Carbon dioxide capture technologies

Dao Sy Duc

Department of Chemical Technology, VNU Hanoi University of Science
19 Le Thanh Tong, Hoan Kiem, Hanoi, Vietnam

Abstract: Global warming and climate change become a serious environmental problem due to the increase of CO_2 concentration in the atmosphere. Several approaches, such as reduction of carbon intensity by using alternatives to fossil fuels such as hydrogen and renewable energy, reduction in energy intensity by the efficient use of energy, and developing efficient technologies for CO_2 capture and storage (CCS), can be applied for mitigating the CO_2 emission and CO_2 concentration in the atmosphere. This paper reviews the current technologies for capturing CO_2.

1. Introduction

The concentration of carbon dioxide (CO_2) in the atmosphere has been increased due to human activities such as the burning of fuels and hydrogen production from hydrocarbons [1], causing a major global environmental problem because CO_2 is the main greenhouse gases responsible for global warming and climate change. As estimated, about 60% of global warming is caused by CO_2 emission [2]. Global warming and climate changes have attracted the attention of many researchers and environmental scientists over the world.
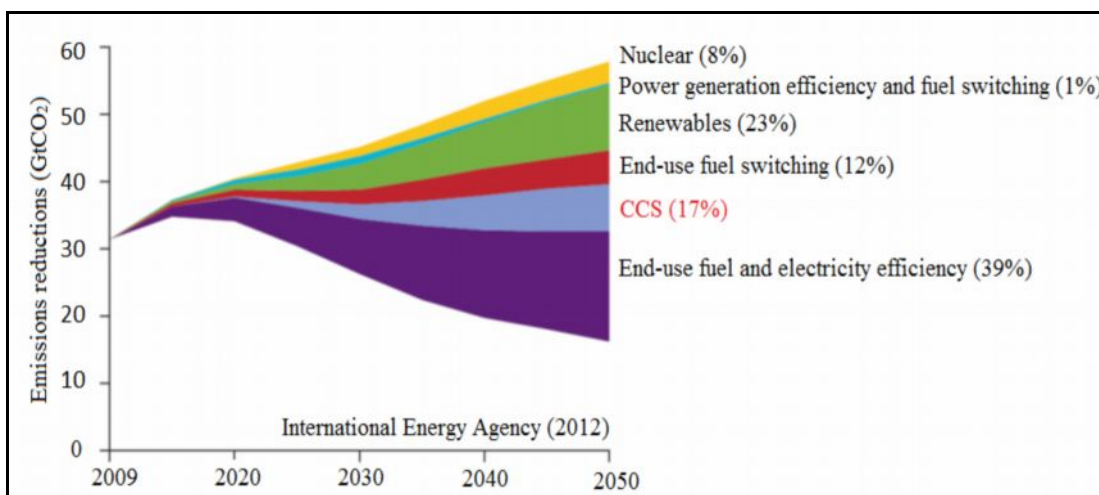

Fig. 1. Scenario for reducing CO_2 emission by 2050 (adapted from IEA [3]).

For reducing the emission of CO_2 into the atmosphere, several approaches, including (i) reduction of carbon intensity by using alternatives to fossil fuels such as hydrogen and renewable energy, (ii) reduction in energy intensity by the efficient use of energy, and (iii) developing efficient technologies for CO_2 capture and

storage (CCS), have been proposed. Among them, CCS has been known as a viable technique for mitigating CO_2 into the atmosphere. The scenario in Figure 1 indicates that about 17% of the CO_2 emission reduction by 2050 is accounted for CCS [3]. CCS refers to a set of methods for the mitigation, remediation, and storage of industrial CO_2 emissions. For more details, this paper reviews the current technologies for CO_2 capture.

Basically, three main systems can be used for capturing CO_2 to mitigate the CO_2 emission including (i) pre-combustion capture, (ii) oxyfuel combustion capture, and (iii) post-combustion capture [4].

- Pre-combustion capture by de-carbonation of the fuels prior to combustion;
- Oxyfuel combustion capture by reengineering the combustion process to produce carbon dioxide as a pure combustion product;
- Post-combustion capture by removing CO_2 from the combustion products.

Pre-combustion capture

Pre-combustion capture involves decarbonation by gasification and reforming of the primary fuel, biomass, or coal. The fuel is contacted and reacted with oxygen and/or air to form a mixture of mainly carbon dioxide and hydrogen [4]. The concentration of CO_2 in this mixture can be ranged 15-50%. Then, the CO_2 can be captured and separated, and the H_2-rich fuel combusted. The aim of these systems is to convert the carbon fuel to carbonless fuel by the transformation of the chemical energy of carbon to chemical energy of hydrogen. High investment costs and decreased short term flexibility are the disadvantages of pre-combustion capture system [3,5].

Oxyfuel combustion capture

In oxyfuel combustion capture processes, a cryogenic air separation or membranes is used to produce pure oxygen which reacts with the fuels, including coal, biomass, natural gas to form a mixture of CO_2 and H_2O. Among the fuels, coal is known as the most suitable candidate for oxyfuel combustion process. After the combustion, water and other impurities are then separated from the flue gas exhaust stream, and high-purity CO_2 is produced [2,4,6-8]. This is the main advantage of the oxyfuel combustion capture because there is no need to use any solvents and/or reagent, resulting in lower operating costs and less environmental problems [2,3]. Moreover, NO_x is not produced during the oxy fuel combustion process, which also is an another advantage of these system. However, oxyfuel combustion capture also exhibited some drawbacks such as a very low SO_x required on leaving burners, the higher temperature materials, and high energy costs of O_2 separation from air [3].

Post-combustion capture

Post-combustion capture, is the most common and widely used process, which involves the separation of carbon dioxide from the combustion products and the flue gases, before discharge to the atmosphere. As shown in Table 1, the combustion products usually contain CO_2, SO_x, and NO_x [2], with the typical CO_2 percentage ranged from 3-14% v/v depending the fuel sources [9]. Post-combustion CO_2 capture is a promising technique because it can be retrofitted to existing plans, allowing the continued operation of valuable resources. Post-combustion capture systems can be applied to already constructed plants, operated with the plant for CO_2 capture, or disconnected to provide maximum power output at times of peak electricity price. However, this method also has some disadvantages, for example (i) the energy requirements for absorbent regeneration is high, (ii) large volumes of solvents are needed, (iii) toxic by-products can be produced during the heating to regenerate the solvents [3]. After separation process, the partial pressure of CO_2 is low, which needs to be compressed for sequestration requirements.

**Table 1. CO$_2$ partial pressure in the flue gas from the combustion systems (adapted from ref. [9])**

Source	CO$_2$ concentration (v/v %)[a]	Pressure of gas stream (kPa)	CO$_2$ partial pressure (kPa)
Gas turbines	3-4	100	3-4
Natural gas fired boilers	7-10	100	7.10
IGCC[b] synthesis gas after gasification	2-20	2000-7000	160-1400
Oil fired boilers	11-13	100	11-13
Coal fired boilers	12-14	100	12-14
IGCC after combustion	12-14	100	12-14

[a] Dry conditions. [b] Integrated gasification combined cycle.

Up to date, a wide range of approaches, including solvents [10-13], membranes [10,14,15], and adsorption [1-5,10,16-18,19-22], have been proposed for post-combustion CO$_2$ capture and separation. Although liquid amine scrubbing is commercially available the process is highly energy-intensive and expensive for CO$_2$ separation from flue gases. Apart from the high energy input required to regenerate the adsorbent the mentioned techniques also have other drawbacks such as solvent evaporation and equipment corrosion [20-22]. The development of efficient techniques for cost-effective CO$_2$ capture, separation and use is therefore of great importance [7,23]. With many advantages comparing with other capture methods, amine-functionalized solid sorbents have attracted much attention, and a lot of research has been devoted to the development of effective CO$_2$ adsorbents. The development of improved adsorbents for CO$_2$ capture and separation from flue gas is considered as a key step in CCS. The following sections will give the detail information about the current technologies for post-combustion capture.

Absorption

At present, the chemical absorption systems are the preferred option for post-combustion CO$_2$ capture. This technique involves a cyclical process in which CO$_2$ is absorbed from a gas stream directed into a liquid, usually an amine. The amine scrubbing technique, has been used to separate CO$_2$ from natural gas and hydrogen since 1930, and was first evaluated in 1994 as a CO$_2$ capture technique [11]. Typically, an absorption system consists of an absorber and a desorber (Figure 2). In the absorber, CO$_2$ from flue gas is captured by reacting with an aqueous alkaline solvent to form a carbamate or a bicarbonate species, depending on the properties of amine, as shown in reactions (1.1) and (1.2) [7]. In the desorber, the absorbed CO$_2$ is stripped from the solution and a captured (~ pure) CO$_2$ stream is followed by a compression process while regenerated liquid is used again for the next absorption and the process continue.
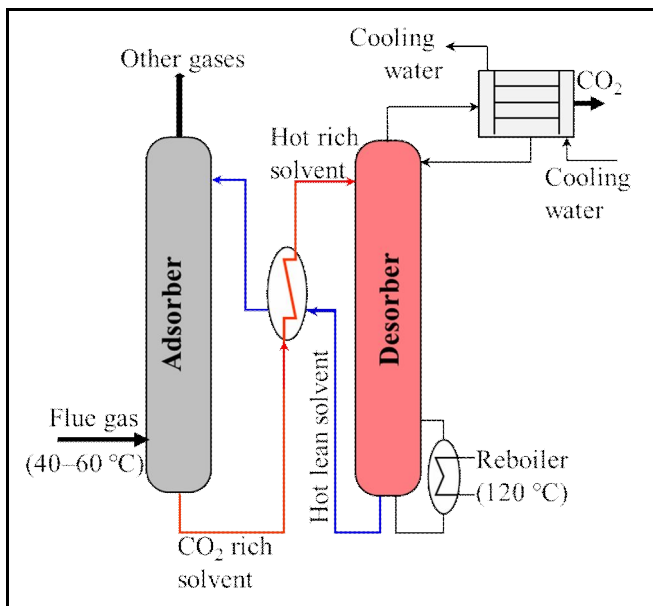
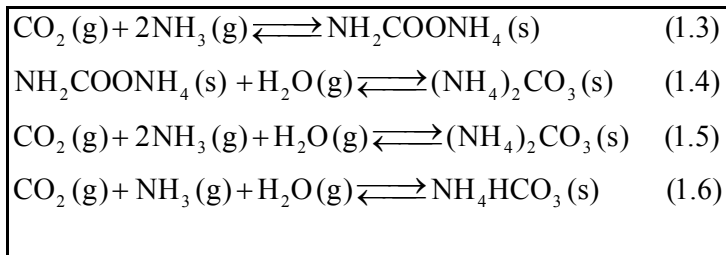**Fig. 2. Solvent absorption system for CO$_2$ capture.**

(1.1)

(1.2)
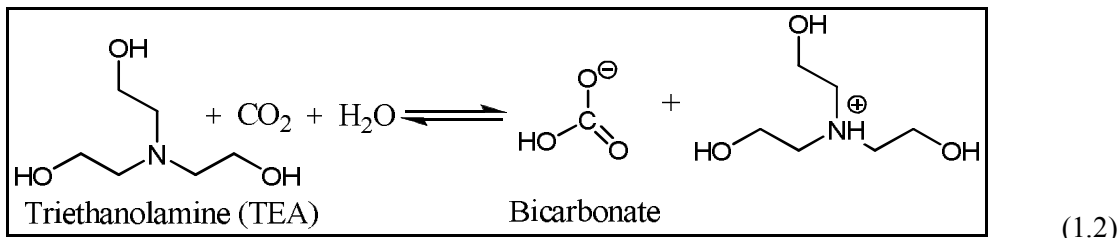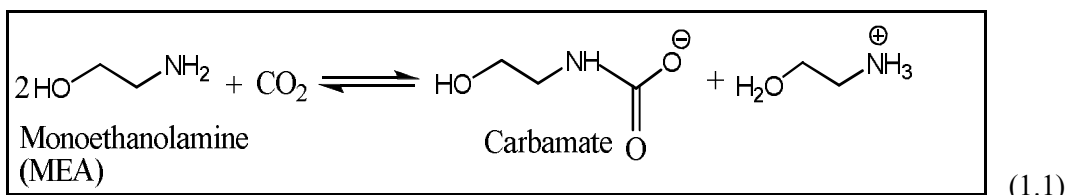
In amine-based chemical absorption, amines can be used in three forms which are primary, secondary, and tertiary (1°, 2°, and 3°) amines. Amines are usually dissolved in water at a concentration below 40 wt.%, typical ca. 20–30 wt.%. For amine scrubbing solution capture, one of the most well-investigated alkanolamines is monoethanolamine (MEA). As shown in reaction (1.1), MEA reacts with CO_2 in a 2:1 ratio to form an anionic carbamate species and a corresponding ammonium cation. In some cases, MEA is combined with secondary or tertiary alkanolamines, such as diethanolamine (DEA) or triethanolamine (TEA) for capturing CO_2. In the case of TEA, the reaction of 1 equav of amine with CO_2 results in the formation of a bicarbonate species (reaction 1.2) rather than a carbamate species due to the steric bulk about the nitrogen center of the TEA. As shown in reactions (1.1) and (1.2), the stoichiometry of the capture reactions has a significant impact on the maximum loading capacity for CO_2, since the tertiary amines react with CO_2 in a 1:1 ratio, while the primary amines interact in a ratio of 2:1. Because the bicarbonate species is comparatively less stable relative to the carbamate species, the energy required to desorb/reverse amine-CO_2 interaction decreases in the order of 1° > 2° > 3° amines [7]. As mentioned, each of amines exhibited the advantages and the disadvantages for capturing CO_2. For example, for regeneration energy and loading capacity, tertiary amines are the most preferred options, followed by secondary, and then primary amines. However, for the highest absorption rate, primary amines are the most suitable candidates, followed by secondary, then tertiary amines [2,7].

Although absorption has been known as the most common technique for capturing CO_2, it has several significant limitations for large-scale CO_2 capture. This technique needs a large amount of energy to regenerate the solvents, to compress the CO_2, and to run the pumps and the fans in the operating process, resulting in a significant energy penalty [24]. Note that the energy penalty for solvent regeneration is a key disadvantage of amine scrubbing solution, because a lower concentration of amines (usually below 40 wt.%) results in larger amount of water which must be heated to regenerate the sorbents [7]. On the other hand, the amine solutions are believed that relatively unstable toward heating, resulting in a limitation of the regeneration temperatures available for full regeneration of the capture materials. Additionally, the decomposition of the amine results in a reduction in capture performance over time, diminishing the lifetime of the solutions [7]. The alkaline amine solutions are also corrosive toward the equipments [25], the primary and secondary amines volatilize extensively during the regeneration, which limit the application of amine scrubbing technology.

CO_2 can be also separated from flue gases by using ammonia-based absorption process [2,26-28]. In this process, ammonia solution absorbs CO_2 by the formation of ammonium carbonate and ammonium bicarbonate, as shows in reactions (1.3) to (1.6). Studies of ammonia-based absorption for the greenhouse gas absorption have been noticed after the investigation of Bai and Yeh [29]. Comparing to the amine-based absorption process, ammonia-based process has some advantages. First, ammonia-based process has the higher absorption capacity compared to amine-based system [26]. Ammonia-based process can be used for capturing all three major acidic gases including CO_2, SO_2, and NO_2 in a single process which is expected to reduce the total cost and the complexity of the emission control systems. The heat of absorption of the reaction between ammonia and its derivatives and CO_2 is lower than that of amine-based absorption process, resulting in an advantage of having a lower regeneration energy [2,26-28]. The possibility of utilizing the major by-products including ammonium nitrate and ammonium sulfate as the fertilizer components is also another advantage of the absorption based on ammonium solutions. However, the high volatility of ammonia, and the loss of

ammonia during the regeneration process because of elevated temperature are recognized as the main drawbacks of aqueous ammonia chemical absorption process [2].

$$CO_2(g) + 2NH_3(g) \rightleftharpoons NH_2COONH_4(s) \qquad (1.3)$$
$$NH_2COONH_4(s) + H_2O(g) \rightleftharpoons (NH_4)_2CO_3(s) \qquad (1.4)$$
$$CO_2(g) + 2NH_3(g) + H_2O(g) \rightleftharpoons (NH_4)_2CO_3(s) \qquad (1.5)$$
$$CO_2(g) + NH_3(g) + H_2O(g) \rightleftharpoons NH_4HCO_3(s) \qquad (1.6)$$

Membrane

Membrane technology, as shown in Figure 3, is an effective method for CO_2 separation. Gas separation with membranes has emerged into a commercially viable method since 1980s. Basically, membranes are similar to filters, by separating specific component from a mixture gas in a feed stream [2]. A membrane works as a semi-permeable barrier in which the CO_2 passes through this barrier more easily than other gases. Most membranes used for gas separation and purification are non-porous, and the polymeric or ceramic membranes are of particular interest in gas separation applications. The separation takes place according to the morphology of the membrane which is based on the different transport mechanisms. CO_2 is separated from a mixture of gases by a membrane by a partial pressure difference of CO_2 across the membrane and/or a reversible chemical reaction with carriers like amines and carbonates in the membrane.
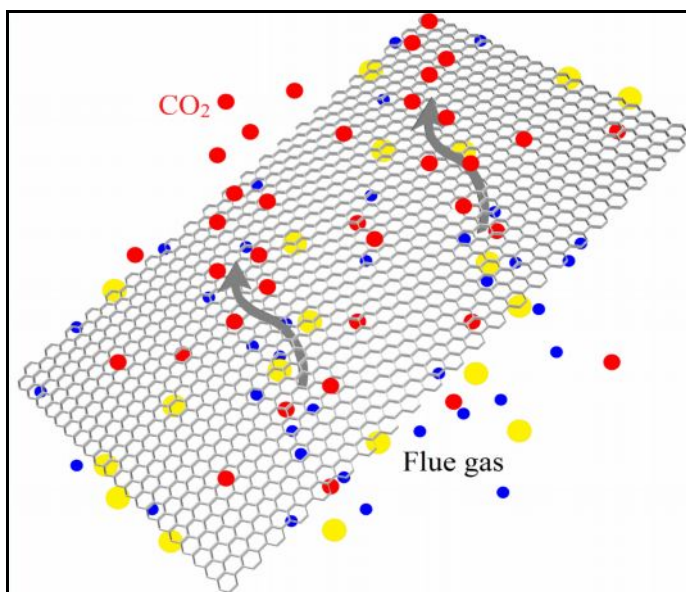
Fig. 3. Membrane system for CO_2 capture.

Membrane technologies have some advantages. One of the advantage is its simplicity, the chemicals is not required to regenerate the absorbent or adsorbent [30]. In addition, the much smaller equipments are required. The main cost for the CO_2 separation using membrane is the energy required to make a large enough pressure difference across the membrane to drive separation. Choi *et al.*[16] reported that membranes could be highly efficient mass-separating agents, especially when the species which are to pass through the membrane were present in a high concentration. Therefore, membrane processes are effective for pre-combustion CO_2 capture. However, membrane process not likely to be the most efficient techniques for the post-combustion CO_2 capture, because the exhaust gas contains CO_2 with low concentration, ca. 4-15% v/v [3,5]. In contrast, adsorption technique that will be discussed in the following paragraphs is suitable for post-combustion CO_2 capture.
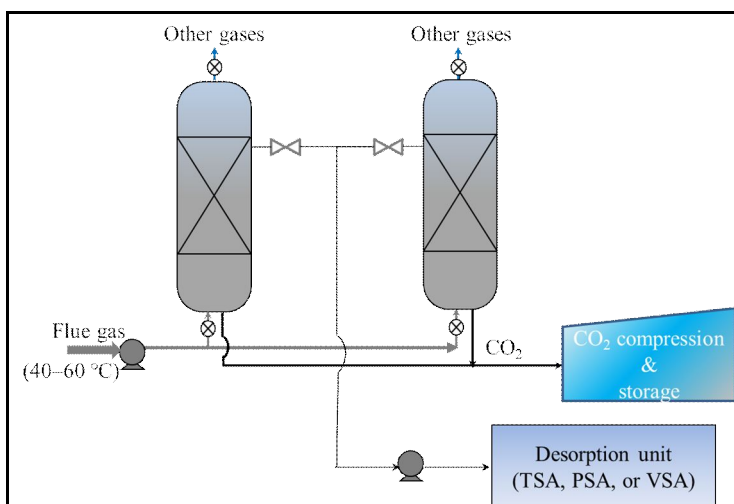
Fig. 4. **Adsorption system for CO$_2$ capture.**

Adsorption

As described in Absorption technology, the energy penalty for solvent regeneration is a key disadvantage of amine scrubbing technology because of high heat capacities of alkanolamine solutions. The lower heat capacities of solid sorbents has led to their investigation as new and effective materials which are expected to result in a lower energy penalty for CO$_2$ capture and separation, especially for regeneration process. Regarding the energy and heat, the reaction heat, the sensible heat, and the vaporization heat of the solid sorbents are lower than those of amine scrubbing solution, results in a lower regeneration energy [7].

In the adsorption processes (Figure 4), a gas or mixture of gases contacts with small porous particles, which can selectively adsorb or complex with CO$_2$ for its effective separation from the gas mixture. Adsorption is effective for the separation of dilute mixtures of gases. CO$_2$ can be adsorbed onto the sorbents by weak intermolecular forces or by strongly via covalent bonding, which termed physisorption or chemisorption, respectively. Therefore, the heat of adsorption of chemisorption processes is higher than that of physisorption processes [31]. Generally, the heat of adsorption is in the range of 60-95 kJ/mol for chemisorption processes [32-37] and 25-50 kJ/mol for physisorption cases [31,37,38]. However, the heat of physisorption of CO$_2$ in some zeolite has been reported to be as high as 55-66 kJ/mol [39].

Conclusions

Global warming and climate changes have attracted the attention of many researchers and environmental scientists over the world due to the increasing of CO$_2$ concentration in the atmosphere. For mitigating the concentration of CO$_2$, many techniques can be applied, such as (i) reduction of carbon intensity by using altenatives to fossil fuels such as hydrogen and renewable energy, (ii) reduction in energy intensity by the efficient use of energy, and (iii) developing efficient technologies for CCS have been proposed. Among them, CCS has been known as a viable technique for mitigating CO$_2$ into the atmosphere. Among the current technologies for post-combustion capture, chemical absorption system has been known as the most common technique for capturing CO$_2$, it has several significant limitations regarding the regeneration energy for large-scale CO$_2$ capture. Using adsorption technique can overcome the disadvantages of absorption.

References

1. Mello, M. R.; Phanon, D.; Silveira, G. Q.; Llewellyn, P. L.; Ronconi, C. M. Amine-modified MCM-41 mesoporous silica for carbon dioxide capture. *Microporous Mesoporous Mater.* 2011, *143*, 174.
2. Sabouni, R.; Kazemian, H.; Rohani, S. Carbon dioxide capturing technologies: a review focusing on metal organic framework materials (MOFs). *Environ. Sci. Pollut. Res*. 2014, *21*, 5427.
3. International Energy Agency:

www.iea.org/publications/freepublications/publication/technology-roadmap-carbon-capture-and-storage-2013.html.

4. Haszeldine, R. S. Carbon capture and storage: how green can black be? *Science* 2009, *325*, 1647.
5. Pires, J. C. M.; Martins, F. G.; Alvim-Ferraz, M. C. M.; Simões, M. Recent development on carbon capture and storage: an overview. *Chem. Eng. Res. Des.* 2011, *89*, 1446.
6. Olajire, A. A. CO_2 capture and separation technologies for end-of-pipe applications - a review. *Energy* 2010, *35*, 2610.
7. Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. Carbon dioxide capture in metal-organic frameworks. *Chem. Rev.* 2012, *112*, 724.
8. Boot-Handford, M. E.; Abanades, J. C.; Anthony, E. J.; Blunt, M. J.; Brandani, S.; Dowell N. M.; Fernández, J. R.; Ferrari, M.-C.; Gross, R.; Hallett, J. P.; Haszeldine, R. S.; Heptonstall, P.; Lyngfelt, A.; Makuch, Z.; Mangano, E.; Porter, R. T. J.; Pourkashanian, M.; Rochelle, G. T.; Shah, N.; Yao, J. G.; Fennell, P. S. Carbon capture and storage update. *Energy Environ. Sci.* 2014, *7*, 130.
9. IPCC. *IPCC special report on carbon dioxide capture and storage.* Cambridge University Press, 2005.
10. Kenarsari, S. D.; Yang, D.; Jiang, G.; Zhang, S.; Wang, J.; Russell, A. G.; Wei, Q.; Fan, M. Review of recent advances in carbon dioxide separation and capture. *RSC Adv.* 2013, *3*, 22739.
11. Rochelle, G. T. Amine scrubbing for CO_2 capture. *Science* 2009, *325*, 1652.
12. Hasib-ur-Rahman, M.; Larach, F. CO_2 capture in alkanolamine-RTIL blends via carbamate crystallization: route to efficient regeneration. *Environ. Sci. Technol.* 2012, *46*, 11443.
13. Dai, N.; Mitch, W. A. Influence of amine structural characteristics on *N*-nitrosamine formation potential relevant to postcombustion CO_2 capture. *Environ. Sci. Technol.* 2013, *47*, 13175.
14. Kim, E.; Lee, T.; Kim, H.; Jung, W.-J.; Han, D.-Y.; Baik, H.; Choi, N.; Choi, J. Chemical vapor deposition on chabazite (CHA) zeolite membranes for effective post-combustion CO_2 capture. *Environ. Sci. Technol.* 2014, *48*, 14828.
15. Pera-Titus, M. Porous inorganic membranes for CO_2 capture: present and prospects. *Chem. Rev.* 2014, *114*, 1413.
16. Choi, S.; Drese, J. H.; Jones, C. W. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* 2009, *2*, 796.
17. Zhang, Z.; Huang, S.; Xian, S.; Xi, H.; Li, Z. Adsorption equilibrium and kinetics of CO_2 on chromium terephthalate MIL-101. *Energy Fuels* 2011, *25*, 835.
18. Lee, S.-Y.; Park, S.-J. A review on solid adsorbents for carbon dioxide capture. *J. Ind. Eng. Chem.* 2015, *23*, 1.
19. Choi, S.; Drese, J. H.; Eisenberger, P. M.; Jones, C. W. Application of amine-tethered solid sorbents for direct CO_2 capture from the ambient air. *Environ. Sci. Technol.* 2011, *45*, 2420.
20. Wang, J.; Chen, H.; Zhou, H.; Liu, X.; Qiao, W.; Long, D.; Ling, L. Carbon dioxide capture using polyethyleneimine-loaded mesoporous carbons. *J. Environ. Sci.* 2013, *25*, 124.
21. Zhang, X.; Zheng, X.; Zhang, S.; Zhao, B.; Wu, W. AM-TEPA impregnated disordered mesoporous silica as CO_2 capture adsorbent for balanced adsorption-desorption properties. *Ind. Eng. Chem. Res.* 2012, *51*, 15163.
22. Feng, X.; Hu, G.; Hu, X.; Xie, G.; Xie, Y.; Lu, J.; Luo, M. Tetraethylenepentamine-modified siliceous mesocellular foam (MCF) for CO_2 capture. *Ind. Eng. Chem. Res.* 2013, *52*, 4221.
23. Chu, S. Carbon capture and sequestration. *Science* 2009, *325*, 1599.
24. Kothandaraman, A. *Carbon dioxide capture by chemical absorption: a solvent comprarison study.* PhD Thesis. Massachusetts Instiute of Technology, Massachusetts, US, 2010.
25. Nainar, M.; Veawab, A. Corrosion in CO_2 capture process using blended monoethanolamine and piperazine. *Ind. Eng. Chem. Res.* 2009, *48*, 9299.
26. McLarnon, C. R.; Duncan, J. L. Testing of ammonia based CO_2 capture with multi-pollutant control technology. *Energy Procedia* 2009, *1*, 1027.
27. Jilvero, H.; Normann, F.; Andersson, K.; Johnsson, F. The rate of CO_2 absorption in ammonia-implications on absorber design. *Ind. Eng. Chem. Res.* 2014, *53*, 6750.
28. Toro-Molina, C.; Bouallou, C. Comparison of post-combusion CO_2 capture by solutions of ammonia and organic amines: assessment using direct and indirect contactors. *Energy Procedia* 2014, *63*, 550.
29. Bai, H.; Yeh, A. C. Removal of CO_2 greenhouse gas by ammonia scrubbing. *Ind. Eng. Chem. Res.* 1997, *36*, 2490.
30. Ho, M. T.; Allinson, G. W.; Wiley, D. E. Reducing the cost of CO_2 capture from flue gases using membrane technology. *Ind. Eng. Chem. Res.* 2008, *47*, 1562.

31.   Wilcox, J. *Carbon capture.* Springer Science + Business Media, 2012.
32.   Satyapal, S.; Filburn, T.; Trela, J.; Strange, J. Performance and properties of a solid amine sorbent for carbon dioxide removal in space life support applications. *Energy Fuels* 2001, *15*, 250.
33.   Qi, G.; Fu, L.; Choi, B. H.; Giannelis, E.P. Efficient CO_2 sorbents based on silica foam with ultra-large mesopores. *Energy Environ. Sci.* 2012, *5*, 7368.
34.   Wang, J.; Long, D.; Zhou, H.; Chen, Q.; Liu, X.; Ling, L. Surfactant promoted solid amine sorbents for CO_2 capture. *Energy Environ. Sci.* 2012, *5*, 5742.
35.   Ebner, A. D.; Gray, M. L.; Chisholm, N. G.; Black, Q. T.; Mumford, D. D.; Nicholson, M. A.; Ritter, J. A. Suitability of a solid amine sorbent for CO_2 capture by pressure swing adsorption. *Ind. Eng. Chem. Res.* 2011, *50*, 5634.
36.   Liu, Y.; Liu, J.; Yao, W.; Cen, W.; Wang, H.; Weng, X.; Wu, Z. The effects of surface acidity on CO_2 adsorption over amine functionalized protonated titanate nanotubes. *RSC Adv.* 2013, *3*, 18803.
37.   Samata, A.; Zhao, A.; Shimizu, G. K. H.; Sarkar, P.; Gupta, R. Post-combustion CO_2 capture using solid sorbents: a review. *Ind. Eng. Chem. Res.* 2012, *51*, 1438.
38.   Delgado, M. R.; Arean, C. O. Carbon monoxide, dinitrogen and carbon dioxide adsorption on zeolite H-Beta: IR spectroscopic and thermodynamic studies. *Energy* 2011, *36*, 5286.
39.   Siriwardane, R. V.; Shen, M.-S.; Fisher, E. P. Adsorption of CO_2 on zeolites at moderate temperatures. *Energy Fuels* 2005, *19*, 1153.

*****