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Recent enlightening strategies for co_2 capture: a review

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Abstract. The global climate change has seriously affected the survival and prosperity of mankind, where greenhouse effect owing to atmospheric carbon dioxide (CO_2) enrichment is a great cause. Accordingly, a series of down-to-earth measures need to be implemented urgently to control the output of CO_2. As CO_2 capture appears as a core issue in developing low-carbon economy, this review provides a comprehensive introduction of recent CO_2 capture technologies used in power plants or other industries. Strategies for CO_2 capture, e.g. pre-combustion, post-combustion and oxyfuel combustion, are covered in this article. Another enlightening technology for CO_2 capture based on fluidized beds is intensively discussed.

1. Introduction

Energy is a major foundation for a country's economic development. Now 90% of global energy consumption comes from fossil fuels [1]. However, the excessive utilization of fossil fuels has led to accumulation of greenhouse gases, which contribute to global warming. Global warming will lead to the rise of sea levels and the ablation of glaciers. It will not only break ecological balance, but also influence the development of human. According to the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report [2], the globally averaged temperature increased by 0.89[0.69 to 1.08] ℃ between 1901 and 2012. It has been predicted that the global average temperature will rise by 0.3-0.7℃ between 2016 and 2035.

The warming rate of earth's surface is proportional to the atmospheric CO_2 concentration. Scientific studies [3] show the concentration of CO_2 in the atmosphere has increased by more than 20% since 1958. By 2013, global CO_2 emissions reached 32.2 $GtCO_2$, up 2.2% from the previous year. Figure 1 shows the top ten emitting countries in 2013 [4]. China produced the most CO_2 (about 9 $GtCO_2$), occupying 28% of global emissions. The accumulation of CO_2 makes the largest contribution to global warming, so a series of down-to-earth measures need to be urgently implemented to control the output of CO_2. Riahi et al. had a modeling study of CO_2 capture incorporating factors of energy demand, demographic, economic and alternative policy [5]. They concluded CO_2 capture was one of the most reliable policies for CO_2 reduction.

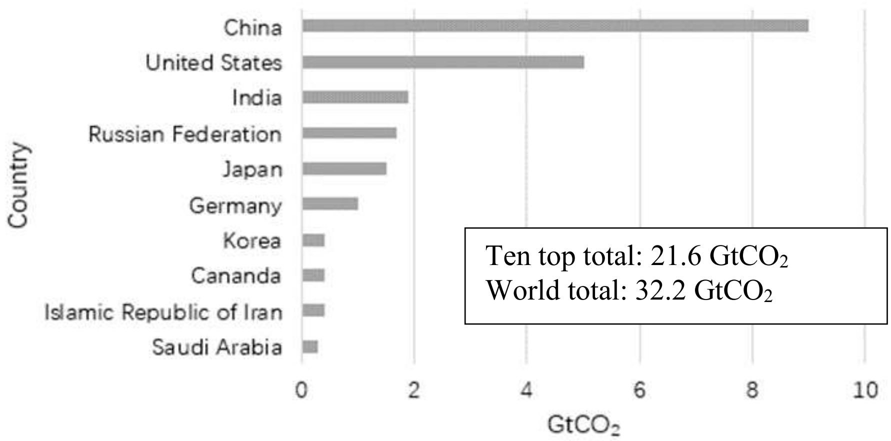

Figure 1. Top ten emitting countries in 2013

2. CO_2 Capture

CO_2 capture is a process of capturing and collecting CO_2 from flue gas of power plants or other factories, such as chemical fertilizer plants, cement plants and so on. The collected CO_2 will be transported to a suitable location by several means of transportation such as motor carriers, railway, ship and pipelines [6]. Then, the CO_2 can be used in caustic soda industry, sugar industry, food industry and so on.

Three different approaches of capturing CO_2 are widely used: pre-combustion, post-combustion and oxyfuel combustion. Each method has its own advantages and disadvantages (Table 1).

Table 1. Comparison of three approaches

Method	Advantages	Disadvantages
Pre-combustion	High CO_2 levels, easy separation	Complicated process, high cost
Post-combustion	Simple process, more branches	Low CO_2 levels
Oxyfuel combustion	High CO_2 levels, low cost of separation	High cost of oxygen supply

2.1. Pre-combustion.

Pre-combustion capture technology can be found in typical integrated gasification combined cycle (IGCC) power plants [7]. The fossil fuel is first gasified to produce syngas, a mixture of H_2 and CO. In the process of gasification, a mixture of CO_2 and H_2 is produced before the combustion reaction [8]. If CO_2 is completely separated herein, only water will be produced after combustion to reducing CO_2 emissions significantly. Figure 2 shows the illustrative diagram of pre-combustion [9].

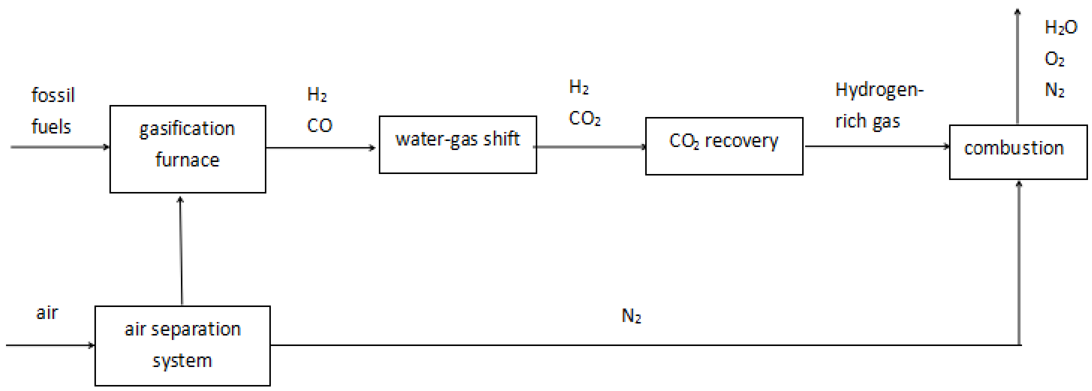

Figure 2. CO_2 pre-combustion capture

At present, pre-combustion capture has been adopted by a raft of proposed IGCC and poly-generation power plants, such as Future Gen in America and Green Gen in China [10]. In general, there are three commercialized methods: Rectisol method, Selexol method and MDEA method.

Allied Chemical Company (now owned by Norton) developed Selexol technology successfully in 1960s [11]. This process uses Union Carbide Selexol solvent, a physical solvent made of dimethyl ether polyethylene glycol [$CH_3(CH_2CH_2O)_nCH_3$]; where *n* is between 3 and 9 [12]. Selexol process can be used to remove CO_2 and H_2S under a low temperature condition and to regenerate absorbent by depressurization [13]. Absorption is accomplished under low temperature (0-5 ℃) operation. Desorption of the rich Selexol solvent takes place at low pressure by vacuuming or stripping. The solvent can be applied to remove SO_x, CO_2, H_2O as well as aromatic compounds (BTEX) as required. Desiccation of the flue gas is necessary before entering the Selexol unit [13]. According to Southern Company, they planned to convert partial CO into CO_2 and H_2 in a 582 MW IGCC project in Kemper County, using Selexol technology to capture 65% of total CO_2 emissions. About 1.1-1.5 million CO_2 would be sold for oil displacement every year [14]. The advantages of this method are low steam tension, less toxicity and low corrosiveness while the disadvantage is the hydrocarbon losses.

MDEA is a weakly basic solvent which will desorb after absorbing acid gases. It can be regenerated by reducing the pressure and flashing. MDEA method was first used in desulfurization until BASF company in Germany developed a novel process to capture CO_2 using MDEA in 1980s [15]. Then MDEA method was introduced into China and developed rapidly. Between late 1980s and early 1990s, Nanjing Chemical Industry Research Institute pushed out a characteristic decarburization system by MDEA method [16]. The first industrial installation went into production in 1991. So far, more than 100 devices have been put into production [17]. Many researchers pay close attention to the composition of MDEA. Zhang Xuemo chose primary amine and secondary amine as activators to increase the absorption speed of solution [18]. Double activators can also reduce CO_2 partial pressure on liquid phase surface, which is conducive to CO_2 absorption. Another innovation point is based on double physical and chemical performance of MDEA. Making full use of its physical property can reduce energy consumption. Semi lean solution is used to absorb most of the CO_2 while tiny amounts of lean solution is used to guarantee cleanliness. Under normal circumstances, amine decarburization process can reach the highest proportion of up to 8:1 when the ratio of semi lean solution and lean solution is 3-4:1 [18]. Application results [19] show that MDEA method can not only reduce energy consumption, but also achieve an excellent absorption effect. In addition, MDEA has many intrinsic advantages, such as good stability, small volatility, and low hydrocarbon solubility and so on.

Rectisol process uses chilled methanol as a solvent, the process is usually operated at -34 to -73 ℃ [20] due to high pressure of methanol. It is best suited when quantities of ethane and heavier components are limited. Rectisol process can be tracked back to the research work of Lurgi Company and Linde Company in 1950s. In 1954, Lurgi Company built up the world's first rectisol industry project at Sasol Company [21]. Rectisol process gets great attention in China. Although it is a relatively mature technology, it still has a bigger research space in energy conservation. In 2013, Shenhua Group invented a coupling method of rectisol and CO_2 capture [22]. The method includes the following steps: desorption will be operated after methanol absorbs acid gases. Then a steam of CO_2 will be separated. After purification and concentrated capture, CO_2 concentration in the exhaust gas can reach up to 95%. This process combines and optimizes rectisol process and CO_2 membrane separation and capture process, resulting to investment reduction. In the same year, Cui Sijing came up with a coupling method of rectisol and CO_2 liquefaction separation [23]. Firstly, partial CO_2 in the exhaust gas will be liquefied. Then methanol will be used to absorb the rest of CO_2. By this way, methanol circulating volume can be reduced, which can reduce energy consumption of liquid delivery in the production process. In 2014, a kind of shunting type low temperature methanol washing technology was developed independently by Shanghai International Engineering Consulting Company [24]. This system can deal with impurities such as BTX and has low energy consumption. Rectisol process is most applicable when dealing with the combination process with desulfurization and decarbonization. The merits include more stable absorbent, less corrosive as well as high thermal and chemical stability [25].

2.2. Post-combustion

Post-combustion capture removes CO_2 from waste gas, which mainly consists of CO_2 and N_2, using chemical or physical methods. This type of technology can be directly used in traditional power plants, so it saves a large amount of construction cost. Figure 3 shows the illustrative diagram of post-combustion [9].

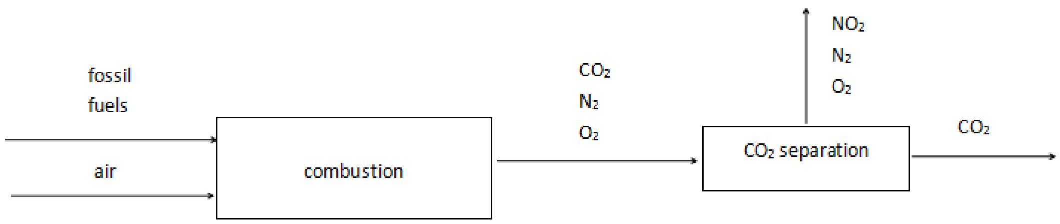

Figure 3. CO_2 post-combustion capture

Post-combustion contains many kinds of adsorption methods: physical absorption, chemical absorption, adsorption and membrane [26]. Among the many options used for CO_2 post-combustion capture from waste gases, there is an increasing interest in using adsorption process as a long-term alternative for CO_2 capture. It has many potential advantages [27], such as greater capacity, low energy regeneration, selectivity and so on. Therefore, adsorption progress will be intensively discussed in the following. Adsorption processes can be broadly classified into two types according to the principles of adsorption and desorption: by regulating the pressure or the temperature [28].

Pressure swing adsorption (PSA) is a novel method of CO_2 adsorption and separation technology. It was processed by karstrom and Guerrin Dumine simultaneously in 1960s [29]. In China, the technology was first developed by Southwest Chemical Research and Design Institute [30]. The basic principle of PSA is the selective adsorption of adsorbents, which is represented in different capacity, velocity and adsorption force.CO_2 will be adsorbed at high pressure while it will be released at low pressure in order to achieve the purpose of CO_2 capture and adsorbents regeneration. In the primary stage of PSA, it was generally believed that this method with higher cost and energy consumption was difficult to be promoted and applied. With the improvement of technology, structure of adsorption tower, circulation design as well as adsorbents [31] have been promoted. Current multi-tower circulation devices are based on Skarstrom circulation [31]. Because of high concentration of CO_2, low energy consumption and investment, PSA technology has been widely applied. However, there are still some problems should be solved urgently.

①Improve circulation design or develop novel adsorbents with stronger adsorption capacity of CO_2 [32].

Normally, CO_2 adsorbents include molecular sieve, activated carbon, silica gel, activated alumina, etc [33]. Regardless of types of adsorbents, the adsorption capacity of CO_2 is stronger than other components in the mixed gas, which is caused by the intrinsic molecular structure and molecular polarity of CO_2. Actually, there are still 5% water vapor cannot be removed in the treated flue gas [32]. And adsorbents tend to adsorb water vapor ahead of CO_2, so that the adsorption of CO_2 is reduced. In conclusion, it is necessary to improve circulation design or develop novel adsorbents with stronger adsorption capacity of CO_2. Based on four bed molecular sieves, American researchers substituted a novel type of hydrophobic carbon molecular for original 5A zeolite molecular sieve [34]. The whole process was improved by omitting air predrying sector, in which only two adsorption beds were needed. This breakthrough not only improved the adsorption capacity of CO_2, but also reduced the operation complexity greatly.

②The negative effect caused by pressure drop [32].

The existence of pressure drop has a negative effect on pressing process, pressure reducing progress and flushing progress. The reduction of system pressure will lead to high energy consumption and low recovery of CO_2.

Temperature swing adsorption (TSA) is the earliest physical adsorption method used in industry. In general, solid adsorbents have a strong adsorption capacity of CO_2 at high temperature while it becomes weak at low temperature. And the adsorption capacity of other gases (such as N_2) is small in the two temperature conditions. Based on this characteristic, adsorption progress is carried out at a lower temperature and then adsorbents can be regenerated by heating. At last, adsorbents will be cooled for next circulation. The adsorption progress can be continuously carried out by the use of a plurality of adsorption beds [35]. When some strong adsorption components cannot be separated completely by PSA, TSA shows obvious advantages. J. Merel et al. [36] used zeolite as adsorbents when they studied the separation performance and energy consumption of TSA technology. Results show that the energy consumption of TSA is a little higher than that of amine absorption method. This disadvantage can be made up by making full use of waste heat from power plants. Another advantage of TSA is slow heating rate and cooling rate, limiting the circulation time [37]. In order to avoid the disadvantages of TSA when dealing with hot gas, the concept of electrical thermal swing adsorption (ETSA) has been proposed by Fabuss and Dubois [38]. The adsorbent needs to be an electrical conductor. The process uses heat generated by Hall Effect to release CO_2. Grande C.A. and Rodrigues A.E. [39] carried out a systematic study on ETSA. Rodrigues research group [40, 41] studied to capture CO_2 from flue gas by ETSA progress, using honeycomb integrated activated carbon as adsorbent. Under this operation, the recovery of CO_2 was over 89% and the purity was up to 16%.

A coupling method of PSA and TSA has also been developed. Pugsley et al. [42] systematically studied the performance of a pressure–temperature swing adsorption (PTSA) process in a circulating fluidized bed. PTSA progress combines vacuuming and heating together, which is suitable for strong adsorption components. Compared with VPSA, PTSA enhances the driving force effectively and reduces the mass transfer resistance, so that it can adopt a higher adsorption pressure and reduce the power consumption of the vacuum pump. Compared with TSA, PTSA can lower regeneration temperature to reduce the heat consumption [35]. Tlilil et al. [28] tested different effects of CO_2 capture by 5A zeolite molecular sieve. The recovery and purity were nearly 99% by PTSA progress, far higher than PSA and TSA. M. G. Plaza et al. [43] adopted different progress to test CO_2 production capacity and recovery rate of activated carbon. Results showed that PTSA had the best effect in primary circulation with the maximum production capacity of 1.9mol/ (kg·h).

2.3. Oxyfuel combustion

Oxyfuel combustion chooses pure oxygen or oxygen enriched air instead of ordinary air as combustion medium. Principal combustion products are CO_2, water vapour and redundant oxygen. After condensation, concentration of CO_2 in flue gas can reach to 80%-98%, so the separation cost is low. Figure 4 shows the illustrative diagram of oxyfuel combustion [9].

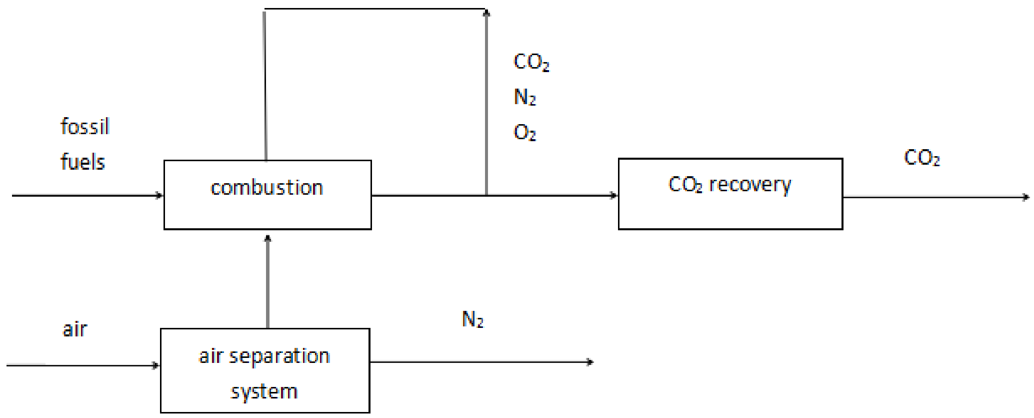

Figure 4. CO_2 oxyfuel combustion capture

The system of an oxyfuel combustion power plant mainly includes: air separation unit (ASU), boiler or gas turbine, flue gas processing unit and CO_2 processing unit (CPU) [44]. A nearly pure steam of CO_2 and water vapor will be produced after oxyfuel combustion; and then CO_2 can be separated from the steam by desiccation and low temperature purification processes. The application of oxycombustion for coal fired power plants are mainly two types: oxy-PC and oxy-CFB [44]. However, the application of oxyfuel combustion faces a series of challenges [45]. The first one is design of next generation oxyfuel boiler. The combustion process needs to be optimized for reduced formation of NOx. The second one is the energy consumption of O_2 production. Cryogenic air separation is only applicable to large scale oxygen production. In conclusion, oxyfuel combustion is still in a stage of demonstration.

3. Summary

Reduction of atmospheric CO_2 is becoming an urgent issue as global temperature is increasing overwhelmingly. In order to control CO_2 concentration, CO_2 capture has been widely adopted. Through this view, the following conclusions can be drawn:

①Pre-combustion capture is usually applied in IGCC power plants. CO_2 separation was finished before the combustion, so the size of separator can be reduced, which helps to improve system efficiency. However, the regeneration section will cause energy penalties. So it is necessary to optimize the conversion process and invent high temperature adsorbents.

②Post-combustion capture separates CO_2 from waste gas after combustion. This method can be applied to traditional power plants directly, so it saves a large amount of construction cost. The engineering design challenge is the partial pressure of CO_2 is relatively low while the flue gas temperature is relatively high.

③Oxyfuel combustion capture is a promising method with a better effect. It applies to different kinds of power plants, including large coal-fired and gas-fired units. But this method still has certain problems. The first one is to lower furnace temperature to avoid corrosion. The second one is to improve related technology to reduce the cost.

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