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A Review of Post-combustion CO_2 Capture Technologies from Coal-fired Power Plants

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Abstract

Reducing CO_2 emissions has become a worldwide research topic. Of all the sources of CO_2 emissions, power plants burning fossil fuels, especially coals, account for a very large portion. For CO_2 capture from existing coal-fired power plants, post-combustion technology is thus far considered the most viable method due to its “end-of-pipe” characteristic. Chemical absorption or scrubbing process is currently the technology most likely to be implemented in the near future but rather energy-intensive. Membrane-based CO_2 separation process in recent years appears to be a competitive substitution for conventional chemical absorption technology. This paper reviews the basic process designs of chemical absorption and membrane-based separation processes for CO_2 capture, as well as corresponding optimization methods including optimizing operational parameters, process modifications, membrane module types and so forth. In addition, some energetic and economic estimates from other researchers for these two CO_2 capture technologies are summarized. It is found that membrane-based separation process does not possess obvious advantage over MEA-based chemical absorption process at the typical 90% CO_2 capture degree in terms of both energy consumption and cost. Therefore, various optimization methods have not changed the fact that CCS technology will lay more burdens on power plants unless they can get enough allowances from government. In recent years, hybrid system with the target of utilizing more than one single capture technology seems to be new direction from the perspective of capture process design. However, it still needs to be further investigated.

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1. Introduction

1.1. Global CO_2 emission

The Fifth Assessment Report from the Intergovernmental Panel on Climate Change (IPCC, Working Group I) states that human activity (greenhouse gas emission) is the major cause of the warming observed since the mid-20th century [1]. Among these human activities, energy consumption accounts for the largest part of greenhouse gas emission [2]. Till 2014, CO_2 concentration (397 ppm) is about 40% higher than that in the mid-1800s, with an average growth of 2 ppm/year[2]. Renewable energy is a solution to reducing CO_2 emission, however, a MIT study [3] shows that coal use will increase by 2050 under foreseeable scenario. Worldwide, burning coal is still the cheapest way of generating electricity and coal is relatively abundant in large energy-consuming countries [4]. So far carbon dioxide capture and storage (CCS) is considered the most promising technology to sequestrate CO_2 from large stationary sources of CO_2 emissions**.**

1.2. CCS technologies

According to IPCC report 2005 [1], CCS can be applied to large point sources. The captured CO_2 can be compressed and transported for storage in geological formations, in ocean, in mineral carbonates, or used as feedstock for industrial processes. Basically, there are three main routes of CO_2 capture systems: post-combustion, pre-combustion, and oxy-fuel combustion [5]. For post-combustion capture, CO_2 is sequestrated from flue gas after fuels have completely burned. Pre-combustion capture involves the so-called integrated gasification combined cycle (IGCC) system, i.e. the syngas that is generated from coal gasification, mainly composed of CO and H_2, is reformed by steam to produce a mixture of CO_2 and H_2. The CO_2 is removed before H_2 is combusted in the combustion chamber of the gas turbine. Finally, in the case of oxy-fuel combustion, coal is burned in nearly pure oxygen to produce flue gas with high CO_2 concentration which is almost ready for transport and storage. Figueroa et al [5] summarized the inherent advantages and disadvantages for the three pathways. They believe that pre-combustion capture is applicable to gasification plants and oxy-fuel combustion can be applied to new-built power plants. As currently all conventional coal-fired power plants combust fuels directly in a boiler to generate power [4], post-combustion capture as an “end-of-pipe” technology is a more viable option for existing coal-fired power plants.

1.3. Post-combustion capture for coal-fired power plants

Post-combustion capture unit is designed to be placed after traditional purification systems as depicted by Oexmann [6]. The diagram is shown in Fig.1. Under this scenario, contaminants in the exhaust gas such as NO_x, SO_x, and particulate matters can be reduced to a very low level prior to CO_2 capture process. Many post-combustion capture technologies are proposed and being investigated these years, including chemical absorption [7], adsorption [8], membrane separation [9], Ca-Looping technology [10], and cryogenic fractionation [11] etc. Most of them are not commercially implemented for CO_2 capture in power plants. One major barrier to the application of post-combustion capture technology in coal-fired power plants is the low partial pressure of CO_2 in the flue gas. The flue gas is present at atmospheric pressure and the CO_2 concentration is within 13-15% [12], so the driving force for CO_2 separation is very low. Another problem is that the flow rate of flue gas is usually 5-10 times larger than streams usually treated in natural gas and chemical industries [4].

Of all these post-combustion technologies mentioned above, chemical absorption is considered so far the most suitable one and most possible to be implemented in the near future [13]. Although many solvents are tested for chemical absorption process, monoethanolamine (MEA) is undoubtedly the most extended solvent [14]. In recent years, many research institutes and companies are collaborating on operating larger-scale demonstration power plants with chemical absorption process and great progresses have been made. Wang et al [15] give us an overview of worldwide research programmes in chemical absorption technology for CO_2 capture. Aside from those projects, a pilot CO_2-scrubbing plant at Niederaussem was commissioned as the first of its kind in Germany in the summer of 2009 [16]; a 1 tonne CO_2/hour CO_2 post-combustion capture pilot plant has been operated at Dong power plant in Denmark [17]; SaskPower's demonstration power plant with CCS, Boundary dam [18], is the first and largest commercial-CCS project which has successfully captured 1 million ton CO_2 by July, 2016.

However, despite the fact that chemical absorption technology is more mature, its character of being energy-intensive is still motivating many scientists to find alternatives. Membrane-based separation [1] as an emerging technology is a very promising competitor. Unlike chemical absorption process, in most cases, there is no chemical reaction in membrane-based separation process and thus it has less environmental impact. In addition, the energy consumption is expected to be much less than chemical absorption technology.

The purpose of this paper is to review some recent researches of MEA-based chemical absorption and membrane-based separation technologies, covering process design, energetic performance, and cost estimation. Additionally, some researches on developing hybrid CO_2 capture systems are introduced as well.

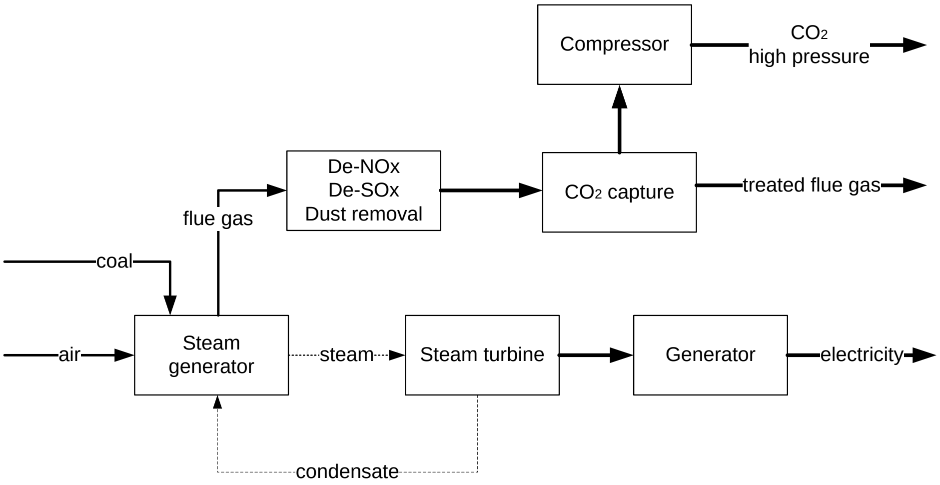


Fig.1. Schematic diagram of a power plant with post-combustion CO_2 capture [6]

2. Chemical absorption

2.1. MEA-based CO_2 absorption process

A typical chemical absorption process for not only MEA but many other solvents is shown in Fig. 2. The flue gas enters the absorber at the bottom and flows upwards while the solvent solution goes downwards, forming a counter flow. Through the contact of these two streams, part of CO_2 in the flue gas is absorbed into amine solution. Then the solution with absorbed CO_2, which is usually called rich-loading solution, is pumped up to the head of the other column, the stripper. In the stripper, there is also a counter flow occurring with rich-loading solution flowing down the column and stripping steam generated in the reboiler upwards. With the heat from the stripping steam, chemical bonds between CO_2 and the solvent are broken so that CO_2 is carried up by the ascending steam towards the overhead condenser. Whilst the condensed steam is directed back to the stripper as a reflux, the product stream with high CO_2 purity (around 99%) is obtained. Then the product stream can be compressed for transportation to storage sites. At the bottom of the stripper, the amine solution which is termed as lean-loading solution is circulated back to the head of the absorber. Before entering the absorber, the lean-loading solution with relatively high temperature (about 120 ℃) is used to increase the temperature of the rich-loading solution to recover some heat. Sometimes the condensate from the overhead condenser is sent back to the absorber instead of the stripper because it could decrease the temperature in the stripper and thus more solvent regeneration energy is needed [19].

To ensure sufficient contact surface in both the absorber and the stripper, trays or packings (random or structured) are applied inside the columns. For CCS applications, MacDowell et al [20] think that structured packing is a better choice as it is commercially available, has large surface area, and has a low pressure drop along the column.

One significant indicator of this process is termed CO_2 capture degree, the ratio of CO_2 amount in product stream to that in the flue gas which reflects the ability of a capture system to sequestrate CO_2 from the flue gas. Rao and Rubin [21] suggests that the optimal CO_2 capture degree should lie in the range of 80-90% considering economic. In most designs, this value is set to be 90% [6, 22-24].

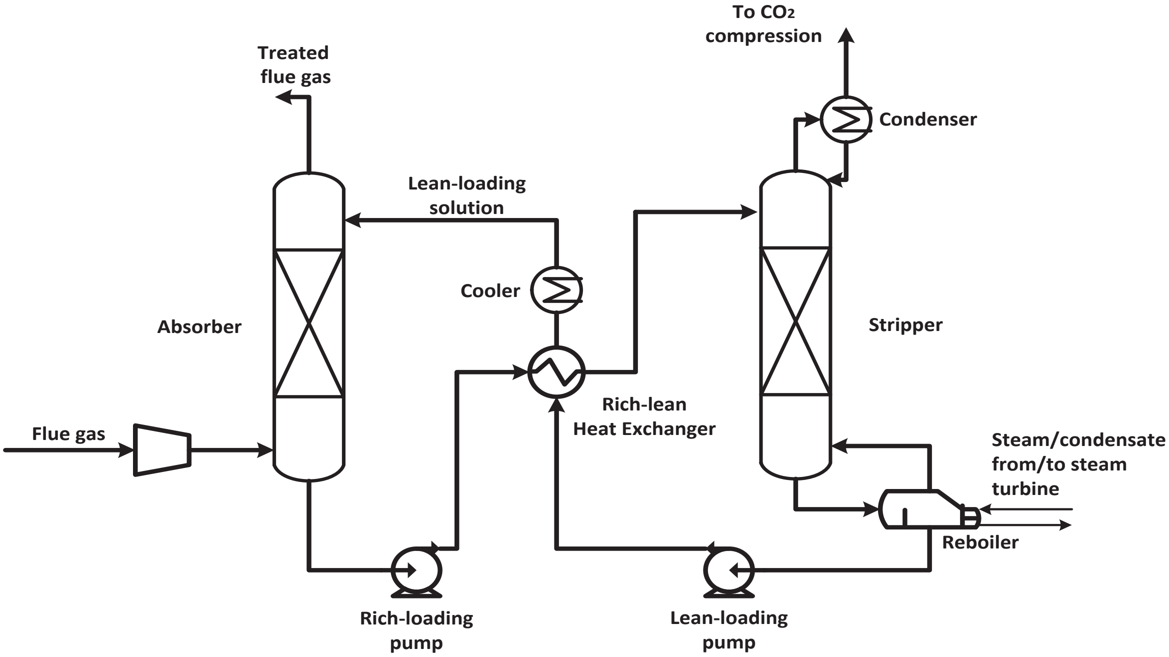


Fig. 2. Schematic of a basic chemical absorption process for CO_2 capture

2.2. Optimizations to chemical absorption process

In chemical absorption process, solvent regeneration in the reboiler accounts for the most energy consumption (reboiler duty). For a 600MW coal-fired power plant, the regeneration of MEA in the chemical absorption process consumes 3.8-4.0 GJ/tonne CO_2 [23]. Efforts to reduce energy requirement are generally being made on three major aspects: optimizing operational parameters, process modifications, and developing better solvents. As this review paper only focuses on process technology, the former two aspects are to be introduced.

For operational parameters, considerable work investigating optimal specifications for this process have been published. According to these researches, there are several factors influencing solvent regeneration energy: CO_2 loading in lean-loading solution (CO_2 lean-loading), MEA concentration, and pressure in the reboiler etc. [23, 25]. It is found that CO_2 lean-loading has an optimal value for CO_2 capture. Basically, the reboiler duty is comprised of three parts [6]: 1) the sensible heat to increase the temperature of rich-loading solution; 2) the heat to generate the stripping steam; 3) the heat to strip the absorbed CO_2 from the amine solution. At low CO_2 lean-loadings, generating the stripping steam is dominant in the thermal energy requirement while heating up solvent at the inlet of stripper is dominant at higher values of loadings. Therefore, a CO_2 loading leading to the minimum reboiler duty is expected. Different optimal values are obtained in different researches though.

Higher solvent concentration could also save energy but adversely bring problems of erosion and solvent degradation. The operation pressure in reboiler or in the stripper is another main influence factor. Increasing the pressure results in a decrease of regeneration energy, but maintaining higher pressure inevitably requires more auxiliary power. In addition to these factors above, other influence factors such as solvent temperature, height of absorber and stripper, the temperature of solvent and so forth are all more or less relevant to the reboiler duty. Abu-Zahra et al [23] believe a reduction of about 20% in the thermal energy consumption is realistic by optimizing these specifications.

On the other hand, modifying the process is also a way of minimizing energy consumption. Moullec et al [26] did a thorough review of 20 elementary modifications from literatures and patents, and classified them into 3 categories based on their effects on the process: 1) absorption enhancement; 2) heat integration; 3) heat pumps. The basic concept of ‘absorption enhancement’ is to increase the CO_2 loading in the rich-loading solution at the bottom of the absorber. Higher CO_2 rich-loading means higher CO_2 capacity of the solvent and thus results in reduced solvent flow rate and the sensible heat of the reboiler duty. The general idea of ‘heat integration’ is to establish heat transfers between streams so that waste heat can partially be recovered so that reboiler duty can be reduced. ‘Heat pump’ is to increase the heat quality by sacrificing more mechanical work. Under each category, several sub-classes of modifications are clearly illustrated and discussed. Moreover, some of these process modifications can be combined to realize further optimization.

In all the 20 cases of modification, MEA is regarded as reference solvent but how these modifications affect energetic performances of chemical absorption process depends on the kind of solvent. One example given in this paper is that intercooled absorber (ICA) has little effect on MEA whereas it can reduce 7% reboiler duty for a mixture of aminomethylpropanol (AMP) and piperazine (PZ) [26]. It is also stated by authors that these modifications will inevitably increase the capital cost and the overall complexity, and sophisticate the operability. Therefore, which of these modifications should be adopted depends on specific conditions. What also should be noted here is that most of these modifications have been assessed via modeling work but only a few of them are validated by experimental results at appropriate scale.

Currently, there are no big technical barriers to the application of chemical absorption technology. The biggest resistance to its implementation is still the high energy requirement and the consequent rise of cost for power generation. Therefore, a large number of papers concentrate on how to reduce the energy consumption as well as to realize optimized integration of the chemical absorption process in a coal-fired power plant. However, as the requirement of the final CO_2 product for transportation is strict (CO_2 purity > 95%, pressure = 110 bar), the decrease of energy requirement by optimizing operational specifications or modifying the whole capture process is very limited. Moreover, these modifications are usually implemented at the sacrifice of the operability and cost [26].

3. Membrane-based separation

3.1. Membrane-based separation process

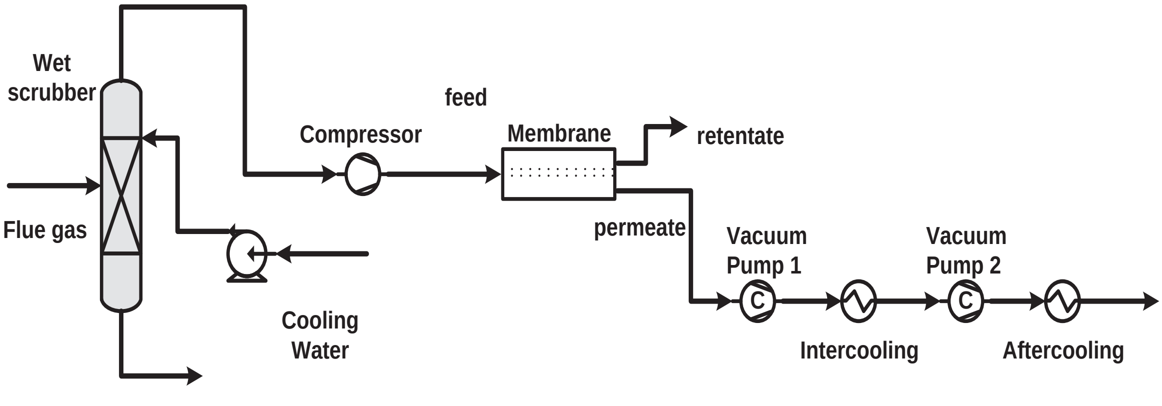


Fig. 3. Schematic of a membrane separation process

Fig. 3 illustrates a basic CO_2 capture process using membrane separation. Before entering the membrane module, a wet scrubber is often used to cool down the flue gas to the operational temperature of the membrane. Inside the membrane module, a portion of CO_2 permeate through the membrane and a stream (permeate gas) with higher CO_2 concentration is gained on the permeate side. The left part of the flue gas is called retentate gas. As mentioned above, the partial pressure of CO_2 is very small so that compressor and vacuum pump are used to increase the partial pressure difference between the feed and the permeate side. Similar to CO_2 capture degree in chemical absorption process, separation degree is used to indicate the proportion of CO_2 separated from flue gas [9].

Compared to chemical absorption process, the membrane separation process apparently is simpler and contains less components. The major energy consumption comes from compressor and vacuum pump.

3.2. Membrane material and module design

It is well known that membrane material plays a significant role in separating CO_2 from flue gas. There are two main properties of membrane material for gas separation [27, 28]: permeability and selectivity. The former mainly affects the separation degree and the latter the CO_2 concentration in the permeate gas (CO_2 purity).

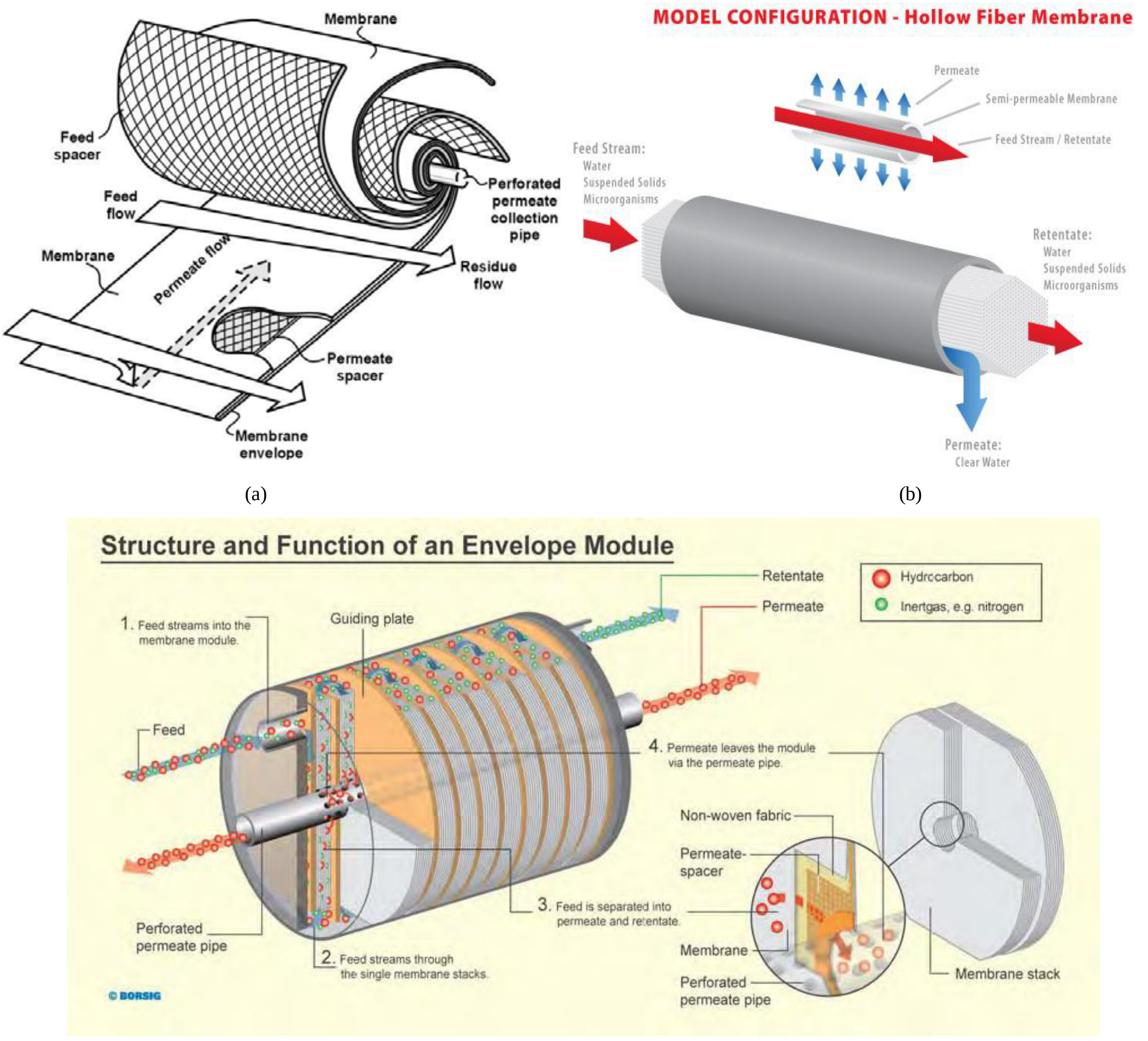
Membrane material generally can be divided into three types [28, 29]: ceramic membrane (inorganic), polymeric membrane (organic) and hybrid membrane. Hybrid membrane, which is aimed at utilizing advantages of both materials, consists of both inorganic and organic membrane material. Ramasubramanian and Ho [30] reviewed membranes that can be used for CO_2 separation and analyzed their pros and cons. Polymeric membranes, such as PolarisTM [5] and Polyactive® [31] which are now commercially available, are usually operated under low temperature and possess better thermal stability as well as mechanical strength compared with ceramic membranes. In addition, polymeric membrane is easier to be manufactured with large area. A special kind of polymeric membrane called facilitated transport membrane [32] is often discussed independent of other polymeric membranes as its transport mechanism is distinct. Although facilitated transport membranes demonstrate very high selectivities and permeabilities, its permeance which is dependent on membrane thickness and reliability still need to be further improved [30]. Ramasubramanian and Ho [30] also suggest that ceramic membranes including silica and zeolite membranes give a better permeability-selectivity trade-off. However, fabricating defect-free layers and product with large surface area are much more difficult than polymeric membranes. As mentioned in the second section, the flow rate of flue gas is usually very large, large area membrane is required for CO_2 separation due to the limitation of material properties. Therefore, polymeric membrane material is currently the most realistic option for CO_2 capture from coal-fired power plant.

Apart from membrane material, the configuration of the membrane module is another important influence factor for CO_2 separation. For polymeric membranes, three kinds of module configurations are mostly adopted: spiral wound [33, 34], hollow fiber [35] and envelope [36]. An important indicator to evaluate membrane module is packing density and it equates to the surface area of membrane per volume inside the module. Fig. 4 [33, 36, 37] illustrates the structures of three types of membrane modules. The characteristic of each configuration is clearly reflected in their names. A typical spiral wound type module is illustrated in Fig. 4(a), a product of Synder Filtration [33]. The packing density for this type of module is in the range of 100-400 m^2/m^3 [36]. Hollow fiber module generally has the highest packing density (up to 30000 m^2/m^3 [38]). As shown in Fig. 4(b), a cylindrical vessel is filled with bundled strands of hollow fibers. In the envelope type module, the envelopes or discs are stacked layer by layer with a permeate pipe through the centers as shown in Fig. 4(c). Several layers of membrane are wrapped around a central collection pipe. The packing density usually lies within the range of 300-1000 m^2/m^3 [38]. For both spiral wound type and envelope type modules, there are spacers placed between two membrane layers to provide space for feed gas.

Table 1. Comparison of membrane modules [39]

Module type	Spiral-wound	Envelope	Hollow fiber
Packing density (m^2/m^3)	<1000	200-500	<10,000
Pressure drop	High and longer permeate path	Moderate	High in the fibers
Cleaning	Hard	Medium	Chemical washing or replaced
Manufacturing	Easy and cheap	Easy	Cheap
Cost (€/m^2)	8-37	40-150	2-8

Luhr [39] in his dissertation summarized not only packing densities but also other important traits for different membrane modules. Part of his summary is listed in Table 1. In terms of cost and packing density, hollow fiber has advantages over two other types. However, fibers could be easily blocked by the particulate matters and must be completely replaced, which is not very friendly for the existing power plants. Hägg [40] in her book presented some commercial-scale membrane suppliers for us.



(a) (b)

(c)

Fig. 4. Membrane module [33, 36, 37]: (a) spiral wound (b) hollow fiber (c) envelope

3.3. Optimizations to membrane-based separation process

The system shown in Fig. 3 is a single-stage membrane-based separation system. It is already found that single-stage system cannot yield desired product with high CO_2 capture degree and purity. This is because the separation process is restricted on one hand by the low CO_2 partial pressure difference， and on the other hand by the trade-off relationship between CO_2 capture degree and CO_2 purity [9, 27]. Therefore, multi-stage or cascade membrane separation becomes a viable option. Two-stage separation system is more widely investigated as it is found that three-stage provides no advantages [41, 42].

Fig. 5 [43] illustrates a two-stage membrane system for CO_2 separation. The permeate gas from the first stage is compressed and then directed to the second stage to be further separated. In this scheme, the retentate stream from the second stage is recirculated to the feed side so that the CO_2 concentration increases. Multi-stage system cannot change the fact that CO_2 partial pressure difference is very small, so compressor and vacuum pump are still needed to increase driving force. Ho et al [44] compared the effects of these two scenarios of producing driving force and found that vacuum pump strategy requires larger membrane area but could save 35% capture cost. Especially, the two-step vacuum design is adopted for it can meet lower energy requirement while provide enough pressure change. According to Lin et al [45] and Merkel et al [4], two-stage vacuum pump system consumes less energy than compressor but larger membrane area is inevitable. Additionally, an expander is often placed after the second membrane to recover some energy from gas expansion. The most obvious advantage of multi-stage system is that it is capable of achieving high CO_2 capture degree and purity simultaneously, a capture degree of 90% and purity of 95% are achievable [4, 43].

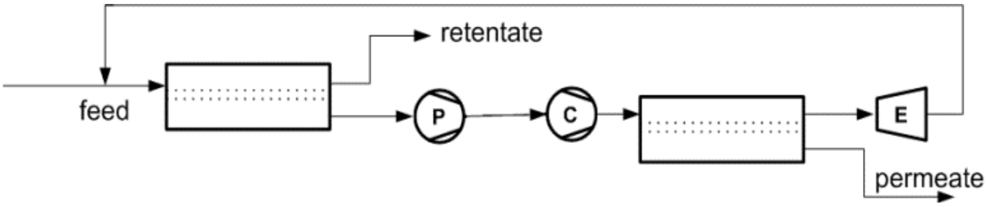


Fig. 5. Schematic of two-stage membrane system [43]

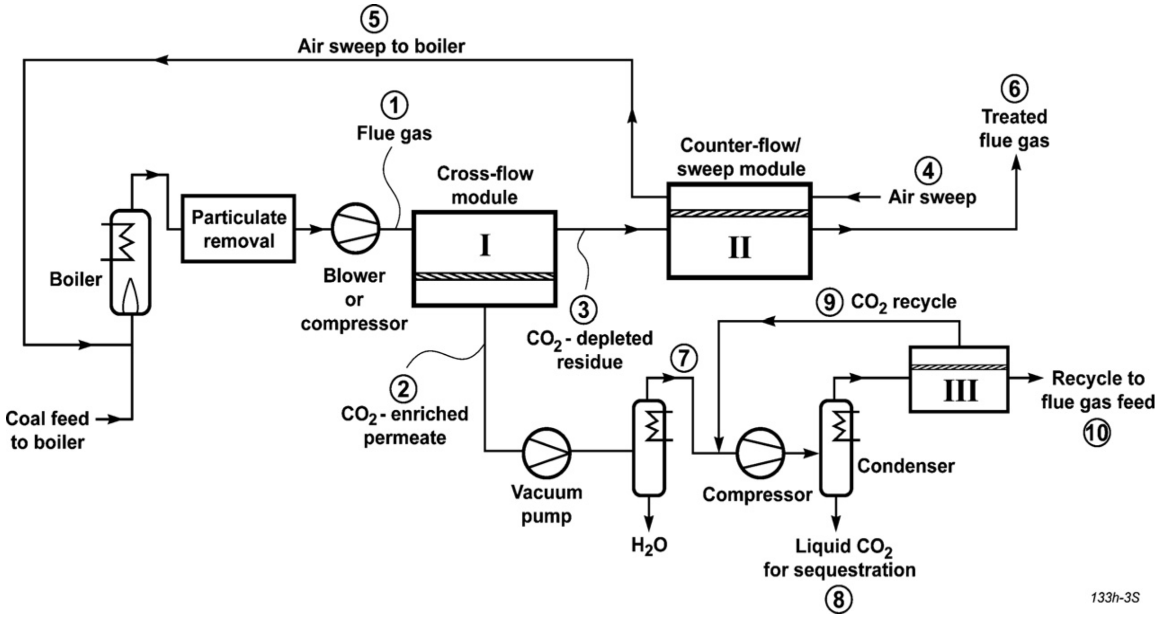


Fig. 6. Flow diagram of a two-step counter-flow/sweep membrane process to capture and sequester CO_2 in flue gas [4]

From the point of increasing the driving force for CO_2 permeation in the separation process, an approach is to use sweep gas, usually air, across the permeate side [46]. Fig. 6 demonstrates a two-step membrane system using sweep gas which is the incoming combustion air. The sweep air enters the second-stage membrane module on the permeate side, forming counter flow with the stream on the feed side. Then the CO_2 that accumulates on the permeate side will be carried away by the sweep gas so that the CO_2 partial pressure difference will increase. After the permeate gas is mixed with the sweep gas, it is very hard to separate the CO_2 from the mixture. So this stream is recycled to the boiler and the flue gas with higher CO_2 concentration can be obtained. Merkel et al in their paper [4] made a comparison between two-stage membrane system with and without sweep gas. For a 600MW power plant with 90% CO_2 captured by membrane, it is found that the membrane area needed decreases from 3.0 to 1.3 million square meters and power dropped from 145 to 97 MW by adopting sweep gas technology.

Although the membrane-based separation technology has a great potential to be a low energy and low-cost solution to controlling CO_2 emission, its application is still constrained by several practical problems. Limited by the capability and energy consumption of current compressor or vacuum pump, the pressure difference created by compressor or vacuum pump is within a certain range and thus very large membrane area is required to deal with typical flue gas [4, 32, 43, 47]. Both the volume of membrane module and cost would be obstacles. Compared to conventional chemical absorption technology, membrane-based separation is still young and immature. For the time being, most tests of membrane-based separation process are under lab-scale. Therefore, its performance in pilot-scale and full-scale power plants must be studied before being fully implemented.

4. Energetic and economic performances of chemical absorption and membrane-based separation processes

4.1. Energetic and economic impacts of chemical absorption with MEA on coal-fired power plants

As mentioned in the second section, many researches nowadays concentrate on the impacts of the integration of the chemical absorption process in existing coal-fired power plants. This section is to summarize recent energetic and economic evaluations from literatures. It is believed now that extracting steam from turbine to provide energy for solvent regeneration is the most effective approach [22, 48-51], which would naturally cause efficiency loss for coal-fired power plants. Therefore, investigating the integration of CO_2 capture system to power plants is a significant task regarding implementation.

A large number of studies focus on optimized integration of chemical absorption process into existing power plants. It is well known that commercial implementation of chemical absorption system with MEA for CO_2 capture will occur in the near future [48]. Its impacts on whole power plant are mostly evaluated by simulation work, though there are some demonstration power plants with MEA-based chemical absorption process. By far there are not simulation tools particularly designed to represent complex interactions between CO_2 capture unit and coal-fired power plant. Currently the most common method of evaluating the integration is simulating CO_2 capture unit and power plant separately and coupling them by transferring operational data. The energy consumption of CO_2 compression for transportation is often taken into account as well.

Roeder and Kather [52] used EBSILON® Professional to set up a model for a 600MW coal-fired power plant and Aspen Plus® to simulate chemical absorption process with MEA respectively. They investigated the influences of the CO_2 capture system on this reference power plant under different loads. It is found that the efficiency penalty of the power plant with 90% degree increases from 10.7% to 11.4%-pts as the load decreases from 100% to 40%, Decreasing CO_2 capture degree to 75% could recover 5% additional power. Oexmann [19] in his doctoral dissertation managed to reflect interactions between power plant and chemical absorption process by developing his own semi-empirical model for chemical absorption in EBSILON® Professional. His model has been validated by experimental results from a pilot plant and proves to be able to very well represent actual function of chemical absorption. This semi-empirical model was integrated into a power plant with an output of 1137MW to investigate the impacts of the overall CO_2 capture process. For MEA-based chemical absorption process, the reboiler duty is 3.58 GJ/tonne CO_2 and the net efficiency penalty is 10.36%-pts according to his simulation. A report by Ramezan et al [48] shows us a very complete study performed to evaluate the technical and economic feasibility of integration of amine-based CO_2 capture technology to an existing coal-fired power plant with an output of 450MW. Different cases with varied CO_2 capture degrees (96%, 90%, 70%, 50% and 30%) are tested. For the case of 90% capture degree, the net efficiency penalty is 10.5%-pts. In the article of Cifre et al [53], coal-fired power plants were simulated in EBSILON® Professional as well and chemical absorption process with MEA were implemented in CHEMASIM. A C++ code was developed by authors to couple these two softwares and apply the results from the chemical absorption process to the power plant model. Two reference coal-fired power plants, a 600MW hard coal and a 1000MW lignite power plant, were studied in this paper. The efficiency losses caused by CO_2 capture and compression are 14 and 16%-pts, respectively. Aside from energetic assessments, some researchers also have done cost evaluations. Similarly, these estimates more or less are based on some assumptions, such as fuel price, interest rate, operating time etc. Some energetic and economic evaluations from literatures are shown below in Table 2.

Although improvements have been made to this technology, the situation of high energy penalty and cost has not fundamentally altered. It can be seen from the table that with 90% CO_2 capture degree, the efficiency loss caused by CCS unit are all around 10%-pts in different literatures. According to the estimation of Abu-Zahra et al [54], the total specific investment of the power plant will increase from 980 €/kW without CO_2 capture to 1865 €/kW with CO_2 capture. In the report of National Energy Technology Laboratory (NETL) [48], the total investment cost will increase by 1,319 $/kW. This report also shows that a nearly linear relationship exists between percent CO_2 capture and total investment cost.

Table 2. Energetic and economic evaluations of chemical absorption process using MEA solvent

Reference	Output of power plant (MW)	CO_2 capture degree (%)	Efficiency loss (%-pts)	Reboiler duty (GJ/tonne CO_2)	CO_2 capture cost (€/tonne CO_2)	CO_2 avoidance cost (€/tonne CO_2)	Cost of electricity (€/MWh)
[23, 54]	600	90	-	3.29	-	37	56
[48]	450	90	10.5	-	53	79	62*
		70	8.1		57	85	47*
		50	5.7		60	89	32*
		30	3.3		69	101	21*
[13]	500	90	-	-	-	53	86
[52]	600	90	10.7	-	-	-	-
[43, 53]	600	50	5.8	-	-	-	-
		70	8.2				
		90	10.5				

* Incremental value

4.2. Energetic and economic impacts of the membrane-based separation process on coal-fired power plants

As stressed earlier, experiments to test CO_2 separation using membrane were mostly operated in labs. Hence simulation is thus far the major method to predict the performance of the membrane-based separation process for large-scale power plants. The methods to evaluate its impacts on power plants are basically the same as those applied for chemical absorption.

For the implementation of membrane-based separation process in coal-fired power plants, many papers on process-modeling are published. Zhao et al [41, 43] used PRO/Ⅱ to simulate CO_2 separation process for a 600MW reference power plant with multi-stage membrane separation systems. Both energetic and economic analyses were done and the results were compared with chemical absorption process. Their cascade membrane system was tested under three CO_2 separation degrees: 50%, 70%, and 90%. The unit price of the membrane used for simulation is assumed to be 50 €/m^2. It is concluded in their paper that only under 50% and 70% separation degree is this system attractive considering energy requirement and cost. It is important to be noted that the exhaust gas in their scheme only consists of CO_2 and N_2. The influences of other gases such as O_2 and H_2O need to be further studied. Low et al [28] found that the existence of water vapor has a small positive sweep effect which is able to enhance CO_2/N_2 separation.

Instead of studying CO_2 capture process in isolation, Zhai and Rubin [55] simulated a complete power plant with CCS using the Integrated Environmental Control Model IECM. They tested the performances of both single- and multi-stage membrane systems. Types of coals (bituminous, sub-bituminous and lignite) and power plants (subcritical, supercritical and ultrasupercritical) are as well considered important influence factors. It is concluded from the paper that efforts to produce highly permeable membranes are more economical than increasing CO_2/N_2 selectivity.

Maas et al [56] also estimated the energetic and economic results for a membrane-based separation process for CO_2 capture. Being operational under 25℃, the cascade membrane system designed by authors reaches the lowest energy consumption. A conclusion is drawn from their research that the cost of CO_2 allowances must exceed 37 €/tonne CO_2 to make membrane-based separation technology economically advantageous.

Some energetic and economic estimates are illustrated in Table 3. In contrast to chemical absorption technology, much less papers on overall evaluation of CCS using membrane in coal-fired power plants are published. According to these results, it can be found as well that membrane-based separation process does not have apparent advantages over chemical absorption technology in terms of energy and cost at 90% separation degree. The fact that large membrane area and mechanical work are needed make membranes technology less competitive than initially expected. In general, membrane property is still the key factor constraining the application of membrane-based separation process.

Table 3. Energetic and economic evaluations of membrane-based separation process

Reference	Output of power plant (MW)	Operating temperature (℃)	Permeance (Nm^{3}m^{-2} h^{-1}bar^{-1})	CO_2 capture degree (%)	Efficiency loss (%-pts)	Membrane area(Mm^2) 1st/2nd	CO_2 avoidance cost (€/tonne CO_2)	CO_2 capture cost (€/tonne CO_2)	Cost of electricity (€/MWh)
[43]	600	30	0.5	50	4.3	6.62/0.24			
				70	6.8	13.92/0.34			
			3	70	6.4	2.44		31	
[55]	450	30	1000gpu	90			72[a]	42[a]	106[a]
							47[b]	31[b]	89[b]
[56]	600	25	3	90	9.6	0.40/0.07	45		91
		30	4.3		11.1	0.29/0.04			
		50	5		14.2	0.24/0.03			

[a] Without air sweep. [b] With air sweep

5. Hybrid system

The development of CCS has mainly focused on using single CO_2 capture technologies in the past. Even though numerous optimization methods involving process modification, material manufacture, optimized integration to power plants and so forth have been made use of, implementing either MEA-based chemical absorption or membrane-based separation process is still energy-intensive or costly.

As noted in previous sections, MEA-based chemical absorption technology is most likely to be implemented in the near future for CO_2 capture. It is not the technical barrier but high energy consumption and cost that stop this relatively mature technology from being put into operation in conventional coal-fired power plants. The discovery of a highly energy-saving solvent would be a breakthrough. In terms of membrane-based separation, as a competing technology, its performance is highly restricted by inherent properties of material as well. Recently, a few studies brought forward the concept of hybrid capture system, combining multiple CO_2 separation technologies.

Membrane Technology & Research, Inc. (MTR) and the University of Texas at Austin (UT Austin) are among the pioneers in the development of hybrid capture technology. They collaborated on hybrid membrane-absorption capture systems which combine MTR’s air-swept Polaris™ membrane contactor with UT Austin’s 5m piperazine advanced flash stripper capture technology [57]. Two variations of theirs schemes are illustrated in Fig. 7. In the series arrangement (Fig. 7(a)), the flue gas is firstly treated in the chemical absorption unit and approximately 50% of the CO_2 can be removed. Then the stream exiting the stripper with 10% CO_2 goes through the membrane unit and the left CO_2 in the stream is further mitigated. As a whole, 90% removal of CO_2 in the flue is achieved. In the parallel arrangement (Fig. 7(b)), the flue gas is split and directed to the absorber and the membrane respectively. The major advantage of the parallel arrangement is that the volume of the flue gas to be treated in the chemical absorption system largely decreases and the absorber can be of only half its normal size. In both schemes, the permeate gas in the membrane is driven by the sweep gas back to the boiler as combustion air so that the CO_2 concentration in the flue gas is higher (around 20%). It is concluded that in the series case the solvent regeneration energy is less required and in the parallel case the capital costs will decrease compared to conventional chemical absorption process. A project of bench-scale test for this system was initiated in 2014 and a 0.1MW SRP pilot plant located at UT Austin was to be modified for testing [58]. The actual energetic and economic performances await experimental test.

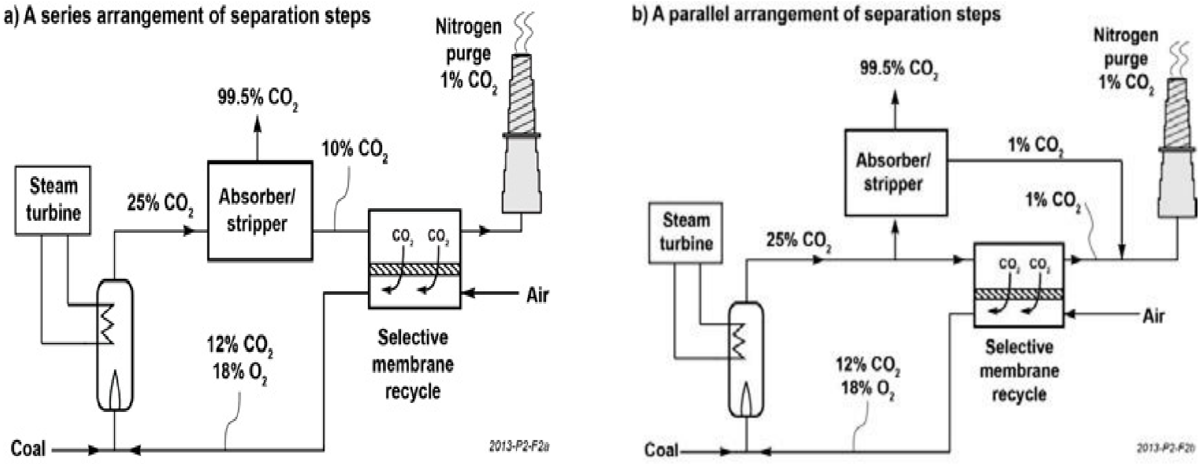


Fig. 7. Hybrid CO_2 capture system [57]

University of Kentucky is also working on a hybrid system combining membrane with chemical absorption [59]. In their design, a membrane device is installed after the absorber and prior to the stripper. The membrane media could concentrate carbon loading in the solution coming from the absorber by permeating a majority of the water and rejecting a major fraction of carbonate/bicarbonate species. Moreover, the ammonia solution on the permeate side can be recycled to the absorber for additional CO_2 capture.

Another idea of hybrid system was designed for gas turbine but may as well be modified for CO_2 capture from coal-fired power plants. Its schematic is shown in Fig. 8. The whole process can be divided into 3 steps [60]: 1) recycling: a fraction of the flue gas is redirected to the gas turbine to increase the CO_2 concentration; 2) a CO_2-selective membrane is sequentially applied to elevate the CO_2 concentration to c.a. 50%; 3) pre-concentrated CO_2 is then fed to a absorber where the CO_2 will be absorbed by a low energy consuming sorbent.

Apart from designs above, cryogenic technology is also investigated as a candidate for hybrid system. In fact, Fig. 6 already illustrates a hybrid system combining membrane separation with cryogenic technology. The CO_2-enriched permeate gas from the first-stage membrane is dehydrated and afterwards sent to a compression-condensation-membrane loop. High-purity CO_2 liquid can be obtained here and ready for sequestration.

However, Scholes et al [61] believe that this scheme presented in Fig. 6 results in dilution of oxygen in the burner and eventually reduces the overall efficiency of the power plant. Hence they considered the addition of an air separation membrane to pre-treat sweep air. This additional configuration as shown in Fig. 9 ensures that the CO_2 recovered in the second-stage membrane does not dilute O_2 concentration. In addition, a simplified process is also studied, where the membrane unit in the compression-condensation-membrane loop is removed. The optimized process successfully reduces the CO_2 avoidance cost to less than US $32 per tonne, whereas its practical application may be limited by sophisticated configuration.

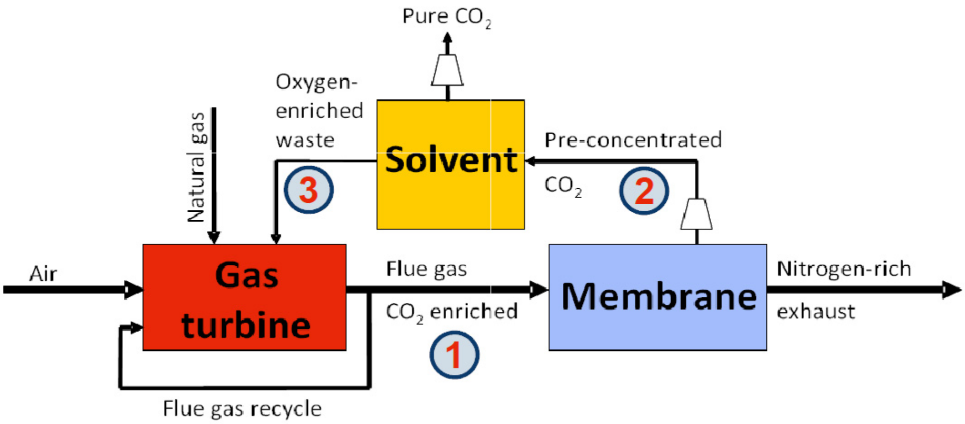


Fig. 8. Schematic of hybrid absorber-membrane CO_2 capture system [60]

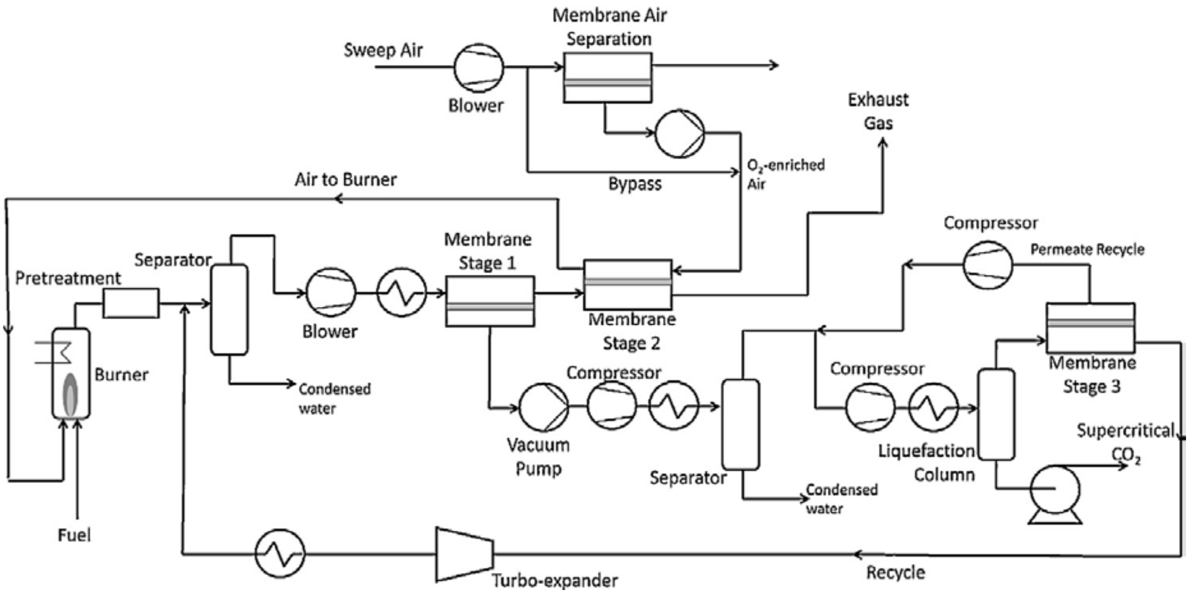


Fig. 9. A modified two-step membrane process to capture CO_2 using sweep gas [61]

Zhao et al [62] and Belaissaoui et al [63] respectively investigated a hybrid process comprised of membrane and cryogenic separation via simulation study as well. Their designs are similar, i.e. a membrane is installed prior to cryogenic separation unit to pre-concentrate CO_2. The major difference is the specific configurations of their cryogenic separation parts. The hybrid process simulated by Belarssaoui et al [63] consumes 3GJ/ton CO_2 with a CO_2 capture degree above 85% and CO_2 purity higher than 89%. According to the research of Zhao et al [62], their hybrid system possesses lower efficiency loss than MEA-based absorption and cascade membrane system when the CO_2 separation degree is below 90%.

We can find that these hybrid systems appear to be more energy-saving or economical. Although there are not enough data, especially experimental data, to prove that hybrid system is really feasible yet, this concept at least is a possible direction for future CCS when we are faced with those bottlenecks in single capture technologies.

6. Summary and conclusions

This paper has reviewed chemical absorption technology (mainly MEA-based process) as well as membrane-based separation technology. Widely studied methods and ideas of improving two technologies are introduced. In addition, some estimates of their energetic and economic performances are collected from the work of other researchers. Several conclusions are drawn as follow:

- A variety of optimization methods have been made to minimize energy consumption as well as cost for conventional chemical absorption process. However, the fact that this technology is energy-intensive and costly has not fundamentally altered.
- Membrane-based separation technology, which was initially expected to be able to compete with chemical absorption, only shows advantages at lower CO_2 capture degree (<90%). Its CO_2 capture ability is highly restricted by properties of current membrane materials.
- It is very hard to compare the energetic and economic results in literatures and draw universal conclusions because these researches were usually operated based on distinct conditions and assumptions.
- From the perspective of process design, the emergence of hybrid system could possibly take CCS one step further towards practical application. By taking advantage of each single capture technology, the overall energy requirement and cost have a great potential to be decreased. This hybrid concept will definitely strengthen the collaborations between scientists from distinct research fields.

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