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CO₂ capture from coalbed methane using membranes: a review

Na Zhang¹ · Zhen Pan¹ · Zhien Zhang² · Wenxiang Zhang³ · Li Zhang¹ · Francisco M. Baena-Moreno⁴ · Eric Lichtfouse⁵

Abstract

Coalbed methane is an abundant form of natural gas extracted from coal beds. Coalbed methane is viewed as a cleaner energy source versus petroleum and coal combustion because methane extraction, transport and use are more efficient and less polluting. However, coalbed methane contains high amounts of CO_2 that induce solidification during liquefaction. Therefore, CO_2 has to be reduced below 2% to meet the pipeline transportation standards. In addition, CO_2 capture would reduce the amount of gas emissions to the atmosphere, thus mitigating global warming. Here, we review membrane absorption, which is an advanced method for CO_2 capture from coalbed methane, by controlling the gas and liquid phases separately during the operation process. We compare CO_2 removal methods for various coalbed methane sources. Parameters influencing CO_2 removal by membrane absorption are discussed to conclude that CO_2 capture efficiency is improved by increasing the flow rate, temperature, and absorbent concentration, reducing the gas flow rate, and selecting a mixed absorbent. We also explain the principles, processes and applications of CO_2 membrane absorption.

Keywords Coalbed methane \cdot CO₂ capture \cdot Membrane \cdot Absorption \cdot Greenhouse effect

Introduction

Coalbed methane is a clean energy source, but accidental discharge into the atmosphere wastes resources, and induces serious climate warming, threatening the environment and human living conditions (Huang et al. 2018). With the increasing CO_2 emissions, the greenhouse effect

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is increasing, and carbon dioxide capture has been recognized as a viable option to reduce carbon dioxide (Yan and Zhang 2019). Currently, the methods for CO_2 capture mainly include solvent absorption, adsorption, low-temperature distillation, synthetic hydrates, and membranes (Huang et al. 2018; Lv et al. 2012b).

With the changing energy economy in recent years, the consumption of naturally occurring gas has been increasing. Because petroleum and coal are rather exhaustible resources, a production peak is expected in the future. Thus, coalbed methane, which is a high-quality energy source, has been continuously produced (Li et al. 2018a, b). China is rich in coal resources and has the third largest coalbed methane reserve in the world after Russia and Canada (Li et al. 2018c; Su et al. 2018). The world's geological coalbed methane resources amount to approximately 2.68×10^{14} m³. Russia, the USA, China, Canada, and Australia account for 90 vol% of the world's total coalbed methane resources (China: 12 vol.%) (Liu et al. 2018c; Su et al. 2018).

The concentration of CH_4 in coalbed methane is about 97% (Mallick and Prabu 2017), and the energy released by combustion of 1 m³ CH_4 is 35.9 million J, which is equivalent to the combustion of 1.2 kg of standard coal (Hao et al. 2018). However, when directly discharged into air by

accident or negligence, CH_4 produces a huge greenhouse effect, which is approximately 21 times stronger than that of CO_2 . Also the CH_4 destructive capacity of the ozone layer is approximately seven times higher than CO_2 (Daeho 2018; Warmuzinski 2008). Moreover, other problems are caused, such as increasing surface temperature, frequent climate variations, and aggravating greenhouse effects (Kim and Kim 2018; Lewis et al. 2011; Li et al. 2018a; Luis et al. 2012). Therefore, accidental coalbed methane emissions have caused widespread concern worldwide.

Figure 1a presents the coalbed methane productions of the world's major coalbed methane producers from 2006 to 2014, showing an increase in China. Figure 1b depicts the production and utilization of coalbed methane in China from 2011 to 2017 (Zheng and Zhao 2018). Although China's annual coalbed methane production is very high, the utilization rate is relatively low.

Since 2008, China's coalbed methane production has increased significantly to more than 2.832×10^8 m³/a (a: annually, per year) (Moore 2012). The development of coalbed methane is essential for improving the safety of the domestic coal mine production, relieving the market gas supply pressure, and protecting the ecological environment (Qin and Ye 2015). The development of coalbed methane resources not only reduces the emissions of greenhouse gases and ensures an optimized energy exploitation, but also reduces natural disasters such as explosions and spontaneous combustions (Cheng et al. 2017; Fan et al. 2017). As a consequence, China has introduced several policies to promote the development of the coalbed methane industry within the National Thirteenth Five-Year Plan. The Chinese national energy administration has established a strategic goal to achieve a coalbed methane production of 2.40×10^{10} m³ in 2020 to accelerate the cultivation and development of the coalbed methane industry and to promote a clean energy production and consumption revolution (Kim et al. 2017; Li et al. 2018a; Sarhosis et al. 2016; Zhou et al. 2014).

Figure 2 shows the storage state of coalbed methane in the ground and its extraction and separation processes (Liu et al. 2018a). Significant progress has been made in the construction of pipelines for coalbed methane in China, with a capacity of more than 4300 km and 18 billion cubic meters per year (https://www.in-en.com/article/html/energy-2258091.shtml). However, the high amounts of CO_2 in the coalbed methane exploitation cause a solidification in subsequent liquefaction. This affects the natural gas treatment process and the quality of the natural gas. Therefore, a coalbed methane decarburization is necessary to reduce the CO_2 concentration to values below 2% to meet the pipeline transportation standard (Bhadra and Farooq 2011; Datta and Sen 2006; Xu et al. 2018).

 CO_2 capture from other gas mixtures by hollow fiber membrane absorption, and other methods for methane decarburization methods have been reported (Chen and Cui 2012;



Gas production and utilization (×10⁸ m³)



Fig. 1 a Gas production of the world's major coalbed methane-producing countries. The coalbed methane production in the USA far exceeds that of the other four countries, and the coalbed methane production in China exhibits an upward trend (bcm: billion cubic meters). Reproduced from Ju et al. (2019), with permission from Elsevier; **b** China's coalbed methane extraction and utilization from 2011 to 2017. With the continuous development and utilization of energy, the utilization of coalbed methane has shown an increasing trend

Fan et al. 2018; Fang et al. 2019; Lee et al. 2019; Li et al. 2019). However, to the best of our knowledge, coalbed methane decarburization by membrane absorption has been rarely reported. For instance, Yan et al. (2015b) studied the use of membrane absorption in flue gas decarburization. They mainly investigated the effect of the membrane structure and various influencing factors on the decarburization efficiency. Anand et al. (2002) investigated the decarburization process of biogas by membrane absorption. However, these studies have not focused on coalbed methane decarburization.

Here, we explore the feasibility of using hollow fiber membrane absorption to remove CO_2 from coalbed methane. We



Fig. 2 Coalbed methane production. As the coal is mined, coalbed methane is separated from coal. Coalbed methane is used after pipeline transportation and decarburization. Reproduced from Liu et al. (2018a), with permission from Elsevier

present applications and methods for membrane absorption in decarburization systems. For example, a mathematical model is used to determine how the membrane absorption method changes the decarburization efficiency. This method improves decarburization and acid gas removal versus conventional methods (Zhang et al. 2014b). Then, the "CO₂ capture technology for coalbed methane" section compares methods for the capture of CO₂ from coalbed methane. In the "CO₂ capture by membrane absorption" section, the principles of the membrane absorption and the main factors controlling the capture of CO₂ are discussed. Furthermore, the application of membrane absorption to other gases is reported in "Membrance absorption applied to other gases" section.

CO₂ capture technology for coalbed methane

Currently, the methods for removing CO_2 from coalbed methane mainly include solvent absorption, adsorption, low-temperature distillation, synthetic hydrates, and membranes (Table 1). Solvent absorption is a gas separation technology that separates the components with the highest solubilities from a mixture with a liquid absorbent (Chen and Wen 2015). Lei and Yao (2013) added different additives (piperazine, ethanolamine, and diethanolamine) to methyl diethanolamine to capture CO_2 from coalbed methane. The results show that the absorption performance of the methyl diethanolamine solution increases highly after the addition of the additives. However, the regeneration ability of the mixed solution decreases to a certain extent because the regeneration performance of the additives is lower than that of methyl diethanolamine. Furthermore, it was discovered that diethanolamine has a better absorption performance than methyl diethanolamine and a better regeneration performance than ethanolamine.

Wan (2014) simulated the decarburization process of coalbed methane with methyl diethanolamine in an absorption tower and analyzed the effect of the pristine and activated methyl diethanolamine concentration on the CO_2 capture efficiency of the system. The results show that the larger the mass fraction of the methyl diethanolamine solution, the stronger the decarburization efficiency. Zhang et al. (2019) modeled the decarburization of coalbed methane

with four amine solutions, i.e., diethanolamine, ethanolamine, triethanolamine, and 1-(2-hydroxyethyl) pyrrolidine. 1-(2-Hydroxyethyl) pyrrolidine induces a high decarburization efficiency even at low absorbent concentrations because it exhibits a high chemical reaction constant for CO₂. When the 1-(2-hydroxyethyl) pyrrolidine concentration increases from 0.4 to 0.9 M, its decarburization efficiency increases by 46.9%. Furthermore, Chen and Wen (2015) considered the corrosion and degradation of an amine solution in the coalbed methane decarburization process. The advantages of the solvent absorption method are the simple equipment, low energy consumption, low investment, and high purity of the products. The disadvantages are the slow absorption and regeneration of the solution.

Pressure swing adsorption is the selective adsorption of a separated gas mixture through adsorbents under different partial pressures (Ebner and Ritter 2009). Tao et al. (2019) used a pressure swing adsorption device to remove CO₂ from natural gas with a high CO₂ content. The decarburization efficiency reaches 66% for a CO_2 content of 30–50% and pressure of 7 bar. However, the purity of the final product CH_4 is insufficient to meet the general natural gas demand. Based on the experimental data of the pressure swing adsorption, they investigated the effects of the pressure with simulations. According to their results, the CH₄ purity can reach 98% when the pressure is reduced to 1 bar. Thus, the pressure is a critical factor for achieving the required separation performance. Engelhard used the Molecular GateTM adsorption technology to decarbonize coalbed methane by compressing the feed pressure in a more traditional pressure swing adsorption mode (Ebner and Ritter 2009). Moreover, Daeho (2016) studied the coalbed methane decarburization through vacuum pressure swing adsorption. The advantages are the mature technology, simple equipment, low operating costs, and high methane recovery rate. However, it consumes much energy and strongly depends on the adsorbents.

Cryogenic distillation usually includes a mechanical method to liquefy the gas and exploits the difference in the gas boiling points to conduct the rectification. Thus, the different gas components can be separated and a high-purity gas is obtained (Chen 2017; Lv et al. 2013). Wang et al. (2014) used the cryogenic distillation technology to liquefy and separate components of coalbed methane at low temperatures and pressures simultaneously. For an increase in the methane concentration in the coalbed methane from 22 to 27%, the methane recovery rate increases slightly to approximately 98.7%. For an increase in the methane concentration from 27 to 45%, the methane recovery rate decreased slightly but was still above 98%. Moreover, Sun and Zhu (2009) designed a cryogenic liquefaction separation equipment for coalbed methane with a 50% air volume and a daily processing capacity of 5.67×10^4 m³. It simultaneously completes the liquefaction and separation processes and exhibits a CH_4 recovery rate of 82.19%. At this stage, cryogenic rectification is a matured technology with a high product purity and CH_4 recovery rate. The drawbacks of the method are the high energy consumption, large investment, complex equipment, and unsuitability for low-concentration and small-scale coalbed methane fields.

Hydrate separation of CO₂ is a new carbon capture approach (Meng et al. 2018), which exploits the different pressures of the gas components in the mixture to form hydrates in a solution and achieve the separation (Liu et al. 2018b; Pan et al. 2018). The study demonstrates that the required pressures for the CH₄ and CO₂ hydrate formation are 2.65 MPa and 1.22 MPa under equal conditions, respectively (Wang et al. 2013). Therefore, the CO_2 separation from coalbed methane through this method can be achieved by controlling the temperature and pressure. Hence, gas components of CO₂ that easily form hydrates can be separated from the gas phase to purify the coalbed methane (Lv et al. 2013). In another work (Zhong et al. 2014), the CH_4 recovery rate reaches 46.1% at 283.4 K and 2.6 MPa. After the secondary hydration separation, the CH₄ volume fraction increases from 30 to 72%. The key of the coalbed methane hydrate separation technology is to determine the thermodynamic conditions for the separation of different components to improve the separation efficiency. The technology provides a high storage density, convenient transportation, simple process, and oxygen-free products. However, it requires a high operating pressure, constitutes a high safety risk, and exhibits high costs and a low methane recovery rate.

The membrane absorption method has attracted much attention owing to its large gas-liquid contact area, fast mass transfer rate, high operational flexibility, no liquid ubiquity and mist entrainment, and simple equipment (Anand et al. 2002). Compared with traditional separation methods, the membrane absorption method is efficient and requires low investments and maintenance costs for the coalbed methane treatment (Gabelman 1999; Kaldis et al. 2004; Medina-Gonzalez et al. 2012). Zeng et al. (2017) first studied the coalbed methane decarburization by combining pressure swing adsorption and the membrane separation technology. The results show that the CH₄ loss rate can be reduced by at least 61.5% with respect to the loss rates of the individual methods. Daeho (2018) used a hollow fiber membrane with a countercurrent flow structure to absorb CO_2 from coalbed methane. The selected coalbed methane composition in the simulations was 90% CH_4 and 10% CO₂. According to the results, increasing the effective length and number of fiber membranes and the gas pressure or decreasing the gas flow rate can improve the CH₄ recovery rate and purity. Moreover, Zhang et al. (2019) used a membrane contactor for coalbed methane decarburization by establishing a mathematical model. The results show that the decarburization efficiencies can be increased by 30% and 46% for an increased liquid flow rate and absorbent concentration, respectively. The decarburization efficiency is significantly better than that of a single membrane contactor (maximal increase of 47%). However, the gas mixture only contained CO_2 and CH_4 . Thus, other gas components should be investigated in future studies.

At present, the membrane absorption method is widely applied for natural gas purification because of the high CH₄ concentrations in gas streams. Tang et al. (2014) compared the effects of single methyl diethanolamine solutions and its blended solutions with diethylenetriamine or triethylenetetramine on the CO_2 absorption capacity during natural gas decarburization. They discovered that the CO₂ absorption capacity is enhanced when diethylenetriamine or triethylenetetramine is added. Faiz and Almarzougi (2010) used hollow fiber membrane contactors to capture CO₂ from natural gas at high pressures up to 50 bar with physical and chemical absorbents. In addition, Kang et al. (2017) investigated CO₂ capture from natural gas containing 70% CO₂. According to the results, the CO₂ capture efficiency increases from 33.3 to 91.3% when the pressure is increased from 1 to 60 bar. In this study, the capture of high CO₂ concentrations from natural gas was investigated with a membrane contactor process at elevated pressures for the first time. Furthermore, Al-Saffar et al. (1997) studied the decarburization of natural gas via membrane absorption. The advantages of this technology are the low energy consumption, low operating costs, and no secondary pollution. In addition, the membrane life could hinder further pilot-scaled applications of this technology.

Based on a comparison of multiple coalbed methane decarburization methods, the membrane absorption method exhibits advantages regarding the process flow, energy consumption, operating costs, and decarburization efficiency. Owing to the coalbed methane characteristics, simple development concept, and environmental protection, the membrane absorption method is more suitable for coalbed methane decarburization treatments and will become a hot spot in this research field.

CO₂ capture by membrane absorption

Principle

The membrane absorption method is a novel separation process that combines membrane separation and absorption. It usually employs microporous membranes. During the process, the gas and liquid phases flow through both sides of the membrane contactor and contact at a fixed gas–liquidphase interface. The membrane itself is not gas selective but acts as a barrier to separate the absorbent and gas. The CO_2 diffuses through the membrane to the liquid phase owing to a concentration gradient. Theoretically, the membrane pores allow the CO_2 gas molecules to pass the membrane section without a high-pressure driving force. Thereby, one mainly relies on the selective absorption of the absorbent to separate mixed gases (Li and Chen 2005; Liang et al. 2013). The basic principle (for a hydrophobic porous membrane) is shown in Fig. 3a. The main driving force of the technology is the gas concentration difference. First, CO_2 from the gas mixture reaches the surface of the membrane pore and diffuses through the membrane pores to the gas—liquid twophase interface. Next, CO_2 reacts with the absorbent in the tube side (Boucif et al. 2008; Genceli et al. 2018). After the purification, the CH_4 gas in the coalbed methane separates from the gas mixture. Figure 3b demonstrates the CO_2 separation process from coalbed methane through membrane absorption.

Effect of absorbent type

The absorbent type in the membrane absorption has an important effect on the CO_2 capture from coalbed methane. The absorbent choice should consider the absorption efficiency, mass transfer rate, chemical stability, and recycling performance. In addition, physical properties such as the degradability, toxicity, corrosivity, and volatility of the absorbent and the chemical compatibility with the membrane material must be considered. The development of the CO_2 absorbent use is depicted in Table 2.

Although water was used as absorbent owing to the easy access, the method exhibits a low capture efficiency. Afterward, amine solutions were applied worldwide (Amrei et al. 2014; Nakhjiri et al. 2018; Pashaei et al. 2016; Stowe and Hwang 2017; Yuan et al. 2017). Marzouk et al. (2010) conducted an experimental study on CO₂ capture in a mixed gas $(9.5\% \text{ CO}_2/90.5\% \text{ CH}_4)$. They compared the effects of water, sodium hydroxide solution, and ethanolamine solution on the CO_2 flux and capture efficiency. The results show that both sodium hydroxide solution and ethanolamine solution have higher CO₂ flux and capture efficiency than water. Boributh et al. (2013) and Al-Marzouqi et al. (2009) selected water and ethanolamine as absorbents to remove CO₂ from mixed gases (10% CO₂/90% CH₄). They concluded that ethanolamine has a better CO_2 separation ability than water. Because sodium hydroxide and ethanolamine solutions react chemically with CO2. Hence, their decarburization efficiencies are significantly higher.

Because amine absorbents exhibit volatilization, large losses, high corrosivity, and poor thermal degradation in decarburization processes, their application in the CO_2 capture and separation is limited. To improve the compatibility with the membrane materials, amino acid salt solutions are employed in membrane absorption systems (Li et al. 2018c). An amino acid salt solution exhibits the same absorption performance and capacity as an amine absorbent, exhibits a low

Fig. 3 a CO₂ transport in a membrane contactor. The main driving force of the technology is the gas concentration difference. First, CO₂ from the gas mixture reaches the surface of the membrane pore and diffuses through the membrane pores to the gas-liquid two-phase interface. Next, CO2 reacts with the absorbent in the tube side: **b** process flow diagram of gas separation. After the mixed gas is separated by the membrane contactor, the absorbent is subjected to gas-liquid separation treatment to recycle the absorbent. At the same time, the decarburized gas is collected and stored



volatility and good resistance to oxidative degradation and thermal degradation (Fang et al. 2015). Rahim et al. (2015) conducted CO_2 capture experiments with a gas mixture of 10% CO_2 and 90% CH_4 . The experimental results show that the decarburization efficiency of the amino acid salt solution is better than that of the amine solution. Furthermore, Simons et al. (2010) compared the effects of amino acid salt solution and ethanolamine on the decarburization efficiency in a mixed gas (20% $CO_2/80\%$ CH_4). The results reveal that amino acid salt solutions exhibit competitive capability in capturing CO_2 . Moreover, with the rise of nanomaterials, research on the enhancement of CO_2 absorption with nanofluids has gradually emerged.

Nanofluids exhibit high absorption efficiency, absorption capacity, thermal conductivity, and stability (Hajilary and Rezakazemi 2018; Kim et al. 2018). Rezakazemi et al. (2019) selected carbon nanotube and SiO₂ nanofluids for the separation of CO₂. As presented in Fig. 4, the

 CO_2 separation efficiencies of the carbon nanotubes and SiO_2 nanofluids as absorbents are superior to that of water. Taheri et al. (2016) added SiO_2 and Al_2O_3 nanoparticles to a diethanolamine absorbent to form a nanofluid for the decarburization of mixed CO_2/CH_4 gas. The experimental results show that the decarburization efficiency of the $SiO_2/$ diethanolamine nanofluids is 40% higher than that of a pure diethanolamine solution. Furthermore, the decarburization efficiency of Al_2O_3 /diethanolamine nanofluids is increased by 33%. In addition, Zhang et al. (2018a) promotes the CO_2 absorption through nanofluids.

Owing to the low regeneration and absorption rate of a single absorbent, researchers have employed mixed solutions as absorbents and achieved great progresses. Zhang and Shu (2014) compared the reproducibility and CO_2 absorption properties of sodium glycinate and potassium glycinate by adding triethanolamine. The results show that the addition of low triethanolamine concentrations can increase the



Fig.4 Effects of gas flow on CO_2 capture efficiency of different nanofluids. The CO_2 separation efficiencies of the carbon nanotubes (CNT) and SiO_2 nanofluids as absorbents are superior to that of water. Reproduced from (Rezakazemi et al. 2019), with permission from Elsevier

CO₂ absorption capacity. Moreover, Zhang et al. (2014a, b) employed a mixed methyl diethanolamine/N-aminoethyl piperazine solution as absorbent and polypropylene hollow fiber membranes to conduct a comprehensive parametric study on the CO₂ absorption behavior. According to the results, the N-aminoethyl piperazine and methyl diethanolamine mixture has a higher CO₂ absorption capability. Mesbah et al. (2019) developed a mathematical 2D model and used a hollow fiber membrane contactor to separate CO₂ from a CO₂/ CH₄ gas mixture with a mixed solution of 2-methylpiperazine and potassium carbonate as absorbent. They discovered that increasing the 2-methylpiperazine concentration from 0.1 to 0.5 mol/L can significantly improve the CO_2 capture efficiency (up to 98%). Table 3 summarizes the conditions and parameters of the membrane absorption tests conducted in the literature.

According to the previously presented analysis, the mixed solution has a higher absorption efficiency and recycling efficiency when subjected to a decarburization treatment than a single absorbent. This is because the mixed solution can overcome the disadvantages of a single absorbent and concentrates the advantages of different absorbents, thereby improving the absorption efficiency and increasing the absorption capacity.

In summary, the main gas component selected by most researchers is CH_4 , which is also the main component of coalbed methane. Therefore, the previously mentioned research studies are also applicable to coalbed methane decarburization. In practical applications, different

proportions of the solution should be mixed based on the actual needs to achieve a high decarburization efficiency and high reproducibility of the solution.

Effect of gas-phase parameters

The gas-phase parameters mainly include the gas composition, pressure, and flow rate of coalbed methane. These parameters have a great influence on the absorption process of a CO₂ film. Generally, the capture efficiency of CO₂ decreases with increasing gas velocity. However, the mass transfer effect works oppositely. This is because the residence time of the gas phase in the membrane decreases sharply. Hence, the boundary layer of the gas phase becomes thinner gradually, and a part of the CO2 is separated from the membrane contactor before fully reacting with the absorbent, which weakens the capture efficiency. Simultaneously, the increase in gas velocity reduces the resistance of the mass transfer process, thus enhancing the mass transfer effect between the gas-liquid reactions. Lv et al. (2012a) studied the capture efficiency of CO₂ at different flow rates with a polypropylene hollow fiber membrane module. The results show that the capture efficiency decreases with increasing gas flow rate and increases with increasing absorbent flow rate.

Daeho (2018) used a hollow fiber membrane with a countercurrent flow structure to absorb and remove CO₂ from coalbed methane. The composition of the selected coalbed methane in the simulation process was 90% CH_4 and 10% CO₂. According to the numerical simulation results, the purification efficiency of CH₄ is inversely proportional to the change in the gas flow rate. Furthermore, Zhang (2016)simulated the effect of the absorbent flow rate on the CO_2 capture efficiency. The results show that when the gas flow rate increases from 0.28 to 1.40 m/s, the CO₂ capture efficiency decreases by approximately 50%. Yan et al. (2007) obtained similar trends with a potassium glycinate solution. Moreover, Zhang et al. (2019) selected coalbed methane $(14\% \text{ CH}_4/86\% \text{ CO}_2)$ as feed gas and used an alcohol amine solution to decarbonize coalbed methane. The results show that the CO₂ concentration at the membrane outlet increases with increasing gas flow rate. When 0.5 M diethanolamine, ethanolamine, triethanolamine, and 1-(2-hydroxyethyl) pyrrolidine and gas flow rates of 0.3-0.8 m/s are applied, the CO_2 capture efficiency in the membrane decreases by 55.7%, 51.2%, 47.5%, and 59.9%, respectively.

Logically, an increasing system pressure increases the CO_2 concentration in the gas phase. However, with increasing gas pressure, the driving force of the mass transfer process increases. Hence, more CO_2 molecules can enter the gas–liquid interface through a membrane pore and react with the absorbent, which improves the CO_2 capture efficiency (Cozma et al. 2015; Dindore et al. 2004). Mansourizadeh

et al. (2010) used a polyvinylidene fluoride hollow fiber membrane to absorb CO_2 in a mixed gas and analyzed the effect of the gas-phase pressure on the mass transfer. When the CO_2 pressure increases from 1×10^5 to 6×10^5 Pa, the CO_2 flux increases from 1.25×10^{-3} to 6.5×10^{-3} mol/m² s, and the CO_2 capture efficiency increases by 50%. Razavi et al. (2013), Mansourizadeh (2012), and Gao et al. (2018) validated this conclusion in subsequent studies.

The CO_2 content in coalbed methane is generally 10–20%. The higher the CO_2 ratio, the thicker the boundary layer of the gas phase, and the diffusion of a large amount of CO_2 in the membrane pores is hindered, which decreases the total mass transfer coefficient. Simultaneously, parts of the CO₂ and absorbent have not completely reacted and leave the membrane contactor, which results in a decrease in the CO_2 capture efficiency. Zhang (2016) studied the effect of the CO₂ content on the capture efficiency through simulations. When the CO_2 content is increased from 10 to 20%, the decarburization efficiency is reduced by approximately 50%. At constant solubility, the CO₂ amount participating in the permeation reaction remains constant, and the amount of CO₂ increases. Thus, the decarburization efficiency decreases. Yan et al. (2007) and Chen et al. (2004) obtained the same behavior for the efficiency through experimental studies.

The CH₄ content in coalbed methane is 86–97% (Flores and Flores 2014; Mallick and Prabu 2017; Zhang et al. 2019). Because of the low CO₂ content in the initial stage of coalbed methane mining, coalbed methane can be directly burned. However, as the CO₂ content in coalbed methane continues to increase, hydrated solids block the pipeline when low temperatures and high pressures are encountered during the pipeline transportation. To improve the utilization efficiency of coalbed methane and reduce safety hazards in the transportation process, a decarburization treatment is required. As mentioned above, the coalbed methane decarburization efficiency can be improved by increasing the gas-phase pressure, reducing the gas flow rate and the percentage of CO₂ during the coalbed methane decarburization treatment.

Effect of liquid-phase parameters

Liquid-phase parameters play a key role in the improvement in the CO_2 capture efficiency. The effects of the CO_2 capture efficiency on the liquid concentration, flow rate, and temperature are summarized in this section. According to the two-phase theory, the CO_2 absorption mainly occurs in the liquid-phase boundary layer (Lewis et al. 2011). Starting from the shell side, CO_2 enters the liquid-phase boundary layer through the membrane pores and is quickly absorbed by the absorption liquid. As the concentration of the absorbing liquid increases, the concentration of the active component that absorbs CO₂ in the boundary layer of the liquid phase increases. This can increase the chemical reaction rate of CO_2 and the solute dissolved in the liquid phase (Yan et al. 2014a). Hence, the CO₂ concentration in the liquid film is rapidly decreased, and the liquid film resistance is lowered, which improves the CO₂ removal efficiency. Zhang (2016) studied the effect of the changing absorbent concentration on the CO₂ capture efficiency through experiments. The results show that when the concentration of the absorbent increases from 0.1 to 1 mol/L, the CO₂ capture efficiency is increased by 61.8%. Eslami et al. (2011) used numerical models to study the effect of different concentrations of a potassium glycinate solution on the CO₂ capture efficiency in polytetrafluoroethylene hollow fiber membrane contactors. According to their results, when the absorbent concentration is increased from 0.5 to 3 M, the CO₂ capture efficiency is increased by approximately 14%.

With increasing absorbent flow rate, the disturbance of the liquid in the tube is strengthened, the thickness of the boundary layer is reduced, the mass transfer resistance of the liquid phase is reduced, and more fresh absorbents react with the CO_2 molecules. Thus, the decarburization efficiency is improved (Zhang et al. 2019). Zhang (2016) simulated the effect of the absorbent flow rate on the CO₂ capture efficiency. The results show that when the absorbent flow rate increases from 0.015 to 0.085 m/s, the CO₂ capture efficiency increases by approximately 30%. Lv et al. (2012a) used 0.5 mol/L ethanolamine to capture CO₂ with polypropylene hollow fiber membranes. The effect of the liquidphase flow on the absorption performance for 8-46 mL/min was studied at a constant feed gas flow. The results show that when the liquid-phase flow rate is increased, the CO₂ capture efficiency increases by 49%. This conclusion has been verified in subsequent studies (Ansaripour et al. 2018).

In addition to increasing the flow rate of the absorbent, increasing the absorbent temperature helps to increase the CO_2 absorption efficiency (Eslami et al. 2011; Yan et al. 2007). Shirazian et al. (2009) compared the decarburization rate of an absorbent at 298 K and 288 K. The decarburization rate increases by approximately 10% with the increase in temperature. Moreover, Mansourizadeh et al. (2010) studied the effect of absorbent temperature on CO_2 capture efficiency. When the absorbent temperature was increased from 283 to 313 K, the CO_2 mass transfer rate was increased by approximately 58.6%. Wu et al. (2012) studied the effect of changes in the absorbent temperature on the CO_2 capture efficiency and mass transfer rate. When the absorption temperature is increased from 298 to 325 K, the CO_2 capture rate and mass transfer rate are increased by 30% and 40%, respectively.

According to the previous analysis, increasing the concentration, flow rate, and absorbent temperature can improve the CO_2 capture efficiency. However, owing to the required temperature control for the membrane material in

the membrane contactor while the absorbent temperature is being changed, the actual material characteristics should be controlled to maximize the capture efficiency.

Effect of membrane contactor structure

At present, there is no study focusing on the effect of the membrane contactor structure on the CO_2 capture from coalbed methane. The main components of coalbed methane and natural gas are CH_4 and CO_2 , whereas the main components of flue gas are N_2 and CO_2 . Although their compositions are slightly different, the common essence is the removal of CO_2 from the mixture. The research on the impact of membrane contactor structures on CO_2 removal from flue gas is relatively mature which provides guidelines in the CO_2 separation from coalbed methane. Figure 5 presents the structure of a hollow fiber membrane contactor (Zhang 2015).

Changes in the wall thickness of the fiber membrane affect the direction of the gas movement. Furthermore, increasing the wall thickness prolongs the residence time of the gas in the membrane, thereby increasing the resistance along the path, which makes the diffusion movement more complicated and leads to a decrease in the decarburization efficiency (Rezakazemi et al. 2011). Yan et al. (2015b) studied the effect of the fiber wall thickness on the CO₂ capture efficiency. The results show that the CO₂ capture efficiency decreases with increasing wall thickness. Furthermore, the decarburization efficiency is reduced by approximately 40% owing to the weak reaction between diethanolamine and CO₂. Rezakazemi et al. (2011) reported the same conclusions.

Increasing the effective length of the fiber membrane increases the gas-liquid contact area, which results in a prolonged residence time of the gas in the membrane. Consequently, the CO_2 capture process in the gas is enhanced.

Boributh et al. (2011) selected three different membrane lengths (0.25 m, 0.5 m, and 0.7 m) to compare their CO_2 capture efficiencies. The results show that the decarburization efficiencies for a membrane length of 0.7 m increase by 15.27% (0.25 m) and 3.58% (0.5 m), respectively.

Reducing the inner diameter of the fiber membrane increases the flow rate of the absorbent, which results in an increase in the CO₂ absorption per unit time and in an improvement in the CO₂ capture efficiency. Rajabzadeh et al. (2009) studied the effect of a changing inner membrane diameter on the CO₂ capture efficiency. According to the results, the capture efficiency increases with decreasing inner membrane diameter because the gas-liquid two-phase contact area increases with increasing number of hollow fiber membranes. This results in an increase in the packing density and shell-side mass transfer coefficient. Eslami et al. (2011) investigated the effects on the CO₂ capture efficiency for a liquid flow rate of 0.1 m/s, an absorbent concentration of 0.5 mol/L, and increasing number of hollow fiber membranes from 3000 to 10,000. As a result, the capture efficiency increases from 36 to 100%. Furthermore, Faiz and Almarzougi (2010) used a membrane contactor to remove CO₂ from natural gas under high pressure. The results show that the capture efficiency increases with increasing porosity and decreases with increasing tortuosity factor.

According to the previous analysis, to ensure the overall performance of the membrane module, reducing the wall thickness of the membrane, the inner diameter, and tortuosity factor and increasing the number of membranes, porosity, and effective membrane length are beneficial to the CO_2 capture. The CO_2 capture from coalbed methane through membrane contactor structures will be the future research direction.



Fig. 5 Schematic of hollow fiber membrane contactor. The components of the membrane contactor and the direction of gas-liquid flow can be clearly seen from the structural drawing. Reproduced from Zhang (2015)

Effects of other conditions

In addition to the previously mentioned factors, the connection mode of the membrane module, the direction of the gas–liquid flow, and the fluidity have a certain influence on the CO_2 capture efficiency. Zhang et al. (2019) studied the effect of a single component and series of components on the CO_2 capture efficiency in coalbed methane. According to the results, the decarburization rate of the serial module is evidently better than that of the single module. This is mainly due to the increase in the number of membrane modules, which leads to an increase in the effective membrane length and an increasing gas–liquid contact area and gas–liquid residence time in the membrane. This indirectly strengthens the mass transfer process between the two phases and improves the decarburization efficiency.

Boributh et al. (2011) compared the effects of single, serial, and parallel connection methods on the CO₂ capture efficiency. The results show that the best absorption performance can be obtained with a serial connection. Moreover, Zhang et al. (2018b) studied biogas (40% $CO_2/60\%$ CH_4) CO₂ separation and CH₄ purification in a membrane contactor with an amine solution. By comparing the effects of single membrane module and membrane modules in series on the decarburization efficiency under equal conditions, they proved that the CO₂ separation efficiency and CH₄ purification efficiency increase by 24.4% and 9.8% with serial membrane modules, respectively. Simultaneously, they concluded that the efficiency of the countercurrent state increases by 38.9% and 25.6% compared with that of the downstream state, respectively. The previously mentioned studies demonstrate that the countercurrent flow mode can improve the CO_2 capture efficiency owing to the influence of the driving

force. Therefore, the countercurrent flow mode is currently mainly employed in membrane absorption systems.

The fluidity is mainly described by a laminar flow or turbulent flow. A gas-liquid contact is more sufficient owing to severe disturbances of the turbulences, which enhance the mass transfer between the gas and liquid phases, thus promoting the separation of CO_2 . This has been confirmed in Zhang et al. (2014a, c). In summary, the coalbed methane decarburization efficiency can be improved through a membrane module and countercurrent flow. The effects of different factors on CO_2 capture efficiency are summarized in Table 4.

Membrane absorption applied to other gases

Qi and Cussler (1985) first proposed a method for absorbing CO_2 with hollow fiber polypropylene (PP) membrane contactors. The method is widely applied because of its large gas-liquid contact area, fast mass transfer rate, no mist entrainment phenomenon, large operation flexibility, and small equipment. With the development of the membrane absorption technology in recent years, many research studies on the membrane absorption technology based on hollow fiber membranes have been conducted in China. Figure 6 presents the various application of CO_2 separation from different gases.

As the main source of CO₂, flue gas accounts for approximately 80% of the greenhouse gases (Sutanto et al. 2017). The main components of the flue gas are CO₂ and N₂, and the CO₂ ratio is generally between 10 and 20 vol% (Masoumi et al. 2016; Zhang 2016). Therefore, capturing CO₂ from flue gas is an effective method to control CO₂ emissions. At present, the membrane absorption method is relatively mature

Fig. 6 Application of membrane separator for CO_2 separation in different gases. The membrane separation method can be applied to a variety of gas decarburization treatments. The process of gas–liquid two-phase absorption in the contactor is also shown



in the flue gas decarburization research field. Many studies have been carried out using the membrane absorption method to remove CO_2 from flue gas (Chen and Cui 2012; Lee et al. 2019). Because the emitted flue gas has a relatively high temperature, a high-temperature-resistant membrane material is required for the membrane absorption. Therefore, to remove CO₂ from flue gas through the membrane absorption method, future research will focus on the development of new high-temperature-resistant membrane materials.

China is a coal energy-consuming country, and energy shortages and environmental pollution will seriously hinder the sustainable development of the society (Medeiros et al. 2013). At present, natural gas is the fastest growing energy source in the world. However, natural gas contains acid gases such as CO_2 , which not only cause serious air pollution but also accelerate the corrosion of pipelines and equipment. Furthermore, CO2 reduces the calorific value of natural gas and increases transportation costs (Knoope et al. 2013). Therefore, natural gas must be purified to ensure the safety of natural gas storage, transportation, and use. The membrane absorption method is a process based on the combination of a conventional absorption method and membrane separation. The method does not require high precision and complicated operations of packed columns and an absorption tower when the CO_2 is removed and enables highly efficient decarburization. Therefore, it is considered as a potential candidate that can be developed for natural gas purification (Fu et al. 2012). Many studies have been carried out on this technology (Faiz and Al-Marzouqi 2011; Kang et al. 2017; Rahim et al. 2015; Tang et al. 2014). However, owing to the high pressures required for the decarburization process of natural gas, the membrane absorption method suffers from many technical problems in the decarburization treatment. The membrane material has high requirements under high pressures, which might decrease the anti-wetting property of the membrane material. Thus, research on membrane materials with high-pressure resistances and anti-wetting properties would promote natural gas decarburization.

In response to the growing energy crisis, biogas is currently considered as a renewable energy source that can replace traditional fossil fuels (Amrei et al. 2014; Li et al. 2018c). The main components of biogas are CO_2 and CH_4 , and the CO₂ content is generally between 25 vol% and 55 vol% (Scholz et al. 2013). However, initial biogas contains much CO_2 . Thus, the direct use will reduce the calorific value of biogas. It is essential to decarbonize biogas to improve its efficiency and make it a substitute for natural gas. Because membrane absorption exhibits a high decarburization efficiency, many researchers have used this technology to study biogas decarburization (Sutanto et al. 2017; Yan et al. 2014a, b, 2015a; Zhang et al. 2014c). However, the biogas phase has a higher CO₂ content than coalbed methane and natural gas. Hence, the continuous

Table 1 Comparisons of m	sthods for CO_2 capture (Zhang et al. 2017)		
Methods	Characteristics	Benefits	Drawbacks
Solvent absorption	It separates the components with the highest solubilities from a mixture with a liquid absorbent	Low demand for equipment; low operating cost; low capital investment; high-purity products	Slow absorption; slow regeneration rate
Pressure swing adsorption	The selective adsorption of a separated gas mixture through adsorbents under different partial pressures	Mature technology; low demand for equipment; low operating costs; high methane recovery rate	High energy consumption; strong dependence
Cryogenic distillation	It includes a mechanical method to liquefy the gas and exploits the difference in the gas boiling points to conduct the rectification	Mature technology; high-purity products; high methane recovery rate	High energy consumption; large investment; complex equipment; strong limitations; small scale
Hydrate separation	It exploits the different pressures of the gas components in the mixture to form hydrates in a solution and achieve the separation	High storage density; convenient transportation; simple process; oxygen-free products	High operating pressure; high safety risk; poor economy; low methane recovery rate
Membrane absorption	It has large gas-liquid contact area, fast mass transfer rate, high operational flexibility, no liquid ubiquity and mist entrainment, and simple equipment	Low energy consumption; low operating costs; no secondary pollution	Easy to block; easy to damage; short service life

research and development of high-efficiency absorbents to improve the biogas decarburization efficiency will become a research hot spot in the future.

The main emissions of ships include CO₂, NOx, SOx, CO, hydrocarbons, and particulate matter (Eyring 2005a). Emissions from ship exhaust increase the SO₂ concentration in the atmosphere, which directly harms humans, marine life, and the stability of the entire ecosystem. Because the international community's requirements for environmental protection have increased, ship exhaust emission standards have become more stringent (Eyring 2005b). Owing to the limitations of narrow space in ship exhaust treatment, it is difficult to achieve flexible operation by traditional capture methods. By contrast, the membrane absorption methods are more suitable owing to their unique advantages (large gas-liquid contact area, flexible installation and operation, and simple equipment). At present, membrane absorption is applied to the SO₂ capture from ship exhaust. Qiu et al. (2019) studied the optimization of the microstructures and geometries of hydrophobic ceramic membranes for SO₂ absorption from ship exhaust gases. According to the results, the optimized efficiency can be increased by 16%, and the optimal film thickness and inner film diameter are 1.0 mm and 4.0-6.0 mm, respectively. So far, no scientific article has mentioned the use of membrane absorption to remove CO₂ from ship exhaust gas. This will be the future development direction of the membrane absorption technology.

Conclusion

The membrane absorption method for coalbed methane decarburization is a key technology related to the application prospects of coalbed methane. A variety of separation techniques have been applied for coalbed methane decarburization. The membrane absorption method has the advantages of large gas–liquid contact areas, fast mass transfer rates, no mist entrainment phenomenon, a large operation flexibility, and small equipment. It has been widely applied for CO_2 capture in flue gas, biogas, and natural gas. Although the gas composition and content of coalbed methane are different from those mentioned previously, the decarburization processes are similar. Therefore, we have summarized research studies with different CO_2 and CH_4 mixing ratios. The following conclusions can be drawn:

- 1. Increasing the temperature, concentration, and flow rate of the absorbent during the membrane absorption process and reducing the gas flow rate have a positive effect on the coalbed methane decarburization efficiency.
- 2. The newly applied solvents (e.g., amino acid salts and nanofluids) exhibit high decarburization efficiencies as absorbents. Furthermore, single absorbents can be mixed to achieve a better decarburization effect.
- 3. By changing the structure of the membrane contactor (e.g., increasing the effective membrane length and reducing the membrane wall thickness and membrane inner diameter), the CO_2 can entirely react with the absorbent, which improves the CO_2 capture efficiency.
- 4. The CO₂ capture can be improved by changing the gasliquid flow state and flow direction, such as the flow state of the countercurrent and turbulent flow in the decarburization process.

At present, the membrane absorption method has good application prospects for purification treatments of coalbed methane, flue gas, natural gas, biogas, and ship exhaust. However, unresolved technical problems make large-scale industrial applications impossible and require further research. Based on the current and possible future applications of the membrane absorption technology to achieve large-scale applications, the following recommendations are given:

 At present, the membrane absorption method mainly uses the simulated gas component for CO₂ separation. However, because acid gases such as H₂S and SO₂ can still interfere with the experimental results in the actual

Table 2 Development of absorbent usage for membrane absorption

Absorbent	Benefits	Drawbacks	References
Water	Rich in resources and pollution-free	Low absorption efficiency	Marzouk et al. (2010)
Alkali	High absorption efficiency, large capacity	Strongly corrosive and non-renewable	Lin and Chu (2015)
Inorganic salt	Large absorption capacity and renewable	High-resolution energy consumption	Li et al. (2018c)
Amine	Fast chemical reaction rate, mature technology	Corrosive, high-resolution energy consumption	Amrei et al. (2014)
Amino acid salt	Good compatibility with membrane, non-toxic, strong thermal stability	Poor regeneration	Fang et al. (2015)
Nanofluids	Large specific surface area and surface activity, high absorption efficiency and stability	High equipment requirements and low output	Kim et al. (2018)

Table 3 Membrane absorption test conc	ditions and parameters			
Absorbent	Gas component	Membrane material	Comment	References
Potassium carbonate	5% CO ₂ , 5% H ₂ S, 90% CH ₄	Polypropylene	A scheme of two membrane modules in series was recommended for the simultaneous absorption of CO ₂ and H ₂ S	Faiz and Al-Marzouqi (2011)
Ethanolamine	10% CO ₂ , 10% H ₂ S, 80% CH ₄	Polyvinylidene fluoride, polypropylene	The wetting effects on the decarburiza- tion efficiency of polypropylene and polyvinylidene fluoride membranes were investigated	Faiz and Al-Marzouqi (2009)
Water, diethanolamine, ethanolamine, sodium hydroxide, triethylenetet- ramine	9.5% CO ₂ , 90.5% CH ₄	Polytetrafluoroethylene	Novel design of hollow fiber mem- brane modules suitable for high- pressure operations	Marzouk et al. (2010)
Diethanolamine, diethylenetriamine, ethylenediamine, ethanolamine, tetraethylenepentamine, triethylene- tetramine, water, sodium hydroxide	10% CO ₂ , 90% CH ₄	Polypropylene, silicon rubber	Three different membrane modules were used in this study; the poly- propylene module exhibited the best performance in terms of CO ₂ flux	Al-Marzouqi et al. (2009)
Sodium hydroxide, diethanolamine, potassium carbonate	5% CO ₂ , 95% CH ₄	Tetrafluoroethylene and ethylene copolymers	First report on the long-term opera- tional stability of HFM modules under industrial conditions	Al-Marzouqi et al. (2016)
Ethanolamine, sodium hydroxide	10% CO ₂ , 90% CH ₄	Polypropylene	A comprehensive mathematical 2D model was developed and combined with the chemical absorption for CO ₂ absorption	Al-Marzouqi et al. (2008)
Methyl diethanolamine	45-70% CO ₂ , 55-30% CH ₄	Polyvinylidene fluoride	Capture of high CO ₂ concentrations from natural gas with high-pressure membrane contactors	Kang et al. (2017)
Water, sodium hydroxide, ethanola- mine, sodium chloride	20% CO ₂ , 80% CH ₄ , 50% CO ₂ , 50% CH ₄	Polyvinylidene fluoride	The experiments were performed in a membrane contactor constructed with (0.2 µm pore size) micropo- rous polyvinylidene fluoride hollow fibers. Sodium chloride was used as an additive in the sodium hydroxide aqueous solution	Atchariyawut et al. (2007)
Ethanolamine	15% CO ₂ , 85% CH ₄	Polytetrafluoroethylene	The membrane mass transfer resist- ance calculated with the Wilson plot method predicted the CO_2 concentra- tion profile with a higher accuracy than the theoretical method	Khaisri et al. (2010)
Water, triethanolamine, diethan- olamine, ethanolamine, potassium argininate	40% CO ₂ , 60% CH ₄	Polypropylene	A mass transfer model for the CO ₂ absorption from biogas to potassium argininate solutions was developed	Zhang et al. (2014c)

Table 4	Summary	of the	influence	of	different	factors	on	CO_2	capture	efficiency
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Influencing factor	Effect on CO ₂ capture efficiency	References			
Gas phase					
CO ₂ content	A higher CO_2 concentration results in a decrease in the CO_2 capture efficiency	Yan et al. (2007), Zhang (2016)			
Pressure	Increasing gas pressure improves the CO ₂ capture efficiency	Cozma et al. (2015), Dindore et al. (2004), Gao et al. (2018)			
Flow rate	The capture efficiency of $\rm CO_2$ decreases with increasing gas velocity	Daeho (2018), Yan et al. (2007), Zhang (2016)			
Liquid phase					
Concentration	As the liquid concentration increases, the CO_2 removal efficiency is improved	Eslami et al. (2011), Lewis et al. (2011)			
Flow rate	With increasing the absorbent flow rate, the CO ₂ cap- ture efficiency is improved	Ansaripour et al. (2018), Zhang et al. (2019)			
Absorbent temperature	When increasing absorbent temperature, the CO ₂ capture efficiency increases	Mansourizadeh and Matsuura (2010), Shirazian et al. (2009)			
Membrane contactor structure					
Membrane thickness	Increasing the membrane thickness leads to a decrease in the CO_2 capture efficiency	Rezakazemi et al. (2011)			
Module length	Increasing the effective length of the fiber membrane increases the CO_2 capture efficiency	Boributh et al. (2011)			
Inner diameter	Reducing the inner diameter of the fiber membrane results in an improvement in the CO_2 capture efficiency	Eslami et al. (2011, Rajabzadeh et al. (2009)			
Other conditions					
Gas-liquid flow direction	The countercurrent flow mode can improve the $\rm CO_2$ capture efficiency	Zhang et al. (2018b)			
Fluidity	Turbulent flow can promote the CO ₂ capture efficiency	Zhang et al. (2014a)			
Module number	A serial connection improves the CO_2 capture efficiency	Boributh et al. (2011), Zhang et al. (2019)			

gas composition, the influence of these interference factors on the degassing effect of the actual gas must be considered for more realistic simulation results.

- 2. The research on high-efficiency absorbents should focus on the absorption characteristics of novel amino acid salt solutions and nanofluids in membrane contactors owing to their higher chemical reaction rates and absorption efficiencies and because they are environmentally friendly, thermally stable, and membrane coated.
- 3. When developing a membrane absorption model, the model should be continuously optimized based on the differences in the absorbents, membrane materials, and other influencing factors. Furthermore, the kinetics and thermodynamics of the reaction of new absorbents with CO_2 should be strengthened. Further comprehensive analyses should be conducted to optimize the conditions and maximize the CO_2 absorption efficiency.
- 4. Expanding the application field of the CO_2 absorption through the membrane absorption method: Ship exhaust contains much CO_2 . However, at present, researchers do not focus on the capture of CO_2 from ship exhaust through membrane absorption.

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