Advanced Post-Combustion Carbon Capture and Separation Technologies

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Abstract. The climate crisis caused by global warming has focused on the role of greenhouse gases (GHG), especially that of CO_2, which is the predominant element of GHG. One of the current approaches toward reducing and limiting atmospheric carbon dioxide is through carbon capture and storage. The most commonly used techniques are absorption, adsorption and membrane-based carbon capture. This paper evaluates individual methods of CC currently in use and draws comparisons for the pros and cons. Furthermore, it assesses potential improvements for the future. The absorption method captures industrial carbon emissions due to its maturity and the possibility of retrofitting the technology into existing power plants. The adsorption method can operate through an extensive range of temperatures, which can be utilized in broader scenarios. Membrane technologies have the greatest potential for future development due to their low operational energy; however, further research is required to reduce capital costs and improve performance under certain conditions.

Keywords: Carbon Capture, Adsorption, Absorption, Membrane, Post-Combustion.

1. Introduction

The exponential development of industrialization since the industrial revolution has been established on the significant volume of energy consumption, with coal, natural gas and oil dominating the fuel mix for the world's energy generation. Fossil fuels are hydrocarbons; therefore, the combustion process will inevitably cause huge carbon emissions. Carbon emissions include various harmful gases and substances that create the greenhouse effect, directly or indirectly. Carbon dioxide (CO_2) is the most significant and abundant component of greenhouse gases, and the increase of its concentration in the atmosphere is the primary cause of global warming. Therefore, reducing emissions and accumulating these heat-trapping gases, chiefly CO_2 in the atmosphere, has become the most effective method to alleviate the earth's temperature rise trend. Global CO_2 emissions from the energy sector soared by more than 2 billion tons in just one year, from 2020 to 2021, and this number keeps increasing [1]. The goal of controlling the global mean temperature rise to 2°C in comparison to mid-nineteenth century levels by 2100 was proposed during the Paris Climate Conference in December 2015 and adopted in 2016. The recent report by the Intergovernmental Panel on Climate Change (IPCC) utilized theoretical constructs to create 1,200 technological scenarios to meet the target of less than 2°C temperature rise, using a mixture of these schemes, the majority of which employ CC methods [2]. What further emphasizes the importance of carbon capture technologies is the current progress with renewable energies – encouraging but not enough - the transition stage to fully renewable energy worldwide is taking longer than anticipated. Additionally, CC can be used simultaneously with other methods, such as solar and wind electricity generation and moving away from traditional internal combustion engine-based transportation systems.

Carbon capture and storage (CCS) includes trapping CO_2 at emission sources, for example, coal or natural gas-fired power plants, then sequestering it belowground to prevent it from entering the atmosphere. The energy sector contributes approximately 75% of the greenhouse gas emissions, and up to 90% can be captured industrially. However, according to International Energy Agency (IEA), only 18 large-scale CCS facilities worldwide are in operation, capturing 35 million tons of CO_2 annually. An assessment completed in 2020 by Imperial College London found that the removal of 2,700 gigatons of CO_2 would be adequate to meet the IPCC's global warming aims. This figure is reduced significantly compared to the previous mainstream estimation, which suggests a figure of 10,000 Gt of CO_2 [3,4]. There is still a huge gap between 35 million tons and 2,700 Gigatons; therefore, research efforts should be made to increase the development of the greater worldwide capacity of CCS. This paper examines different post-combustion carbon capture technologies – one of the carbon capture approaches.

2. Post-combustion carbon capture technologies

Post-combustion carbon capture separates and captures carbon dioxide before it enters the atmosphere. Three mainstream methods are absorption, adsorption, and membrane-based methods. These methods are currently the most developed and commercially viable approaches for CO_2 emission reduction. Post-combustion capture involves adapting technology to power plants already in operation to capture CO_2 after the combustion of fossil fuels. The technology utilized for post-combustion capture of CO_2 may also be adapted to capture nitrogen oxides and sulfur oxides from most existing coal-fired power plants. Following separation, the partial pressure of CO_2 is reduced, and compression is utilized to meet the sequestration requirements, which incurs additional costs. Due to solvent regeneration and losses during adsorption, post-combustion CO_2 capture has high energy requirements and thus, demands better solvents to save costs. Although this technology does require huge energy supplies to regenerate sorbents or solvents, its advantages certainly outweigh its drawbacks. First, post-combustion capture can readily be installed in large existing or newly constructed power plants without further upgrade or rebuilding. For example, petrochemical and gas industries and ethylene oxide production plants can utilize the technique for CO_2 emission reduction. Secondly, when post-combustion capture malfunctions, its restoration will be easily regulated and will not cause the termination of the procedure of the entire power system. Last, but not least, it takes a relatively shorter time to create and install the post-combustion capture. Since post-combustion capture can be regarded as a promising and potentially valuable strategy, it is necessary to explore the technique and its positive influence on addressing the global greenhouse effect [5]. Figure 1 shows the scheme of carbon capture process.

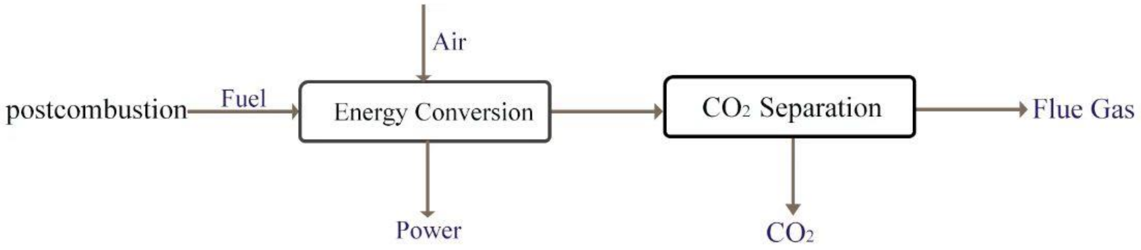

Figure 1. A Scheme of post-combustion carbon capture working process

2.1. Absorption Method for CO2 capture

The absorption method is one of the dominant technologies for CC; according to facility data supplied by the Global CCS Institute, only this CC technology has been commercially used [6]. Figure 2 indicates that the flue gas is initially cooled to 40-60 ºC and passes through the absorption chamber, the solvent absorbs CO_2 inside the flue gas, and any remaining gases are released. Secondly, the solvent containing enriched CO_2 enters the decarbonizing chamber and desorbs using heat, pressure, or an electric swing. At this point, CO_2 is separated, with the solvent transferred to its initial stage [7]. The working process of the solvent sorption method is shown in Figure 2.

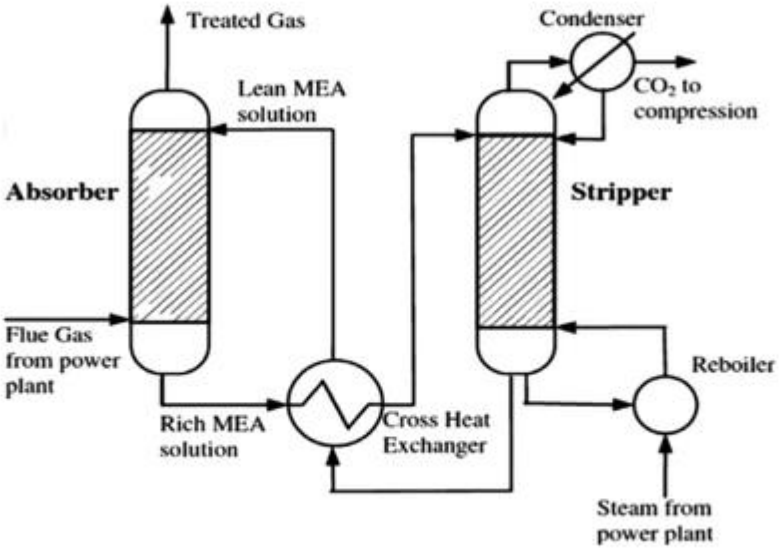

Figure 2. A scheme of the solvent absorption method for CO_2 capture [8]

2.1.1 Physical Absorption

In the physical absorption method, the solvent absorbs CO_2 without chemical reaction and attains weaker bonds between the CO_2 and the solvent, requiring less energy to break the bonds when decarbonizing the solution. The ideal environment for physical absorption involves CO_2 at low temperature and high partial pressure, and CO_2 will be desorbed at reduced pressure and increased temperature.

The most commonly used absorbents are Selexol (dimethyl ether or propylene glycol), Rectisol (chilled methanol), Purisol (N-methyl pyrrolidone), Fluor (propylene carbonate), and Morphysorb (morpholine). In the Selexol process, CO_2 and H_2S can be removed at low temperatures, and the absorber regeneration by pressure reduction or vapor extraction [9]. This procedure gives advantages of low toxicity, low vapor pressure, reduced corrosiveness of solvents and no deterioration. The Rectisol process is preferred for the treatment of sulfur-containing exhaust gases. Its advantages include a non-corrosive and more stable sorbent, easy solvent regeneration and the ability to remove several contaminants in one process. The Fluor process best suits CO_2-containing gases at partial pressures above 60 PSIG. In this process, the CO_2 is highly soluble and selective in the solvent, which is non-corrosive, but the cost is extremely high. The Purisol process and the Morphysorb process are two of the other processes. The former has the advantage of being low energy consuming, while the latter is a relatively new process with operating costs 30-40% lower than those of the Selexol process [10].

2.1.2 Chemical Absorption

In the chemical absorption process, the chemical bonds form between the solvent and the CO_2, and the process is classified as chemical absorption. The operating environment for chemical absorption is low partial pressure and low temperature. And CO_2 is desorbed by temperature swings (heating) and collected.

The most common solvents are anime-based solvents (MEA, DMEA etc.), aqueous ammonia, chilled ammonia, potassium carbonate, bi-phasic liquid solvents, ionic liquids, and sodium hydroxide. Chemical absorption with anime-based solvent is a well-proven technology with low capital cost. Its limitations on it are its relatively low loading capacity and higher energy demand for solvent regeneration, in addition to high solvent loss due to H_2O. Both aqueous and chilled ammonia have reduced energy requirements for absorbent regeneration and lower solvent costs; however, the operating temperature range is reduced. For example, the operating temperature for chilled ammonia is near freezing. Additional advantages for chilled ammonia are higher durability and commercially viable by-products (Figure 3). The advantages of bi-phasic liquid solvents are less corrosive and lower energy requirement for solvent regeneration. The list advantages of potassium carbonate solvent are increased loading capacity, reduced corrosivity, lower solvent cost, and less energy required for absorbent decarbonization. Due to the nature of their dual absorption mode, significant improvements for ionic liquids are that they only release a limited amount of heat during absorption, low volatility, low solvent loss, and high loading capacity. This leads to a significant possibility of minimizing environmental effects created by the carbon capture process. However, the cost is high, and the absorption rate is limited. For sodium hydroxide, raw materials are abundant. Hence, the cost is lowered, but the energy requirement and solvent loss are high [11].

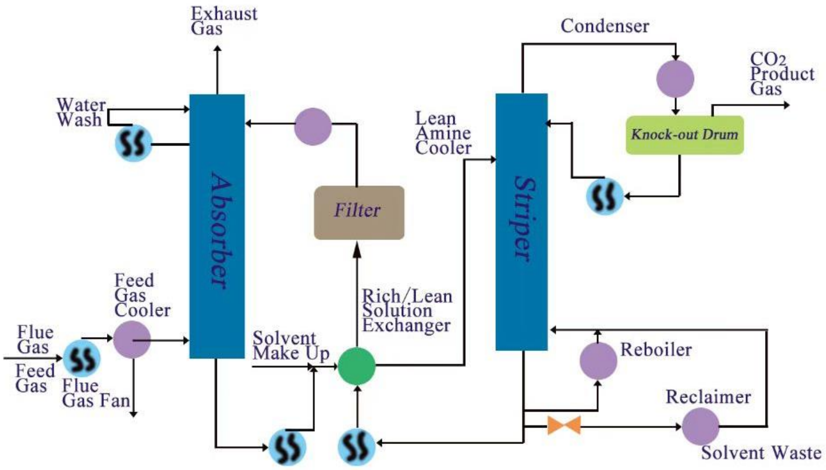

Figure 3. Diagram of the process of an amine-based post-combustion carbon dioxide capture system

From the solvent mentioned above, the use of an amine-based solution is considered to be the preferred choice for post-combustion CO_2 capture (Figure 4). For example, MEA is the most common, most developed, and most demonstrated solvent for carbon capture. Thus, the chemical reaction principle of amine-based solvent will be further investigated. Amines are compounds formed when the hydrogen in an ammonia molecule (NH_3) is replaced by a hydrocarbon group (-R). Every ammonia molecule (NH_3) has three hydrogens attached, which are divided into primary amines RNH_2 such as monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP); secondary amines R_2NH such as diethanolamine (DEA); and tertiary amines R_3N such as methyl diethanolamine (MDEA). These are in order of the number of hydrogens being substituted. While reacting with CO_2, the primary and secondary amines perform as weak alkali, forming carbonates. The reaction is listed as follows:

$$CO_2 + 2RNH_2 = RNHCOO^- + RNH_3^+ \tag{1}$$

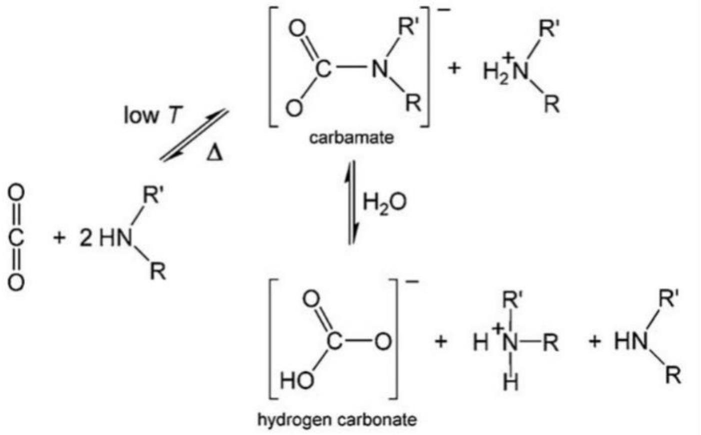

Figure 4. The displayed formula of reaction between primary/secondary amine and CO_2 [12]

According to stoichiometry, one molecule of amine can load up to 0.5 molecules of CO_2.

When tertiary amines react with CO_2, bicarbonate is formed, and the reaction is (Figure 5):

$$CO_2 + R_1R_2R_3N + H_2O = R_1R_2R_3NH^+ + HCO_3^- \tag{2}$$

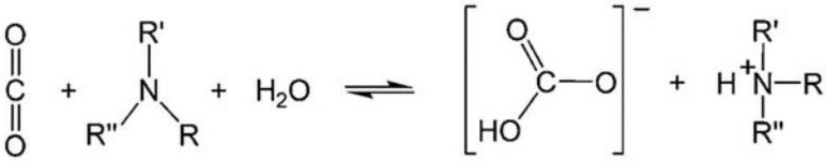

Figure 5. The displayed formula of reaction between tertiary amine and CO_2 [12]

Since one molecule of tertiary amines can react with a single molecule of CO_2, 1 mole of tertiary amine can absorb an ideal maximum of 1 mole of CO_2 [13].

2.2. Adsorption Method

Regarding the adsorption method, CO_2 adsorbs to adsorbents due to surface interactions, and chemical or physical bonds are formed; adsorbents can be either solid or liquid, and the regeneration process of adsorbents starts when the surface of sorbents is saturated with CO_2. The following are different regeneration methods for adsorbents: temperature swing adsorption (TSA) – which raises the temperature to break the bonds, and electric swing adsorption (ESA) – in which electricity is used to heat the sorbents and follows the same principle as TSA (Figure 6). The pressure adsorption (PSA) and vacuum adsorption (VSA) decarbonize by reducing pressure. It has been established that PSA has been prioritized before due to TSA being a time-consuming process, and PSA has lower energy demand.

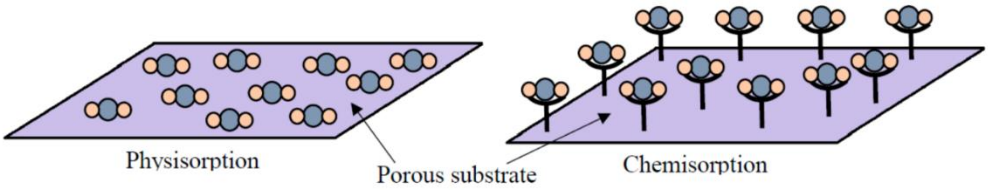

Figure 6. Demonstration of different interactions between the surface of absorbent and gas molecules [5]

2.2.1 Physical Adsorption

Physical absorption occurs when the adsorbate molecules are held to the sorbent by intermolecular forces such as hydrogen bonds and Van der Waals forces. Therefore, the relatively weak forces require less energy for sorbent regeneration than chemical adsorption. Additionally, because it does not involve a large quantity of water to be heated and cooled constantly, which absorption methods require, the process saves a significant amount of energy rather than the carbon capture method using liquid absorbent. The disadvantage for physiosorbed is that they have relatively poor selectivity due to the weak intermolecular force and the presence of water molecules reduces the CC performance.
Factors contributing to physical adsorption efficiency and capacity include partial pressure of CO_2 (surface force), pore structure and surface area of the absorbent, and temperature. Typically, the primary factor of CO_2 loading capacity under higher pressure is the surface area and specific pore volume of the sorbent; however, the pore construction of the adsorbents becomes the most important element in influencing CO_2 when the partial pressure of CO_2 is lowered.

The most commonly used sorbents include molecular sieves, activated carbons, metal-organic frameworks (MOFs), and lithium compounds. Several kinds of typical MOF materials are shown in Figure 7. Active carbons with enriched nitrogen can adhere to an addition of 30% of CO_2 under the condition of 298 k and 1 bar; furthermore, the performance is unaffected by humidity. Molecular sieves include zeolites (aluminosilicates), non-zeolites (aluminophosphates), and silica. These compounds are extremely porous solids that can adsorb both gases and liquids. Metal-organic skeletal compounds are three-dimensional porous crystalline materials. They spontaneously assemble from metal ions and organic ligands and have found wide applications as optical, magnetic, and hydrogen storage materials. Also, their high carbon capture ability is rewarding due to their large surface area. It is closely related to the swing adsorption process, and its adsorption ability is quite restricted to low carbon partial pressure, in which the total pore volume and the surface area cannot be fully utilized. Its adsorption of carbon dioxide under high pressure is nearly ten times higher than that of an air cylinder alone. The metal-organic frame has a variety of structures, including rigid ones and flexible ones. The MOF-210 structure has a Brunauer–Emmett–Teller (BET) surface area of 6240 m^2 g^{-1}, which gives an excellent carbon dioxide storage ability, up taking CO_2 of 2400 mg g^{-1} under 5 MPa and 300K conditions. Previous research has shown the huge potential in the future for MOFs [11,12].

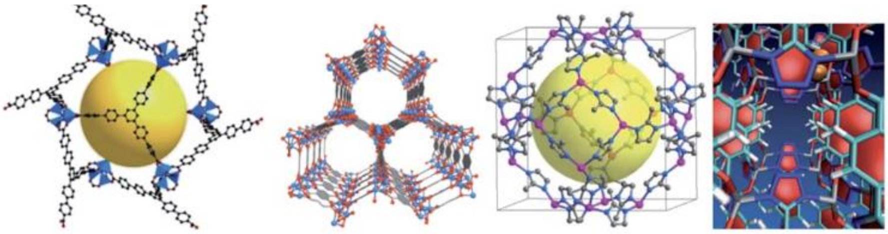

Figure 7. Representative MOF structures, from first to last respectively, are MOF-210: the highest surface area out of current crystalline materials; MOF-74: one of the best CO_2 adsorption materials; ZIF-8: the sodalite zeolitic topology; Zn-TBC: tetrozolate groups provide excellent CO_2 selectivity vs. N_2 [12]

Lithium compounds such as Lithium zirconate and lithium orthosilicate are common sorbents for CO_2 at high-temperature conditions (723 K-973 K), and lithium-based sorbents have very high absorption rates and capacity for CO_2 adsorption. Their chemical reaction equations with CO_2 are:

$$Li_4SiO_4 + CO_2 \rightarrow Li_2SiO_3 + Li_2CO_3 \tag{3}$$

$$Li_2ZrO_3 + CO_2 \rightarrow Li_2CO_3 + ZrO_2 \tag{4}$$

And the theoretical maximum adsorption capacity of Li_4SiO_4 can reach 8.33 mmol g^{-1} [14].

2.2.2 Chemical Adsorption

Chemical absorption occurs when the adsorbate molecules are held by intramolecular forces, such as covalent and ionic bonds. This increases the selectivity of CO_2 because of the stronger forces compared to physical adsorption. Additionally, the process is suitable for CC when the partial pressure of CO_2 is comparatively lower, or flue gas contains water.

The surface area and pore structure of sorbents, the partial pressure of CO_2, temperature, and humidity determine the adsorption efficiency and capacity. Solid amine, alkali, and alkaline-earth metals are the most commonly used sorbents.

Solid amine absorbents consist of porous support on which amine is fixed or attached, and a reversible reaction happens between CO_2 and it. They are presently widely used for CO_2 capture since they provide high adsorption capacities, high CO_2 adsorption rates and relatively easy regeneration. Furthermore, amine-based sorbents are suitable for operating in humid environments, and the presence of water increases their performance. Organic amines can connect porous surfaces by immobilization, impregnation, post-synthesis grafting, or direct co-condensation. The adsorption capacity increased immensely after the remodeling because of the creation of carbamates. An example is the adsorption capacity of the PEI/MCM-41 adsorbent, which is significantly greater than the unmodified MCM-41 under atmospheric pressure and temperature [15].

Regarding alkali metal oxides, such as lithium and sodium oxide, their alkalinity is higher than alkaline earth metal oxide. Li_4SiO_4 and Li_2ZrO_3 are better sorbents than Li_2O because their decarbonization process is less difficult. Na_2O is frequently used to promote alumina chemisorption, demonstrating excellent cyclic durability.

Alkali earth metal oxides, for example, CaO, have magnificent carbon loading capacity ideal for 0.786g CO_2 per gram of CaO. The con of this sorbent is its durability; only 20% of the $CaCO_3$

transforms back to the initial CaO in the eleventh cycle, and the operating temperature is around 600 degrees. The decarbonization happens at 700 degrees. On the other hand, MgO as a sorbent has limited performance due to the low CO_2 adsorption capacity and has limited thermal stability in the regeneration process. However, it can be combined with anhydrous magnesium acetate via thermal decomposition to form mesoporous MgO. Mesoporous MgO is an improvement on both issues by increased surface area and thermal stability. This new sorbent is more desirable for CO_2 adsorption [16].

2.3. Membrane-based Method for CO2 capture

The membrane acts as a selective permeator. It exhibits both higher selectivity and permeability only to specific gases under certain pressure, meaning that only the desired gas of the exhaust is permitted to pass through the membrane while undesired ones are restricted. It separates the different gases according to their difference in diffusivity, solubility, absorption, and adsorption abilities on various materials. Membranes' CO_2 selectivity relies on the material, and the pressure difference of each side of the membranes influences the capture capacity. These properties deem membranes appropriate for systems utilizing high-pressure streams [17]. Additionally, membrane methods do not require regeneration of the sorbent. Therefore, they consume less energy. A complete membrane absorption process is illustrated in Figure 8.

Membrane technologies for CO_2 capture are classified as gas adsorption and gas separation membranes. The difference is that the gas absorption membranes can contact the gas and liquid phases.

The membrane separation technology has the advantage of being easy to operate, energy saving and high efficiency. CO_2 separation utilizing membrane materials is classified into three main divisions: polymeric, dense metal and porous inorganic membranes, which differ in their selectivity for different gases. For example, polymeric and porous inorganic membranes are usually selective for CO_2, while dense metal membranes are usually selective for H_2. The membrane permeance and selectivity are factors that affect its performance. If the CO_2 partial pressure and concentration in the flue gas are low, capture cost may be increased through raised energy consumption since the lower the permeate/feed pressure ratio is, the lower the selectivity is. Also, compared with the single-stage membrane process, the two-stage membrane process can be more practical since the stream can be recycled twice, leading to high CO_2 recovery and improved product purity [18].

Membrane absorption technology uses a hydrophobic microporous hollow fiber membrane to separate the gas from the absorbent solution. The membrane is not highly selective for treating the gas mixture but only keeps the gas mixture and the absorbent solution out of direct contact. Under relatively low-pressure conditions, the gas can diffuse from the gas phase on one side of the membrane through the membrane pores to the liquid phase on the other side and be selectively absorbed by the adsorbent in the liquid phase, thus achieving the effect of separating a component of the gas mixture. This technology solves the problem of low carbon dioxide mass transfer between the gas and liquid phases that exists in the traditional technology, making the gas-liquid contact area larger and avoiding problems such as bulging. Meanwhile, the material's hydrophobic property can prevent the liquid phase's leakage [19].

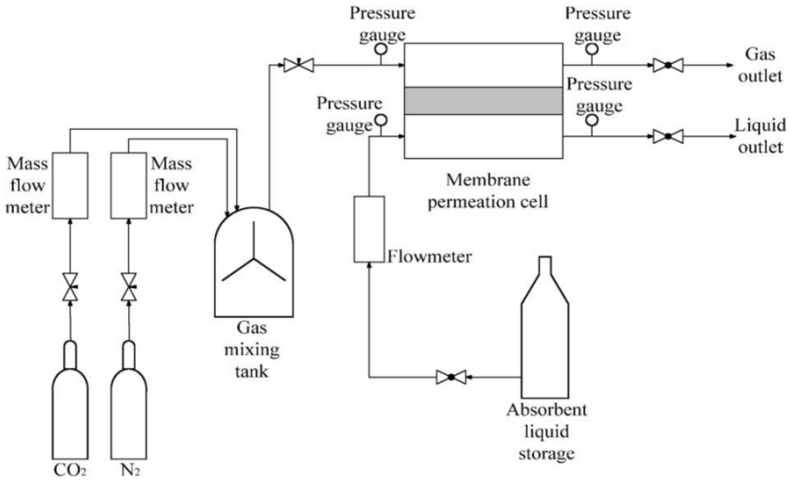

Figure 8. Complete membrane gas absorption system's illustration [19]

3. Conclusion

After a detailed description of all carbon capture methods mentioned above, the advantages and disadvantages of several capture methods regarding absorption, adsorption and membrane technology are compared. The absorption method currently has the highest maturity; however, the operation temperature and durability are limited due to its liquid nature. Cooling of flue gases and replacement of the solvent increase the cost and energy demand of the process. The degradation sorbents used in the adsorption method take significantly longer than absorption, and the range of temperatures suitable for the process is also larger. However, the regeneration process of the solid sorbents is energy inefficient, and the capital cost for the facilities and the sorbents is high.

Further research could investigate their economically viable sorbents and a low energy demand decarbonization process. The membrane technology has a comparatively low energy demand compared to its competitor because no regeneration process has been required, reducing the operation cost for the facilities. The current limitation of this process is the high capital cost for large-scale facilities and performance in the treatment of high-temperature flue gases, which needs to be improved to have a wider application scenario.

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