} = -m_{am} \int_{lean}^{rich} \Delta h_{rxn} (\alpha) d\alpha \tag{1.14}$$

$$Q_{sens} = m_{am}(C_{am} + r_w c_w + \alpha_{lean} C_{CO2})\Delta T \quad (1.15)$$

$$Q_{latent} = m_w \lambda \quad (1.16)$$

$$Q_{regen} = Q_{rxn} + Q_{sens} + Q_{latent} \quad (1.17)$$

where, m_{am} is the molar amount of amine to produce per ton of CO_2 (in mol); Δh_{rxn} is the reaction enthalpy (kJ mol^{-1}); α and α_{lean} are CO_2 loading for rich and lean solutions respectively (mol mol^{-1}); C_{am}, c_w, and C_{CO2} are the heat capacities for amines, water, and CO_2 per ton of CO_2 produced, respectively (kJ mol^{-1} K^{-1}); r_w is the water to amine molar ratio in fresh solution; ΔT is the temperature difference (K); m_w is the molar water vapor per ton of CO_2, and λ is the latent heat (kJ mol^{-1}). In their investigations, researchers finally reported that TETA-TMPDA has the lowest reaction rate and reaction enthalpy (45 kJ/mol), corresponding to other blends.

Liu et al. [42] focused on 12 alkanolamines (including primary, secondary, and tertiary) and created their different aqueous blends with DEEA solvents. The preliminary solvent screening was done by a bubble column reactor. Carbamates and bicarbonates were formed in the lower phase after phase splitting that was taken out from the absorber, and fed to the desorption section. Finally, researchers reported that aqueous blends of DEEA-MEA and DEEA-AEEA showed phase-splitting behavior with higher absorption loading and desorption capacity, as compared with MEA. After selecting these biphasic blends of DEEA-MEA and DEEA-AEEA, they calculated CO_2 loading, CO_2 loading distribution, phase split ratio, and phase split time. The CO_2 loading at 40 ℃ for DEEA-MEA and DEEA-AEEA blends was reported to be 1.56–2.93 mol/kg and 0.86–3.15 mol/kg, respectively. The phase split ratio has a direct relation with CO_2 loading. Approximately 95 % of CO_2 is absorbed in the lower phase and provided CO_2 loading for DEEA-MEA and

DEEA-AEEA solvents to 42.4 % and 66.4 % higher than the benchmark 30 wt% MEA solutions that are beneficial for regeneration purposes. Phase split time was much less for biphasic solvents so formed. ^{13}C NMR analysis was done on the lower and upper phases of CO_2-loaded amine blends. Ultimately, the DEEA-AEEA solvent with a regeneration energy demand of 2.58 GJ/tco_2 was reported to be the best amine blend that showed biphasic characteristics.

Shen et al. [47] reported that solvents blended with biphasic properties could easily be screened by knowing their reaction mechanism. In primary amines, the increase in N_2 molecule decreases carbamate formation. They performed screening on 4 amines that had the potential of phase-splitting properties. Absorption was performed to calculate CO_2 loading in the bubble column in the same manner as absorption rate was calculated by the DSCR. Deuterated water and deuterated chloroform were used for the NMR analysis at 151 MHz of frequency. ^{13}C NMR analyzed that CO_2 absorption was fast and initially occurred with the primary amine, then with the tertiary amine. Based on their entire experiments, they concluded that a blend of TETA+DMCA showed the best results.

Investigations performed by many researchers on biphasic solvents in the last 10 years have been listed in Table 1.8. There are currently 27 commercial CO_2-capture projects in operation worldwide until 2022. The first project was established by the US in 1972, and it was the ‘Terrell Natural Gas Processing Plant’ that captured maximum 0.5 metric tons of CO_2 per year ($MtCO_2$/Y). ‘Alberta Carbon Trunk Line (ACTL) with Nutrien CO_2 Stream’ was the last commercial project established by Canada in 2022 [130]. Table 1.9 represents information corresponding to all the commercial CO_2-capture projects operating from 1972 to 2023.

Table 1.8 Investigations conducted over the past 10 years on biphasic solvents by various researchers.

S. No.	Total Absorbents Screened/ used	Best Absorbent	Split-phase mode	Absorption Temperature (℃)	Regeneration Temperature (℃)	Operating Conditions	References
1.	5	A1 + Activated- DMCA A1 = Not disclosed (selected by screening over 30 amines)	Liquid-liquid	30	75–80	P_{CO2}: 19.4 kPa; Operating time: 2–3 h; Amine concentration: 3–5 M; Total gas flow rate: 100–400 NL/h	Zhang et al. [14]
2.	32	DMCA + A1; A1 + B1 A1-Secondary Alkyl amine B1-Sterically hindered Alkyl amine A1,B1 = Not Disclosed	Liquid-liquid	30–40	75–85	P_{CO2}: 5–50 kPa; Operating time: 2–5 h; Amine concentration: 3–5 M; Agitation rate: 1000 rpm	Zhang et al. [43]
3.	12	DMBA (2 M) + DEEA (4 M)	Liquid-liquid	-	-	Operating pressure: 1 atm.; Semi batch reactor used	Zhicheng et al. [30]
4.	9	MCA (Activator) + DMCA (Promoter) + AMP (Solubilizer)	Liquid-liquid	30–40	80	Amine concentration: 4–5.5 M (Oxidative degradation setup used)	Zhang et al. [16]
5.	4	BDA (2 M) + DEEA (4 M)	Liquid-liquid	40	90	Total gas flow rate: 463 ml/min.; Operating pressure: 1 atm.	Xu et al. [44]

6.	5	MEA + TOU	Liquid-liquid	25	-	Double stirrer cell reactor used; Total gas flow rate: 8.33*10^{-5} m^3/s	Gervasi et al. [1]
7.	5	MEA + 1-Heptanol	Liquid-liquid	40	-	Total flow rate of gas: 200 ml/min. ; Stirring speed: 500 rpm; Semi-batch reactor used	Kim et al. [40]
8.	2	DEEA (5 M) + MAPA (2 M)	Liquid-liquid	40, 60 & 80	100–120	Total gas flow rate: 5 NL/min. ; P_{CO2}: 1–20 kPa	Pinto et al. [22]
9.	50 (Including Blend)	TETA (1 M) + DEEA (4 M)	Liquid-liquid	40–50	80	Pure CO_2 flow rate: 105 ml/min; operating pressure: 1 atm.; absorption time: 90 min.; batch reactor is used.	Ye et al. [38]
10.	2	DETA + Sulfolane + H_2O	Liquid-liquid	40, 80, 110	-	Operating temperature: 313 to 393 K; P_{CO2}: 400 kPa	Luo et al. [106]
11.	3	DETA (1.5/2 M) + PMDETA (3/3.5 M)	Liquid-liquid	40	100–120	Operating pressure: 1 atm.; absorption time: 120 min.	Ye et al. [45]
12.	8	EAE + DEGDEE + H_2O	Liquid-liquid	40–80	-	Operating pressure: 1–100 kPa; P_{CO2}: 0.2 kPa.	Machida et al. [46]
13.	40 (Including	TETA + TMPDA	Liquid-liquid	40, 50, 60	-	CO_2 gas flow rate: 200 ml/min; solution concentration: 4 Molar	Shen et al. [3]

	blends)					(1:3); absorption time: 90 min.; stirring speed: 250 rpm; P_{CO2}: 1.3 and 13 kPa	
14.	13 (DEEA blended with 12 alkanolamine)	DEEA + AEEA	Liquid-liquid	40	100	Gas flow rate (CO_2) = 500 ml/min.; NMR analysis; absorption time: 30 min.	Liu et al. [42]
15.	4	TETA + DMCA	Liquid-liquid	40	-	Total gas flow rate: 200 ml/min; operating time: 120 min.; total amine concentration: 4 M (1:3); NMR analyses	Shen et al. [47]
16.	3	EDA + DMA; EDA + DMF	Solid-liquid	20	T = 50.22, 135.87, & 151.45; Desorption rate = 10 ℃/min.	P_{CO2}: 40 kPa; total gas flow rate = 150 ml/min; Operating pressure: 1 atm.	Li et al. [112]

Table 1.9 List of commercial CO_2 capture projects under operation from 1972 to 2023 [130,132,133].

S. No.	CO_2 Capture Project	Country	Established Year	CO_2 Source	CO_2-capture capacity ($MtCO_2$/Y)		Storage Technique
					Min.	Max.	
1.	Terrell Natural Gas Processing Plant (erstwhile Val Verde Natural Gas Plants)	United States	1972	Natural Gas Processing	0.4	0.5	Enhanced Oil Recovery (EOR)
2.	Enid Fertilizer	United States	1982	Fertilizer Production	0.1	0.2	EOR
3.	Shute Creek Gas Processing Plant	United States	1986	Natural Gas Processing	7	7	EOR
4.	MOL Szank field CO_2 EOR	Hungary	1992	Natural Gas Processing	0.059	0.157	EOR
5.	Sleipner CO_2 Storage	Norway	1996	Natural Gas Processing	1	1	Dedicated Geological Storage (DGS)
6.	Great Plains Synfuels Plant and Weyburn-Midale	United States	2000	Synthetic Natural Gas	1	3	EOR
7.	Core Energy CO_2-EOR	United States	2003	Natural Gas Processing	0.35	0.35	EOR
8.	Sinopec Zhongyuan Carbon Capture Utilization and Storage	China	2006	Chemical Production	0.12	0.12	EOR
9.	Snohvit CO_2 Storage	Norway	2008	Natural Gas Processing	0.7	0.7	DGS
10.	Arkalon CO_2 Compression Facility	United States	2009	Ethanol Production	0.23	0.29	EOR
11.	Century Plant	United States	2010	Natural Gas Processing	5	5	EOR

12.	Petrobras Santos Basin Pre-Salt Oil Field CCS	Brazil	2011	Natural Gas Processing	4.6	4.6	EOR
13.	Yanchang Integrated Demonstration	China	2012	Chemical	0.05	0.05	EOR
14.	Bonanza Bio-Energy CCUS EOR	United States	2012	Ethanol Production	0.1	0.1	EOR
15.	Coffeyville Gasification Plant	United States	2013	Fertilizer Production	0.9	0.9	EOR
16.	Air Products Steam Methane Reformer	United States	2013	Hydrogen Production	1	1	EOR
17.	PCS Nitrogen	United States	2013	Fertilizer Production	0.2	0.3	EOR
18.	Boundary Dam 3 Carbon Capture and Storage Facility	Canada	2014	Power Generation	0.8	1	Various Options Considered
19.	Quest	Canada	2015	Hydrogen Production	1.2	1.2	DGS
20.	Uthmaniyah CO_2-EOR Demonstration	Saudi Arabia	2015	Natural Gas Processing	0.8	0.8	EOR
21.	Karamay Dunhua Oil Technology CCUS EOR Project	China	2015	Methanol Production	0.1	0.1	EOR
22.	Abu Dhabi CCS (Phase 1 being Emirates Steel Industries)	United Arab Emirates	2016	Iron And Steel Production	0.8	0.8	EOR
23.	Illinois Industrial Carbon Capture and Storage	United States	2017	Ethanol Production	0.55	1	DGS
24.	CNPC Jilin Oil Field CO_2 EOR	China	2018	Natural Gas Processing	0.35	0.6	EOR
25.	Gorgon Carbon Dioxide Injection	Australia	2019	Natural Gas Processing	3.4	4	DGS
26.	Qatar LNG CCS	Qatar	2019	Natural Gas Processing	2.2	2.2	DGS

27.	Alberta Carbon Trunk Line (ACTL) with North West Redwater Partnership's Sturgeon Refinery CO_2 Stream	Canada	2020	Hydrogen Production	1.3	1.6	EOR
28.	Alberta Carbon Trunk Line (ACTL) with Nutrien CO_2 Stream	Canada	2020	Fertilizer Production	0.2	0.3	EOR
29.	Enhance Clive Oil Field	Canada	2020	CO_2 Transport/Storage	-	1.12	EOR
30.	Wolf Alberta Carbon Trunk Line	Canada	2020	CO_2 Transport / Storage	-	14.6	EOR
31.	China National Energy Guohua Jinjie	China	2021	Power Generation & Heat	-	0.15	DGS
32.	Climeworks Orca	Iceland	2021	Direct Air Capture	-	0.004	DGS
33.	Sinopec Nanjing Chemical	China	2021	Chemical	-	0.2	EOR
34.	Yangchang Yan'an CO_2-EOR	China	2021	Chemical	-	0.1	EOR
35.	Entropy Glacier Gas Plant	Canada	2022	Natural gas processing	-	0.2	DGS
36.	Red Trail Energy Richardton Ethanol	United States	2022	Ethanol	-	0.18	DGS
37.	Sinopec Qilu-Shengli	China	2022	Chemical	-	1	EOR
38.	Yangchang Yulin CO_2-EOR	China	2022	Chemical	-	0.3	DGS
39.	China National Energy Taizhou	China	2023	Power Generation & Heat	-	0.5	EOR
40.	CNOOC Enping	China	2023	Natural gas processing	-	0.3	DGS
41.	Sinopec Jinling Petrochemical (Nanjing Refinery)	China	2023	Oil refining	-	0.3	EOR

ASSOCIATED CONTENT

Appendix – A and Appendix – B

Figure A1 to Figure A5, related to this chapter, can be found in Appendix–A.

Table B1 and Table B2**,** related to this chapter, can be found in Appendix–B.

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