Research progress of CO_2 separation technology by solvent absorption

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Abstract. The combustion of fossil fuels emits a large amount of CO_2, which causes the greenhouse effect and leads to global warming and poses a serious threat to life on earth. CO_2 capture technology can effectively reduce the concentration of CO_2 in the atmosphere, alleviate the greenhouse effect, and improve the environment. CO_2 capture technologies include absorption, membrane separation and adsorption separation, among which chemical absorption and separation have the advantages of high efficiency, low cost and easy availability of materials. In this paper, the advantages and disadvantages of three main chemical absorption and separation methods (inorganic reagents, organic amines and ionic liquids) adsorb CO_2 are summarized. Among inorganic adsorbents, $NH_3 \cdot H_2O$ can achieve rapid and efficient absorption of CO_2, and it is relatively stable and not easy to degrade. Common types of organic amine adsorbents are monoethanolamine, methanolamine, and sterically hindered amine. However, it is difficult for a single organic amine adsorbent to meet the requirements of high absorption rate, high absorption capacity and low reaction heat at the same time. Therefore, mixing organic amine absorbents with different characteristics can improve their performance in absorbing CO_2. Ionic liquids have the advantages of good thermal stability, very low saturation vapor pressure, and designable structure, and are a new type of CO_2 adsorbent, but ionic liquids have high viscosity themselves. Combining ionic liquids with organic or inorganic porous materials to form loaded ionic liquid materials, which can be used as CO_2 adsorbent not only to improve the separation effect, but also to avoid the problem of high viscosity caused by direct absorption of ionic liquids, thus improving CO_2 adsorption efficiency.

1. Introduction

With the continuous development of China's economy, the consumption of energy has been increasing, and the total primary energy consumption in China reached 4.3 billion tce in 2015, of which fossil energy accounted for 88%. The burning of large amounts of fossil fuels makes China the country with the largest carbon emissions at present, which reached 9.1 billion tce in 2015, accounting for 27.3% of the world's total [1]. The emission of large amounts of CO_2 causes the greenhouse effect, leading to global warming, glacier melting, sea level rise, and precipitation change, which will eventually pose a serious threat to life on Earth. How to effectively control and reduce CO_2 emissions while maintaining economic development and energy demand, so as to achieve a "win-win" situation of sustainable economic development and environmental protection, has become a serious issue for mankind [2]. At the 75th session of the United Nations General Assembly, President Xi Jinping made a major announcement to the world that China will strive to peak its CO_2 emissions by 2030 and achieve carbon neutrality by 2060.

In order to achieve carbon peaking and carbon neutralization, our current goal is to reduce CO_2. CO_2 reduction methods include improving energy efficiency, carbon capture, utilization and storage (CCUS), and Clean energy substitution, etc. Currently, CCUS technology is considered to be one of the most important technologies to control greenhouse gas emissions in the short term [3].CO_2 capture technologies include absorption, membrane separation, and adsorption separation. Adsorption separation is divided into two aspects: physical adsorption and chemical adsorption, and chemical absorption separation has the advantages of high efficiency, low cost, and easy availability of materials. The absorbent is the core of chemical absorption method to remove CO_2. The ideal CO_2 absorber should have the characteristics of fast absorption rate, high absorption capacity, and low energy consumption for regeneration, as well as the characteristics of safety and stability, environmental friendliness, low corrosion of equipment, and good economy [1]. In this paper, the advantages and disadvantages of three main chemical absorption

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separation methods (inorganic reagents, organic amines and ionic liquids) for CO_2 adsorption are summarized in order to provide a reference for the subsequent chemical absorption separation of CO_2.

2. Chemical absorbents

Commonly used chemical absorbents include inorganic reagents, organic amines and ionic liquids, etc. Their main types and advantages and disadvantages of CO_2 absorption are shown in Table 1. They are introduced separately below.

Table 1 Chemical absorbents and their advantages and disadvantages

Chemical absorbent	Type	advantages	disadvantages
Inorganic adsorbent	$Ca(OH)_2$、K_2CO_3、Na_2CO_3、$NH_3{\cdot}H_2O$, etc.	Low cost, non-volatile	Some reagents have low solubility and slow absorption rate
Organic amine adsorbent	Monoethanolamine, methanol amine, sterically hindered amine, etc	Fast absorption rate, strong absorption capacity, high selectivity and removal efficiency, low solvent consumption	High energy consumption, easy foaming and degradation
Ionic liquid	Cations: imidazole, pyridine, pyrrolidine, quaternary amines and quaternary phosphorus ions, etc.; Anions: halogens, boric acids, carboxylic acids and amino acid ions, etc.	Good thermal stability, extremely low saturated steam pressure, and designable construction	High cost, high viscosity

2.1 Inorganic adsorbents

Commonly used CO_2 inorganic adsorbents are $Ca(OH)_2$, K_2CO_3, Na_2CO_3 and $NH_3{\cdot}H_2O$, etc. $Ca(OH)_2$ reacts quickly with CO_2 at room temperature to 750°C, the concentration of Ca(OH)2 solution affects the absorption of CO_2, and saturated $Ca(OH)_2$ solution can absorb more CO_2 than the theoretical amount. However, $Ca(OH)_2$ preparation energy consumption is high, and the preparation process will release CO_2 to limit the application of this method. K_2CO_3 is low cost, non-volatile, less toxic and less degradable than organic amines. However, at low temperatures, the solubility of K_2CO_3 is low, resulting in a slow absorption rate of CO_2. In addition, the KHCO3 generated by the reaction of K_2CO_3 and CO_2 is highly corrosive, and some corrosion inhibitors need to be added, such as V_2O_5, As_2O_3, etc. $NaCO_3$ is generally used to absorb carbon dioxide from the flue, and the purity of carbon dioxide absorbed by this method is very high, up to 99%. The disadvantage is that the cost is too high and the water consumption is serious. $NH_3{\cdot}H_2O$ achieves fast and efficient absorption of CO_2, and is relatively stable and not easily degraded. In addition, The products produced by $NH_3{\cdot}H_2O$ and CO_2 can be used as scrap[4].

In addition to the commonly used inorganic adsorbents for CO_2, there are also some new inorganic adsorbents, Lixia Yang et al. prepared a series of sodium-magnesium complex salt materials for CO_2 uptake using sodium carboxymethyl cellulose as a crystal guiding agent, and it was found that the CO_2 saturation uptake of homogeneous layered sodium-magnesium complex salt was 22.8%. And this reagent has good cycling stability and high potential for industrial application [2].

2.2 Organic amine adsorbents

The common types of organic amine adsorbents include monoethanolamine, methanolamine, and sterically hindered amine, etc. Monoethanolamine (MEA) is a primary amine that is highly alkaline and can react quickly with CO_2 to form a carbamate compound, and when heated, the carbamate will decompose to desorb CO_2. Monoethanolamine has the advantages of fast absorption rate, high absorption capacity, high selectivity and removal efficiency, and low solvent consumption, but CO_2 desorption requires high temperature and therefore high energy consumption, in addition, monoethanolamine is prone to foaming and degradation, and the addition of organic solvents and active agents to the solution can solve these problems [5]. Methyl diethanolamine (MDEA) has good chemical stability, the solvent is not easily degraded, and the absorption volume is large, but the absorption time is long.MEDA plays a catalyst-like role in the absorption of CO_2, but when reacting with CO_2, MEDA must be hydrolyzed before slowly reacting with CO_2 and generating sub-stable bicarbonate, which can lead to a slower absorption rate of MDEA, which is its biggest defect. and some additives can be added to MEDA to speed up its reaction rate. In addition, sterically hindered amine (AMPs) have also attracted attention. These organic amine molecules are characterized by at least one amino group connected to a secondary or tertiary carbon atom in their structure, which makes them have a space-site hindering effect, resulting in unstable carbamates and easy to react with H_2O to form amines and HCO_3^-. Therefore, it is relatively easy to desorb CO_2 after absorption of sterically hindered amine, and their maximum theoretical absorption capacity of CO_2 is 1 molCO_2/mol absorber [6].

Because a single organic amine absorbent is difficult to meet the requirements of high absorption rate, high absorption capacity and low reaction heat. Therefore, mixing organic amine absorbents with different characteristics can improve their performance in absorbing carbon dioxide. The main idea is to absorption rate higher than primary amine or secondary amine as the main body, adding other amines to reduce regeneration energy consumption and improve the overall performance of the absorbent. For example, the addition of MDEA in MEA aqueous solution can significantly reduce the regeneration energy consumption of CO_2 capture [1]. In addition, the mixture of organic amines and alcohols can also improve the CO_2 capture capacity. For example, Sha et al.prepared a butanediol-ethylenediamine system and found that CO_2 can be rapidly activated and converted into a solid CO_2 storage material (CO_2SM) under mild conditions. When the butanediol-ethylenediamine mixed solvent system absorbs CO_2 at 20 °C and desorbs CO_2 at 98.6 °C, the solution has no obvious loss and is considered to be green, efficient and low-cost method for carbon dioxide capture and utilization [7].

In recent years, some CO2 absorption demonstration project using chemical solvents method were built in China (Table 2), their CO2 adsorption capacity is in the range of 60000-1000000 t/a.

Table 2. CO_2 absorption demonstration project using chemical solvents method in China [8]

Project	Location	Scale (t/a)
National Energy Group Jinjie Power Plant Carbon Capture Project	Shanxi Province	150000
Shanghai Shikou Carbon Capture Project of China Huaneng Group	Shanghai	120000
Demonstration project of CO_2 capture and oil displacement in Shengli Oilfield	Shandong Province	1000000
Sinopec Zhongyuan Oilfield CO_2-EOR Project	Henan Province	100000
Xinjiang Dunhua Company Project	Xinjiang	60000

2.3 Ionic liquids

The ionic liquid is a room-temperature molten salt composed of anions and cations [9], the cations mainly include imidazole, pyridine, pyrrolidine, quaternary amine and quaternary phosphorus ions, and the anions are mainly halogen, boric acid, carboxylic acid and amino acid ions. Ionic liquids have good thermal stability, extremely low saturation vapor pressure, and a designable structure. The environmental pollution caused by volatilization is small, and it is easy to be separated from other substances for recycling. Ionic liquids capture CO_2 mainly through its basic group directly capturing CO_2 [10]. The special properties of ionic liquids make them promising for a wide range of applications in CCUS, for example, Lv et al. based on the preparation of ionic liquids [C2OHmim] [Gly] containing multiple amine sites, which have good thermal stability, regenerability and oxygen tolerance, and 1 mol of this ionic liquid can trap 0.575 mol of CO2 [11]. The CO2 adsorption capacity of some other ionic liquids is illustrated in Figure 1[12]. In addition, temperature and pressure affect the solubility of CO2 in ionic liquids, the solubility of CO_2 increases with increasing pressure and decreases with increasing temperature. The type of anion in the ionic liquid also significantly affects the solubility of CO_2. SHARMA et al. found that the order of CO_2 absorption capacity of different ionic liquids is: BF_4^-<DCA^-<PF_6^-< TfO^-<Tf_2N^-[13].

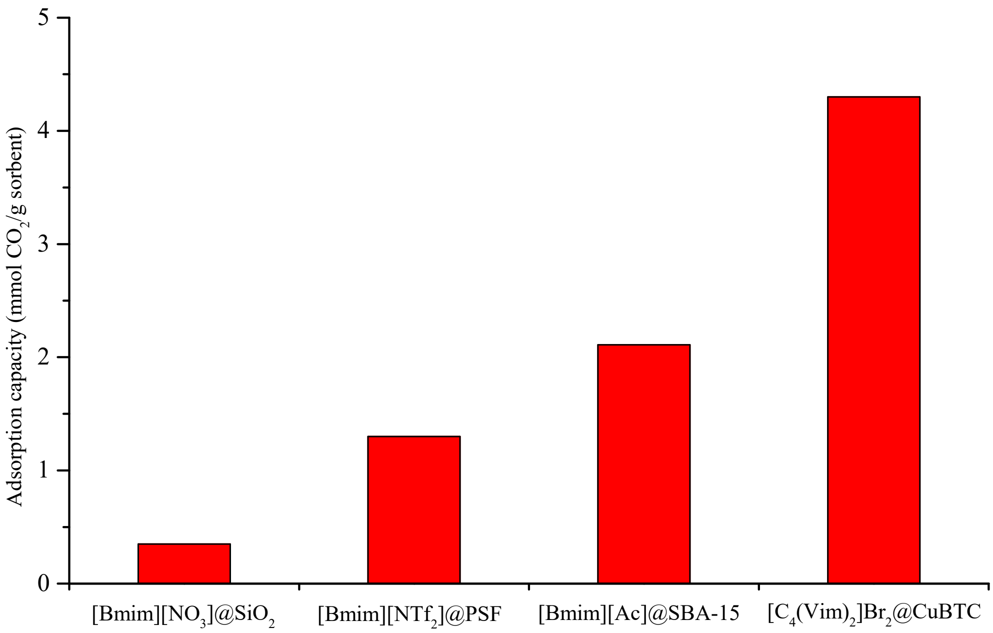

Figure 1. CO_2 adsorption capacity of some ionic liquids

However, the high viscosity of ionic liquids themselves and the formation of hydrogen bonding network structure of ionic liquid-CO_2 system during the absorption process further increases the viscosity. For example, the viscosity of amino acid ionic liquids increases by about 15-30 times after absorbing CO_2 [14], which limits the application of ionic liquids in absorption and separation. In order to solve the above problems, ionic liquids have been combined with organic or inorganic porous materials to form loaded ionic liquid materials, which have the advantages of both ionic liquids and porous materials, As a CO_2 adsorbent, it can not only improve the separation effect, but also avoid the high viscosity problem caused by the direct absorption of ionic liquids, thereby improving the CO_2 adsorption efficiency [15]. Dong et al.loaded two ionic liquids on type A and type B silica gel by impregnation method to investigate the effects of different influencing factors (silica gel type and activation temperature, ionic liquid type and loading, adsorbent pore size distribution) on CO_2 adsorption efficiency. It was found that the obtained adsorbents all had well-developed microporous structures with pore diameters of 0.4-0.8 nm, and the loaded samples had better CO_2 adsorption performance of 3.68% (mass fraction) when the type A silica gel was activated at 500°C and the amount of [bmim]PF6 was 20% [16]. In addition, the method of combining ionic liquid with membrane separation can also improve its CO_2 adsorption performance. This method can greatly reduce the amount of ionic liquid and reduce the complexity and cost of ionic liquid preparation to a certain extent. It also overcomes the disadvantage of slow diffusion of CO_2 in ionic liquids. Vollas et al. developed pyridine-based polyionic liquid composite membranes, and when the mass fraction of ionic liquids was at 45% mass fraction of ionic liquid, the CO_2 flux of the polyionic liquid composite membrane was 11.8 barrer and the CO_2/CH_4 selectivity was 35, and the separation performance was significantly better than that of the pure membrane [17].

3. Conclusion and outlook

The chemical absorption separation method for CO_2 capture has the advantages of high efficiency, low cost and easy availability of materials. This paper summarizes the advantages and disadvantages of three main chemical absorption separation methods (inorganic reagents, organic amines and ionic liquids) for CO_2 adsorption. Commonly used inorganic adsorbents for CO_2 are $Ca(OH)_2$, K_2CO_3, Na_2CO_3 and $NH_3 \cdot H_2O$, among which $NH_3 \cdot H_2O$ can achieve rapid and efficient absorption of CO_2 and is relatively stable and not easily degraded. The common types of organic amine adsorbents are monoethanolamine, methanolamine, sterically hindered amine, etc. However, it is difficult for a single organic amine adsorbent to meet the requirements of high absorption rate, high absorption capacity and low reaction heat at the same time. Therefore, mixing organic amine absorbents with different characteristics can improve their performance in absorbing CO_2. Ionic liquids have the advantages of good thermal stability, very low saturation vapor pressure, and designable structure, and are a new type of CO_2 adsorbent. However, ionic liquid has high viscosity, Combining ionic liquids with organic or inorganic porous materials to form loaded ionic liquid materials, which can be used as CO_2 adsorbent not only to improve the separation effect, but also to avoid the problem of high viscosity caused by direct absorption of ionic liquids, thus improving CO_2 adsorption efficiency.

In general, single organic amines have limited CO_2 absorption capacity, and mixed amine absorbers can combine the advantages of multiple single absorbers, thus having higher absorption capacity and absorption rate as well as lower regeneration energy consumption. However, there are still more problems, such as absorber stability and process system development, which need further research. In addition, the current types of loaded ionic liquids are mainly conventional ionic liquids and amino and carboxylic acid functional ionic liquids, which are limited in variety and are mainly based on single-site interaction with CO_2. In the future, these ionic liquids need to be combined with emerging materials to develop more types of loaded ionic liquids to meet the efficient adsorption and separation of CO_2. Meanwhile, the mechanism of interaction between loaded ionic liquids and CO_2 is still unclear, and more characterization tools are needed to probe the microstructure and macroscopic properties of loaded ionic liquids and to understand the interaction between loaded ionic liquids and CO_2, so as to provide theoretical guidance for the design and preparation of loaded ionic liquids for CO_2 adsorption.

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