Research progress of biogas decarbonization

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Abstract. Taking biogas decarbonization process as the theme, this paper introduces several kinds of process methods for producing dry ice by separating carbon dioxide based on biogas, relevant research results at home and abroad, as well as the advantages and disadvantages of various process methods. Finally, the relevant application cases and the new direction of future development are introduced. This paper introduces the biogas decarbonization process and related equipment, which provides theoretical support for future research.

1. Introduction
China’s new industrialization is advancing steadily, and the characteristic of new industrialization is to use cleaner energy to reduce environmental pollution. At present, with the continuous development of social economy, the use of fossil energy is very huge, which leads to a large number of environmental problems. Biogas is a combustible mixed gas produced by anaerobic fermentation of some organic substances, such as human and animal feces, straw and leaves, under the condition of isolation from the external air (such as in biogas digester or biogas generation tank) through the action of microorganisms. Due to different contents of biogas produced by fermentation of different kinds of organic matter, the physical properties of various gases are also quite different, but biogas mainly contains 60% ~ 70% methane (CH₄), 30% ~ 40% carbon dioxide (CO₂), 1% ~ 5% nitrogen (N₂), and less than 1% gases include hydrogen sulfide (H₂S), ammonia (NH₃), oxygen (O₂), sulfur dioxide (SO₂), hydrogen (H₂) Carbon monoxide (CO). Hydrogen sulfide in biogas will have a strong corrosive effect on equipment and pipelines. In order to improve the calorific value of biogas and recover carbon dioxide with utilization value, biogas must be separated and purified to make biogas a new energy with high added value and high utilization rate.

2. Process for carbon dioxide removal from biogas
The high content of carbon dioxide in biogas will have a great impact on the combustion performance of biogas. The separation and purification technology can not only separate carbon dioxide from biogas, but also the purified high-purity carbon dioxide can be used as refrigerant and solvent for homogeneous reaction. Carbon dioxide separation methods mainly include absorption method, membrane separation method, pressure swing adsorption method, low-temperature distillation method and hydrate separation method rising in recent years [1].
2.1. Absorption method
Absorption method can be subdivided into physical absorption method and chemical absorption method. Physical absorption method is to separate carbon dioxide by using the characteristics of the great difference between the solubility of carbon dioxide in absorbent and other gases in biogas. The chemical absorption method is that carbon dioxide reacts with the absorbent, while other gases do not react with the absorbent [2]. Common absorption solutions include water, alkali solution, alcohol mixture, alcohol amine mixture, etc. Bauer, F. [3] et al. studied the biogas pressurization of 6-10 bar during water absorption, and the countercurrent absorption mode is adopted in the operation tower, but the water absorption water consumption is large. Zhou wenlai [4] measured the solubility data of carbon dioxide in the mixed solvent aqueous solution of N-methyldiethanolamine and sulfolane at 25.0 °C and 40.0 °C, and measured the kinetic data of carbon dioxide absorption by the mixed solvent aqueous solution of N-methyldiethanolamine and sulfolane. Because carbon dioxide dissolved in organic solvent has higher solubility than water, the amount of absorption solution is less than that of water, but desorption is relatively more difficult because of its higher solubility. Wang Zhongcheng and Zhou Peilin [5] studied the absorption capacity of different concentrations of sodium hydroxide and sodium carbonate to carbon dioxide respectively. Li fenrong [6] first used coconut shell activated carbon (MCAC) prepared by microwave heating for adsorption and separation of CO2 / CH4 gas. Based on the absorption method, the adsorption and separation performance of coconut shell activated carbon (MCAC) for adsorption and separation of CO2 / CH4 was quantitatively analyzed and calculated. At the same time, the preparation method and optimal working condition of coconut shell activated carbon (MCAC) were introduced. The absorption method has high requirements for absorbent. The absorbent must have good selectivity for CO2, have large absorption solubility for CO2, stable physical and chemical properties, and have little or no corrosivity to equipment. The alkaline solution and organic alcohol amine solution widely used in industrial production can meet the above requirements, but the desorption process of this kind of absorbent is complex and needs secondary operation, which also has certain requirements for the use site. [7]

2.2. Membrane separation
Membrane separation also uses the different adsorption capacity, dissolution and diffusion capacity of carbon dioxide on the membrane surface to separate carbon dioxide. The membrane is divided into porous and non-porous [8]. Compared with the absorption method, the membrane separation method has the characteristics of small land occupation, good operation flexibility and low operation cost, but the separation performance depends on the material of the membrane and the methane loss is large [9-11]. In order to develop membrane materials with better separation efficiency and performance, researchers have done a lot of work. Liu Qingxiang and Zhang Wenshi [12] briefly described the classification and application of gas membrane technology, and prospected the future development prospect of this technology. Hua Dongyang [13] and others invented a small biogas purification and purification device, which can separate carbon dioxide and hydrogen sulfide in biogas at the same time; Aspen HYSYS chemical simulation software is selected to establish the simulation model of biogas membrane separation, so as to verify the feasibility of simultaneous separation of H2S and CO2, and the size of the unit is designed based on the optimization theory. Ren Xiaoling [14] and others took the composite gas separation membrane made of PEBA of polyethylene oxide (PEO) chain segment as the separation layer membrane material as the research object, tested and analyzed the permeation amount of carbon dioxide, methane, oxygen and other gases in the separation membrane, and concluded that polar molecular gases such as carbon dioxide have extremely high permeation flux, And it has good barrier selection efficiency for non-polar gas.

The membrane separation method is difficult to separate high-purity CO2, because the gas content of each component in biogas is complex and not fixed. If the CO2 content in biogas is too high, it will lead to the "plasticization" of polymeric membrane materials under certain pressure, resulting in the decline of selective permeability [15]. If you want to obtain high-purity CO2, you can combine membrane separation and swing adsorption. The membrane separation method is used for preliminary
separation and pressure swing adsorption for secondary separation. In addition, the feed gas needs to be pretreated, such as dehydration, impurity removal and filtration, so as to prevent the water vapor and hydrogen sulfide in biogas from damaging the equipment [16].

2.3. Pressure swing adsorption

Pressure swing adsorption refers to the method of using pressure to make the gas better adsorbed on the adsorbent and desorbed through decompression [17]. Among them, the process of enrichment and aggregation of substance molecules with lower density on the surface of substances with higher density is called adsorption, while the process of separation is called desorption [18]. Li Jian [19] pointed out the feasibility and optimization of pressure swing adsorption in the recovery and extraction of CO2 gas. As a common method for biogas purification and separation, the research of pressure swing adsorption is also deepening. Feng Chenran [20] and others have developed a set of high-efficiency biogas separation and purification system based on the mechanism and process of biogas purification, which greatly improves the grade of biogas energy and converts the heat energy of biogas into methane chemical energy and carbon dioxide bioenergy. Li Sheng [21] and others studied the compressor special oil for pressure swing adsorption separation of CO2 from biogas, and developed special lubricating oil on the basis of analyzing the process mechanism of biogas separation of CO2. The lubricating oil has good physical and chemical properties, good equipment sealing performance and high CO2 separation efficiency. Chen Shuhua [22] and others measured the separation capacity of 5A and 13X zeolite molecular sieves for methane and carbon dioxide mixture under the condition of low temperature and pressure swing. By changing the conditions such as gas flow, adsorption pressure, filler height and adsorption temperature, they came to the conclusion that 13X has better separation performance. At the same time, the of 13X molecular sieve was analyzed from the perspective of molecular structure to explore the internal causes of its better separation performance. Li Xuefei [23] and others used the self-made carbon molecular sieve (GC-3) as the adsorbent to compare the adsorption capacity with the activated carbon adsorbent for CH4 / CO2 separation sold on the market, and used the pressure swing adsorption test device to explore the advantages and disadvantages of the two adsorbents. It is found that the self-made carbon molecular sieve (GC-3) has good adsorption performance, and the product gas CH4 has the advantages of high volume fraction and stable output gas concentration. Tan Fengguang [24] aimed at a design scheme for the separation and purification of biogas with a daily output of 20000 m3, silica gel was used as the adsorbent for drying, and 4A molecular sieve adsorbent was used for CO2. The separated CH4 meets the standard of vehicle fuel, and the separated CO2 becomes the raw material for making dry ice.

PSA is a mature and widely used process for gas separation. It has the characteristics of low impact by the external environment, small corrosion of pipeline equipment, good equipment economy, good operability and high degree of automation. In recent years, PSA technology has also been continuously improved and upgraded, such as combined adsorption treatment with other methods, vacuum regeneration and desorption, research and improvement of adsorbent, multi bed adsorption, etc., with a good development momentum. However, to extract high-purity methane and carbon dioxide, a large number of adsorption towers are required, and the requirements for equipment are also high, which will greatly increase the investment in equipment.

2.4. Low temperature distillation

Low temperature distillation can also be called low temperature separation technology. Low temperature distillation is to liquefy the gas under high pressure and low temperature according to the different boiling points of each component gas in the biogas mixture, and gradually separate the gaseous methane from the liquid carbon dioxide. Methane obtained by low-temperature distillation has high purity and can also obtain by-products such as dry ice [25]. Zhou Shuxia [26] and others simulated the process of low-temperature liquefaction and separation of CO2 gas from biogas on the Aspen HYSYS platform. By changing the volume fraction of methane and carbon dioxide, the dew point range and separation pressure range of biogas are obtained. At the same time, through the
Experimental verification of the simulation process, a method of industrialized separation of carbon dioxide and purification of biogas is obtained. Based on the working principle of low-temperature distillation, Xu Gang [27] and others simulated a new integrated method of carbon dioxide compression and separation in Aspen plus. The method of multi-stage compression and multi-stage separation greatly improves the separation performance and makes full use of the waste heat in the energy system. Li Xuelian [28] designed and optimized the process of mixed alcohol amine method and low-temperature distillation method based on Aspen HYSYS software. In the early stage, MDEA + Mea mixed amine solution was used, and in the later stage, low-temperature distillation method was used, which can flexibly process the mixture with different concentration ratio, and make the separated methane and carbon dioxide gas have high concentration.

Low temperature distillation is suitable for absorbing and separating the mixture with high CO2 concentration, especially when the CO2 concentration changes greatly. The effect is better for the case of large flow. However, the traditional low-temperature distillation method also has the disadvantages of high energy consumption, large equipment investment, especially large initial investment, and poor effect on the separation of CO2 gas with low concentration.

2.5. Hydrate separation
In recent years, hydrate separation has great development potential in the decarbonization of natural gas and biogas. Hydrate separation uses the phase equilibrium difference of hydrate generated by two different gases, CH4 and CO2. At a certain temperature and pressure, one component in the mixture forms hydrate, and the other component still exists in gaseous state to achieve the effect of separation [29-32]. Zang Xiaoya et al. [33] analyzed and summarized the research on the separation of CO2 from natural gas or biogas by hydrate technology, and analyzed the kinetics and thermodynamics of the separation of CO2 from natural gas or biogas by hydrate method. Gao Peng et al. [34] studied the separation of CO2 from biomass gas. The effects of pressure, gas-liquid ratio and tetrabutyl ammonium bromide (TBAB) concentration on CO2 separation were studied. The separation efficiency was verified by experiments, and the gas loss rate and CO2 concentration after separation were measured and calculated. Fan Minglong et al. [35] simulated the process flow of separating CH4 / CO2 from natural gas by using Aspen HYSYS software, and optimized and analyzed the key process parameters such as pressure, temperature and water content. Through process simulation and corresponding characteristic analysis, it is concluded that the separated CH4 concentration can reach more than 95%, and the generated CO2 hydrate also maintains good stability.

The separation of CO2 from biogas or natural gas by hydrate method is still in the stage of small-scale experimental application. At present, there is no mature hydrate method to separate CO2 for industrial production. Adding additives to hydrate can more effectively separate CO2 and form CO2 hydrate, but the effect of a single additive is not very ideal. In the future, more researchers are needed to develop hydrate separation processes and equipment suitable for industrial production.

3. Conclusion
Biogas resources have broad development prospects and are gradually becoming a new energy alternative to fossil energy. From large and medium-sized biogas engineering enterprises to small biogas digesters in rural areas, this new energy is all over production and life. However, the resource utilization rate of biogas is low, various additional gases are not fully utilized, especially CO2 is not effectively collected, so the economic benefit of using biogas is still not high. In today's era of actively promoting green ecological environment, the collection and utilization of CO2 has become another breakthrough in the development of biogas industry.

China has a vast territory and different crop products in different regions, resulting in different organic substances used for biogas fermentation in different regions. For example, straw is used in northern regions, while cassava residue and bagasse are used in Guangxi. This different temperature conditions and different fermentation raw materials lead to the uncertainty of the concentration of biogas components, which makes the calorific value of biogas not high, the gas concentration changes
greatly, and the separation is difficult. When using biogas for the separation and utilization of each component gas, each region should learn from the advanced technology at home and abroad and optimize the design of the best separation process in combination with the composition of its own gas.

There are many ways to separate carbon dioxide from biogas. Some technologies have been relatively mature, and some technologies need more research and verification. Different processes and technologies also have different advantages and disadvantages, and there are advantages and disadvantages that can complement each other. When determining the separation process of biogas gas separation project, it should not be limited to the use of a single process, but use multi-stage process for step separation, which is conducive to the separation of gas products with high concentration and high added value.

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