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# Alternative pathways for efficient CO<sub>2</sub> capture by hybrid processes—A review



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#### ABSTRACT

CO<sub>2</sub> capture and storage technologies have been recognized as the primary option to mitigate the issue of climate change caused by the utilization of fossil fuels. In the last decades, several CO<sub>2</sub> capture approaches have been developed, such as absorption, adsorption, membrane, cryogenic, hydrate and chemical looping combustion etc. However, the energy penalty is a general challenge for each technology. To overcome the disadvantages of standalone technology, the combination of two or more approaches (namely hybrid CO<sub>2</sub> capture processes) has been considered as a potential option. In this work, the status and development of hybrid CO<sub>2</sub> capture processes is presented in a classification of primary technology as absorption-based, adsorption-based, membrane-based and cryogenic-based. The detail configuration of each hybrid process is introduced. Simultaneously, the characteristics, advantages and potential challenges of each hybrid process are also summarized. Compared to the standalone methods, hybrid processes showed the superiority not only in CO<sub>2</sub> recovery and energy penalty, but also in the installation investment. Therefore, hybrid processes can be a promising alternative to conventional CO<sub>2</sub> capture technologies in future.

#### 1. Introduction

Climate change caused by greenhouse gas emission has attracted increasing concern. In 2012, global  $CO_2$  emission was approximately  $3.17 \times 10^{10}$  t, as shown in Fig. 1 [1]. China is the largest  $CO_2$  emission country (totally  $8.25 \times 10^9$  t) in the world. Combustion of fossil fuels is the dominant contributor for anthropogenic  $CO_2$  emission. According to the report of International Energy Agency (IEA), fossil fuels still account for over 80% of the world energy supply [1]. In China, about 70% of energy is provided by coal and petroleum. The resulting greenhouse gas effect has become more serious in recent years, which greatly affected ecological balance. Therefore, it is urgent to develop effective  $CO_2$  mitigation technologies.

Using clean energy instead of fossil fuels is an effective strategy to mitigate  $CO_2$  emission. However, it is difficult to optimize the structure of energy source in a short term.  $CO_2$  capture and storage (CCS) is a promising countermeasure against global warming. Depending upon different plant configurations,  $CO_2$  emission from flue gas of thermal

power plant can be reduced by three strategies, including pre-combustion capture, post-combustion capture, and oxy-fuel combustion [2,3]. The detail  $CO_2$  capture technologies generally include absorption, adsorption, membrane, cryogenic and hydrate etc. [4]. Nevertheless, the retrofit of CCS units into a power plant would cause a significant decrease in electric output [5]. Merkel et al. reported that an amine system used to capture 90% of  $CO_2$  in flue gas would require about 30% of the power produced by the plant and result in a  $CO_2$  capture cost of 40–100\$ per ton  $CO_2$  [6]. Therefore, reducing the energy requirement of capture is critical to a large-scale commercial application of CCS technology.

Recent years, combination of two or more standalone  $CO_2$  capture technologies, named as hybrid processes, has attracted more and more attention due to the potentially high capture efficiency and low energy requirement. This work is objective to provide a state-of-the-art of hybrid  $CO_2$  capture processes. At the beginning, the challenges of existing  $CO_2$  capture technologies are introduced. Then, the hybrid  $CO_2$  processes mentioned in the literatures are classified in four types, including

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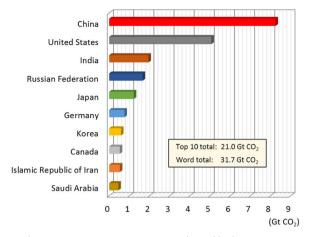


Fig. 1. Top 10 CO2 emission countries in the worldwide in 2012 [1].

absorption based, adsorption based, membrane based and cryogenic based hybrid process. The characteristics (such as source of raw gas, application condition, and  $\mathrm{CO}_2$  capture performance) of each hybrid process are investigated and summarized. An overall comparison of advantages, challenges and potential solutions of each hybrid process is then carried out. Finally, the future trends of hybrid  $\mathrm{CO}_2$  capture processes are also discussed.

#### 2. Challenges of current CO2 capture processes

At present, the major challenge of existing CO2 capture technologies is high energy consumption. For example, as one of the most mature technologies, the energy requirement for solvent regeneration of MEA absorption process varies from 3.0 to 4.5 MJ/kg CO<sub>2</sub>, which contributes around 80% of the total energy consumption [7,8]. According to the annual report of National Energy Technology Laboratory (NETL), integrating of CO2 capture unit (i.e. MEA absorption) into coal-fired power plant would lead to the decrease of total efficiency from 35% to 24.4%, and capturing per ton CO2 approximately consumed 80 US dollar [9]. Sipöcz and Tobiesen evaluated the economic analysis of a 440 MWe natural gas combined cycle power plant with an integrated CO2 removal plant, using an aqueous solution of monoethanolamine (MEA) [10]. Simulation results indicated that net LHV efficiency decreased from 58.29% to 49.48%. Goto et al. reviewed recent studies on the efficiency penalty of coal-fired power plants with CCS [5]. The investigation results indicated that the efficiency penalty for current technologies was about 10%. By reducing the regeneration energy of the CO2 scrubbing solvent by 1 GJ/ton CO2, an approximate 2% efficiency improvement can be expected.

Clausse et al. mentioned that the energy consumption of CO<sub>2</sub> capture processes has to be reduced as low as possible (target around 1 GJ/ ton CO2 is sometimes quoted) while keeping high CO2 recovery (above 90%) [11]. Chemical absorption (conventional MEA) is often defined as a reference process. The heat requested for the amine regeneration, in up to date MEA processes, represents an energy cost ranging from 2.5 to 3.5 GJ/ton CO<sub>2</sub> [8,12]. A recent study by Ho et al. showed that the cost of CO<sub>2</sub> capture (in 2008 terms) from a 500 MW subcritical lignite power plant is over US\$70 per metric ton of CO<sub>2</sub> using commercially available 30 wt% MEA solvent. When advanced heat integration with the power plant is applied, the capture cost decreases to US\$55 per metric ton of CO<sub>2</sub> avoided [13]. As a comparison, the carbon tax of Australia in 2012 was A\$23 per metric ton of CO2 and the European Union Emissions Trading System (ETS) carbon price was €3.5 per metric ton of CO<sub>2</sub>, which means that the current cost of implementing CCS is higher than both the Australian carbon tax and the EU carbon credit price [14,15]. In addition, the application of CCS is also restricted by some specific drawbacks, such as the degradation of solvent, secondary pollution,

installation corrosion, high material cost, non-stability selectivity etc. [16,17]. Table 1 summarized the existing challenges of dominant  $CO_2$  capture processes.

#### 3. Hybrid CO<sub>2</sub> capture processes

So far, the development of  $\mathrm{CO}_2$  capture processes has largely focused on single separation technologies (absorption, adsorption, membranes, cryogenics, etc.). A few studies examined the merits of combining different separation technologies into a hybrid capture process [41]. To overcome the challenges of standalone  $\mathrm{CO}_2$  capture technologies, hybrid processes may be a potential alternative. It usually consists of two or more conventional technologies (i.e. absorption, adsorption, membrane, cryogenic and hydrate etc.). The integration of different technologies may be superior to the standalone process, and avoid their disadvantages [42].

Potential hybrid  $\rm CO_2$  capture processes can be classified into four categories, such as absorption-based, adsorption-based, membrane-based and cryogenic-based hybrid processes. Meanwhile, each category also includes different options in process arrangement, as shown in Fig. 2. A total of 7329 publications on hybrid  $\rm CO_2$  capture technologies in the last decade were depicted in Fig. 3. Among them, approximately 60% (4383 publications) belonged to absorption based hybrid processes, 20% (1448 publications) belonged to adsorption based hybrid processes, 16% (1163 publications) belonged to membrane based hybrid processes, and 4% (335 publications) belonged to cryogenic based hybrid processes.

Screening of suitable hybrid  ${\rm CO}_2$  capture processes highly depends on the properties of feed gas (e.g. CO2 concentration, gas temperature and pressure etc.), the requirement of product (e.g. purity etc.) and the availability of the capture equipment. In addition, CO2 recovery and energy consumption are also significantly affected by the source of CO2 emission when using different capture technologies. It should be noted that for various technologies the types of required energy are different [43,44]. For example, there are two main energy factors that should be considered in the typical MEA absorption processes. One is the thermal energy used for regenerating the solvent and extracting steam from the steam turbine, which dominates the energy consumption of the whole capture process. The other is the electric energy for the machine operation. In the adsorption processes, the type of energy is decided by the way of desorption. Electric energy is dominant in pressure swing adsorption (PSA) to generate pressure difference, and thermal energy is used in temperature swing adsorption (TSA) to provide desorption heat. In membrane gas separation, all the energy required is electric energy to drive compressor or vacuum pump. In the cryogenic and hydrate separation processes, both the cryogenic and high pressure condition and operation of the systems are based on electric energy consumption.

#### 3.1. Absorption-based hybrid processes

#### 3.1.1. Membrane contactor

Membrane contactor is one of the most common hybrid technologies, which is widely applied in  $\mathrm{CO}_2$  capture processes. It is different from the conventional membrane process, which separates gases by selective permeation through a dense membrane separation layer by a solution/diffusion mechanism [45]. The different configuration of membrane contactors is illustrated in Fig. 4. The separation driving force is provided by the partial pressure difference of each gas component across the membrane. The conventional membrane processes require either flue gas compression, permeate side sweep, application of permeate-side vacuum, or a combination of these steps to provide the separation driving force. The integration of absorption and membrane has the benefits of both liquid absorption (high selectivity) and membrane separation (modularity and compactness), and is more effective at low  $\mathrm{CO}_2$  concentration [46–48]. The major disadvantage of membrane contactors is the increased mass transfer resistance, especially

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