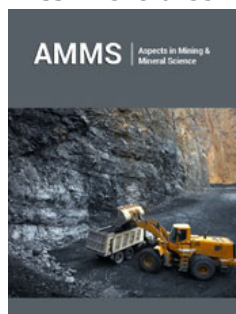Review Article

An Overview of Conventional Techniques and Recent Advancements in CO$_2$ Capture Technologies

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Abstract

CO$_2$ Capture and Utilization (CCU) is a promising technique for reducing global warming. Conventional methods include absorption and adsorption, chemical looping combustion and cryogenic distillation, hydrate-based separation and membrane separation have been used for CO$_2$ separation, but they have certain limitations like high energy intensive, solvent degradation, solvent loss, corrosive nature of the solvents and toxicity of solvents. Novel materials and techniques are always being developed in order to achieve greater optimization. Ionic Liquids (ILs) have demonstrated great potential for cost-effective CO$_2$ separation. Similarly, Supported Ionic Liquid Membranes (SILMs) have also shown effective CO$_2$ separation performance. This review offers the detailed mechanism, advantages and disadvantages and comparison of various conventional methods used for CO$_2$ capture. In addition, different ionic liquids used for CO$_2$ separation have also been discussed in detail. Lastly, Various challenges, and future recommendations in SILMs are identified and explained.

Keywords: Conventional technologies for CO$_2$ capture; Ionic liquids; SILM; CO$_2$/N$_2$ permeability and selectivity

Abbreviations: CO$_2$: Carbon Dioxide; N$_2$: Nitrogen; H$_2$O: Water; CH$_4$: Methane; H$_2$: Hydrogen; GPU: Gas Permeation Unit; IL: Ionic Liquid; TSIL: Task-Specific Ionic Liquid; RTIL: Room-Temperature Ionic Liquid; SLM: Supported Liquid Membrane; SILM: Supported Ionic Liquid Membrane; PF$_6$: Hexafluorophosphate; Tf$_2$N: Bis(trifluoromethylsulfonyl)-amide; BF$_4$: Tetrafluoroborate; C$_2$mim: 1-ethyl-3-methyl-imidazolium; C$_4$mim: 1-butyl-3-methyl-imidazolium; C$_8$mim: 1-octyl-3-methyl-imidazolium; DCA: Dicyanamide; Gly: Alanate; P$_{66614}$: Trihexyl(tetradecyl)phosphonium; PI: Polyimide; PVDF: Polyvinylidene Fluoride; PS: Polysulfone; PES: Polyether Sulfone; PTFE: Poly (Tetrafluoroethylene); MMM: Mixed Matrix Membrane; GHG: Greenhouse Gases; CCU: Carbon Capture and Utilization; C$_5$H$_6$NCl: Pyridinium Chloride; H$_4$P$^+$: Phosphonium; NH$_4$$^+$: Ammonium; Gt: Gigatonnes; IGCC: Integrated Gasification Combined Cycle; ASU: Air Separation Unit; MEA: Mono-Ethanolamine; HSO$_4$$^-$: Hydrogen Sulfate; CILs: Conventional Ionic Liquids; [bmim][PF$_6$]: 1-Butyl-3-methylimidazolium hexafluorophosphate; [bmim][Tf$_2$N]: 1-Butyl-3-methylimidazolium bis[trifluoromethyl)sulfonyl]- imide; [bmim][BF$_4$]: 1-butyl-3-methylimidazolium tetrafluoroborate; [bmim][Ac]: 1-butyl-3-methylimidazolium acetate; [bmim][DCA]: 1-butyl-3-methylimidazolium dicyanamide; [bmim][TCM]: 1-butyl-3-methylimidazolium tricyanomethanide; [bmim][NO$_3$]: 1-Butyl-3-methylimidazolium nitrate; [Bmim][Gly]: 1-butyl-3-methylimidazolium glycinate; [Bmim][Ala]: 1-butyl-3-methylimidazolium L-alaninate

Introduction

Human activities and natural processes contribute to the emission of greenhouse gases like carbon dioxide, nitrous oxide, methane, and halogenated compounds. GHGs absorb infrared radiation and trap heat within the atmosphere, increasing the natural greenhouse effect known as global warming. The amount of CO$_2$ emissions is around 15-20% in the atmosphere and a major contributor in the greenhouse gases [1]. The CO$_2$ emissions from energy related sources of the United States, Japan and European Union declined significantly in 2019, compared with the previous year 2018, but emissions in the rest of the world increased by a same amount which levelling off the overall CO$_2$ emissions [2]. The main problem of the environment today is the maximum CO$_2$ emissions which induce global warming as a result. The earth's climate is differing constantly because of different factors, viz., change in the Sun's intensity, and change in the Earth's orbit, volcanic emissions, and increase in Greenhouse Gas (GHG) concentrations. The increase in the earth's temperature is due to the phenomenon where carbon dioxide (CO$_2$),

methane (CH_4) and other anthropogenic gases absorb the leaving infrared radiations which cause an increase in the temperature of earth [3]. For industrial CO_2 emissions, various Carbon Capture and Storage (CCS) systems are in the development stage. Pre-combustion, post-combustion, and oxyfuel combustion are the three main CCS methods. The mitigation of CO_2 before combustion, which relates to the gasification process to create synthesis gas, is referred to as pre-combustion capture. After that, the synthesis gas can be treated to create H_2 and CO_2 rich streams or converted into chemicals and light fuels by catalysis [4,5]. The oxyfuel combustion method needs the use of pure oxygen for the fuel combustion [6]. Existing plants cannot use either pre-combustion or oxyfuel combustion methods. Post-combustion CO_2 separation methods, on the other hand, may be retrofitted onto existing facilities [7]. Cryogenic separation, amines solvent based absorption, porous solids based adsorption, and membrane separation are all employed in post-combustion CO_2 separation procedures for gas processing and CO_2 capture, respectively [8]. The use of amines to capture CO_2 by post-combustion is a robust approach that may be integrated into existing plants [9]. Despite its great efficiency, the amine-based CO_2 separation technology is neither a long-term ecologically friendly or cost-effective option [10]. Solvent degradation [11,12], equipment corrosion [13,14], solvent escape, and the production of nitrosamines and nitramines are all disadvantages of amine-based chemical solvents [15].

In this work, the conventional methods used for CO_2 separation are comprehensively presented. The mechanism, advantages and disadvantages and comparison of the conventional methods, i.e., absorption and adsorption process, chemical looping combustion, cryogenic distillation, hydrate-based separation, and membrane separation are broadly explained. Ionic liquids, being an attractive solvent with excellent properties are discussed in detail. The use of ILs in combination with membranes is a relatively recent technology for gas separation explored in the last two decades. Supported Ionic Liquid Membranes (SILMs) is among the many forms of IL-containing membranes reviewed in this study.
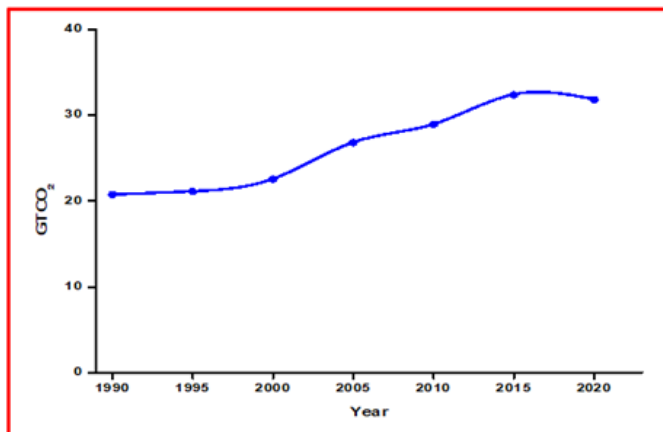
Sources of CO_2 Emissions

Worldwide anthropogenic (GHG) emissions are predominantly because of human activities that includes the consumption of non-renewable energy resources, transportation, industrial processes and emissions from forestry and other land use [16]. According to the Figure 1, the data was published by the European Environment Agency in 2016 and it shows that, among various sources of anthropogenic (GHG) emissions, the fuel combustion sector mainly use for electricity and heat production has the biggest commitment towards greenhouse gas emissions. Similarly, the transport sector has also shown the excess amount of GHG emissions followed by Industrial processes and Agriculture sector [16]. As reported by Netherlands Environmental Assessment Agency In 2018, the development altogether worldwide ozone depleting substance (GHG) emissions (eliminating those from land-use change) continued at pace of 2.0%, coming to 51.8 gigatonnes of CO_2 equivalent [17]. Similarly, the increase in global GHG emissions of 2% (1.0 gigatonnes CO_2) was due to a 2.0% rise in worldwide

CO_2 emissions from fossil fuel combustion and from Industrial processes together with cement production. There was a 1.8% increase in global methane and 0.8% increase in global nitrogen oxide emissions during the same time period [18]. In the 1990s, global fossil fuel CO_2 emissions increased by 0.9 percent per year. In the 2000s, they accelerated to a rate of 3.0 percent per year. Since 2010, they have returned to a slower growth rate, increasing by 0.9 percent per year [19]. Aside from declines in emissions in the European Union and the United States over the last decade, the rise in emissions in China, India, and most emerging nations had also greatly affected global emission trends over the last couple of decades [20].
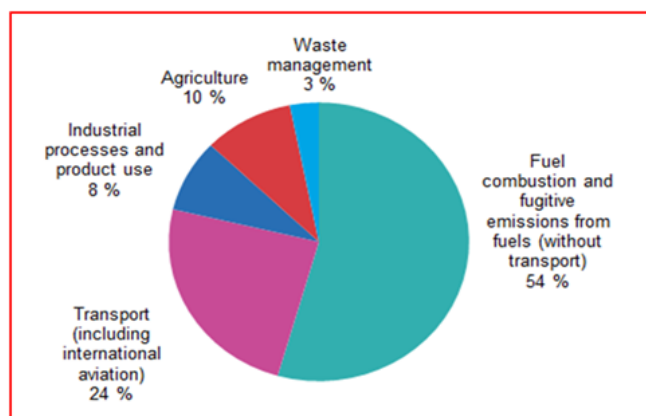
Figure 1: Greenhouse gas emissions by sectors 2016 [16].

In 2019, Global greenhouse gas emissions increased at a 1.1%, reaching 52.4 Gt CO_2 comparable. The main reason for the rise in global greenhouse gas emissions coincided with the rise in global carbon dioxide emissions in 2019. Similarly, the global emissions of Methane increased by 1.3%. This results in CO_2 from fossil fuels accounts for 73% of the total, while methane accounts for 19%. contributed mainly to the rise of global warming [21]. As stated in Figure 2, the International Environment Agency did a study in 2021 and compared the Global CO_2 emissions in the last three decades. Stated that the worldwide CO_2 emissions was nearly 21 gigatonnes in 1990 and then grew up continuously to almost 33 gigatonnes in 2019 but there is a slight decline in 2020 because of the pandemic. As of the most recent statistics, primary energy demand fell by almost 4% in 2020, while worldwide energy-related carbon dioxide emissions fell by 5.8%, the highest annual percentage drop since Second World War. Simplistically, carbon dioxide emissions have been reduced by nearly 2 billion tons [22]. The international climate policy has published the top five CO_2 emitter countries as stated in Figure 3, it indicates that China has the highest CO_2 emissions as recorded 29% globally, followed by the United States which was 16%. Similarly, European Union, India and Russian Federation have also included in the top CO_2 emitters list. The role of China, the United States and European Union is critical because they account for more than 50% of global emissions [23]. In 2019, China has recorded the excess CO_2 emissions of nearly 10 gigatonnes, next off the United States was indicated almost 5 gigatonnes of CO_2 emissions. Additionally, the European Union and India have showed 3.0 and 2.3 gigatonnes of CO_2 emissions respectively [24].

**Figure 2:** Global energy-related CO_2 emissions, 1990-2020 [22].
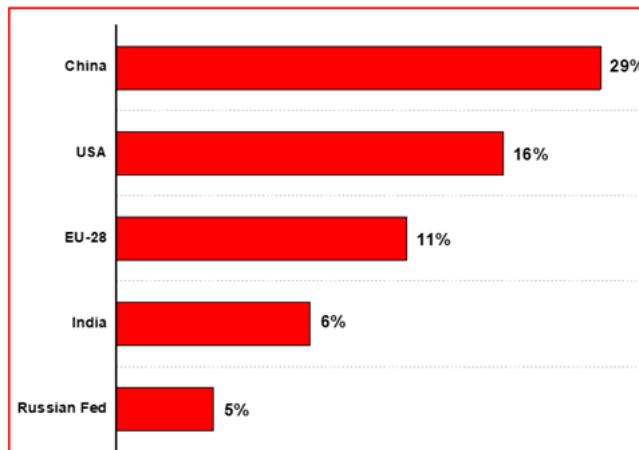
Figure 3: Countries with the largest CO_2 emissions in 2020 [23].

Conventional Technologies for CO_2 Capture

The amount of CO_2 produced during combustion, as well as the type of combustion, have a direct impact on the selection of the suitable CO_2 removal method. The cost of currently available CO_2 capture technologies in the market is high, accounting for 70-80% of the total cost of a complete carbon capture storage system which includes capture, transportation and storage [25]. There have been three basic CO_2 capture methods, each of which is linked to a distinct combustion process, such as post-combustion, pre-combustion, or oxy-fuel combustion, which is shown in Figure 4 and explored in the following section.
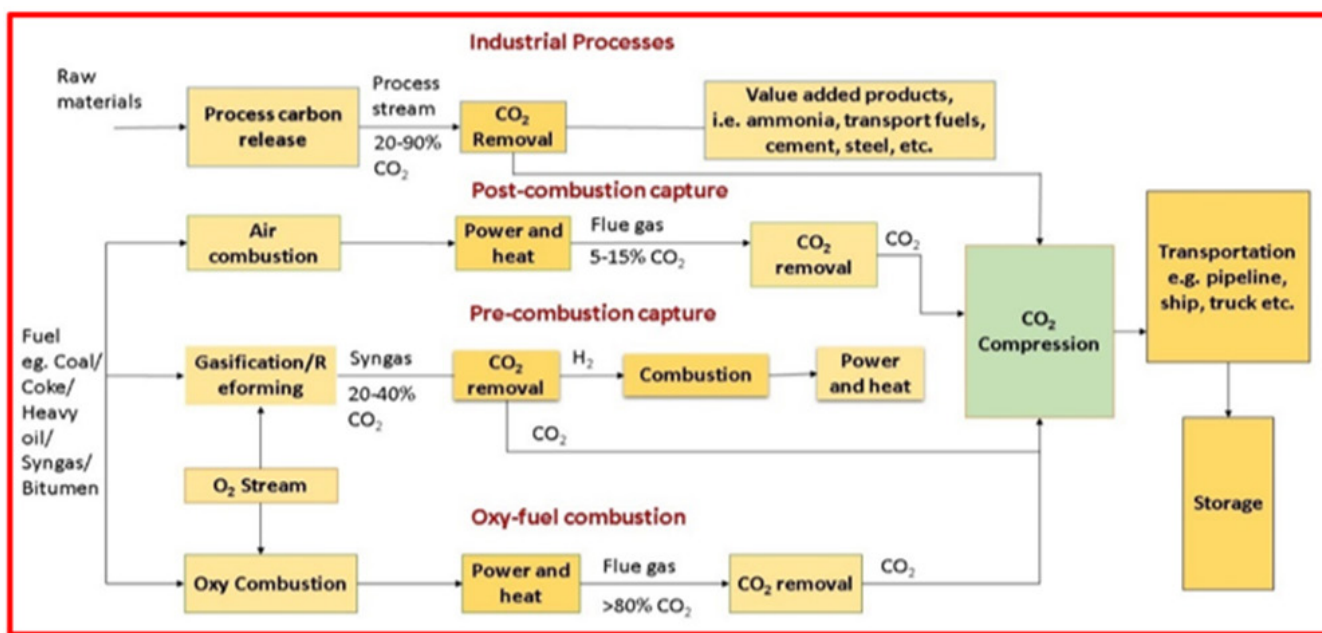
**Figure 4:** CO_2 capture pathways [28].

Post-combustion, pre-combustion, and oxy-fuel combustion

The technologies used for CCS are currently divided into pre-combustion or post combustion systems and named after the point at which the carbon is removed, i.e., before or after the burning of fossil fuels [26]. Another technology, called oxy-fuel combustion, is still in the development phase and will take some time to become industrially acceptable. Power plants use technology similar to that used in several industrial processes, though without the combustion process.

Post-combustion: After burning, this procedure eliminates CO_2 from the flue gas. For retrofitting of the existing power plants, post-combustion technology is the most desirable option. It has been proved on a small scale that the recovery rate of carbon dioxide is as high as 800 tons/day [27]. Although, the main challenge for post-combustion CO_2 capture is its huge parasitic load (power consumed even when the appliance is shut off, that is standby power) [28]. Because the CO_2 level is usually very low (i.e., 7-14% in combustion flow gas for coal fired and for gas fired as low as 4%) [29]. The energy loss and related cost for the capture device reaches the

CO_2 concentration (above 95.5%) required for transportation and storage are raised [30]. National Energy Technology Laboratory of the United States evaluated that post-combustion CO_2 capture would rise the electrical power production cost by 70% [31]. As stated by the Energy Information Agency, the ever-increasing power demand will result in 50% increase in installed coal-fired power generation capacity by 2030 [32]. A new study indicated that the electricity cost for post-combustion in coal and gas fired power plants would increase by 65% and 32% accordingly (Figure 5), [33,34].
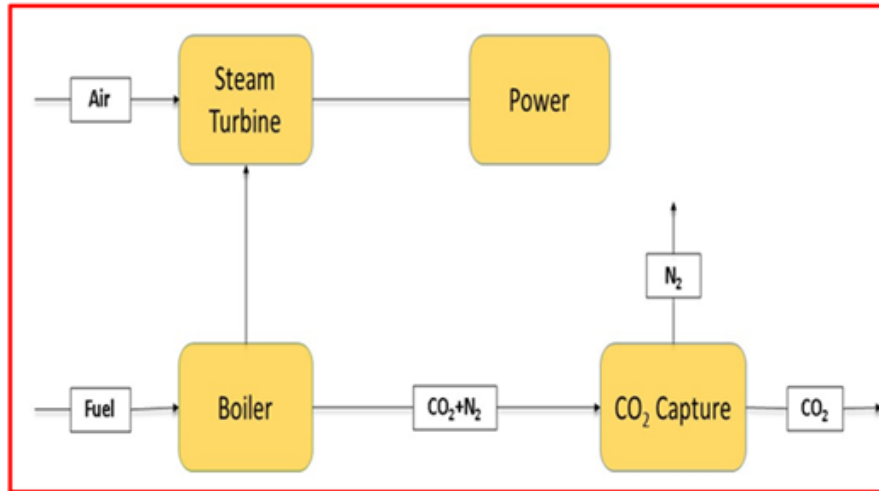
Figure 5: Schematic diagram of post-combustion carbon dioxide capture [34].

Pre-combustion: This technology uses the extraction of carbon dioxide from fossil energy before the combustion process begins [35]. This innovation can additionally be clarified as a responding fuel and O_2 gas to produce carbon monoxide, fuel gas and hydrogen. After the expulsion of carbon dioxide, a pure hydrogen gas is obtained [36]. Carbon dioxide can be acquired by means of integrated gasification. The technology can also be used for power plants that use natural gas as a fuel [37]. The first essential stage in the process of removing carbon from a fuel is to change the fuel to a type that is easy to collect. A reaction between coal, steam, and oxygen gas is a common occurrence in coal-fired power plants, and the reaction takes place at high temperature and pressure [37]. The final product of this reaction is a fuel made from carbon monoxide also as mixture of hydrogen known as syngas. This gas can then be used to generate electricity in power plants by undergoing a combustion process. The energy produced is commonly referred to as IGCC (Integrated Gasification Combined Cycle) energy. The carbon monoxide gas obtained in the first step is converted to carbon dioxide in the second step by reacting with steam. As a result, hydrogen and carbon dioxide are produced. Through a chemical cycle, carbon dioxide is captured using a glycol solvent called selexol (Figure 6). This produces purified hydrogen gas, which is then used to generate electricity in some other plants [38].
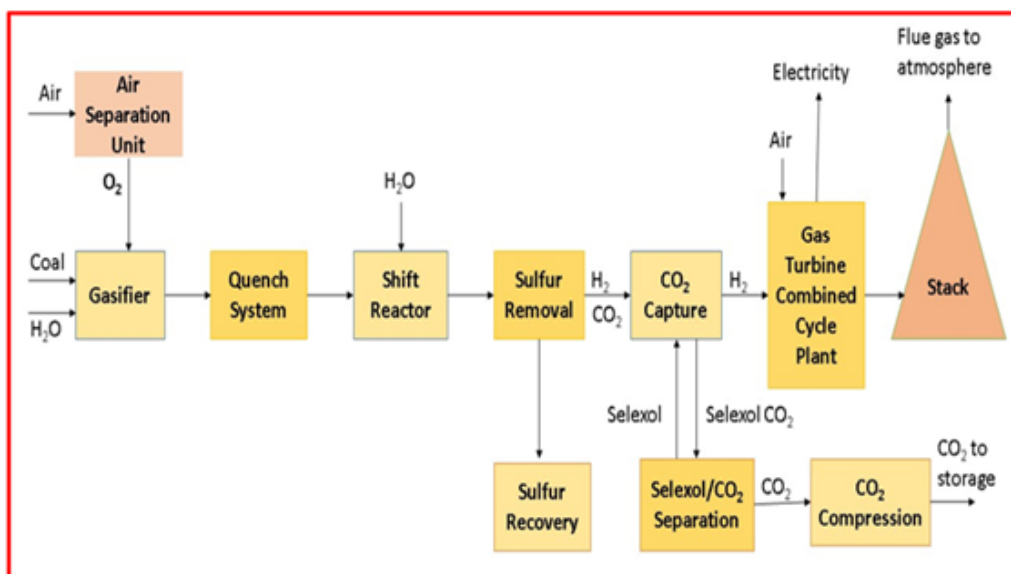

Figure 6: Pre-combustion carbon capture and storage technology [39].

Oxy-fuel combustion: The oxy-combustion method is an alternative to the post-combustion process [39]. This process uses pure oxygen to capture CO_2 and to minimize the nitrogen quantities [40,41]. Fly ash is also removed from the gaseous stream, resulting in exhaust gas that is primarily composed of carbon dioxide and water droplets, with some pollutants such as sulfur dioxide. For the removal of water droplets reducing the temperature and compression used as a medium [42]. One benefit of oxy-fuel combustion versus post-combustion is that it is more economical to capture CO_2 after combustion. Post-combustion requires an expensive system for CO_2 capture [43,44]. An Air Separation Unit (ASU) is used in the oxy-combustion process to remove CO_2, instead of post-combustion which uses CO_2 capture system. The Air separation Unit make all around 95-99% pure oxygen for oxy-fuel system in comparison with Integrated Gasification Combined Cycle plant for the equivalent volume [45]. Air separation unit influences the cost fundamentally to meet the proper environmental guideline, additional gas transformation is frequently required to limit air pollutant concentrations. This will additionally decrease the undesirable materials within the flue gas reprocessing [45-47].

The temperature for burning the use of clean oxygen is in excess of air, for this reason oxy-combustion entails an enormous part of the steam for flue gas getting recycled within boiler to preserve superior running temperature. Modern oxy-fuel boilers have been improved to reduce recycling by employing slagging combustors. The sealing of the system to take care of the required oxygen and nitrogen found inside the gas is another key stage in the design. It prevents the leakage of air into the flue gas. It is also difficult to stop leaks at couplings and flanges, especially along the flue gas duct hence, it is considered as the foremost difficult maintenance issue [48]. Several studies on 30MW thermal power plants that use oxy-fuel combustion technology have been carried out. This system necessitates gas treatments to remove contaminants from the system, which affects the system's performance by about 90% (Figure 7). In a simple cycle, the principle of oxy-combustion can be used [49].
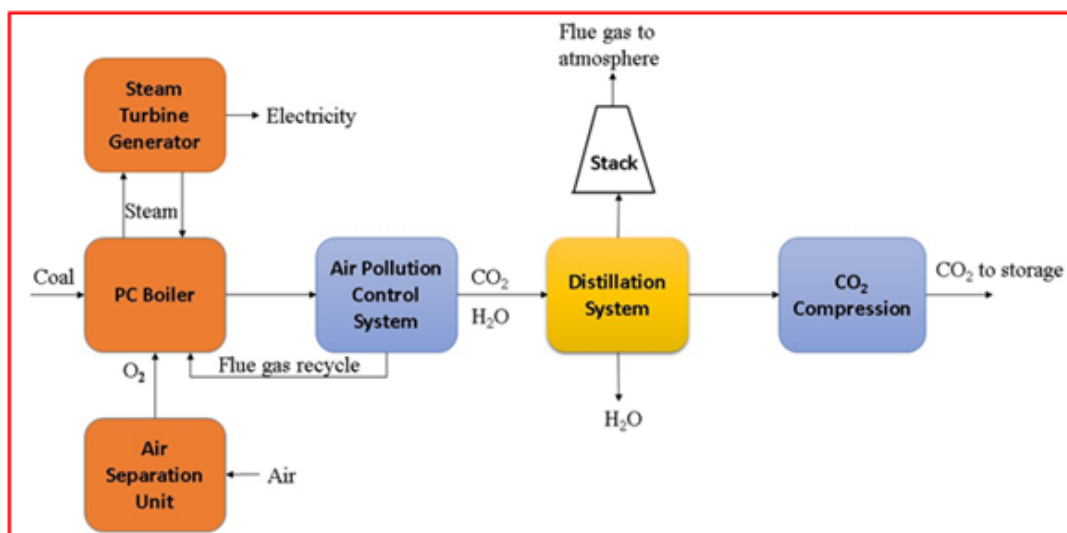
Figure 7: Schematic of oxy-combustion technology used in a coal fired power plant [40].

Comparison of different combustion processes used for carbon dioxide capture

CO_2 capture from carbon fuels comprised of three main strategies i.e. pre-combustion capture, post-combustion capture and oxy-fuel combustion as discussed above. The benefits and drawbacks of each CO_2 capture technology, as well as the conditions of CO_2 emissions (e.g. CO_2 content in the flue gas, gas flow pressure), as presented in Tables 1 & 2; [50,51]. The application area of the pre combustion is coal gasification plant and oxy fuel combustion and post combustion technology have been implemented in coal and gas fired plants [51].

Table 1: Benefits and drawbacks of existing CO_2 capture processes.

Capture Process	Benefits	Drawbacks	References
Pre-combustion	· Maximum CO_2 concentration (~45 vol %) and pressure. · Industrially accomplished in some Mechanical areas.	· Extreme operating pressure and temperature (1.5-2.0Mpa and 190-210 °C). · High energy consumption because of sorbent recovery.	[52,53]
Oxy-fuel combustion	· Lower capital cost · Maximum concentration of CO_2 (80-98%) · Lower expenditure of boiler and different equipment's	· Maximum drop in efficiency and high power consumption because of distinct air separation unit.	[54,55]

| Post-combustion	· A direct way to deal with the retrofitted · More mature than other strategies	· Dilute concentration of CO_2 (5-15 vol %) at near atmospheric pressure · High energy consumption because of solvent/sorbent recovery.	[51,54]

Table 2: Exhaust gases constitution of various carbon capture methodologies [50].

Flue Gas Composition	Pre Combustion [56,57]	Oxy Fuel Combustion [58-60]	Post Combustion [56,57]
CO_2	37.70%	85.00%	10-15%
N_2	3.90%	5.80%	70-75%
H_2	55.50%	---	---
H_2O	0.14%	100ppm	5-10%
CO	1.70%	50ppm	20ppm
O_2	---	---	---
SOX	---	50ppm	<500ppm
NOX	---	100ppm	<800ppm
H_2S	0.40%	---	---

Absorption process

The most generally recognized innovation for post-combustion carbon dioxide extraction is absorption using Mono-ethanolamine (MEA), which consists of two segments: absorption and stripping/desorption, as shown in Figure 8. It is capable of capturing considerable amounts of CO_2 from exhaust gases using fast kinetics and a strong chemical reaction. Although [52-60], there are a few unresolved restraints that should be settled which contains corrosion, solvent degradation and solvent recovery effectiveness [61]. The amines are corrosive and susceptible to degradation by trace components (particularly SOx), which significantly restricts their application. According to a study by Rao & Rubin [62], Solvent degradation is responsible for around 10% of the entire cost of CO_2 capture. Thermal degradation and oxidative degradation are the two basic forms of degradation. Thermal degradation happens in circumstances with high CO_2 partial pressure and large temperature and oxidative degradation occurs because of the excess amount of oxygen present in the flue gases. Besides this, degradation can also occur because of the presence of impurities in the gases like (SOx and NOx). Similarly, MEA is environmentally hazardous because of its volatile nature, and it could be ejected into the environment. Furthermore, it requires an excess quantity of energy (nearly 4 to 6 Mega Joule/kg CO_2) to recover chemical solvents [63]. The national technology laboratory of energy department (DOE/NETL) reports that the MEA-based carbon capture process will raise the electricity cost of new power plant by around 80%-85% and increase plant efficiency by roughly 30% [64].
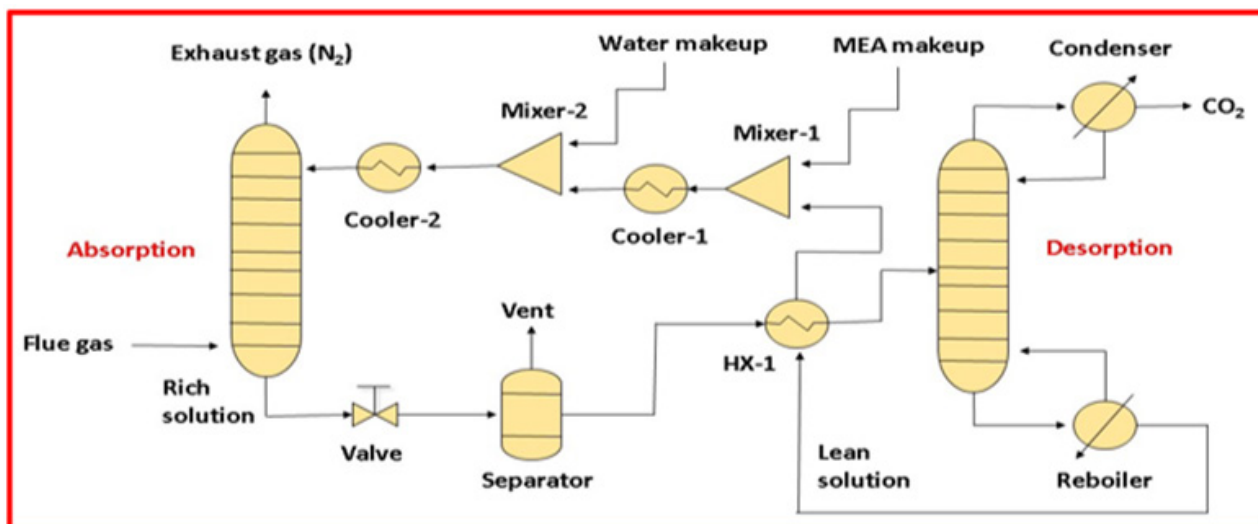
Figure 8: CO_2 recovery from flue gas using a typical chemical absorption system [50].

Adsorption process

Figure 9 depicts a typical physical CO_2 adsorption system, which indicates that a pre-treatment setup is required prior to CO_2 adsorption. Solid adsorbent is placed in each adsorption chamber (such as zeolites, activated carbon or metal organic frameworks, etc.) [65,66]. In most cases, two or three adsorption chambers are

employed throughout the process, with one chamber receiving the raw material for adsorption, the second chamber desorbing the captured CO_2, and the third chamber is on standby to receive the feed [67]. As a result, the system can run constantly. Until far, the majority of CO_2 adsorption systems have been dry. Other restrictions that reduce the efficiency of the process include: 1) low CO_2 selectivity and limited adsorbent capacity. 2) The removal efficiency is lower when compared to other techniques such as absorption and cryogenics. 3) Regeneration and re-use of the absorbent [68-70].
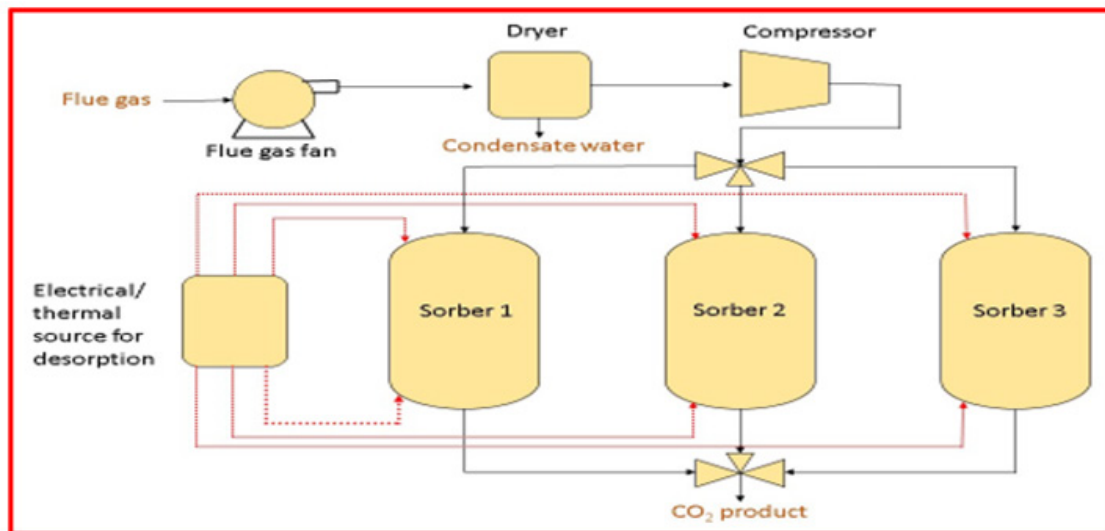

Figure 9: CO_2 capture from flue gas using an adsorption method [50].

Chemical looping combustion

Richter and Knoche propose the technology of Chemical Looping Combustion (CLC) [71]. The solid oxygen carrier circulates between the various portions, dividing the combustion into intermediate oxidation and reduction reactions that are carried out individually. Fine metal oxide particles including NiO, CuO, Fe_2O_3, or Mn_2O_3 [72,73] are suitable oxygen carriers for a primary CLC system with two air and fuel reactors each, as depicted in Figure 10. Between the reactors, the oxygen carrier circulates. The carrier is oxidized by oxygen within the air reactor. The metallic oxide is reduced in the fuel reactor by the oxidation of CO_2 and H_2O by the fuel. The main advantages of CLC can be described as follows [29,74]
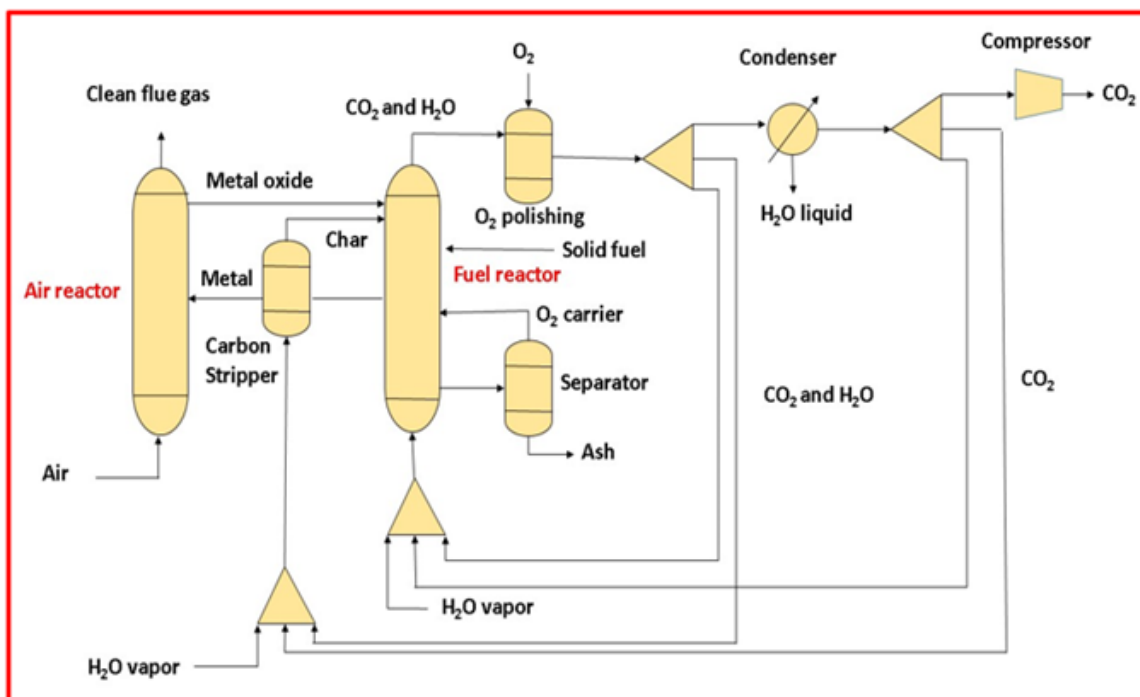

Figure 10: Process flowchart of chemical looping combustion [50].

a. Mainly nitrogen gas is released from the air reactor which is not harmful. 2) Because CO_2 and H_2O make up the exhaust gas flow from the fuel reactor, the CO_2 is frequently separated using a condenser, eliminating the energy expenditures of traditional absorption methods and lowering capital expenses. The bulk of CLC processes have only been tested in the lab, however the technology has some large-scale demonstrations. At the same time, the existing process still has some serious problems (like insufficient oxygen carrier stability and slow redox reaction). Additionally, the de-sulfurization of fuel is also essential to avoid carrier's sulfidation [75]. Before scaling up, other aspects should be considered. The CLC rating is currently based on air and fuel reactors. The ultimate goal, however, is to use the thermal energy contained in the reactor exhaust gases. As a result, parallel to the development of the technology, it is critical to evaluate the usage of CLC for real-world applications [76].

Cryogenic distillation

Holmes and Ryan suggest the traditional cryogenic distillation method for purifying natural gas which is one of the most common separation techniques [77]. The typical cryogenic separation process is shown in Figure 11. The supply gas is first chilled with a pre cooler before being cooled to a low temperature with the help of a heat exchanger. The cooled gas is pumped into the distillation column, which is made up of several vapor-liquid contact devices (like trays or packing materials). The vapor component is separated into two pieces after passing through the distillation column: top and bottom product. A partial condenser extracts the methane isolated from the atmosphere. The CO_2 that has condensed at the bottom of the distillation column is collected. By transferring a portion of the rich CO_2 stream via a reboiler to produce heat for vaporization, a portion of the rich CO_2 stream is returned to the distillation column. The remaining CO_2 stream is separated further, and the pure CO_2 product is taken from the separator at the end.
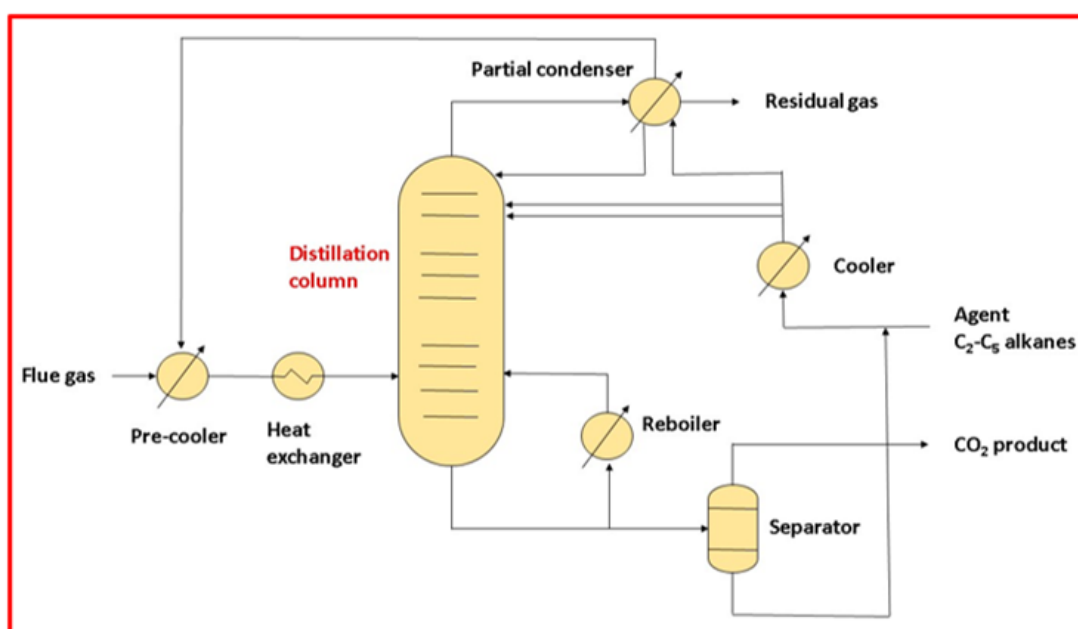
Figure 11: Schematic flow diagram of cryogenic distillation [50].

Despite its widespread commercial use and significant benefits, cryogenic distillation's high energy requirements typically account for more than half of a plant's operating costs [78,79]. Many energy-efficient distillation solutions have been proposed, including cyclic distillation, thermally integrated distillation column, reactive distillation, and thermally connected column, all of which are based on the integration of upgraded processes and technologies [80,81]. Maqsood et al. [82] investigated the intensified side-mounted and integrated switching cryogenic network structure for CO_2 extraction from natural gas [82-84]. The study's findings revealed that utilizing the hybrid cryogenic distillation network, energy consumption was greatly decreased, and methane loss and size requirements were detected, and the technique offers promising results for the purification of sour natural gas reserves [84,85]. With the optimization of the advanced cryogenic networks, the overall profit grew to 69.24 percent [86].

Hydrate based separation

Clathrate hydrates, also known as gas hydrates, are ice-like crystal formations made up of water molecules and additional chemicals such as N_2, H_2, CO_2, and O_2. Inside the cavities of water molecules, these small gas molecules become trapped. The concentration of different gases are different from each other i.e. in the crystal form and in the original mixture of gases [87]. CO_2 separation is defined as the selective separation of CO_2 from a gas mixture between the crystalline solid hydrate phase and the gas phase, resulting in the formation of a hydrate crystal. The minimum pressure required for the production of hydrates at a temperature of 273.9K is roughly 5.56MPa, according to thermodynamics. The pressure of the synthesis gas after the shift reaction is nearly 2 to 7MPa, while the flue gas is almost at atmospheric pressure after combustion. Hence, to increase the rate of hydration formation the gas steam needs compression [88]. To generate hydrates, various promoters have

been tried to lower the equilibrium condition. The most researched promoter is Tetrahydrofuran (THF). The equilibrium of hydrate formation decreases with the addition of THF at any temperature. Similarly, by increasing the THF concentration the pressure of hydrate formation decrease to an optimal concentration of nearly 1 mol% THF. It can be used in industry to remove CO_2 without compressing the exhaust gas appreciably [89]. If 3.2 mol% propane is added to a CO_2/O_2 mixture, the equilibrium pressure for hydrate formation can be decreased by 50%. It should be noted that current kinetic hydrate models are unable to account for the additives system well. It could be upgraded by means of studying particular mechanisms and superior microscopic observations [90,91].

Membrane separation

The phenomenon that causes membrane separation is known as the Knudsen diffusion principle. CO_2 dissolves within the membrane and dissipates at a proportionate rate to the partial pressure gradient. Membranes are semi-permeable barriers made of various materials that, through various mechanisms, can separate various components from a mixture [92]. Organic or inorganic materials are used to make membranes. In non-facilitated membranes, the solution-diffusion process occurs. After being dissolved in the membrane, the permeate diffuses through it. The partial pressure of CO_2 is related to the amount of CO_2 dissolved per unit volume [93]. Furthermore, large-area polymeric membranes are easier to make. A unique sort of polymeric membrane called facilitated transport membrane has a transference process that differs from that of conventional polymeric membranes [94] is frequently studied independently of other polymeric membranes. Table 3 shows a comparison of membrane module.

Table 3: Comparison of different membrane modules [9].

Module Type	Hollow Fiber	Spiral Wound	Envelope
Pressure drop	High in the fiber	High and longer permeate path	Medium
Packing density (m^2/m^3)	<10,000	<10,000	200-500
Manufacturing	Cheap	easy and cheap	easy
Cleaning	Chemical washing/replaced	Hard	medium
Cost (€/m^2)	2-8	8-37	40-150

The two types of membranes utilized in carbon capture are gas separation membranes and gas absorption membranes. In the gas separation membrane system, the CO_2 bearing gas is fed at a high pressure to a membrane separator. Membrane separators are typically formed out of parallel cylindrical membranes. CO_2 preferentially passes through the membrane and is collected on the opposite side at a lower pressure. Membrane separators are typically formed out of parallel cylindrical membranes. CO_2 preferentially passes through the membrane and is retrieved on the opposite side at a lower pressure. A microporous solid membrane separates CO_2 from the gas stream in a gas absorption system. The CO_2 removal rate for a gas absorption system is high because flooding, foaming, channeling, and entrainment are reduced. The equipment required is less than that required for a membrane separator [95]. Figure 12 depicts the two systems.
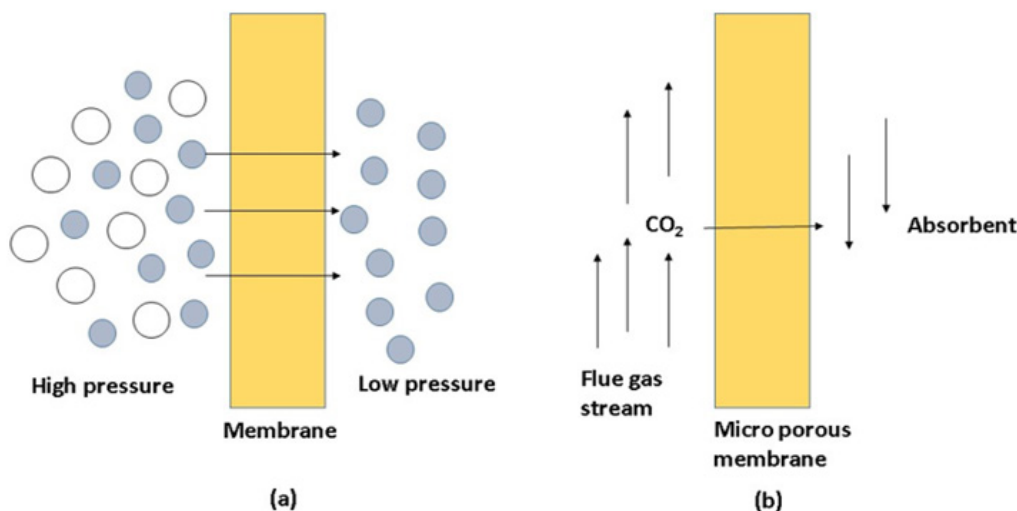
Figure 12: (a) gas separation membrane (b) gas absorption membrane [96].

Comparison of the Different CO_2 Capture Technologies

Carbon capture, which requires CO_2 separation, is often an old procedure that has matured to the point of having a number of full-scale applications. These mechanisms have been the subject of several experimental and computational modelling research. The fundamental advantage of post-combustion capture is that it is simple to integrate with existing power plants; nevertheless, CO_2

partial pressure and concentration in flue gases are low. A minimal concentration of CO_2 should be achieved for transportation and storage. Carbon capture requires a large amount of additional energy and expenses to achieve a minimum necessary concentration. The degradation of solvent and severe corrosion of the utilized equipment is done by using the chemical absorption procedure for the removal. As a result, this process of preparing CO_2 for transit and storage necessitates a large investment in solvents and other equipment. These might result in a 70 percent increase in the cost of producing electricity [96,97]. New solvents are being researched in order to reduce the cost of carbon capture. This method has a high capital and operating cost due to large size of the equipment.

Carbon collection before combustion is generally used in process industries. There are full-scale CCS facilities in some of the industries that use this approach [98]. In the gas mixture, the amount of CO_2 is far higher than the conventional mixture of flue gas. In comparison with post combustion, low energy is needed in this process because of the higher pressures and the lower volume of gas, but the energy penalty is still high. Pre-combustion is mainly used in combined cycle integrated gasification technique. This technology requires a large auxiliary system to operate smoothly. Consequently, this system's capital costs are too high compared with other systems. Some pilot operations are under development and oxy-fuel combustion is also used in several small-scale demonstration units [51,99,100]. The most promising milestone for oxygen fuel combustion is a 50MW thermal demonstration power plant built in Texas by Net Power employing the Allam cycle idea and ensures almost zero emissions. This method offers some other advantages such as reduction of the size of the equipment, compatibility with different types of coal and a chemical plant on-site [100]. In addition, certain technical uncertainties require more investigation to apprehend the complete operation. The carbon capture chemical looping combustion process is still currently in progress. It is not yet commercially implemented. This method must be used for further research. As there is no flame, thermal NOx is not produced, and the air reactor outlet stream is environmentally harmless [74]. It will be much more attractive than other processes when a correct oxygen carrier is developed in CLC. While there is a great potential for a cheap and cheap energy solution to the control of CO_2 emissions in membrane-based separation technology, its application is still limited by several practical issues. The pressure difference produced by a compressor or vacuum pump is limited by the capability and energy consumption of the current compressor or vacuum pump within certain ranges, and therefore the typical flue gas requires a very large membrane area [9,101]. In comparison to traditional chemical absorption technology, membrane-based separation is still in its infancy. The majority of membrane-based separation studies are now conducted on a small scale in laboratories. As a result, its performance in pilot and full-scale energy plants must be evaluated before it can be fully implemented [9].

Advantages and Disadvantages of CO_2 Separation Processes

High energy consumption is the main challenge of CO_2 separation methods. Each process has also certain disadvantages, such as secondary pollution [102], solvent degradation , high cost of equipment [29] and limited selectivity [63], which restrict its application and development. To address the constraints of a single separation procedure, hybrid mechanisms should be a viable option. Combining several techniques can improve separation performance while avoiding drawbacks. The hybrid process, however, is fully independent. Various CO_2 separation processes, such as absorption, adsorption, membrane, cryogenic and hydrate, etc., have been developed in the past few decades. Cryogenic and hydrate are low-temperature processes in CO_2 capture approaches. Cryogenic processes are gases which are converted at very low temperatures to their liquid phase. Hydrate is a solid hydrate process [103]. In this process, hydrogen units are implemented to strengthen the formation of hydrate and reduce the conditions of equilibrium [104]. For cryogenic and hydrogen conditions, low temperatures and high pressure are required. Absorption and adsorption are widely applied in many industrial fields and are relatively mature processes. Membrane based separation method is considered as one of the most widely studied and rapidly growing processes of separation for efficient pollutant treatment [105,106]. Researchers are committed to not only optimizing operating parameters, but also inventing new membrane materials and membrane processes in order to address some of the drawbacks of membrane-based separation procedures and boost separation performance even further [107].

Ionic Liquids for CO_2 Capture

Ionic liquids (ILs) are organic molten salts with a variety of desirable properties, including no vapor pressure above the liquid surface, thermal stability, and low volatility [108,109]. ILs have the most appealing property of being tailor-made, which means that the properties of ILs can be adjusted by changing the cations and anions to produce specific compounds for specific applications [110,111]. ILs are classified as non-volatile because their vapor pressure is relatively low in environmental conditions. ILs are known for their exceptional lubricating and hydraulic characteristics. Similarly, the acidity and basicity trends of ILs is adjustable and it can both absorb and emit gases [112].

Comparison of CO_2 Capture Using Ionic Liquids with Amine Based Solvents

As mentioned in the introduction, carbon capture methods are classified into three types: pre-combustion, post-combustion, and oxy-combustion. Among these approaches, post combustion is suitable for retrofitting facilities, while industrialized absorption systems mostly use post-combustion technology. Because of their high CO_2 capacity, amine-based solvents are the current absorption technique solutions. The efficiency of ILs for CO_2 collection in

comparison to amines determines their practical uses. It is claimed that ILs can be tuned to have a reasonable CO_2 solubility without the side effects associated by using amine-based solvents [113]. Because amine-based solvents are volatile, systems that employ them require a lot of energy during the solvent regeneration step, which adds to the overall cost of the CO_2 capture process. Using ILs as non-volatile solvents can considerably reduce or even eliminate this expense. Because of their volatility, amine-based solvents are not ecologically friendly. They are naturally unstable, leading in the formation of hazardous poisonous compounds such as nitrosamines, nitramines, and amides. It should be noticed that nitrosamines are of particular concern since they are carcinogenic and toxic to humans even at small concentration [114]. Because of their negligibly low vapor pressure, ILs are classified as non-volatile. It implies they do not evaporate and so do not pollute the atmosphere. As a result, solvent losses are low in case of ILs.

Conventional ILs capture carbon by physical absorption. It is noteworthy that changing the cations/anions in ILs can increase CO_2 solubility, but their CO_2 capture capability is still poor compared to other commercial carbon capture methods, such as amine-based solvents, which are already available [115]. Mono Ethanol Amine (MEA) is more efficient than other alkanolamines as an absorption solvent. The following is the order of absorption rate for amines: MEA>DEA>AMP>DIPA>MDEA [116]. For a general overview, Table 4 compares CO_2 capture methods using conventional ILs with the most often used commercial solvents. Table 5 compares the benefits and drawbacks of three different ionic liquid composition systems [117-119].

Table 4: Comparison of properties of conventional ILs with commercial solvents used for CO_2 capture [117-119].

| Variable	Chemicals for CO2 Capture				
	Conventional ILs	Task-Specific ILs	MEA (30 %wt)	DEPG	PC
Absorption type	Physical	Chemical	Chemical	Physical	Physical
Vapor pressure (bar) at 25 °C	1.33×10^{-9}	1.33×10^{-9}	8.5×10^{-4}	9.73×10^{-7}	1.13×10^{-4}
Viscosity (cP)	20-2000	50-2000	18.98	5.8	3.0
CO_2 solubility (mol of CO_2/mol of IL) at 1 bar and 20-40 °C	>2.51	1.6	50-85	3.63	3.41
$\Delta Habs$ (kJ/mol CO_2) at 1 bar and 40 °C	~10–20	~40–50	~85	~14.3	~15.9
Selectivity					
CO_2/CH_4	8-35	---	---	15	26
CO_2/H_2	50-150	---	---	77	126
H_2S/CO_2	2-10	---	1-2	8.8	3.3
CO_2/N_2	30-100	---	---	50	117
Cost	200 \$/5gr	400 \$/5gr	370 \$/1L	80 \$/1L	117 \$/1L

Table 5: Benefits and drawbacks of three different ionic liquid (IL) mixture systems [114].

Type	Benefits	Drawbacks
Conventional ILs (CILs)	▪Energy consumption is lower than traditional solvents. ▪High CO_2 selectivity	▪High viscosity
Task-specific ILs	▪When compared to CILs, they have a better CO_2 storage capacity (because of functional groups)	▪Compared to CILs, they possess higher viscosities ▪Complex synthesis procedures
IL-alkanolamine-water mixture	▪They have low viscosities compared to CILs ▪When compared to CILs, there is a higher rate of CO_2 dissolution	▪Not ecologically friendly as pure ILs ▪This kind of IL has lower amine loss and energy utilization than amines, but greater than CILs.

Supported Ionic Liquid Membranes for CO_2 Capture

A SILM is a three-phase liquid membrane system in which the IL is retained in the pores of the support material by capillary forces. Polymeric and inorganic membranes are the most common support materials. Due to the relatively high viscosity of IL, there are three techniques for preparing SILM: direct immersion, vacuum, and pressure. Each of these methods can have a significant impact on the operation performance of SILM [120]. Several SILMs were produced, for example, by soaking a hydrophilic PVDF membrane in six phosphonium-based ILs [121]. Miyako et al. [122] reported the formation of a SILM by submerging a hydrophobic PP film in [BMIM] PF_6. The produced SILMs employing this approach are typically acceptable for transport studies for the extraction of organic molecules [123]. SILMs containing [BMIM] [Cl, BF_4 or NTf_2], which were produced using the pressure technique, and the resulting SILMs verified that each of the ILs had completely filled the holes of support material. As a result of this approach, it is possible to utilize the SILMs for pervaporation studies even at higher pressures [124-126]. Figure 13 Shows the number of publications related to CO_2 capture/separation through ionic liquid-based membranes in the previous decade [127]. The CO_2 permeability and selectivity of SILMs is summarized in Table 6.
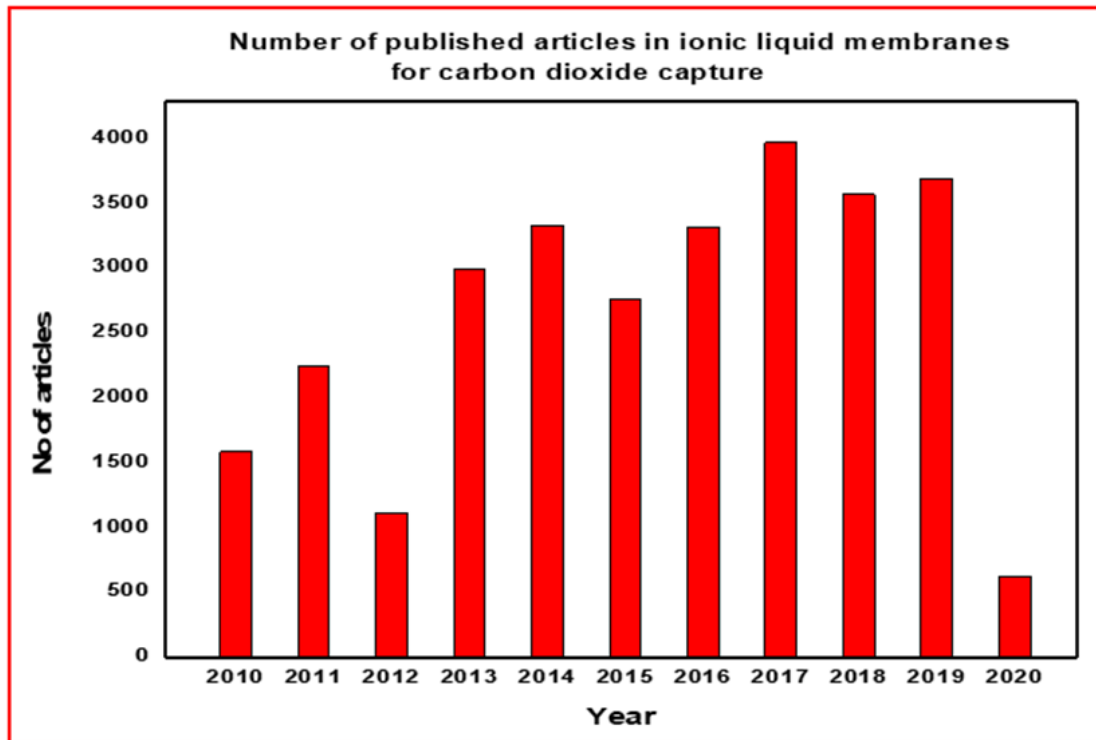
Figure 13: Published articles in ionic liquid based membranes for CO_2 capture [127].

Table 6: Permeability and selectivity of CO_2 and N_2 gases using SILMs.

ILs	Polymers	CO₂	N₂	Selectivity CO₂/N₂	Conditions	Ref
		Permeability (Barrer)				
$[C_6mim][NTf_2]$	PIM-1	2240	90	25	303 k	[129]
$[C_4mim][NTf_2]$		4590	212	22		
$[C_2mim][NTf_2]$		6650	332	20		
[Dems][TFSI]		5800	193	30		
[Bdim][TFSI]	PSF	3600	130	27	308 k	[130]
[Bmim][TFSI]		3000	107	28	7 bar	
Cyphos 102		637	15.3	41.5		
AMMOEN™100	PVDF	93.9	1.79	52.6	303 k 3 bar	[131]
$[Bmim][BF_4]$		93.9	5.04	52.3		
$[Set_3][NTF_2]$		747	18.4	26.2		
[Emim][OTf]		486	14.3	34		
$[MtdFHim][NTf_2]$		210	13	16		
$[MnFHim][NTf_2]$	PES	280	14	21	296 k 1.85 bar	[132]
$[MpFHim][NTf_2]$		320	12	27		
[Bmim][NTf2]	PI	34.4	1.34	25.7	308 k	[133]
$[N_{2224}]_2[maleate]$	PES	2840	---	218.5	313 k 0.1 bar	[134]

CO_2 Permeability and Selectivity of SILMs

A gas molecule is generally transported across an IILM in three steps: (1) absorption in the ILM's upstream surface, (2) diffusion across the ILM matrix, and (3) desorption in the ILM's downstream face. The permeability and selectivity can be found by the following equations [128].

$$Permeance_i = \frac{Permeating\,flux_i}{Driving\,force_i} = \frac{mol}{m^2.s.pa} \quad (1)$$

$$Permeating\,flux_{ji} = \frac{Permeate\,flowrate_i}{Membrane\,Area} = \frac{mol}{m^2.s} \quad (2)$$

$$Driving\ force_i = \Delta P_i = P_i^{feed} - P_i^{permeance} = Pascal \quad (3)$$

$$Permeability_i = Permeance_i \times Membrane\ thickness = \frac{mol.m}{m^2.s.pa} \quad (4)$$

$$Selectivity = \frac{Permeability_i}{Permeability_j} \quad (5)$$

Conclusion and Future Recommendations

This paper examines the complete mechanism, usage, benefits, and drawbacks of conventional technologies used for CO_2 capture. Conventional methods have issues with solvent loss, corrosive nature of the solvents, toxicity of solvents, and high energy usage in solvent regeneration. ILs play a critical role in CO_2 capture processes [129-134]. The unique features of ILs lead them to a wide range of applications. For CO_2 separation, a variety of SILMs, including supported ionic liquid polymer membranes has been thoroughly investigated. The CO_2/N_2 permeability and selectivity of various ionic liquids with polymer membranes are investigated comprehensively. The CO_2/N_2 permeability and selectivity is substantially improved by choosing the appropriate size of porous support. Similarly, choosing the suitable membrane support, resulting in superior membrane performance at low and high gas pressures. The testing methods for SILMs must be improved significantly before commercialization.

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