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Review on cryogenic technologies for CO₂ removal from natural gas

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Abstract CO₂ in natural gas (NG) is prone to condense directly from gas to solid or solidify from liquid to solid at low temperatures due to its high triple point and boiling temperature, which can cause a block of equipment. Meanwhile, CO₂ will also affect the calorific value of NG. Based on the above reasons, CO₂ must be removed during the NG liquefaction process. Compared with conventional methods, cryogenic technologies for CO₂ removal from NG have attracted wide attention due to their non-polluting and low-cost advantages. Its integration with NG liquefaction can make rational use of the cold energy and realize the purification of NG and the production of by-product liquid CO₂. In this paper, the phase behavior of the CH₄-CO₂ binary mixture is summarized, which provides a basis for the process design of cryogenic CO₂ removal from NG. Then, the detailed techniques of design and optimization for cryogenic CO₂ removal in recent years are summarized, including the gas-liquid phase change technique and the gas-solid phase change technique. Finally, several improvements for further development of the cryogenic CO₂ removal process are proposed. The removal process in combination with the phase change and the traditional techniques with renewable energy will be the broad prospect for future development.

Keywords cryogenic CO₂ removal, purification of natural gas (NG), biogas upgrading, CH₄-CO₂ binary system

1 Introduction

With the rapid development of the global economy, the conflict between economic development and environmental protection is becoming increasingly intensive. The

issue of carbon emissions is one of the environmental issues of global concern. At present, 54 countries in the world have reached their peak carbon emissions, accounting for 40% of the total global carbon emissions. China has become one of the largest energy consumers and greenhouse gas emitters in the world [1]. China's CO₂ intensity of GDP (gross domestic product) in 2030 is expected to drop by over 70% than that in 2005, and the CO₂ emissions will peak before 2030 and as early as possible [2]. Promoting energy efficiency and optimizing energy structure are effective in facilitating the transition toward a low-carbon society. Therefore, the development of clean energy has become increasingly important [3]. As one of the clean fossil energy sources, natural gas (NG) has attracted intensive interest in recent years [4]. In the near future, with the promotion of social development and welfare, a huge amount of NG will be demanded. However, NG production in China is insufficient, and thus the vast NG needed has to be imported [5]. NG is mainly traded by pipelines and in the form of liquefied natural gas (LNG). Therefore, it is usually liquefied to reduce its volume to facilitate storage and transportation [6]. At present, LNG is playing an increasingly important role in the global NG industry chain, and its share of trade has also increased significantly [7]. Meanwhile, the research of the performance of the LNG process is drawing more and more attention and the equipment applied in the LNG process is also studied by many research groups [8]. The main components of NG are alkanes, of which CH₄ accounts for the vast majority. In addition, CO₂ is regarded as an impurity that has attracted much attention in NG. Its presence will affect the calorific value of NG, and it is easy to pass into a solid form under low-temperature conditions, causing a block of equipment and pipelines. On the other hand, in the presence of water, CO₂ will combine with it to form acid, causing corrosion to equipment. At present, because the most commonly used plate-fin heat exchanger (PFHE) in the LNG industry is very sensitive to CO₂ impurities, the industry requires that the content of CO₂ in the feed gas entering the LNG cold box should not exceed 50 [9]. Therefore, the feed

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gas needs to first go through the CO₂ removal equipment before entering the cold box to be liquefied.

Conventional CO₂ removal methods include chemical absorption methods (such as into aqueous solutions of MDEA, MEA, DEA), physical absorption methods (such as Selexol [10], Purisol [11]), adsorption methods, membrane separation and cryogenic separation. Both chemical absorption and physical absorption are traditional methods with mature technology and have wide applications. The adsorption, membrane separation, and cryogenic separation are all newcomers. They are still pursuing advancements in technology and have relatively few applications. CO₂ removal is widely used in industries such as the coal chemical industry, power plants, and oil fields. The development of CO₂ removal from NG has been relatively mature. At present, there have been many engineering and commercial applications for CO₂ capture and storage (CCS), but the deployment of large-scale CCS projects has been slow. Of the 37 large-scale CCS projects in the world, more than half have not yet been constructed and operated, and they are in various stages of development [12].

The principle of the chemical absorption method is to use an absorbing liquid that can chemically react with CO₂ and absorb it, and then decompose and release CO₂ when heated. This method has a high CO₂ removal accuracy and is suitable for removing various concentrations of CO₂ in the feed gas. However, the regeneration of the solution requires a lot of energy and will cause corrosion to the equipment. In addition, the absorption and the regeneration tower occupy a large area [13]. The working principle of the physical absorption method is to realize the absorption and desorption of CO₂ by alternately changing the operating pressure and temperature between CO₂ and the absorbent, but the absorbent does not react with CO₂ and is mostly an organic solvent [14]. The advantage of the physical absorption method is that the regeneration energy consumption of the solution is relatively low, but the disadvantage is that the purification effect is poor. Therefore, the physical absorption method is generally used for rough removal, and the equipment area is relatively large.

The adsorption method uses solid adsorbents (activated carbon, zeolite, molecular sieves, etc.) to selectively and reversibly adsorb CO₂ to separate CO₂ in the feed gas. The amount of gas adsorbed changes with the change of pressure and temperature. As a result, CO₂ separation can be achieved through periodic temperature and pressure changes. According to this characteristic, the adsorption separation method is divided into pressure swing adsorption (PSA) and temperature swing adsorption (TSA) [15]. As temperature changes need to be equipped with corresponding heating and cooling equipment, energy consumption and investment are relatively high. In addition, large periodic changes in temperature will also affect the life of the adsorbent. Therefore, the

application of TSA is less. The PSA process is a purification technology that has developed rapidly in recent years. This process has a low energy consumption, high product purity and flexible adjustment, but generally requires the parallel use of multiple adsorption towers [16], with a lot of equipment and more investment. In addition, the issue of adsorbent regeneration needs further study.

The membrane separation method is a method of separating mixed gas by the selective permeability of the membrane. The equipment that uses membrane separation to remove CO₂ is relatively simple, occupies a small area, and has a low energy consumption [17]. Membrane separation is suitable for processing gases with high CO₂ contents. In remote areas where operations need to be reduced, membrane separation is more appropriate [18]. The main disadvantage of membrane separation is that there is a considerable amount of methane permeation loss. Therefore, the hydrocarbon loss is relatively large, and it is difficult to obtain high-purity gas, which restricts its application.

Cryogenic CO₂ separation is a physical process in which CO₂ is condensed or sublimated under low-temperature conditions. After the mixed gas is compressed and cooled several times, the phase of CO₂ is changed, thereby separating CO₂ from the mixed gas [19]. According to different types of phase transition, the phase change of CO₂ is divided into the gas-liquid phase change and the gas-solid phase change, which will be discussed in detail in Section 3. The main restricting reason for the development of cryogenic CO₂ removal is that an additional refrigeration system is required to provide the cold energy required for phase change during the application, which is considered to have a high energy consumption and is not suitable for stand-alone use [20]. However, in the NG liquefaction process, the existing cold energy can be used to purify NG and produce by-product liquid CO₂ under low-temperature conditions, avoiding the huge compression cost of traditional CO₂ capture devices, and the by-product liquid CO₂ can be used in enhanced oil recovery (EOR). Therefore, integrating the cryogenic removal of CO₂ with the NG liquefaction process is a very promising solution.

Many of the CO₂ separation methods mentioned above that can be used to remove CO₂ from CH₄ can be used to capture CO₂ from flue gas in places such as coal-fired power plants. Many scholars have conducted numerous researches on flue gas decarbonisation and summarized the future development and technological research progress [21–23]. However, the process conditions for removing CO₂ from NG and capturing CO₂ from the flue gas after combustion are quite different. The main difference between the two is the partial pressure of CO₂ in mixed gas and purity requirements. When removing

CO₂ from NG, the feed gas is usually pressurized to a higher pressure (generally more than 3000 kPa), whereas the pressure of the flue gas is generally only slightly higher than the atmospheric pressure (about 101 kPa) [24]. In addition, for the decarbonisation of NG, especially for LNG, the CO₂ content is strictly restricted. Consequently, the amount of CO₂ that needs to be removed is relatively large. Therefore, it is necessary to summarize the existing technologies for removing CO₂ from CH₄, and find out the existing problems and future development directions, instead of simply imitating the technology for removing CO₂ from flue gas.

Regarding the technology of removing CO₂ from NG, many studies have been conducted. Rufford et al. [24] summarized the traditional and emerging processes for the removal of CO₂ and N₂ from NG, but for the cryogenic CO₂ removal process, only the commercialized Ryan-Homes (R-H) process, the controlled freeze zone (CFZ) process demonstrated by the pilot plant and CryoCell process were discussed. Maqsood et al. [20] summarized and studied the conventional cryogenic methods and non-traditional methods of the CO₂ cryogenic separation technology, but the summary of the properties of the CO₂-CH₄ binary mixture was limited, and the new technologies in recent years were not included. Song et al. [25] summarized the development and challenges of the cryogenic-based CO₂ capture technology, but the technologies mentioned were not very clearly classified, except an introduction to the classic cryogenic technology. At present, most of the review papers on the cryogenic removal of CO₂ only summarize classic technologies, and there is not enough introduction to the basis of thermodynamics.

To more clearly sort out the development context of various technologies in order to explore the development potential, in this present paper, the characteristics of the CH₄-CO₂ binary mixture are summarized and analyzed in detail. The research on the phase equilibrium and frost point of the binary system are summarized from two aspects of experimental research and theoretical calculation, which provides a scientific basis for the removal of CO₂ from NG at low temperatures. In addition, the cryogenic CO₂ removal technologies are classified and sorted from the perspective of phase change. Starting from the two categories of gas-liquid phase change and gas-solid phase change, the design and optimization of cryogenic CO₂ removal are summarized, which not only includes classic technologies but also incorporates emerging processes developed in recent years. The key parameters and energy consumption of different technologies are also summarized in the form of tables, which are clear and easy to read. After the systematical analysis of the current research status and progress, suggestions for further research on the cryogenic CO₂ removal from NG are proposed, and the current challenges and future improvements are pointed out.

2 Characteristics of the CH₄-CO₂ binary mixture

The development of the CO₂ cryogenic removal technique requires a full understanding of the characteristics of the CO₂-CH₄ binary mixture. Therefore, it is necessary to have a detailed study of the solid-liquid-gas phase behavior of the binary mixture. The qualitative pressure-temperature diagram for the CO₂-CH₄ binary system [26] is shown in Fig. 1. When the mixture composed of CH₄ and CO₂ reaches thermodynamic equilibrium at a certain temperature and pressure, it will decompose into vapor, liquid, and solid phases. As the temperature is lower than the temperature of the GF line in Fig. 1, CH₄ will also be frozen as a solid phase, so it is not considered in the LNG field. In the other region of Fig. 1, the solid phase will be pure CO₂, while the liquid and vapor phases will consist of both CO₂ and CH₄. With the different CO₂ content, the shape of the two-phase line is different, so is the intersection point with the three-phase line.

More specifically related relevant research has been performed since the 1950s, and the characteristics of the binary mixture of CO₂-CH₄ have been discussed in detail experimentally and theoretically. With the development of the NG industry, the research in this area has become more in-depth. In recent years, in particular, there have been more studies on CO₂ frost points. In this section, the phase behavior of the CH₄-CO₂ binary mixture and the study of the CO₂ frost point will be summarized.

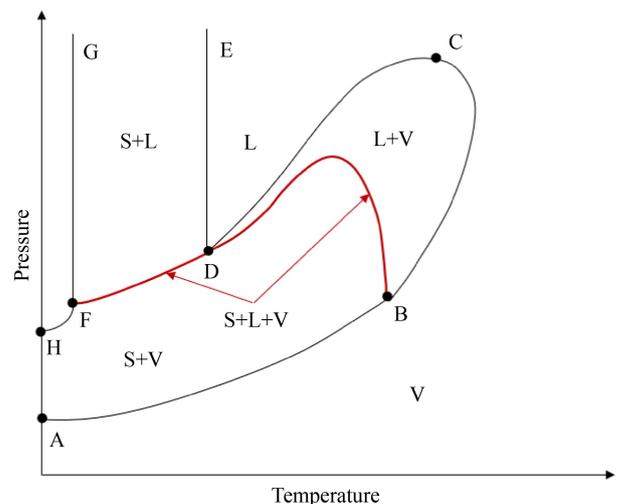


Fig. 1 Qualitative pressure-temperature diagram of CO₂-CH₄ binary system.

2.1 Experimental studies

Numerous experimental studies on the phase behavior of the CH₄-CO₂ binary mixture and the CO₂ frost point have been conducted, whose key parameters are summarized in Table 1.

Donnelly and Katz [26] used experimental methods to obtain the critical locus of the CO₂-CH₄ binary system solid-liquid equilibrium and the course of the triple-point locus in the temperature range of 194.54–215.65 K at a pressure of 0.92–5.39 MPa and extrapolated the qualitative three-phase diagram of the binary system. The conclusion showed that the three-phase curve would show a maximum value in the gas-liquid equilibrium zone. Pikaar [27] used a non-sampling method to determine the vapor-liquid, vapor-solid CO₂, and liquid-solid CO₂ equilibrium of the CH₄-CO₂ binary system in the range of 1%–20% CO₂ in mole fraction and designed a sampling method to determine the composition of vapor and liquid in equilibrium with solid CO₂ at a pressure of up to 10.13 MPa and temperature from 113.15 to 210.15 K. Davis et al. [28] measured the pressure and temperature from the triple point of CO₂ to 97.54 K along the solid-liquid-vapor locus. The vapor phase composition range was determined by the sampling method in the 0.1%–10% CO₂ composition range, and the liquid phase composition range was determined by the crystallization point determination of 11 CH₄-CO₂ mixtures (CO₂ ranging from 0.16% to 20% (mole fraction)). Kurata and Im [29] reported a study of the vapor and liquid compositions at equilibrium in the presence of solid CO₂ by using a sampling method. The experiment was conducted in the temperature range of 165.21 to 210.21 K and the pressure between 1.89 and 4.84 MPa.

Agrawal and Laverman [30] used a non-sampling visual technique to measure the frosting points of the CH₄-CO₂ mixture in the solid-vapor region and measured two CH₄-N₂-CO₂ mixtures whose composition were intentionally selected to be similar to typical NG. The study of this composition is also of great significance to the LNG industry. Le and Trebble [31] used a non-sampling visual observation technique to measure the solid-vapor equilibrium of CO₂ in the NG mixture. In the pressure range of 0.96–3.01 MPa and the temperature

range of 168.6–187.7 K, the frost points of a CH₄-CO₂ binary mixture containing 1.00%, 1.91%, and 2.93% (mole fraction) CO₂ were measured. In addition, while keeping the CO₂ composition unchanged, the effect of adding C₂H₆ and N₂ to the CH₄-CO₂ binary system on the frost point was investigated. Zhang et al. [32] obtained new experimental data for the CO₂-CH₄ system in the concentration range of 10.8% to 54.2% CO₂ in mole fraction. These data are very important for evaluating the thermodynamic model of process simulation. Shen et al. [33] and Gao et al. [34] designed a new experimental device and measured the SLE (solid-liquid equilibrium) of the CO₂-CH₄ binary system based on a static analysis method, and compared the data with the experimental data published. Thanaraju [35] used the observation method to test the dew point of carbon dioxide and NG in PVT equipment and compared it with the result predicted by HYSYS. Xiong et al. [36] used static analysis to collect SVE (solid-vapor equilibrium) data of CO₂ in a wide range of components, temperature, and pressure in NG industry applications. The sampling and analysis were performed at equilibrium.

2.2 Theoretical studies

Due to the limitation of time, cost, measurement, and other practical factors, the experimental operation of the frost point and the phase behavior of the CH₄-CO₂ binary system are complicated. Alternative theoretical calculation models or numerical simulation methods are hoped to be found to estimate the state of the mixture under specific working conditions. Therefore, many scholars have summarized different calculation models and simulation methods for the characteristics of the CH₄-CO₂ binary mixture, as presented in Table 2.

Starting from the thermodynamic relationship of phase equilibrium, Yi [37] established the three-phase equilibrium model of CO₂ crystallization in light hydrocarbon

Table 1 Experimental research on phase behavior and CO₂ frost points of CH₄-CO₂ binary mixture

Ref.	Composition of the mixture (mole fraction)	Temperature/K	Pressure/MPa	Methods
[26]	CH ₄ + CO ₂ (20.5%–86.5%)	194.54–215.65	0.92–5.39	Non-sampling visual observation and sampling
[27]	CH ₄ + CO ₂ (1%–20%)	113.15–210.15	0.41–10.13	Non-sampling visual observation and sampling
[28]	CH ₄ + CO ₂ (0.16%–20%)	97.54–216.15	0.028–4.87	Sampling
[29]	CH ₄ + CO ₂ (vapor:0.6%–17.5%, liquid:1.83%–74%)	165.21–210.21	1.89–4.84	Sampling
[30]	CH ₄ + CO ₂ (0.12%–10.67%)	137.5–198	0.17–2.78	Non-sampling visual observation
[31]	CH ₄ + CO ₂ (1%–2.93%)	168.6–187.7	0.96–3.01	Non-sampling visual observation
[32]	CH ₄ + CO ₂ (10.8%–54.2%)	196.5–210.3	0.29–4.45	Dynamic analysis
[33]	CH ₄ + CO ₂ (0.0213%–2.8960%)	112–169.9	0.093–2.315	Static analytic
[34]	CH ₄ + CO ₂ (0.0213%–2.8960%)	113.15–169.7	–	Static analytic
[35]	NG + CO ₂ (69.14%, 39.37%)	253–285	0.3–10.5	Observation
[36]	CH ₄ + CO ₂ (0.5%–20.1%)	153.15–193.15	0.219–3.038	Static analytic with sampling

mixture by using the PR equation, and proposed the calculation method of the CO₂ freezing method in the cryogenic separation device. Zhu and Chen [38] modeled the phase equilibrium characteristics and state of the CO₂-CH₄ system, put forward the phase state judgment criteria and procedures, and proposed a modified Clausius-Clapeyron formula to describe the gas-solid equilibrium. Agrawal and Laverman [30] used the BWR equation of state to calculate the phase equilibrium of the CO₂-CH₄ and CO₂-CH₄-N₂ mixture systems. ZareNezhad and Eggeman [39] used the PR equation of state to predict the CO₂ freezing point of a mixture of hydrocarbon liquid and vapor and proposed a secondary temperature correlation equation to express the interaction of

CO₂ and CH₄ under low-temperature conditions. The overall AAD between experimental and predicted CO₂ freezing temperatures was found to be about 0.26%. Hlavinka and Hernandez [40] used the ProMax software to simulate the temperature and pressure conditions of solid CO₂ formed during the liquefaction of different components of NG and compared them with the experimental results of others, indicating that relatively accurate results could be obtained under various conditions. Hu et al. [41] used the HYSYS software to predict the temperature of solid CO₂ formed in NG, but he did not compare it with the actual experimental data. Jiang et al. [42] established liquid-solid and vapor-solid equilibrium models based on the principle of phase

Table 2 Theoretical research on characteristics of CH₄-CO₂ binary mixture

Ref.	Methods	Phase equilibria	Data points	Average absolute deviation (AAD)
[37]	PR equation of state	SLVE	–	–
[38]	Equivalence fugacity model	SVE SLE SLVE	25	10.08%
[30]	BWR equation of state	SVE	16	0.39%
[39]	PR equation of state	SVE SLE	58	0.26%
[40]	ProMax simulation	SVE SLE SLVE	4 (Donnelly and Katz) 8 (Davis et al.)	0.90% 2.84%
[41]	HYSYS simulation	–	–	–
[42]	HYSYS simulation	SLE SVE	28 (SVE) + 11 (SLE)	0.57% (SVE), 0.66% (SLE)
	PR equation of state			3.35% (SVE), 3.39% (SLE)
[32]	SRK equation of state	SVE	17	0.31%
	PR equation of state		5	0.43%
[43]	HYSYS simulation	SVE	5	0.97%
	Charting		5	1.17%
[44]	PR equation of state	SVE SLE	–	5.67% (SLVE), 0.85% (SVE), 1.84% (SLE)
	Yokozeki equation of state	SLVE	–	5.15% (SLVE), 0.77% (SVE), 1.98% (SLE)
[45]	SRK equation of state	SLVE	–	2.48%–7.14% (SRK), 1.11%–7.13% (PR)
	PR equation of state			
[46]	Helmholtz free energy explicit equation of state	VLE	–	–
[47]	Reference state of hypothetical fluid	SVE SLE	–	3.056% (RKS) 2.742% (PR) 0.160% (GERG-2008)
[48]	PC-SAFT equation of state	VLE SVE SLE	–	0.3%–2.80%
[49]	Modified Dalton's law of partial pressure	SVE SLE	15 (SVE) + 9 (SLE)	1.64% (SVE), 0.51% (SLE)
[50]	Global Gibbs energy minimization algorithm	SVE	–	2.98% (SVE)
		SLE	18	0.7% (SLE)
		SLVE	–	2.0% (SLVE)
[51]	Phase stability analysis algorithm	SVE SLVE	–	5.86% (SVE) 4.27% (SLVE)

Notes: SLE—solid-liquid equilibrium; SLVE—solid-liquid-vapor equilibrium; SVE—solid-vapor equilibrium; VLE—vapor-liquid equilibrium.

equilibrium using the PR equation of state and compared the results calculated with the results simulated by the HYSYS software and the experimental data. Zhang et al. [32] used the SRK equation of state to calculate the fugacity and modeled the CO₂ solid-forming conditions by using a solid fugacity model based on the sublimation pressure of pure CO₂, and used the thermodynamic model to predict the CO₂ frost points in the presence of methane.

Xiong et al. [43,52] used the PR equation to calculate the frosting temperature of CO₂ in the CH₄-CO₂ binary system and proposed that it was feasible to remove CO₂ by sublimation separation in the NG liquefaction process. In addition, they also compared the results calculated, the results simulated by HYSYS, and the graph lookup results with the experimental data. The results obtained by the three methods were in good agreement with the experimental data. Riva et al. [44] compared two different methods to represent the solid-liquid, solid-vapor, and solid-liquid-vapor equilibrium of CH₄-CO₂ mixtures. De Guido et al. [45] developed a thermodynamic methodology based on the cubic equation of state to predict the solid-liquid-vapor equilibrium of CO₂ mixtures. In addition, they also proposed an algorithm for solving an isobaric-isothermal flash coupled to a phase stability analysis in 2021 [51]. The proposed method can be used to determine suitable operating conditions for the process of separating CO₂ by freezing. Mao et al. [46] improved the Helmholtz free energy explicit equation of state to calculate the PVT_x and vapor-liquid equilibrium of the CH₄-CO₂ mixture, whose calculation accuracy is close to the experimental data. Li et al. [47] used a new hypothetical fluid reference state thermodynamic method to replace the LSE model based on the Antoine equation to calculate the fugacity of solid CO₂. Compared with the experimental data, the calculation results had a higher accuracy in complex NG systems. Of these methods, the improved GERG-2008 method had the highest accuracy. de Ozturk et al. [48] used the PC-SAFT equation of state to simulate the phase behavior of the hydrocarbon-CO₂ system at different temperatures and pressures. The results showed that this equation of state could accurately predict VLE (vapor-liquid equilibrium), SVE, and SLE with a set of binary interaction parameters that were independent of temperature and pressure. Kong [49] used the modified Dalton's law of partial pressure to predict the freezing point temperature of CO₂ in the binary system and compared it with other methods. The results indicated that the proposed model was very consistent with the experimental data and had a wide range of versatility. Tang et al. [50] derived composition-independent correlations of solid-vapor and solid-liquid and introduced these correlations into a Gibbs energy minimization algorithm with the stability variable of phase to predict the phase diagram of the CH₄-CO₂ binary system.

3 Classification of cryogenic CO₂ removal techniques

According to the different phases of CO₂ when it is captured, the cryogenic CO₂ removal techniques can be divided into the gas-liquid phase change and the gas-solid phase change. The cryogenic removal based on the gas-liquid phase change is also called liquefaction separation, which uses the difference in boiling point between CO₂ and other components and uses cold energy to liquefy and separate CO₂. The most commonly used method is cryogenic distillation. The cryogenic removal based on the gas-solid phase change is also called sublimation separation, which uses the difference in frost point between CO₂ and other components and uses cold energy to solidify and separate CO₂. For mixed gases with a high CO₂ concentration, the gas-liquid phase change is usually used, and when the CO₂ concentration is low, the gas-solid phase change is usually used [9]. In addition, there are also studies based on combined phase change. The research progress of the CO₂ removal process according to these three categories will be introduced respectively in this section.

3.1 Cryogenic removal based on gas-liquid phase change

A lot of research have been conducted on gas-liquid phase change separation. In previous research, the feed gas needed to pass through pretreatment equipment before entering the distillation tower, or the tower needed to be operated under specific temperature, pressure, and composition conditions to avoid solid production. However, none of these methods could achieve satisfactory results. Holmes and Ryan [53] proposed the Ryan-Holmes process in 1982, which was the earliest and most classic conventional cryogenic distillation process. To avoid the solidification of CO₂ in the distillation tower, one or more heavy hydrocarbon additives between C₂-C₅ or other nonpolar liquids which were miscible with methane at the column conditions were added to the distillation tower to reduce the freezing temperature of CO₂. For gases with a high CO₂ content, the method was economical and effective and did not require a pre-separation device. The flow chart of the R-H process was shown in Fig. 2.

The feed gas passed through two heat exchangers, in which it was pre-cooled and then cooled to a low temperature to be partially liquefied, and then introduced into the distillation tower. CH₄ was discharged from the upper part of the distillation tower through the condenser, and part of it was refluxed to the bottom. Part of the bottom product was recovered through the reboiler, and the other part entered further separation equipment to separate other components, such as ethane-plus components. The agent that prevented solidification could also be separated from the bottom of the separation equipment,

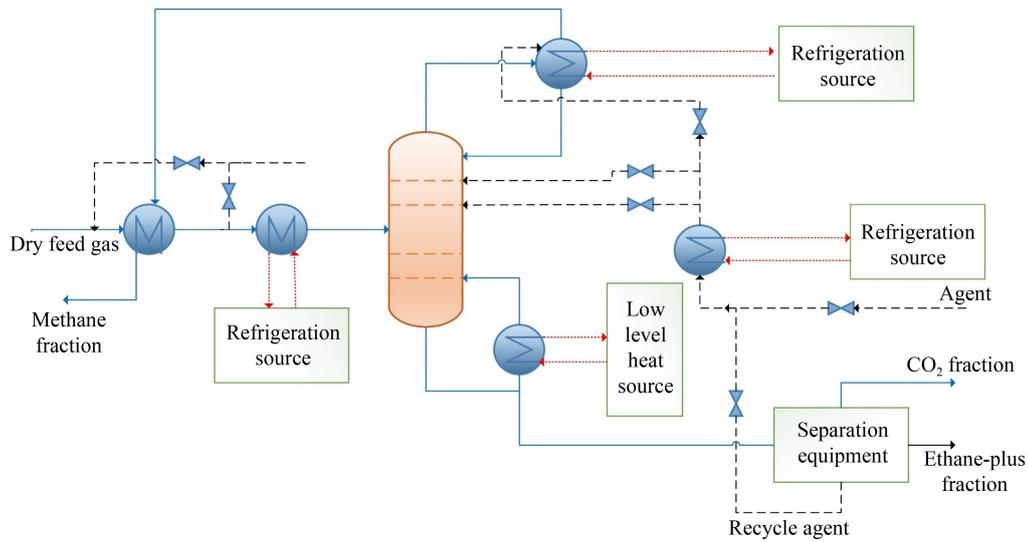


Fig. 2 Ryan-Holmes process.

cooled by the heat exchanger, and then introduced into the process from several different entry points. It was worth noting that the agent should avoid entering from the first tray at the top of the distillation column to avoid entrainment in the product fluid. For example, it entered from the distillation column or the inlet of the pre-cooling heat exchanger and so on. Agent lines are indicated by dashed lines.

Based on the R-H process, many scholars have made improvements to optimize the technology and reduce energy consumption. Valencia and Denton [54] innovatively used helium (He) as an additive to prevent CO₂ from freezing when removing CO₂ from CH₄ by distillation. However, since it was difficult to separate He from CH₄, the purity of the final product was affected. In 1988, Atkinson et al. [55] proposed to use two distillation towers with different working pressures, that was, a dual-pressure distillation tower to remove CO₂ from NG. The emergence of dual-pressure distillation towers is an important node in the cryogenic CO₂ removal technology based on gas-liquid change. In this way, the product could meet the requirements of pipeline gas transmission.

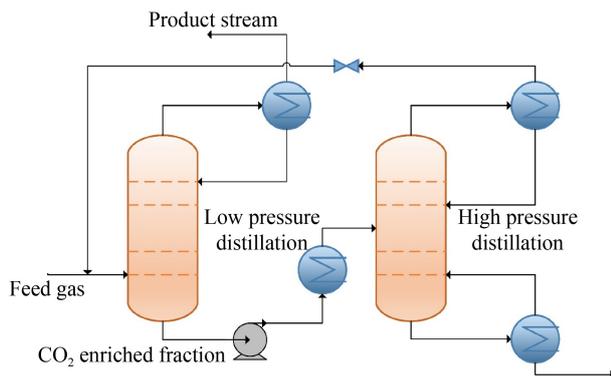


Fig. 3 Dual-pressure distillation tower process.

Figure 3 is the schematic flow diagram of this process, in which cold and heat source supply modules were omitted, and these modules were almost the same as those in the R-H process. Such a dual-pressure distillation operation could avoid the use of additives. However, for the two distillation columns in the system, the operating pressures must be carefully selected, otherwise, it may cause the freezing of CO₂.

ZareNezhad and Hosseinpour [56] proposed a new extractive distillation technology that did not use external solvents based on the dual-pressure distillation tower for sharp separation of CO₂ from the recovered hydrocarbon streams in EOR fields from CO₂-rich gases. The flow chart is depicted in Fig. 4. Although the feed gas simulated had no CH₄ component, it contained C₂, C₃, and C₄ components, which was of guiding significance for the purification of actual NG. The heavy component C₄₊ produced from the bottom of the C₂/C₃ stripper was added to the top of the CO₂ stripper to break the azeotrope that usually occurred in the cryogenic CO₂ stripper, i.e., to break the azeotrope formed by CO₂ and C₂H₆.

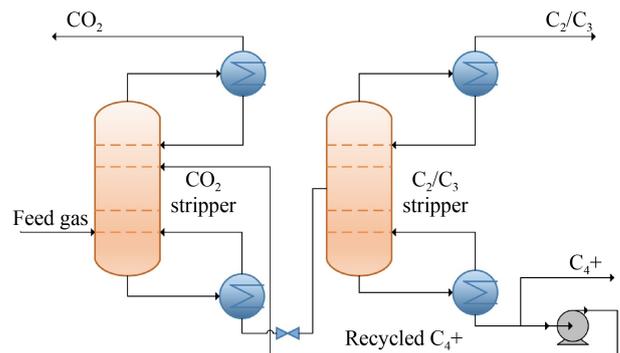


Fig. 4 Extractive distillation process for CO₂ separation (adapted with permission from Ref. [56].)

In 2012, Berstad et al. [9] simulated the R-H process on the commercial software Aspen HYSYS, in which C_5 was used as the additive. The simulation results demonstrated that using this process to remove CO_2 from NG from 50.6% in mole fraction to 50 ppm required three distillation towers. The number of trays was 19, 16, and 62 respectively. In addition, they pointed out that integrating the NG liquefaction process with the CO_2 removal process could reduce the overall energy consumption of the system. The increase in the number of distillation towers and trays had an adverse effect on total cost and operation. Subsequently, in 2014, Roussanaly et al. [57] simulated the MDEA chemical absorption process, the Selexol physical absorption process, and the R-H process in HYSYS under the same feed gas conditions and product requirements, and then compared the three processes in many aspects. The results suggested that in the case of high CO_2 content, the chemical solvent technology would lose its energy efficiency advantage due to its large equipment, while the cryogenic technology was a compact and energy-saving option. Pellegrini proposed a cryogenic CO_2 removal process using distillation towers in 2014 [58], the essential idea of which is to use a dual pressure distillation tower. As manifested in Fig. 5, the feed gas enters the distillation tower (T-1) at a working pressure of 4.5 to 5.5 MPa with CO_2 at the bottom and a mixture of CO_2 and CH_4 at the top. Then, the top product or part of the top product was heated to a temperature higher than the dew point of the stream at the pressure of the subsequent second distillation tower. The top of the second distillation tower was the CH_4 product, and the bottom product stream was pressurized and returned to the first distillation tower. Subsequently, they analyzed the refrigeration cycle required for this process, and the results indicated that the cascade refrigeration cycle has a higher performance [59]. In addition, they also studied

the application of this process in biogas upgrading and compared the performance with other technologies [60].

From 2016 to 2019, Yousef et al. [61–64] from the Department of Mechanical Engineering, School of Engineering, Alexandria University, conducted in-depth studies on the removal of CO_2 in low-temperature biogas and simulated the processes they proposed in HYSYS. They arranged the parameters to avoid frosting and made full use of energy. The combination of the distillation tower and flash separator made the separation effect better. In 2016, they proposed a process of low-temperature technique for separating CO_2/CH_4 mixtures with avoiding CO_2 freeze-out to upgrade the biogas as an alternative to the conventional biogas upgrading technologies [61] as plotted in Fig. 6. The raw gas which was common biogas containing 40% CH_4 and 60% CO_2 in mole fraction was first pressurized to 4.98 MPa by four-stage compressors and was cooled to 308 K by a water cooler in the middle of each stage. The pressurized feed gas first exchanged heat with the reboiler of the distillation tower to make full use of the heat of the high-temperature gas, then entered HX2 and was further cooled by the distillation tower product stream, and finally was cooled to 208 K by the auxiliary refrigeration device and entered the distillation tower. Finally, the purity of CH_4 in the top product stream could reach 94.5% (mole fraction). It was worth mentioning that the content of CO_2 in the bottom by-product (liquid CO_2) could be as high as 99.7% (mole fraction), which could be easily transported by pressurizing it to 11 MPa.

In 2017, they analyzed the impact of different operating conditions on the occurrence of CO_2 freezing in the process based on the existing cryogenic CO_2 removal process of typical biogas mixture ($CH_4 + CO_2$) [62], including tray number, column feed pressure, reflux ratio, feed CO_2 mole concentration and feed column temperature, which provided a theoretical basis for

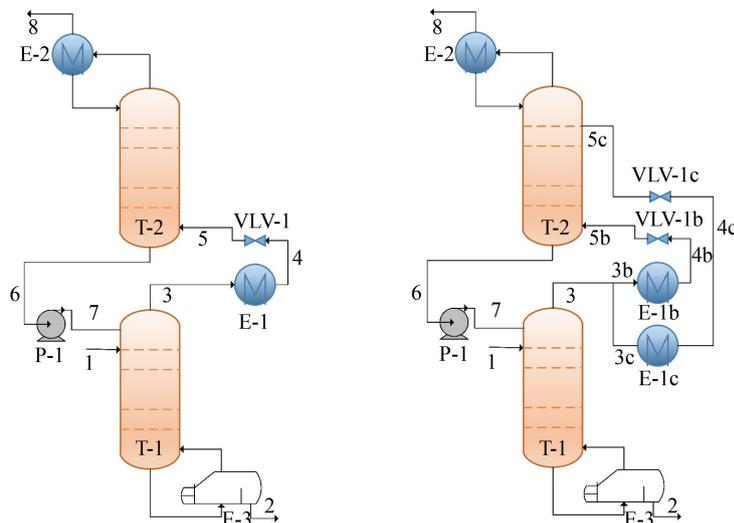


Fig. 5 Process scheme of removal of CO_2 from acid gas.

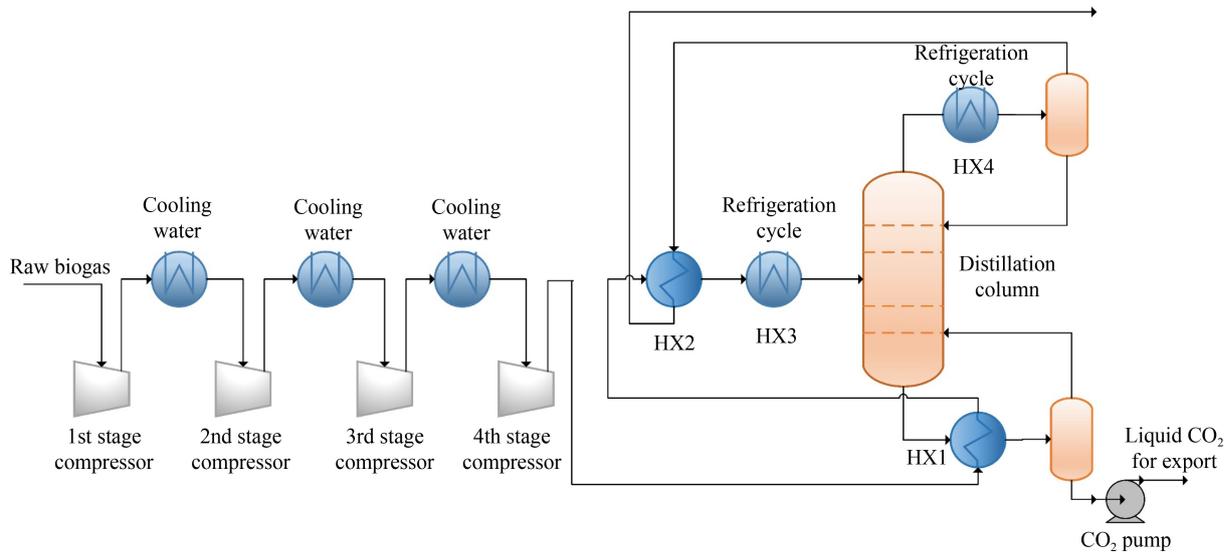


Fig. 6 Principal process flow diagram of low-temperature CO₂ removal from biogas.

subsequent in-depth research. Subsequently, in 2018, they continued to introduce a low-cost and low-complexity cryogenic distillation upgrade process that used two distillation towers for purification [63], to more flexibly respond to changes in operating conditions, and reveal new operating areas to achieve higher product purity. Finally, they not only produced high-purity CH₄ (97.12%, mole fraction) but also produced the valuable by-product liquid CO₂ (99.92%, mole fraction). The operating pressures of the two distillation towers were 4.98 MPa and 4.76 MPa respectively, and the optimal reflux ratio was 2.8.

In 2019, they proposed a low-temperature method combining distillation and flash [64]. As exhibited in Fig. 7, the highest CH₄ purity (97.2%, mole fraction) could be achieved with only one distillation column, which not only simplified the equipment complexity but

also achieved the lowest energy loss. The difference between the previous study was that the top product passed through the throttle valve to cause a sudden pressure drop, so that the volatile components in the mixture raised and recovered, thereby improving the final purity of CH₄.

Although the use of the cryogenic distillation technology to remove CO₂ has been widely used in industry and has achieved certain benefits, it has a high demand for energy, which accounts for more than 50% of the operating cost of the plant [65]. In addition, the volume of the distillation column is large, which requires a high footprint for the factory, and the equipment required for multi-column rectification is complicated. To meet the product purity requirements, the number of distillation tower plates is large, and the operation of multiple towers in series will also increase the complexity of the

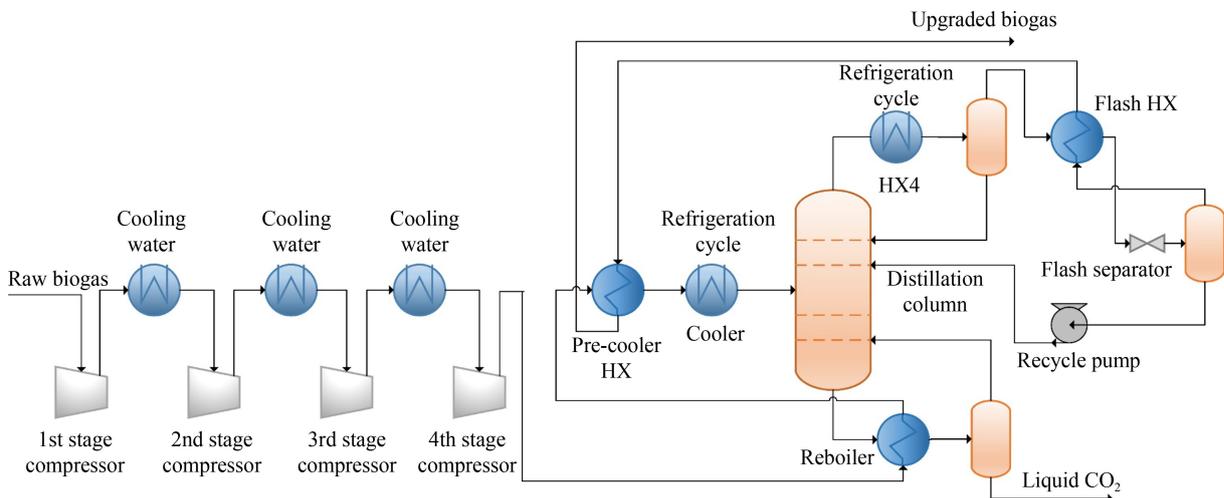


Fig. 7 A low-temperature removal of CO₂ from biogas combining distillation and flash.

equipment. If additives are used to avoid freezing, there also exists the problem of additive removal. Therefore, system integration, technology enhancement, energy saving, and emission reduction need to be applied to the improvement of this technology.

3.2 Cryogenic removal based on gas-solid phase change

Even though the development of the cryogenic CO₂ removal technology based on gas-solid phase change started late, and there are still relatively few related studies in the field of NG, many scholars are still keen on using this method to capture CO₂ in the flue gas. The technology can be used as a reference for NG purification. Takeuchi et al. [66] proposed a scheme to use the cold energy of LNG to solidify and separate CO₂ in the flue gas, which could make full use of the cold energy of LNG and reduce energy waste. It provided a reference for the system integration of CO₂ removal and liquefied NG in future research. In 2005, Clodic et al. [67] proposed a cryogenic process based on frosting and defrosting to separate CO₂ in flue gas, as displayed in Fig. 8. This process used two heat exchangers to work alternately in the CO₂ removal part, when one frosted, the other defrosted. The experimental results showed that this process could remove 90% of the CO₂ in the flue gas. Meanwhile, they also showed that the energy loss of their technology was lower compared to MEA absorption for capturing CO₂ from two similar coal-fired power plants. Based on the previous research, Chang et al. [68] combined cryogenic CO₂ separation with landfill gas liquefaction, aiming to remove CO₂ in the form of frost. The basic process flow was similar to that of Clodic et al. [67], and heat and mass transfer analysis and heat exchanger size design were performed. This process can achieve CO₂ removal at atmospheric pressure or higher pressure. Bi and Ju [69] proposed a cryogenic CO₂ separation process for the new LNG purification cold

box. The cryogenic CO₂ removal adopting the one-use-one-stand mode was applied under high-pressure conditions to realize the integration of NG purification and liquefaction. The basic working principle was similar to that of Clodic et al. and Chang et al., but the application conditions and energy supply methods were different. The alternate frosting-defrosting working mode mentioned above would result in a waste of energy during the rewarming process, and the change of high and low temperature would cause damage to the equipment. In addition, more valves and pipes were used in the process than in the conventional process, and the switching of the valve required the addition of a control system.

Tuinier et al. [70] proposed using a cryogenic bed to condense and remove CO₂ from the flue gas and combining the cold energy of LNG gasification to adsorb CO₂ at low temperatures. Both theoretical calculations and experimental results showed that CO₂ could be well separated from the flue gas. Moreover, this method could also be used to pretreat biomass gas, whose CH₄ recovery rate and processing capacity were significantly better than conventional vacuum pressure swing adsorption methods. Compared with other capture technologies, cryogenic beds have the advantages of not requiring chemical adsorbents and high-pressure operation, but their insulation should be improved to avoid sensible and latent heat loss. There are certain advantages when integrating it with the LNG process, but if there is no LNG cold source, an additional chiller is required, and the energy consumption is relatively high. Schach et al. [71] used the Aspen plus simulator to simulate the process of anti-sublimation to capture CO₂ in flue gas and compared it with the amine absorption method. The results showed that the cryogenic process had a better performance in terms of energy requirements. Lee et al. [72] proposed the use of a cyclone separator to separate solid CO₂ and LNG. After the liquefaction process was

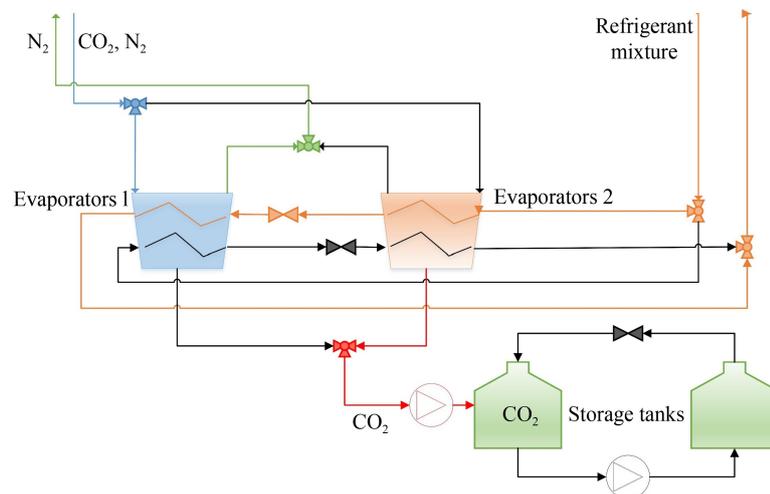


Fig. 8 Cryogenic process based on frosting and defrosting.

completed, LNG and CO₂ solids were passed into the separator together, but only the experiment was designed and the test was not completed. At the same time, the life of the motor under low-temperature conditions would be seriously affected. Therefore, the feasibility of this design still needed to be considered.

In 2014, Song et al. [73] used a Stirling refrigerator to capture CO₂ in the flue gas at low temperatures. The CO₂ was sublimed in the crystallization tower through multi-stage cooling, and the resulting dry ice was stored. The effects of different flue gas flow and cold head temperature on CO₂ sublimation, energy consumption, and heat conduction were studied through experiments and theoretical calculations [74,75]. However, since the difficulty of frost layer scrapping, this method had not been piloted and applied so far. Yuan [76] designed a CO₂ low-temperature sublimation capture process based on the expansion cycle, as presented in Fig. 9. The calculation results showed that the double nitrogen expansion process was more energy-efficient than the single nitrogen expansion process. Meanwhile, a CO₂ sublimation visualization testbed was built to investigate the CO₂ sublimation mechanism. In his design, the CO₂ solid separated by the solid-gas separator entered the solid compressor, was pressurized and liquefied and stored.

Lin et al. [77] and Xiong et al. [78] achieved cryogenic removal of CO₂ impurities through the pressurized liquefied NG (PLNG) solution and integrated the cryogenic CO₂ removal device into the process to achieve CO₂ sublimation removal. However, the LNG produced by this scheme must be stored and transported at a certain pressure. Once the pressure was reduced, not only a large amount of flash gas would be generated, but also a large amount of CO₂ solid would be precipitated due to the decrease in temperature. Furthermore, they did not explain how to remove solid CO₂ from the heat exchanger. Baccioli et al. [79] used HYSYS to simulate the liquefaction unit of a bio-LNG plant. Comparing the parameters of the conventional process and cryogenic CO₂ removal process, the results showed that the

cryogenic process did not require feed gas pretreatment and could achieve ideal energy consumption. Babar et al. [80] used the data from the existing literature to verify the effectiveness of HYSYS in the prediction of thermodynamic data of the CO₂-CH₄ binary system and optimized the cryogenic CO₂ removal process based on the packed bed. The corresponding experimental results showed that the pressure and temperature inside the packed bed had a significant impact on process efficiency by changing the composition of the top stream.

3.3 Cryogenic removal based on combined phase change

In the research of the cryogenic CO₂ removal process, many scholars combined gas-solid separation with gas-liquid separation, i.e., used a combined phase change method to separate CO₂. Of these methods, the most representative was the controlling freeze zone process proposed by Valencia and Denton [81]. The specially designed distillation tower allowed CO₂ solids to appear within a controllable range during the distillation process. The distillation process was the same as that in Fig. 2, except that the internal structure of the distillation tower was different, which was shown in Fig. 10. Thomas and Denton [82] built a CFZ experimental device, and the operation proved the feasibility of the process. The CO₂ content of the gas at the top of the rectification tower could be reduced to several hundred parts per million (ppm), and the methane loss was only 0.5%. Kelley et al. [83] conducted a detailed analysis on the process of combining CFZ and acid gas reinjection, and the results showed that this process has less equipment investment and a higher acid gas profit than the Selexol and R-H processes. In addition, the CFZ process had a low operating cost, high safety, and compact structure, making it more suitable for offshore NG installations. The ExxonMobil Upstream Research Company has successfully demonstrated the CFZ technology through a commercial demonstration plant in Wyoming [84]. Most of the captured CO₂ at ExxonMobil's commercial

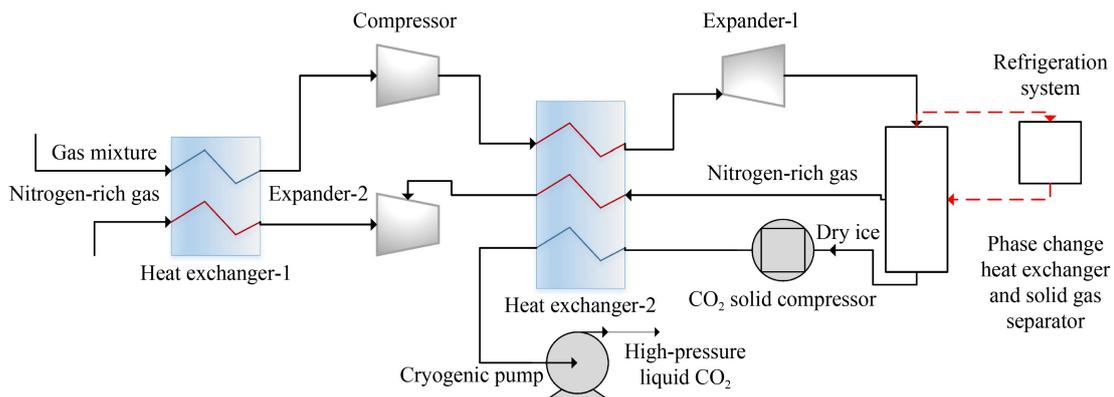


Fig. 9 Cryogenic sublimation capture process based on the expansion cycle.

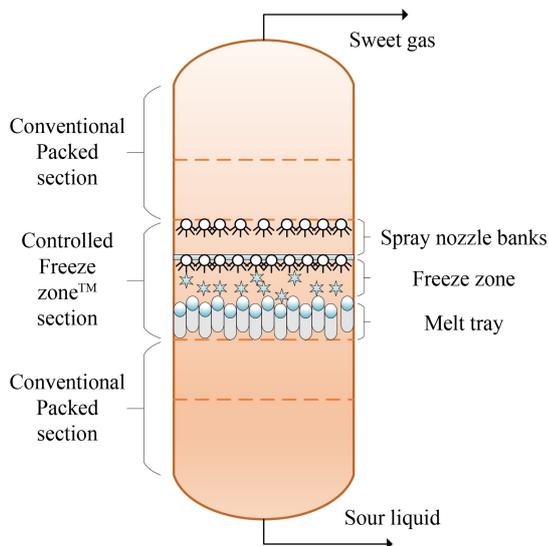


Fig. 10 Internal structure of the distillation tower of the CFZ process.

demonstration plant is used for EOR, and can add to the economic viability of producing sour NG reserves.

Hart and Gnanendran [85] proposed a CryoCell process based on gas-liquid-solid three-phase separation, as shown in Fig. 11, to remove CO₂ from NG. The process used a gas-liquid-solid three-phase separator to separate, and solid CO₂ was heated and melted, and then sent to geological storage together with liquid CO₂. They verified the reliability of the simulation method through experimental tests and then simulated the Cryocell process and the MDEA process. The results showed that the Cryocell process had a lower energy consumption and a lower equipment investment. The advantage of the CryoCell process was that no additional heating system was required, which was more suitable for gases with a high CO₂ content. Maqsood et al. [86] proposed a hybrid cryogenic distillation network using both cryogenic packed beds and distillation towers, as shown in Fig. 12, to separate CO₂ from CH₄, and studied the feed gas containing 72% (mole fraction) and 50% (mole fraction)

of CO₂, respectively, and studied the best location of the cryogenic packed bed. In addition, they also studied a traditional cryogenic extractive distillation network composed of multiple distillation towers with butane as an additive, and performed the simulation with the Aspen Plus software. The results showed that the cryogenic network had a great potential in energy saving and consumption reduction and could effectively reduce the equipment size of the NG purification process.

4 Summary and outlook

The cryogenic CO₂ removal technology can produce CO₂ as a high-purity liquid by-product while purifying NG, which has huge development prospects in the NG industry. Experimental and theoretical studies on the characteristics of CH₄-CO₂ binary mixtures and cryogenic CO₂ removal technologies in recent years have been classified and summarized in this paper. Compared to other CO₂ removal technologies, the cryogenic CO₂ separation has the following advantages. First, no chemical solvents are required, which will reduce the cost of frequently needed consumables and do not produce corrosion. In addition, this can also avoid the use of solvent recovery devices. In addition, no additional heating systems are required, which will reduce the heat consumption. Moreover, by-product liquid CO₂ can be used for EOR or other applications. Furthermore, if an integrated system is used and so is the cold energy from the regasification of LNG, the required cold energy can be obtained at a relatively low cost, and the system is highly economical. In Section 2, the characteristics of the CO₂-CH₄ binary mixture system are summarized experimentally and theoretically. Key parameters of experimental studies and models and methods of theoretical studies are listed in Tables 1 and 2, respectively. From the summary, it can be seen that most of the experiments were performed within 110–220 K at 0–5 MPa, and the CO₂-CH₄ binary mixture phase behavior and frost point were studied by observation and

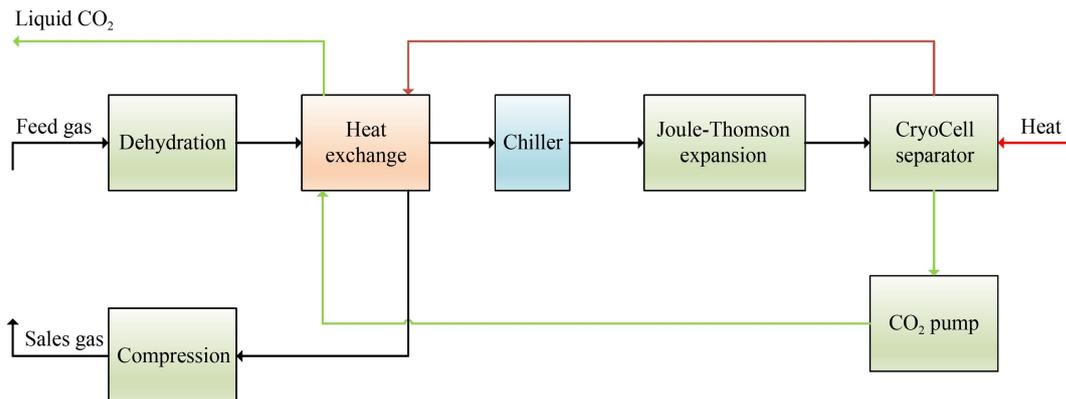


Fig. 11 Flow diagram of the CryoCell process.

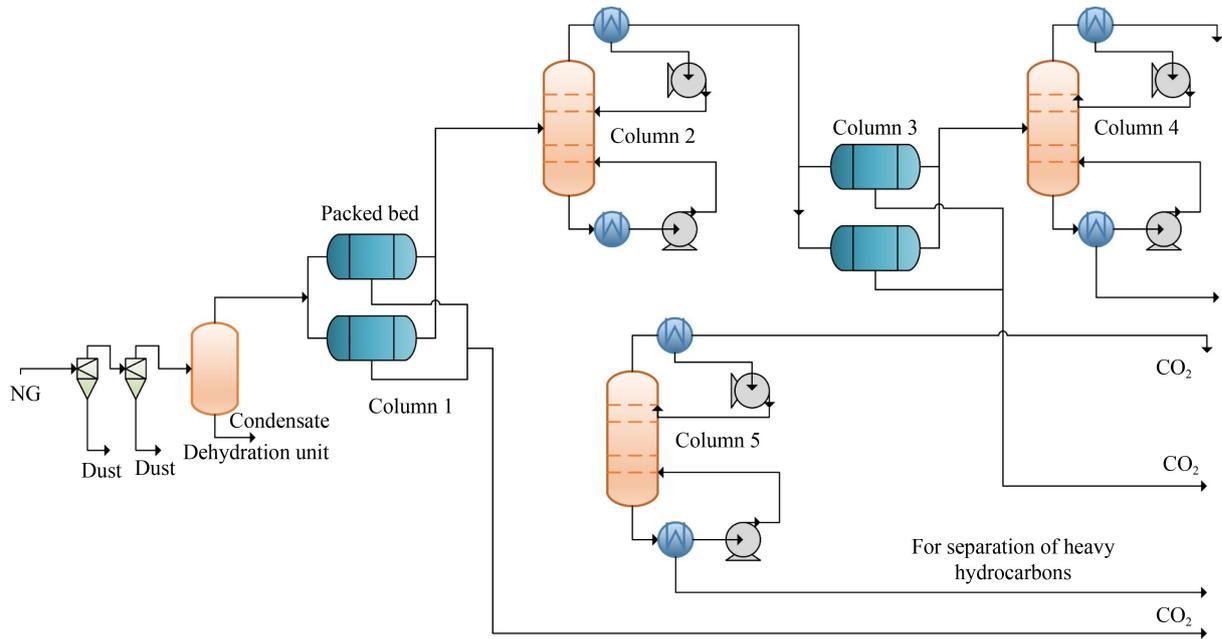


Fig. 12 Schematic of the hybrid cryogenic distillation process.

using the sampling methods. The AAD of theoretical prediction is less than 10%, most of which are between 0.2%–3%, which is in good agreement with the experimental data. In Section 3, numerous researches for the cryogenic CO₂ removal technique in NG are presented and discussed. Different separation mechanisms, process structures, and working conditions lead to different separation effects and power consumption. The differences between those cryogenic CO₂ removal systems based on key parameters are listed in Tables 3 and 4, respectively. It can be found that in the previous cryogenic CO₂ removal techniques, more researches are conducted on technologies based on gas-liquid phase change, while technologies that use gas-solid phase change are mostly applied in the field of flue gas purification. There are few applications of this technology in the field of NG, and the researches on cryogenic CO₂ removal technologies based on combined phase change are even more inadequate. In addition, the removal technologies based on gas-liquid phase change are mostly used for high CO₂ content feed gas, and the removal technologies based on gas-solid phase change are more suitable for the purification of feed gas with a lower CO₂ content. The purity of product CH₄ obtained by using the cryogenic CO₂ removal technology based on gas-liquid phase change is mostly higher than 95%, even up to 99.9%. At the same time, high-purity liquid CO₂ for EOR can be obtained by using this technology. Moreover, it can also be observed from Tables 3 and 4 that the cryogenic CO₂ removal technology is mostly used for feed gas with a higher CO₂ content. The energy consumption of cryogenic CO₂ removal is lower than of the commercial chemical absorption method whose energy consumption is between 3.0 and 4.2 MJ/kg CO₂

[87]. In response to this, Langè et al. [88] also analyzed the economy of the traditional MDEA washing process and the low-temperature CO₂ removal process. The results show that when H₂S is not considered in NG and the CO₂ content is higher than about 8%–9% (mole fraction), the low-temperature technology has better economic efficiency.

In general, compared with other technologies, the cryogenic CO₂ removal technology can obtain the high-pressure, high-purity by-product CO₂, which can store part of the cold energy. At the same time, it can obtain high-purity products. However, the cold source is the biggest problem that restricts the development of this technology. Although LNG is an ideal cold source, it limits the geographic location of the application of the cryogenic CO₂ removal technology. If an additional chiller is used to provide cooling capacity, its energy consumption will be higher. In addition, other impurities in the raw gas will also affect the operation of the equipment during the cryogenic CO₂ removal process. For example, water will freeze and block the equipment when the temperature drops, which cannot be ignored. Therefore, purification needs to be considered to avoid these effects. From the review of the above-mentioned cryogenic CO₂ removal technologies, it can be found that most researchers use chemical software such as Aspen HYSYS, Aspen Plus, PROCESS, and even their own programs for physical property analysis and simulations. At the same time, different processes have been proposed and the impact of key parameters on the process has been analyzed according to different feed gas components. In addition, most studies only propose corresponding feasible processes, detailed numerical analysis is incomplete, and the refrigeration system required for cryogenic removal is

Table 3 Differences between proposed CO₂ removal techniques based on gas-liquid phase change

Author	Ref.	CO ₂ concentration in feed gas/(mole fraction)	Operating conditions	Product purity of CH ₄ /(mole fraction)	By-product purity of CO ₂ /(mole fraction)	Duty of distillation/MW	Specific energy consumption/(MJ·kg ⁻¹ CO ₂)	Method	Additive
Holmes and Ryan (1982)	[53]	50%	Pressure: 3.44–4.13 MPa; trays: 5–18; reflux ratio: 1.0–5.22	97.5%–99.02%	97.9%–99.72%	Reboiler: 1.25–3.23 Condenser: 0.52–1.74	–	PROCESS SM simulation	<i>n</i> -butane
Valencia et al. (1985)	[54]	67%	Pressure: 5.51 MPa; trays: 20; reflux ratio: 2.42	Pipeline gas specifications	–	Reboiler: 2.86 Condenser: 0.91	–	Exxon program	He
Atkinson et al. (1988)	[55]	7%	Pressure: 4.2, 4.995 MPa	98.6%	90%	–	–	–	–
Berstad et al. (2012)	[9]	50.6%	Pressure: 4 MPa; trays: 19, 14, 62; reflux ratio: 1.69, 1.57, 1.61	98.7%	94.35%	Reboiler: 63.1 Condenser: 74	1.58	HYSYS simulation	C ₃ + ⁺
Roussanaly et al. (2014)	[57]	50%	Pressure: 4.4, 3.1, 6.1 MPa; trays: 19, 14, 62	97.5%	90.9%	–	–	HYSYS simulation	C ₃ + ⁺
Pellegrini et al. (2014)	[58]	Up to 80%	Pressure: 4.5–5.5, 3.8–4.3 MPa; trays: 15–30	98%–99.9%	99.9%	–	–	RKS equation of state	–
Yousef et al. (2016–2019)	[61]	40%	Pressure: 4.98 MPa; trays: 11; reflux ratio: 2.8	94.5%	99.7%	Reboiler: 1.371 Condenser: 0.684	1.377	HYSYS simulation	–
	[62]	40%	Pressure: 4.94 MPa; trays: 10; reflux ratio: 2.5	94.4%	99.5%	Reboiler: 0.119 Condenser: 0.0805	1.66	HYSYS simulation	–
	[63]	40%	Pressure: 4.98 MPa, 4.76 MPa; trays: 13, 11; reflux ratio: 2.8, 2.8	97.12%	99.92%	Reboiler: 0.192 Condenser: 0.1248	1.79	HYSYS simulation	–
	[64]	40%	Pressure: 4.91 MPa; trays: 15; reflux ratio: 3.089	95.45%	99.26%	Reboiler: 0.0753 Condenser: 0.1073	1.19	HYSYS simulation	–

Table 4 Differences between proposed CO₂ removal techniques based on gas-solid and combined phase change

Ref.	Feed gas composition (mole fraction)	Feed gas condition	Operation conditions	Effect	Total energy/ MJ·kg ⁻¹ (CO ₂)	Method	Proposed process
[67]	81.39%N ₂ + 11.63%CO ₂ + 6.98%O ₂	333 K, 0.12 MPa	Frost: 156 K; defrost: 217 K, 0.52 MPa	90%CO ₂ removal	0.65–1.25	Experiment	Two alternate heat exchangers
[68]	–	–	112 K	5.7 × 10 ⁻⁶ ppm CO ₂	–	Analysis and calculation	Heat and mass transfer analysis
[69]	1%CO ₂ + 99%CH ₄	293 K, 0.7MPa	132.5 K, 5 MPa	2 × 10 ⁻³ ppm	–	HYSYS simulation	Anti-sublimation process
[70]	75%N ₂ + 20%CO ₂ + 5%H ₂ O	373 K, 0.1 MPa	123 K	–	–	Experiment and simulation	Cryogenic bed
[71]	15%CO ₂ + 7%H ₂ O + 75%N ₂ + 3%O ₂	312.8 K, 0.1 MPa	155 K	90%CO ₂ removal	1.03	Aspen Plus simulation	Anti-sublimation process
[72]	5%CO ₂ + 95%CH ₄	–	6 MPa	–	–	Experiment	Cyclone separator
[73–75]	87%N ₂ + 13%CO ₂	298 K	168 K	85%CO ₂ removal	3.4	Experiment and Numerical simulation	Stirling refrigerator
[76]	80%N ₂ + 20%CO ₂	300 K, 0.1 MPa	0.106 MPa, 140–165 K	41.2%–95.9% CO ₂ removal	0.32–8.53	Experiment and EES simulation	CO ₂ sublimation visualization test
[77, 78]	99.5%CH ₄ + 0.5%CO ₂	308.15 K, 15 MPa	164.5 K, 1.5 MPa	5 × 10 ⁻⁵ ppm CO ₂	–	HYSYS simulation	PLNG process
[79]	40%CH ₄ + 59%CO ₂ + 0.5%H ₂ S + H ₂ O	303 K, 0.150 MPa,	195 K, 3.44 MPa	3%(mole fraction) CO ₂	5.22 MJ/kg bio-LNG	HYSYS simulation	Cryogenic upgrading bio-LNG plant
[80]	75%, 90%CO ₂ + CH ₄	–	133.4–167.4 K, 0.4–1.4 MPa	0.09%–0.85% (mole fraction)CO ₂	0.094–2.5 MW	HYSYS simulation and experiment	Cryogenic packed bed
[81]	79.6%CH ₄ + 18.5% CO ₂ + 1.5%N ₂ + others	311 K, 4.134 MPa	183.7–226 K, 3.79 MPa	0.234%(mole fraction) CO ₂	–	Exxon program	CFZ process
[82]	31.3%CH ₄ + 58%CO ₂ + 9.7%N ₂ + others	301.5 K, 7.2 MPa	–	0.3%(mole fraction) CO ₂	20% less than Selexol	Experiment	CFZ process
[85]	13%, 21%, 40%, 60%CO ₂ + CH ₄	208–223 K, 5.5–6.5 MPa	–	3%, 4%, 14%, and 26% (mole fraction) CO ₂	0.734–0.845	CryoFlash and HYSYS simulation	CryoCell process
[86]	50%–70%CO ₂ + 39.7%–20%CH ₄ + others	–	4 MPa	0.006%–0.1% (mole fraction)CO ₂	235–262 MW	Aspen Plus simulation	Hybrid cryogenic rectification network

not introduced in detail. Therefore, the numerical reference value of the calculation of total energy consumption is quite limited. From the perspective of the optimization of key parameters, most optimization studies use the total energy consumption as the objective function. Due to the complexity of equipment cost estimation, there is currently a lack of optimization research on the total cost.

Simplifying equipment to improve equipment compactness and enhancing the CO₂ removal effect to improve product purity still plays an important role in the process of cryogenic CO₂ removal from NG. Several promising developments in the design and optimization of future cryogenic CO₂ removal processes may include:

1) The integration of NG purification and liquefaction will be the future development trend, so the compactness of the equipment for the cryogenic CO₂ removal process has attracted more and more attention. Compared with the traditional large-scale purification process, different design features should be considered to meet the needs of offshore LNG ships or the needs of small-sized equipment in scattered gas fields.

2) At present, most researches are only based on gas-liquid phase change or gas-solid phase change. These two processes are suitable for different feed gas components. Therefore, more attention should be paid to researches based on combined phase change to achieve a better purification effect through the combination of different technologies.

3) With close attention to NG with a high CO₂ content such as biogas and landfill gas, the cryogenic CO₂ removal process of different components of raw gas should be studied in detail. The most suitable process at different CO₂ contents should be explored to adapt to the difficulties in choosing the appropriate process.

4) Most previous studies have selected the total energy consumption or specific power consumption of the CO₂ removal module as the objective function for optimization. However, the refrigeration system is also an important part of the cryogenic CO₂ removal process and needs to be considered in the overall design of the system.

5) In the study of the cryogenic CO₂ removal process, dynamic simulation is not mentioned. Because the specific parameters and status of CO₂ liquefaction or solidification under low-temperature conditions will change with time, static analysis cannot enable researchers to have a deeper understanding of the process. Therefore, the development of a more competent optimization algorithm used in dynamic simulation to obtain global optimal parameters will be beneficial to process design and optimization.

6) Low-grade energy or renewable energy such as solar energy and geothermal energy can be combined with the cryogenic CO₂ removal processes, such as pre-cooling through absorption refrigeration, which can reduce energy consumption to a certain extent.

5 Conclusions

The detailed characteristics of the CH₄-CO₂ binary mixture and the development of cryogenic CO₂ removal from NG in recent years are summarized and comprehensively reviewed in this paper. The experimental and theoretical studies on the phase behavior and frost point of the CO₂-CH₄ mixture are discussed. Most of the experiments were conducted in the range of 110–220 K and 0–5 MPa. Observation and sampling methods are widely used in the experiments. The average absolute deviation of theoretical prediction is less than 10%, most of which are between 0.2% and 3%, which is in good agreement with the experimental data. According to different mechanisms, the cryogenic CO₂ removal techniques are divided into two processes based on the gas-liquid phase change and the gas-solid phase change. In the previous removal technologies, the most used process is based on the gas-liquid phase change, and the processes based on the gas-solid phase change have gained attention in recent years. The purity of product CH₄ obtained from the cryogenic CO₂ removal technology based on gas-liquid phase change is mostly higher than 95%, even up to 99.9%. At the same time, high-purity liquid CO₂ for EOR can be obtained by using this technology. It should be noted that for feed gas with a high CO₂ content, the cryogenic CO₂ removal technology is more suitable than conventional methods. In addition, the development focus on the cryogenic CO₂ removal techniques based on gas-liquid phase change is the reduction of equipment volume and the improvement of product purity. The techniques based on the combination of the phase change have attracted more and more attention. Considering the existing technologies, the cryogenic removal technology based on the gas-solid phase change is more mature in the field of flue gas. Therefore, it is necessary to continue to explore it in the field of NG, especially the removal of solid CO₂.

Cryogenic CO₂ removal from NG can purify NG to a purity of more than 90% CH₄. In particular, the cryogenic removal technology based on gas-liquid phase change and combined phase change can even achieve a purity of 95% and above. In addition, the technology can also produce high-purity liquid CO₂ by-products, which can be used to enhance oil recovery. Moreover, the challenges and future improvements are identified, and the combination of the cryogenic CO₂ removal techniques with renewable energy, the integration of the purification and liquefaction of NG, and the combination of different processes will be important directions for future development.

Notations

AAD	Average absolute deviation
CCS	CO ₂ capture and storage

DEA	Diethanolamine
EOR	Enhanced oil recovery
GDP	Gross domestic product
He	Helium
LNG	Liquefied natural gas
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
NG	Natural gas
PFHE	Plate-fin heat exchanger
PLNG	Pressurized liquefied natural gas
ppm	Parts per million
PSA	Pressure swing adsorption
R-H	Ryan-Holmes
SLE	Solid-liquid equilibrium
SLVE	Solid-liquid-vapor equilibrium
SVE	Solid-vapor equilibrium
TSA	Temperature swing adsorption
VLE	Vapor-liquid equilibrium
PSA	Pressure swing adsorption
R-H	Ryan-Holmes
SLE	Solid-liquid equilibrium
SLVE	Solid-liquid-vapor equilibrium
SVE	Solid-vapor equilibrium
TSA	Temperature swing adsorption
VLE	Vapor-liquid equilibrium

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