

Sustainable Agriculture Reviews 38

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Sustainable Agriculture Reviews 38

Carbon Sequestration Vol. 2 Materials
and Chemical Methods

 Springer

Sustainable Agriculture Reviews

Volume 38

Series Editor

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Sustainable agriculture is a rapidly growing field aiming at producing food and energy in a sustainable way for humans and their children. Sustainable agriculture is a discipline that addresses current issues such as climate change, increasing food and fuel prices, poor-nation starvation, rich-nation obesity, water pollution, soil erosion, fertility loss, pest control, and biodiversity depletion.

Novel, environmentally-friendly solutions are proposed based on integrated knowledge from sciences as diverse as agronomy, soil science, molecular biology, chemistry, toxicology, ecology, economy, and social sciences. Indeed, sustainable agriculture decipher mechanisms of processes that occur from the molecular level to the farming system to the global level at time scales ranging from seconds to centuries. For that, scientists use the system approach that involves studying components and interactions of a whole system to address scientific, economic and social issues. In that respect, sustainable agriculture is not a classical, narrow science. Instead of solving problems using the classical painkiller approach that treats only negative impacts, sustainable agriculture treats problem sources.

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ISSN 2210-4410 ISSN 2210-4429 (electronic)
Sustainable Agriculture Reviews
ISBN 978-3-030-29336-9 ISBN 978-3-030-29337-6 (eBook)
<https://doi.org/10.1007/978-3-030-29337-6>

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Chapter 10

Cryogenic CO₂ Capture



Aminah Keshavarz, Maryam Ebrahimzadeh Sarvestani,
and Mohammad Reza Rahimpour 

Abstract To alleviate the global warming issue arising from emission of greenhouse gases involving CO₂ through burning of fossil fuels CO₂ recovery and its utilization and storage has been known as an appropriate choice. With this purpose in mind, various CO₂ recovery methods have been applied recently including adsorption, membrane, hydrating, chemical looping, biofixation, and absorption. Among these strategies, cryogenic CO₂ capture technique has become more attractive. However, there are some challenges including capture cost, impurities and cold energy sources which encounter utilization of this technique.

In this investigation, the major technologies and strategies of capturing CO₂ which is exhausted from the combustion of fossil fuels are summarized, and also the features of cryogenic routes for CO₂ capture have been reviewed. Also, the future prospect of the improved cryogenic processes is discussed. According to the consequences of this study, cryogenic CO₂ capture methods can be utilized for the industrial scale and eliminate the problems associated with physical sorbents and chemical solvents. Also the integration of two or more conventional CO₂ capture technologies can minimize the disadvantages of standalone process. These processes, named as hybrid system, compared to the standalone technology indicated the superiority in terms of energy penalty, the installation investment, and CO₂ recovery.

Keywords CO₂ capture · Usage and storage · Cryogenic CO₂ capture technique · The combustion of fossil fuels · Cryogenic routes · Cold energy sources · Hybrid system · Energy penalty · The installation investment · CO₂ recovery

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© Springer Nature Switzerland AG 2019
Inamuddin et al. (eds.), *Sustainable Agriculture Reviews* 38, Sustainable
Agriculture Reviews 38, https://doi.org/10.1007/978-3-030-29337-6_10

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Abbreviations

CFZ	Controlled Frosting Zone
CO	Carbon monoxide
CO ₂	Carbon dioxide
DeNO _x	The process of NO _x reduction
EOR	Enhanced Oil Recovery
H ₂	Hydrogen
H ₂ O	Water
LNG	Liquefied Natural Gas
MEA	Monoethanolamine
O ₂	Oxygen
VPSA	Vacuum Pressure Swing Adsorption

10.1 Introduction

The climate change arising from greenhouse effect has attracted global concern, recently. Therefore, it is necessary to utilize fossil fuels in a way that environmental challenges including global warming can be restricted (Bozzano and Manenti 2016). Generated CO₂, as one of the greenhouse gases, from combustion of fossil fuel contributing significantly to the climate change (Zhang 2018). Figure 10.1 demonstrates that among various emission sources, CO₂ is mainly produced and exhausted from Coal-fired power station throughout the world (Song et al. 2019).

A promising approach to alleviate CO₂ emissions is to capture it from large sources such as iron-steel, cement industry and coal-fired power station (Li et al. 2013). CO₂ emissions could be decreased about 80–90% if a traditional coal-fired power station is modified by providing CO₂ recovery units (Metz et al. 2005; Stewart and Hessami 2005). Researchers have investigated different technologies of CO₂ capture and separation, and the major issue is the improvement of novel structures

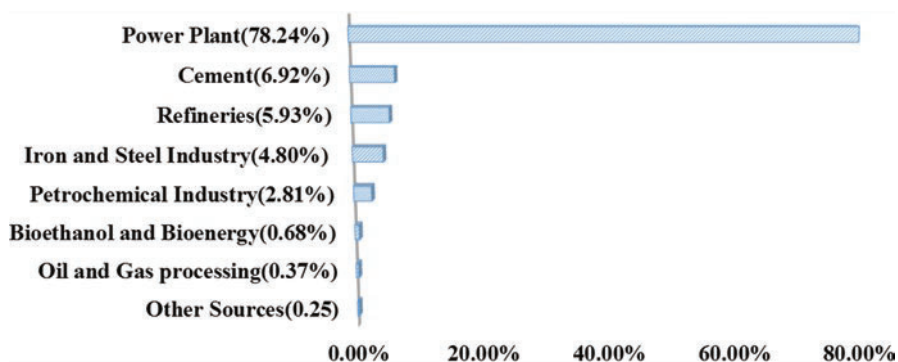


Fig. 10.1 Breakdown of the dominant CO₂ emission sources in 2014

or materials that can permit an optimal capture efficiency and the minimum energy penalty. CO₂ capture strategies generally includes adsorption, membrane, absorption, hydrate and cryogenic (Amrollahi et al. 2012; Liu et al. 2017; Miller and Stöcker 1989; Wang et al. 2015).

The main target of CO₂ capture process is its removal and storage. The flue gas is mostly comprised of nitrogen and 5–20 vol% carbon dioxide. Moreover, it includes water and impurities such as nitrogen oxide and sulphur, depending on the process and feedstock. It can be extremely costly to compress and store the flue gas completely. Thus, before storage in geological formation, it is essential to obtain purified form of CO₂. Around 50% of the entire cost can be attributed to the capture stage of the CO₂ recovery process. Therefore, the development of capture technologies has come into sharp focus of many researchers. The selection of suitable capture method highly depends on particular discharge condition (Olajire 2010). The flue gas condition, as the primary criterion, contains its temperature, composition, CO₂ concentration, and flow rate (Porter et al. 2015). Additionally, the characteristics of the targeted production including transport pressure, and CO₂ purity or discharged standards including H₂S, NO_x, and SO_x also have an important effect on the capture technology selectivity (Song et al. 2017a, b). For instance, the captured CO₂ have to be compressed to 110 bar to ease transportation and storage (Ali et al. 2017; Skaugen et al. 2016).

One conventional route for CO₂ separation is the application of cryogenic techniques, which has dominant benefits such as preventing the chemical solvents usage and no pollution. In order to develop an efficient cryogenic methods, a comprehensive evaluation of current processes in terms of advantages and disadvantages is required (Berstad et al. 2013; Maqsood et al. 2017; Pan et al. 2013; Song et al. 2019; Thomas and Denton 1988). In this study, the applications of the CO₂ capture process and its potential are discussed. In general, CO₂ which is mainly produced through burning of carbon-based fossil fuels can be captured through three main technologies. These strategies are divided into pre-combustion, oxy-fuel combustion and post-combustion.

10.2 Pre-combustion Carbon Dioxide Capture

The carbon existed in the fuel gas reacts with H₂O and O₂ to produce CO₂, CO and H₂ via partial oxidation or autothermal reforming. Besides, CO₂ and H₂ are produced through water-gas shift reaction which contains approximately 20–40% CO₂ and 60–80% H₂. Subsequently, CO₂ is captured and H₂ is passed through the fuel cell or combustion chamber (Deng et al. 2010). Coal gasification is mostly conducted through pre-combustion via a cyclic gasification system. One of the main benefits of this capture technique is the H₂ production which can be used as a green source of energy because combustion of hydrogen only creates water (Ma et al. 2017). Furthermore, it can be applied in many fields including in energy vehicles, fuel batteries, chemical industry (Deng et al. 2010).

10.3 Oxy-Fuel Combustion Carbon Dioxide Capture

The combustion of fuel in pure O₂ occurs in the process of oxy-fuel combustion, leading to a high concentration of CO₂ in the flue gas. Therefore, compared to the post-combustion technology, the CO₂ purification in this technology is easier (Mathekgga et al. 2016; Stanger et al. 2015). Furthermore, lesser proportion of NO_x exists in the flue gas when this process is applied. Oxy-fuel combustion integrated with fluidized bed burners and powdered coal combustion could be a satisfactory alternative strategy. For a given input of coal, a fluidized bed burner has the ability to decrease the flue gas flow while keeping a high temperature of furnace which is the important advantage of this technique in comparison to the powdered coal combustion (Mathekgga et al. 2016). If oxy-fuel carbon capture facilities were retrofitted due to the air separation, the compression and purification stages, the coal-fired power stations' efficiency would be decrease about 10–12% (Escudero et al. 2016). In order to carry out the CO₂ capture process efficiently through oxy-fuel combustion, minimization of energy requirement should be conducted through optimization of the process.

10.4 Post Combustion Carbon Dioxide Capture

Fuel burns in the air in the process of post-combustion, and produce CO₂. Nevertheless, the concentration of produced CO₂ from the typical post combustion process is approximately low usually about 4–14%, and the process is carried out in atmospheric pressure. Thus, a disadvantage of this method for separation is the reduction of driving force because of the diluted CO₂ and low pressures. As a result, in order to recover CO₂ appropriately to obtain CO₂ concentration of more than 95.5% which made it suitable for storage and transport, high energy is required (Leung et al. 2014). However, Post-combustion units of CO₂ capture can be put with available coal-fired power station directly by a bit retrofitting, and this process has been applied at pilot-scale plants compared to the oxy-fuel combustion and pre-combustion (Abu-Zahra et al. 2007; Oh et al. 2016).

10.5 Low Temperature Carbon Dioxide Capture Strategies

Cryogenic processes separate CO₂ from feed gases via utilizing different desublimation and condensation instruments. This technology can gain higher CO₂ purity and recovery than other separation methods. Several types of CO₂ recovery processes through cryogenic method have developed until now. By way of illustration, the advanced cryogenic can be exemplified with the advantage of inhibiting blockage of undesired compounds involving H₂O as well as enhancing energy efficiency through reducing energy requirements (Berstad et al. 2013; Brunetti et al. 2010).

10.5.1 Cryogenic Distillation CO₂ Capture

Among the most prevalent cryogenic processes for CO₂ recovery is cryogenic distillation can be exemplified. In this regard, Holmes and Ryan proposed a conventional process of cryogenic distillation (Holmes and Ryan 1982). Figure 10.2 demonstrates the summarized fractionation process in which the feed stream enters the distillation section after two stages of cooling. The distillation column consists of packing materials or trays which are contacted devices of vapor-liquid. Methane as the top product is removed by a partial condenser, and desublimated CO₂ as the bottom product is gathered. The stream of rich CO₂ is passed through reboiler to be recycled and provide heat of vaporization. The recovered CO₂ is then further purified.

Operational conditions for the conventional cryogenic distillation are high pressures and super low temperatures which separate components based on the differences in their boiling temperatures. Vapor CO₂ or liquefied CO₂ are manufactured during the process at high pressure. By this technique, storage cost decreases. However, in the range of higher and lower pressure at the top of columns, column choking and solid formation cause operating problems.

An extractive distillation technology was proposed by Holmes et al. (1983) and Holes and Rayan (1982). They added heavier hydrocarbons in the distillation condenser to prevent CO₂ solidification. Valencia and Denton added helium to improve the CO₂ capture from methane and prevent CO₂ solidification, but helium removal from methane was quite difficult (Valencia and Denton 1985). For the CO₂ removal from natural gas, Atkinson et al. presented a dual-pressure distillation system (Atkinson et al. 1988). This process was comprised of two distillation columns that operated at different pressures to inhibit CO₂ solidification. The product of the sec-

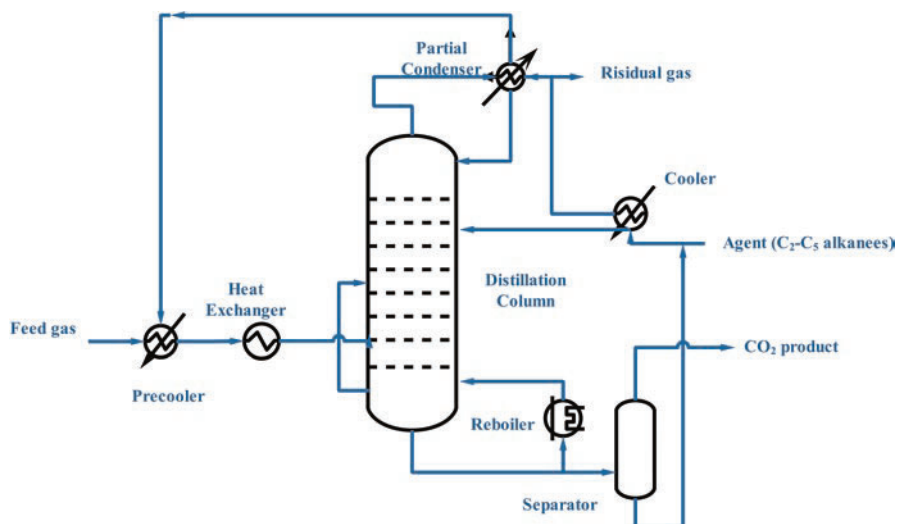


Fig. 10.2 Process flow diagram of cryogenic CO₂ capture via Rayan Holmes technology

ond column was methane, however, to prevent CO₂ solidification, the pressure of the columns must be accurately selected. Berstad et al. simulated a three distillation columns network via adding pentane, using Aspen HYSYS to separate CO₂ from natural gas (Berstad et al. 2012).

Masqsood et al. presented a detailed classification of the cryogenic processes based on condensation and sublimation (Masqsood et al. 2014a, b, c). The cryogenic technologies are divided to the non-conventional, conventional, and hybrid systems. They forecasted the solid formation in the distillation process inside the loop. According to the investigation results, the solid formation can be kept off by increasing the pressure of distillation column or utilizing extractive distillation. Also, a hybrid cryogenic network conformation for CO₂ capture from natural gas was proposed by Masqsood et al. (Masqsood et al. 2014a, b, c). The obtained results demonstrated a significant decrease in the size of equipment, energy requirement and methane loss by utilizing the networks of intensified integration cryogenic distillation. The optimized cryogenic network enhances the overall profit to 69.24%.

Although cryogenic distillation has major benefits and extensive industrial application, energy requirement of this process for the plant is nearly 50% of operating costs (Ebrahimzadeh et al. 2016; Li and Bai 2012). Process intensification and hybrid technologies such as thermally coupled columns, reactive distillation, cyclic distillation, and a hybrid distillation column have been developed to improve energy efficiency (Jana 2016; Kazemi et al. 2016).

Yousef et al. proposed a process of cryogenic distillation via biogas upgrading. This method included two distillation columns that operated at different pressures (Yousef et al. 2018). The optimum distillation pressures for the first and second columns were 4983 kpa and 4763 kpa. For the first column, 13 trays at 2.8 reflux ratio, and for the second one, 11 trays at 2.8 reflux ratio were the optimum numbers. The advantages of this process were high purity of biomethane nearly about 97.12%, mol and liquid CO₂ about 99.92% as by-products.

10.5.2 External Cooling Loop Cryogenic Carbon Dioxide Capture

Energy source is one of the main challenges for capturing of CO₂ based on cryogenic. In cryogenic technologies, the effective method for reduction of energy consumption is to utilize a process of thermal swing, an exterior cooling loop, or a system of carbon extraction and reuse cold energy from sources. Baxter et al. developed a hybrid cryogenic system via an exterior cooling loop which involved:

1. flue gas was dried and cooled.
2. flue gas was compressed and cooled until CO₂ changed to the solid form.
3. gas was expanded to further chill it.
4. an amount of CO₂ precipitated.
5. CO₂ was pressurized.

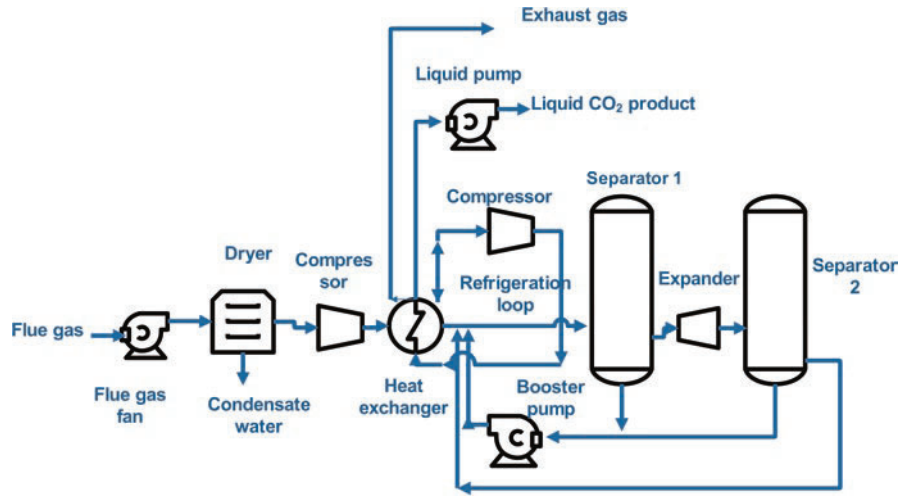


Fig. 10.3 The schematic flow diagram of CO₂ capture via low temperature process

6. CO₂ and residual flue gas were heated again by the incoming gases (Baxter et al. 2009; Jensen 2015).

According to Fig. 10.3 at the end of the process, CO₂ was captured as the liquid phase, and a stream of N₂-rich was discharged. This technology has some conformations that can save energy of liquefied natural gas (Jensen 2015). This ability handles the energy requirement for CO₂ removal via applying a stored refrigerant. Furthermore, this method becomes profitable when integrates with the traditional power plants by renewable power source. The average total energy consumption of External cooling loop cryogenic carbon dioxide capture is around 0.98 MJ_{electrical}/kg CO₂, which is less energy-intensive than other traditional processes (Safdarnejad et al. 2015).

10.5.3 Cryogenic Packed Bed

Tuinier et al. developed cryogenic CO₂ capture process using dynamically cooled packed bed (Tuinier et al. 2010). The basis of separation is the differences in the dew points and the composition of components in the natural gas. There are no plugging problems or pressure drops in this technology. Cryogenic packed bed contains moving interface to separate CO₂ and water, simultaneously. A process cycle includes three main steps: cooling down the bed, capturing CO₂ and recovering steps, as shown in Fig. 10.4. During the first step, refrigerated N₂ gas flow is fed to the cooling cycles. Feed gas is passing through the packed bed to capture water and CO₂. A packed bed, containing borosilicate tubes, is encompassed by a vacuum jacket. At the surface of packing bed, CO₂ and water desublimates and condense by cooling

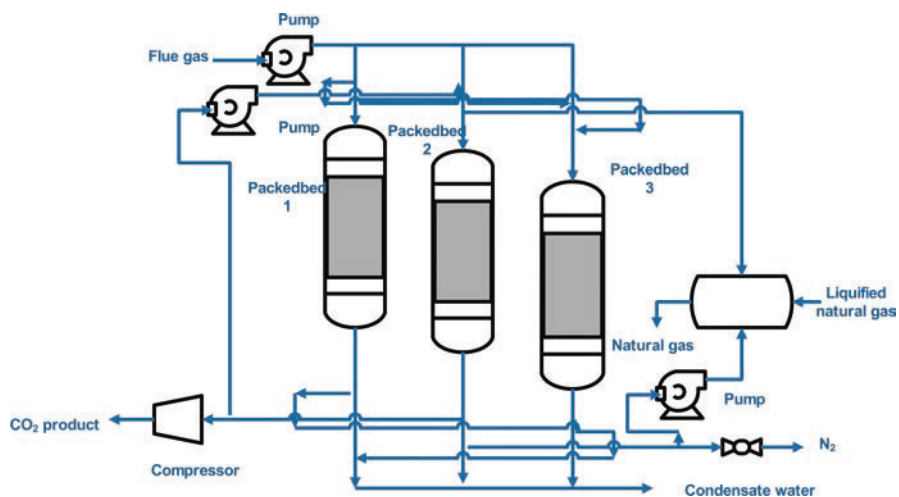


Fig. 10.4 Process flow diagram of cryogenic CO₂ capture via packed bed

down of the flue gas. In the last step, CO₂ by recycling CO₂ and water via recycling air are recovered. All these steps should operate parallel in the beds, to reach continuous performance of the process. The separation process is performed in the atmospheric pressure. Experimental validation is described by 1D pseudo-homogeneous model, and axial temperature, mass deposition and concentration are compared with numerical model.

Dynamically operated packed beds based on cryogenic CO₂ removal were proposed by Tuinier et al. Liquefied natural gas was utilized as the cold energy and the packed beds are made of steel monolith (Tuinier et al. 2011). Simultaneous separation of both carbon dioxide and water based on the sublimation points is the benefit of this method. Also, pressure drop and clogging could be avoided in the dynamic packed bed based on cryogenic separation and by this process, there is no need for chemical absorbent. Tuinier and his team utilized the packed bed to upgrade biogas at cryogenic condition (Tuinier and van Sint Annaland 2012). Volume percentage of the captured water and CO₂ from the flue gas is 1% and 10%, respectively, and compared to the conventional method, the productivity and CH₄ recovery in the cryogenic technology can be increased to 94.3%. Installation investments and energy consumption is lower than the process of vacuum pressure swing adsorption. (Tuinier et al. 2011).

Abulhasan et al. developed the cryogenic packed bed system for high concentration and pressure of CO₂ (Ali et al. 2014). According to the experimental validation, energy requirements with a low CO₂ concentration for both cryogenic systems including packed-bed and distillation are similar and with a high CO₂ concentration, the cryogenic distillation separation consumes more energy than the cryogenic packed-bed technology. In addition, for the cryogenic packed bed technology CO₂ capture concept, a simulation and nucleation investigation with validated results was presented utilizing 1-D pseudo homogenous model. Abulhasan et al. used series packed-bed pipelines to capture and dehydrate CO₂ from natural gas, simultane-

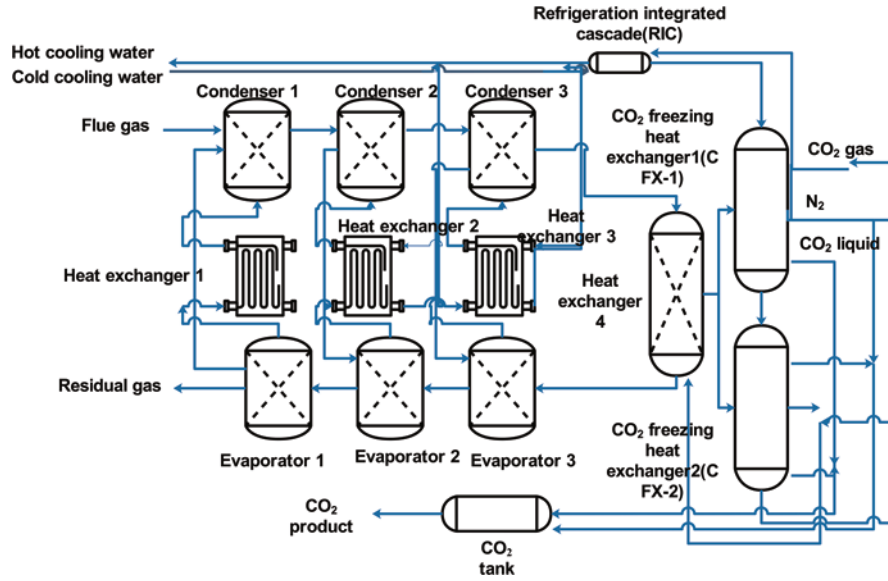


Fig. 10.5 The schematic flow diagram of CO₂ capture by de-sublimation technology

ously (Ali et al. 2016). The advantages of this strategy are clean and efficient pipelines in the packed beds with low cost. Also, in the next study, optimization of cryogenic packed bed system was carried out to investigate the temperature and pressure effect of each bed (Ali et al. 2018). Product purity can reach up to 94% and hydrocarbon losses decrease from 39% to 16%.

Although the process of cryogenic packed-bed for CO₂ capture compared to vacuum pressure swing adsorption (VPSA) processes and monoethanolamine (MEA) absorption has higher potential, several drawbacks involving thermal insulation and the amount of H₂S in raw biogas, require to be dealt with before the commercial utilization. In order to obtain high removal of H₂S, and thereby enhancing the operating costs, it is necessary to keep the packed bed in a low temperature about $-150\text{ }^{\circ}\text{C}$. The cryogenic processes require the cold energy, and liquefied natural gas as the cold source is economical (Abatzoglou and Boivin 2009).

10.5.4 CO₂ Cryogenic De-sublimation

An efficient CO₂ capture based on cryogenic process was developed by Clodic et al. and Clodic and Younes, in which CO₂ was condense on the surface of heat exchangers (Clodic et al. 2005a, b). According to the Fig. 10.5, the overall process contains five sections:

1. cleaning up the flue gas with condensation removal and chilling to $-40\text{ }^{\circ}\text{C}$,

2. utilizing heat exchange between low and high content of flue gas,
3. refrigeration stage,
4. frosting of CO₂ via applying heat exchange,
5. CO₂ recovery process (Pan et al. 2013).

The operation conditions for this technique were 60 °C and 120 kpa, in which a 660 MWe boiler with a 15.47% CO₂ concentration was observed (Clodic and Younes 2003). The de-sublimation energy consumption was about 3.8–7.2% of the power station efficiency (Clodic et al. 2005a, b). Their investigations for two coal-fired power plants demonstrated that the energy penalty of this study compared to the absorption processes reduced. One of the benefits of this technique is that defrosting CO₂ on the surface of the heat exchanger from the solid phase to liquid, permits recovery of fusion heat (Clodic et al. 2005a, b). Before evaporation, to chill mixture of refrigerants, the heat of fusion is applied (Clodic and Younes 2003). During operation, to avoid unacceptable high increase in pressure and clogging, the humidity of the flue gas should be removed. Materials were utilized for making the heat exchangers must have good mechanical stress and thermal conductivity. The freezing point of flue gas usually containing 15% CO₂, was –99.3 °C from a coal-fired power plant (Song et al. 2014).

Cryogenic de-sublimation method for capturing CO₂ is a compact process with no contamination. To study the dynamic de-sublimation process for cryogenic CO₂ capture in the gas mixture, Wang et al. proposed a transient model which includes a tube-in-tube heat exchanger with the nitrogen coolant, three control volumes, and the wall containing the layer of solid CO₂ and the mixture (Wang et al. 2018). The model has been validated by experimental results. The results show that the solid layer generated via de-sublimation should be considered during simulation, and before capture stage, the wall is not required to be precooled. During the process, low energy consumption and high mass diffusion can be gained at low velocity flow and high concentration of CO₂ supply.

Also Yu et al. developed the numerical and analytical model of cryogenic CO₂ capture technology in a de-sublimating heat exchanger to calculate the rate of desublimated CO₂ through the heat exchanger, outlet temperature of gas mixture and liquid temperature, CO₂ mole fraction and temperature distribution (Yu et al. 2017).

10.5.5 Stirling Cooler Strategy

A Stirling cooler strategy for capturing CO₂ at cryogenic condition with heat recovery was proposed by Song et al. (2012a, b). Figure 10.6 demonstrated this system which contains three sections: a pre-frosting section, main frosting section and storage, and each section is cooled via a free-piston of Stirling cooler. For the separation of H₂O

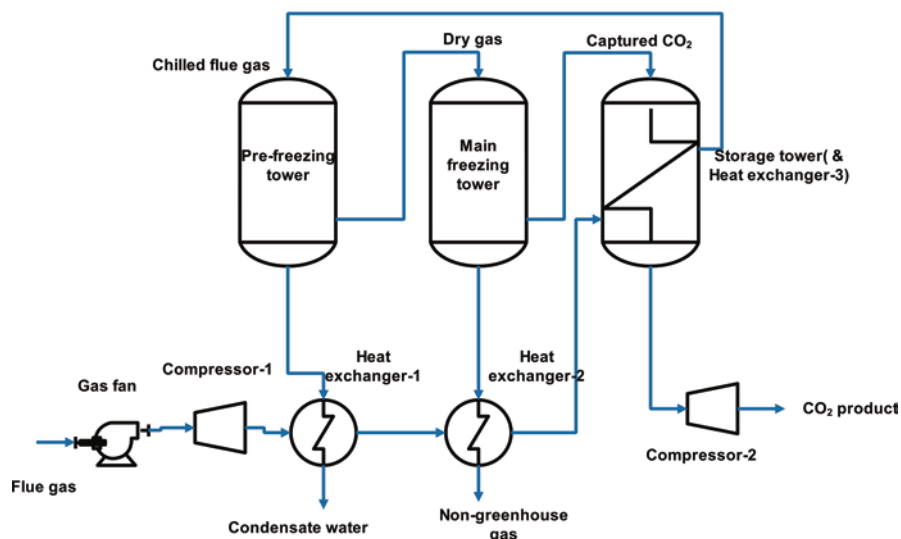


Fig. 10.6 Process flow diagram of cryogenic CO₂ capture by Stirling cooler strategy with heat recovery

in the feed gas by condensation, the pre-frosting section is cooled via the Stirling cooler-1. The extra heat of the main-frosting tower is taken away via Stirling cooler-2 at the temperature of de-sublimation. Moreover, the freeze CO₂ is collected in the storage tower which is cooled via Stirling cooler-3, and The emission gas is sent to the environment. The details of this route can be observed in reports of Song and his team (Song et al. 2012a, b, 2018a, b). This process hasn't been applied for a large-scale or pilot plant, because simulated gas condition greatly differs from the flue gas emitted from the industry for instance, CO₂ concentration, flow rate impurities, and temperature. Thus, in the future works, investigators should focus more on this challenge of Stirling coolers process of cryogenic CO₂ capture (Song et al. 2017a, b).

10.5.6 CryoCell System

Cool Energy Ltd. developed the Cryocell system and examined with other industrial companies in Western Australia (Hart and Gnanendran 2009). Figure 10.7 described the CryoCell process configuration. According to this method, the first step is dehydration of feed gas for lowering water characterizations nearly about 5 ppm, in order to manage the downstream of cryogenic systems. Then, the dehydrated gas passes through heat exchanger to chill the CO₂ until achieving the freezing point. Before

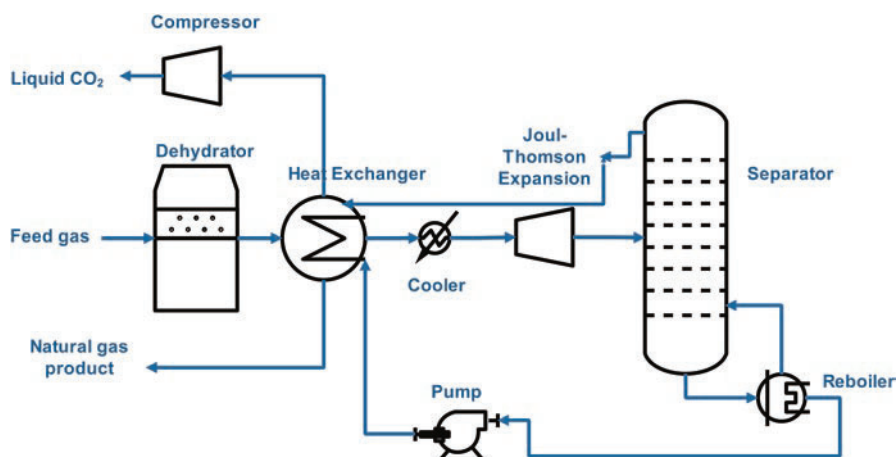


Fig. 10.7 The schematic flow diagram of CO₂ capture via the Cryocell system

liquid is passed through the CryoCell separator, it is expanded through a Joule-Thomson valve.

10.5.7 Controlled Frosting Zone

Some developing countries such as China, recommended replacing natural gas, as a green source of energy, with coal to reduce the air pollution made by coal combustion (Rufford et al. 2012). However, sour impurities such as H₂S and CO₂ in natural gas must be removed since these compounds influence its combustion and transport. CO₂ to H₂S ratio differs enormously through geographic regions (Kelley et al. 2011). One of the most efficient methods of removing CO₂ and H₂S from the sour gas is a controlled frosting zone technology. Figure 10.8 shows the whole process in which the utilized tower can be divided into three zones including upper distillation tower, down distillation tower and controlled frosting zone (CFZ). First, the feed stream is passed through a pre-cooler. Then, the low temperature feed stream is delivered to the controlled frosting zone via a spray nozzle. The company of ExxonMobil Research applied this technology successfully through a commercial manifestation plant of Wyoming. ExxonMobil company utilized majority of the captured CO₂ for Enhanced Oil Recovery (EOR) (Parker et al. 2011).

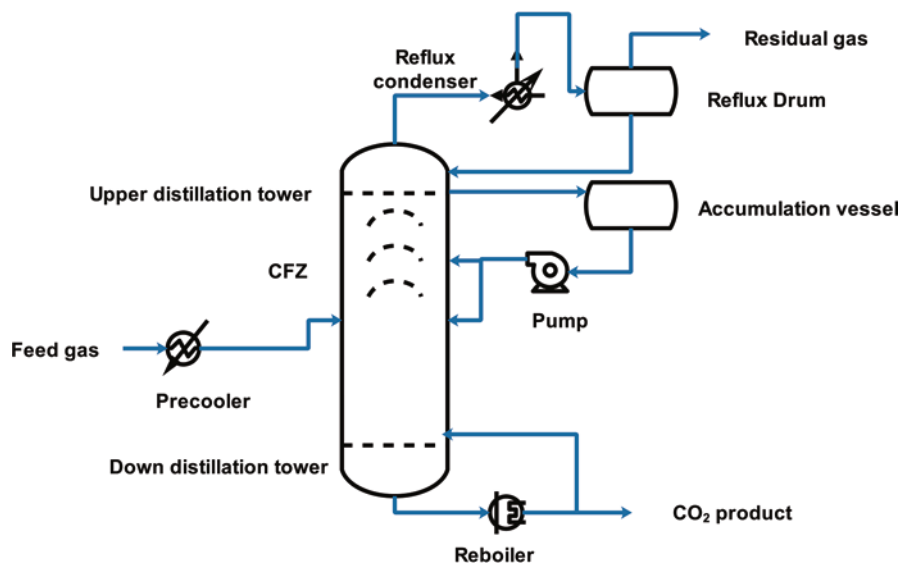


Fig. 10.8 Process flow diagram of cryogenic CO₂ capture by controlled frosting zone technology

10.6 Hybrid Methods for CO₂ Capture

CO₂ capture methods such as cryogenics, adsorption and membrane have some limitations. For example, when high purity and high recovery CO₂ ratio is needed, utilization of membrane technology is very expensive (Wu et al. 2017). Also, when concentration of CO₂ is low, the feed stream of cryogenic process becomes very expensive in terms of energy requirement. It is reported that cryogenic process is suitable when the CO₂ concentration in the feed gas is more than 40 v/v% (Tuinier et al. 2011). Likewise, adsorption process for capturing CO₂ is viable in the high concentration of CO₂ stream.

From all the statements above, it can generally be concluded that the mentioned processes can be regarded economical if the concentration of CO₂ in the feed stream is high enough. Therefore, the major purpose of a hybrid system is integration of various methods and materials to decrease energy consumption, and thereby achieving higher efficiency for CO₂ capture process.

Hybrid processes are divided into 5 technologies including membrane-absorber, membrane-cryogenic, membrane-adsorption, chemical absorption-electrolysis and the solar thermal electrochemical technique (Asif et al. 2018). Cryogenic process in comparison to the membrane process based on the phase change properties. Percentage of CO₂ is one of the factor that influences the temperature of CO₂ desublimation in the cryogenic separation. Integration of membrane process with cryogenic increases CO₂ capture rate, and energy consumption of the cryogenic process decreases by enhancement of liquefaction temperature (Song et al. 2017a, b).

Belaissaoui et al. utilized this idea and developed a membrane-cryogenic system to decrease energy requirement and achieve efficient CO₂ capture for this hybrid system (Belaissaoui et al. 2012). Shafiee et al. used a genetic algorithm to optimize a flow sheet in the membrane-cryogenic system for CO₂ removal (Shafiee et al. 2017). According to this study, at 1.249 GJ/ton of CO₂ energy penalty, 97.9% permeate purity can be achieved for the optimal conformation of integration or hybrid system. In this hybrid system of CO₂ capture, first the inlet stream is fed to a membrane stage to produce concentrated CO₂. In the second section, the gas stream containing concentrated CO₂ is passed through a cryogenic system to achieve the desired product. Energy consumption in the hybrid system can be attributed to both membrane and cryogenic stages. The consequences demonstrated that for 85% recovery of CO₂ ratio and 89% CO₂ purity, 3 GJ/ton CO₂ minimum energy is required, and therefore this system is economical compared to the membrane processes. Moreover, Belaissaoui et al. investigated the effect of inlet concentration of CO₂ on the energy requirement of a membrane-cryogenic system (Belaissaoui et al. 2012). The results showed that at an inlet concentration of CO₂ between 0.1 to 0.3, for 85% purity of CO₂, energy consumption of membrane-cryogenic system is less than other single-stage processes including cryogenic separation, membrane process and conventional absorption process through MEA solvent.

Jean and his team studied a hybrid system process to determine the optimum range of operating conditions for the process (Fong et al. 2016). This integration technique has three sections: vacuum swing adsorption, membrane section and cryogenic. They installed the cryogenic separation instead of the multi stage compression of CO₂ to obtain high purity of products and manufacture liquid carbon dioxide. For optimization of the hybrid system, a new methodology combining with exergy analysis was used in their applied hybrid system, flow rate of refrigerant, multi-stage compression and decreasing temperature of cryogenic separation can influence the rate of recovery. The results demonstrated that for a recovery percentage of 94.4%, a minimum loss of energy of 1.6 GJ/ton of CO₂ was obtained.

A novel strategy using a low-temperature of membrane-cryogenic system instead of a conventional hybrid system or capturing of CO₂ was proposed by Song et al. (2018a, b). The consequences showed that CO₂ recovery and energy requirements have been improved by this novel process. Moreover, the energy requirement of a conventional membrane-cryogenic integration system for CO₂ capture could be decreased to 1.7 MJ/kg CO₂ by utilizing this strategy for a coal-combustion power plant.

Song et al. presented an improved process of cryogenic CO₂ capture utilizing heat generation to further reduction of total energy (Song et al. 2013). This technology consists of three parts: pre-freezing tower, main freezing tower and storage tank. These three parts are cooled by stirling coolers. Also, Hasse et al. implemented the same idea using air liquid membrane in which membrane sections were based on a hollow fiber integrated with cryogenic separation (Hasse et al. 2013). Their studied indicated that a good integration of CO₂ selectivity and permeability happened utilizing air liquid at low temperature.

A hybrid process including production of liquefied natural gas(LNG), oxy-fuel power generation system and cryogenic CO₂ capture was proposed by Mehrpooya et al. (2017a, b). In their study, the effect of operating parameters in the system and its components were investigated through thermodynamic simulation. The energy efficiency for the oxy-fuel power system and liquefaction process of natural gas obtained are 69% and 51%, respectively. According to the obtained results, this process could be used for the actual plant designation.

10.6.1 Cryogenic-Hydrate Technologies

High pressure and low temperature are the main conditions for both hydrate and cryogenic CO₂ capture processes (Surovtseva et al. 2011). In the first step of this process, feed gas is condensed via cryogenic at $-55\text{ }^{\circ}\text{C}$ in which concentration of CO₂ is expected to be decreased to 75 mol%. In comparison with the traditional standalone cryogenic distillation methods, the cryogenic-hydrate CO₂ capture process operates at lower energy requirement and cost. Also captured CO₂ as the form of solid hydrate at nearly $1\text{ }^{\circ}\text{C}$ decreases concentration of CO₂ down to 7 mol% (Sreenivasulu et al. 2015). Promoters such as tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium nitrate, tetrabutylammonium fluoride, tetrabutylphosphonium chloride, and tetrabutylphosphonium bromide are usually applied in hydrate unit not only to intensify formation rate of hydrate, but also to lower equilibrium condition such as high pressure (Ma et al. 2016).

10.6.2 Cryogenic –Membrane Technologies

The performance of gas separation in the membrane process depends strongly on the ambient temperature. Mostly, with the reduction of operating temperature, the permeability of membrane reduces while the selectivity enhances (Hasse et al. 2013). When operating temperature was below $-20\text{ }^{\circ}\text{C}$, it demonstrated two or four times enhancement in the selectivity of CO₂/N₂ with minimum CO₂ permeation loss. Long term of bench-scale test containing the mixture of CO₂/N₂ at sub temperature conditions has affirmed the increased separation performance observed at lab-scale translated to the commercial modules of membrane (Hasse et al. 2013; Kulkarni et al. 2012).

10.6.3 Low Temperature Absorption Technologies

Monoethanolamine (MEA) can be possibly utilized in the early step of commercial scale plants of post-combustion CO₂ capture (Wang et al. 2011). Using MEA is accompanied by high energy requirement due to thermal degradation, oxidation made by O₂, heat-stable salts' formation, and rich solvent regeneration (Pfaff et al. 2010; Qi et al. 2013). Thus, to tackle the mentioned drawbacks, the chilled ammonia process can be a good alternative for MEA absorption process (Hanak et al. 2015). The CO₂ absorption process using chilled ammonia is usually conducted in the temperature of 2 to 10 °C. In general NH₃ exhibits superior features than CH₄ in terms of low energy requirement for regeneration, non-corrosive, commercial availability, comparatively low price, and relatively high capacity of CO₂ absorption (Hanak et al. 2015; Zhao et al. 2012). Additionally, the integration of low temperature stations can effectively prevent NH₃ volatility in the absorber (Strube and Manfrida 2011).

A summary of different cryogenic processes based on the hybrid CO₂ capture technologies and their application for various gas sources is shown in Tables 10.1, and 10.2 demonstrates the benefits and limitations of hybrid processes for cryogenic CO₂ capture. A combination of cryogenic and hydrate methods as Cryogenic-hydrate hybrid can obtain high CO₂ recovery in the pre-combustion CO₂ capture. Nevertheless, to apply this method for an industrial scale, more comprehensive studies are required. Cryogenic CO₂ capture technology, integrating with membrane CO₂ capture process, requires less energy (Sun and Kang 2016). When chilled ammonia absorption applied into post-combustion CO₂ capture, a high recovery of

Table 10.1 Summary of hybrid processes for cryogenic CO₂ capture

Hybrid technologies	Product purity	Phase state	Gas source	Energy consumption	References
Cryogenic-hydrate	95 mol% to 97 mol% CO ₂	Liquid	Integrated gasification combined cycle power plant	–	Surovtseva et al. (2011)
Cryogenic-absorption	93.8 wt%	Gas	Coal fired power plant	1.163GJ/t CO ₂	Hanak et al. (2015)
Cryogenic-membrane	98.3 mol%	Liquid	Coal fired power plants	1.215GJ/t CO ₂	Anantharaman et al. (2014), Scholz et al. (2013), Shafiee et al. (2017), and Zhao et al. (2012))
			Biogas	–	
			Coal fired power plants	1.249 GJ/t CO ₂	
			Coal fired power plants	48 £ ₂₀₀₈ /t CO ₂	
Cryogenic-adsorption	99.9992% CO ₂ and 99.99955% CH ₄	Gas	Raw natural gas	–	Grande and Blom (2014)

Table 10.2 Benefits and limitations of hybrid processes for cryogenic CO₂ capture technologies

Hybrid technologies	Benefits	Limitations	References
Cryogenic-membrane	Large enhances in CO ₂ /N ₂ selectivity	Humidity sensitivity Capital cost enhancement	Clodic and Younes (2003) and Hasse et al. (2014)
	Long term stability (about 8 months)	Reduction of the membrane module productivity	
Cryogenic-hydrate	Low energy demand and capture cost	Low CO ₂ recovery	Bak et al. (2015), Ramezan et al. (2007), and Surovtseva et al. (2011)
	High CO ₂ recovery	Lab scale	
Chilled-adsorption	Low theoretical regeneration heat (0.67 GJ/t CO ₂ vs. 1.92 GJ/t CO ₂ for MEA)	Flammability and toxicity	Hanak et al. (2015)
	Avoid ammonia loss because of evaporation	High volatility	

CO₂ is obtained. But, the energy consumption for regeneration have to be more decreased.

CO₂ can be obtained in various phases, such as vapor-solid, vapor-liquid or a combination such as CO₂ slurry in the hybrid processes of cryogenic CO₂ capture. CO₂ product as liquid form requires both high pressure condition and the cryogenic temperature. CO₂ product as solid form is mostly captured under lower temperature in comparison to the liquid form (Song et al. 2018a, b).

Transportation and utilization stage for CO₂ capture technologies have to be considered. For transportation, the easiest form of CO₂ product is liquid phase with high pressure (Clodic et al. 2005a, b). Although, in the de-sublimation method, capture cost is low, the transport cost^s goes up significantly in solid form (Tuinier et al. 2010). Thus, before transportation and heat recovery, there should be a suitable scheme to transform the produced CO₂ into the liquid or gas phase. Some researchers assessed the benefits of hybrid CO₂ capture technologies in comparison to the standalone technologies. (Fong et al. 2014, 2016).

10.7 Advantages and Limitations of CO₂ Capture Methods Based on Cryogenic Process

The usual routes for high content of CO₂ are capture and usage or storage. To deliver the CO₂ product to specified sites, pipeline transport and compression are necessary. Because of the long distance between the CO₂ recovery unit and the unit where it needs to be delivered for utilization and storage, it is vitally important to purify the recovered CO₂ as much as possible. In fact, if the purity of recovered CO₂ is high enough, it is feasible to compact it to the desirable pressure before it is transported.

CO₂ is captured as different phases, namely, solid, liquid or a combination of both, during the cryogenic technologies. Cryogenic CO₂ capture methods can reach higher purity of CO₂ over 99.9% in comparison with other separation routes, owing to desublimation inherent properties. Consequently, with such purity of CO₂, production of various chemical substances that can be used in other industries including fertilizer, industrial food, is more possible through biological or catalytic reactions for instance, artificial photosynthesis and steam methane reforming. Besides, when CO₂ is recovered through the cryogenic technique, not only the need for extra compression processes is eliminated and thereby lower energy is consumed, but also it is a cold source of energy, meaning that it is useful to be combined with the processes at which low temperature is required, such as membrane, liquefaction of natural gas. The energy storage for the process of CO₂ capture based on cryogenic by integrating a cryogenic technique with a refrigeration loop of an open natural gas, was designed by Baxter's group (Hasse et al. 2013; Kulkarni et al. 2012). The total process consists of three sections:

1. energy saving, in which production of liquefied natural gas(LNG) enhances by 40% to utilize excess energy.
2. equilibrium, in which production of LNG equalizes the requirement from the plant to operate the process of carbon capture based on cryogenic.
3. energy recovery, in which production of LNG reduces by 70% to decrease the parasitic loss.

Table 10.3 indicates the summary of benefits and challenges of the CO₂ removal technologies based on low temperature via various cold sources. Installing cryogenic system is extremely restricted by the accessible cryogenic sources, because the energy requirements are considerable for cryogenic methods. Refrigeration and compression are usual routes utilized to supply cryogenic condition. Although liquefied natural gas could be a good option for the energy source, it is greatly subjected to the scale, location, and other characteristics of the natural gas plant. Also, one of the most important cryogenic sources are coolers. The total energy demand increases, when the chilling in the cryogenic systems is supplied by refrigeration. The performance coefficient of a common refrigerator which chills to -140 °C is usually 0.5, indicating that the used electrical energy is approximately double of the thermal energy (Tuinier et al. 2011). One of the solution to decrease the consumed energy of refrigeration and compression is to recover the heat of the cold products of CO₂ and residual gas (Hasse et al. 2013; Sreenivasulu et al. 2015).

Capture cost is the principal challenge related to the large-scale organization of CO₂ cryogenic capture. For instance, around 80% of the overall cost is attributed to compression and capture, 10% for storage, and 10% for transportation. (Hanak et al. 2015; Qi et al. 2013). Siriwardhana et al. and Raksajati et al. denoted that for a conventional process of MEA absorption, the CO₂ capture expense is nearly 55 USD\$/ton CO₂ (Siriwardhana et al. 2011). In comparison, in Europe and Australia are 3.5 €/ton CO₂ and 23 AUD\$/ton CO₂, respectively, that limits severely the commercial application of cryogenic process (Raksajati et al. 2013).

Table 10.3 Advantages and challenges of cryogenic CO₂ capture technologies

Category	Advantages	Challenges	Energy source	References
Distillation	Prevent compression cost		Compressor and cooler	Baxter et al. (2009)
	Be pumped to storage units easily			
	Water saving possible			
	No corrosion	High instillation cost		
	No foaming possible	Capital cost for pressure difference		
	Energy saving potential			
	Remove other pollutants(SOX, HCL, Hg, NO ₂) simultaneously			
Packed-bed	Surface area to volume ratio of the column		Liquid nitrogen gas	Lively et al. (2012) and Tuinier and van Sint Annaland (2011))
	Remove H ₂ O and CO ₂ simultaneously			
		Directly be effected by the availability of LNG		
	Atmosphere			
De-subliamtion	Pilot demonstration	Undesired mechanical stresses	Liquefied natural gas	Clodic et al. (2005a, b)
	Lower energy consumption than MEA absorption	Freeze CO ₂ adversely influences heat conduction		
	Atmosphere	H ₂ O can't be tolerated		
		Directly be effected by natural gas location		
Stirling cooler	Remove H ₂ O and CO ₂ simultaneously	Exergy loss because of temperature difference	Stirling cooler	Song et al. (2012a, b)
	Energy storage possible	Lab scale		
	Lower energy consumption than MEA absorption	Difficulty of freeze layer scrapping		
	Atmosphere			

(continued)

Table 10.3 (continued)

Category	Advantages	Challenges	Energy source	References
Cryocell	No process heating system required	High compression power need More suitable for high concentration of CO ₂ (more than 20%)	Chiller	Hart and Gnanendran (2009)

Table 10.4 Comparison of capturing performance for cryogenic CO₂ capture technologies

Cryogenic technologies	Phase state	CO ₂ recovery	Gas sources	Energy consumption	References
External cooling loop	Liquid	95.6 mol%	Raw natural gas	1.401 kWh/kg CO ₂	Ebrahimzadeh et al. (2016)
Packed-bed	Liquid	99.%	Coal fired power plants(10 vol% CO ₂ , 89 vol% N ₂ , 1 vol% H ₂ O)	1.8 MJ _{electrical} /kg CO ₂	Tuinier and van Sint Annaland (2011)
De-Sublimation	Liquid	90%	Coal fired power plant(12% CO ₂)	1.18 GJ _{electrical} /ton CO ₂	Pan et al. (2013)
Stirling cooler	Solid	85%	Coal fired power plants (13% CO ₂ and 87% N ₂)	3.4 MJ _{thermal} /kg CO ₂	Song et al. (2018a, b)
Cryocell	Liquid	–	Raw natural gas (20–35 mol% CO ₂)	–	Hart and Gnanendran (2009)
Controlled frosting zone	Liquid	98–99%CH ₄	Raw natural gas(8–71% CO ₂)	–	Carpenter (2015)

Table 10.4 demonstrates the capture operating of existing CO₂ capture based on cryogenic. For a common CO₂ capture process, there are two kinds of costs involving capital cost and operational cost. The major energy-intensive instruments in cryogenic CO₂ methods, are pumps and compressors, and also heat exchangers for CO₂ liquefaction and condensation (Clodic et al. 2005a, b; Tuinier et al. 2010). On one hand, the capital cost of conventional adsorption and absorption processes is lower than that of cryogenic processes because their equipment sizes (in the absence of using a large adsorption/absorption tower) are smaller. On the other hand, the operational cost of cryogenic routes is lower than conventional adsorption and absorption due to eliminating sorbent/solvent regeneration costs. However, different technologies of CO₂ capture performance by various types of energy characters. (Song et al. 2012a, b; Zhao et al. 2012).

Operating temperature is one of the main factor that highly influences the efficiency of cryogenic CO₂ capture techniques. As expected, the efficiency enhances with reducing operating temperature. The efficiency of CO₂ capture based on cryogenic condition is extremely affected by the networks of heat exchanger. The multi

heat exchangers with optimal thermal conductivity and viscosity can help a reduction in the exergy destruction.

The difference of temperature between the ambient condition and the cryogenic process would cause heat loss, and consequently reduce the total efficiency. To decrease energy loss, a vacuum interlayer could be an efficient route. The heat exchangers' materials must be carefully chosen to ensure its proper performance at low temperatures, as well as sustaining mechanical stresses and heat conductivity. The frozen CO₂ on the heat exchanger surface might adversely influence heat transfer between the solid and gas phase. While many researchers have studied the process of frost formation, most of these research is referred to humidity. There is a difference between the behavior of frost CO₂ and humidity, and the overall process is comprised of three step:

1. crystal emergence,
2. frost emergence,
3. formation of frost.

The existence of other compounds is another key factor that influences the CO₂ freezing process. Thus, frost CO₂ of flue gas in comparison with that of CO₂, consists of a complicated deposition process, and additional efforts would be required.

When water converts to the ice under low temperature condition, it can cause the clogging of equipment and pipes. Also, any humidity should be eliminated via the pretreatment units to reach a high efficiency of capturing in cryogenic methods. Tuinier et al. proposed the process of cryogenic packed bed based on the differences in the sublimation and dew points of various components. Respectively, CO₂ and H₂O can be desublimated and condensed on the packed bed at different situations (Tuinier et al. 2011).

Additionally, corrosion of the entire facilities and the heat exchanger can occur by acidic impurities. DeNO_x treatment and an efficient desulfurization must be carried out prior to cryogenic CO₂ capture that would cause an increase in the cost of process. Some researchers have designed a novel process of cryogenic CO₂ capture that could eliminate other pollutants such as NO_x, PM, SO_x, and mercury, simultaneously to alleviate the negative impact of the impurities. Fazlollahi et al. provided an advanced method of cryogenic process to remove all species which are less volatile compared to CO₂ and desublimates CO₂ and other pollutants (Fazlollahi et al. 2016).

10.8 Conclusions

In this review, the development of CO₂ capture based on cryogenic is summarized. This process has some advantages in comparison with other technologies including adsorption, chemical looping, membrane, hydrating, and absorption. There is no need of chemical adsorbents or absorbents and chemical solvent for recovery plants in the cryogenic technology. CO₂ can be reached at high pressure and can be utilized

for enhanced oil recovery. By this technology, operating cost decreases because heating systems are not required. One of the beneficial features of cryogenic CO₂ capture technologies is that CO₂ with high purity can be produced in either solid form or liquid form, which is profitable for utilization, transport and storage. Additionally, exergy destruction because of high temperature differences is one obstacle that encounters industrial scale utilization of cryogenic technique. Thus, this method should be studied more comprehensively to provide higher efficiency.

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