Methods and Applications of Carbon Capture

Submitted: 20 December 2018
Submission Type: [A]

Introduction

Since the Industrial Revolution, coal, natural gas, and other fossil fuels have been used to power human civilization. Consumption of these fuels has grown at a roughly exponential rate. The combustion of fossil fuels yields two main products: water vapor and carbon dioxide. Water is a harmless byproduct because it is not produced in sufficient quantities to have a noticeable effect on the global environment. About 1% of the atmosphere is composed of water vapor, and natural water reservoirs such as lakes and oceans can easily absorb the water produced by fossil fuel combustion.[1] In contrast, only .04% of the atmosphere is carbon dioxide.[2] There are no natural reservoirs of carbon dioxide to absorb the products of hydrocarbon combustion, so if carbon dioxide is introduced to the atmosphere in large amounts, it simply stays there.

There are a multitude of consequences to an increase in the atmospheric concentration of carbon dioxide, including ocean acidification and increases in global temperature.[3,4] The latter is causing sea levels to rise and storms to become more frequent and violent. One study on the effects of climate change in the US found that the average annual direct property damages from tropical storms in coastal US states could double or even triple.[5]

Climate change and ocean acidification have already impacted ecosystems around the globe. It is important to curb CO_2 emissions in order to minimize the damage that CO_2 emissions will do in the future. One way to reduce carbon emissions is through carbon capture and sequestration (CCS). CCS involves extracting CO_2 from a mixture of gases, compressing it into a liquid, and storing it, generally deep underground.[6] As with any extraction process, high quantities and concentrations make for more efficient capture. In the case of CCS, the highest quantities and concentrations of CO_2 can be found in fossil fuel power plants.[7] Suggestions have been made to use CCS to capture CO_2 from the atmosphere, but capturing CO_2 with this method is expensive due to the low atmospheric concentration of CO_2.[8]

There are three main methods of carbon capture that are technologically mature enough to be applied at an industrial scale in the near future. Amine-based post-combustion capture, pre-combustion capture, and oxy-fuel combustion. There are other methods of carbon capture that are still in their infancy, including supercapacitive swing adsorption (SSA) and adsorption via metal-organic frameworks (MOFs)[9,10] These techniques have been shown to work in an experimental setting, but they have not been proven to work on an industrial scale.[11]

This report will focus on CCS where carbon is collected from a power plant rather than collected from the atmosphere. Each method of carbon capture listed above will be explained at a molecular level. The advantages and disadvantages of each method will be discussed, and the potential for optimization through continued research will be assessed.

Discussion

Post-Combustion Amine Absorption

In fossil fuel burning power plants that use post-combustion capture, the fossil fuel is burned in the same manner as a power plant that does not use CCS; however in a plant with post-combustion capture, the flue gas is bubbled through an aqueous amine solution.[12] Amines are basic when dissolved in water, and carbon dioxide is acidic. When the CO_2 rich flue gas is bubbled through a basic solution, the carbon dioxide reacts with water to form H_2CO_3 which subsequently reacts with free hydroxide ions to form water and HCO_3^-. The bicarbonate ion then bonds with the positive ion created by the dissolution of the amine, locking the bicarbonate into the solution.[13] This is the simplest amine absorption process.

Most amines use more complicated reactions, and many bind directly to the CO_2 itself to form a carbamate. Once saturated with carbon dioxide, the amine bicarbonate solution is transported away from the flue gas stream and heated to about 120°C.[14] This gives the bicarbonate ions enough energy to decompose into hydroxide ions and carbon dioxide gas. At these temperatures, some water vaporizes and joins the CO_2. The carbon dioxide gas and water vapor are transported to a condenser where water vapor is converted to liquid water. This leaves pure CO_2 that can be compressed and sequestered.

Post-combustion carbon capture has the advantage of being a mature, well established technology. It can easily be retrofitted to an existing power plant because it does not require special combustion conditions.[15] A power plant that implements post-combustion capture experiences a significant decrease in efficiency. About 30% of the power it produces goes to capturing carbon dioxide from flue gas.[16] CCS using the amine-based absorption process costs about \$100 per ton of CO_2.[17] In the US, the government gives tax credits, capped at \$75 million, to companies that store CO2 underground. The current rates are \$10 per ton of CO2 pumped into a depleted oil field and \$20 per ton pumped into a deep saline aquifer. This is not enough to make CCS economically advantageous, but legislation is being considered to raise these rates.[18] Amine solutions degrade when used for CCS, and these degraded amines can be dangerous environmental pollutants.[19] Proper disposal procedures are costly. Post-combustion capture is not economically favorable for the majority of fossil fuel power plants. The only way to achieve widespread implementation of post-combustion capture is with government intervention by means of new regulations or heftier tax credits.

Pre-Combustion Capture

In pre-combustion capture, carbon is chemically extracted from the fossil fuel before combustion occurs. One pre-combustion capture technique begins with the partial oxidation of the fuel with oxygen gas and water vapor to create a mixture of carbon monoxide and water vapor.[20] This creates a chemical equilibrium with the species CO, H_2O, CO_2, and H_2. Water vapor is added in large amounts to decrease the relative concentrations of the other species. Following Le Chatelier's Principle, carbon monoxide reacts with the water until it is of negligible concentration, and carbon dioxide and hydrogen are produced. At normal reaction temperatures, the equilibrium constant for this reaction strongly favors the products CO_2 and H_2.

At equilibrium there are measurable amounts of CO_2, H_2, and H_2O. The amount of CO is negligible. These products are then piped away and cooled to condense the water vapor into liquid water, separating it from the desired products. The carbon dioxide is separated from the hydrogen, compressed, and transported to a sequestration facility while the hydrogen gas is ready to be used as a fuel.

Pre-combustion capture is more useful for purer fossil fuels like natural gas and petroleum and less useful for coal because impurities can interfere with the chemical processes that extract the carbon. In general, pre-combustion capture techniques have the potential to be more energy efficient than post combustion capture.[21] Pre-combustion capture requires large reactors and separators that are expensive to add on to an existing power plant, so retrofitting power plants with pre-combustion capture technology is not feasible.

Oxy-fuel Combustion

Oxy-fuel combustion differs from post-combustion and pre-combustion capture in that the fossil fuel is burned in pure oxygen instead of air. This vastly decreases the amount of impurities created during fossil fuel combustion. The resulting flue stream is almost all carbon dioxide and water vapor which can easily be separated by cooling the mixture below the boiling point of water.

Power plants that use oxy-fuel combustion produce virtually zero carbon emissions because the reactions in their reactors have two products, water and carbon dioxide with only trace amounts of contaminants. This method of carbon capture is capable of burning virtually any fossil fuel, even poor quality coal.[22] The main disadvantage of oxy-fuel combustion is the energy cost of creating pure oxygen. Cryogenic distillation of air is the most mature technology for producing pure oxygen at an industrial scale.[23] Even so, using this method to produce enough oxygen to burn coal would use about 10% of the energy produced by the power plant.[24] 10% is a significant amount, but it is far less than the 30% figure associated with post-combustion capture via amine absorption. There is significant potential for this technology in areas like Australia, where natural gas and petroleum are expensive but low-quality coal is plentiful.[25]

Supercapacitive Swing Adsorption (SSA)

SSA is a relatively new technology, and carbon capture using SSA is being explored by current research. SSA has been used to separate carbon dioxide from nitrogen and other gases. In carbon capture via SSA, there are numerous different materials for cathodes and anodes and a variety of salts that can be used for the capturing solution. To discuss all of them is beyond the scope of this paper. The design used in one particular experiment[26] will be discussed as a case study to provide a concrete example of a functional way to capture CO_2 using SSA. To simulate the composition of a stream of flue gas in a power plant, a mixture of CO_2 and N_2 is fed into the capacitor. In this design, CO_2 from the stream dissolves in water, becoming HCO_3^- and H^+. Much of the HCO_3^- is adsorbed to electronic double layer on the aluminum anode, increasing its concentration there. Al from the anode is oxidized to Al^{3+} and bonds with the HCO_3^- on the anode to form carbonaceous precipitates such as

$[NaAlCO_3(OH)_2][Al(OH)_3]_3$. The electrons that are left at the anode during the oxidation of aluminum generate a current that supplies electrons for reduction at the cathode. At the cathode H^+ ions from the dissolution of H_2CO_3 are reduced to make H_2 gas, a useful fuel unto itself. If this SSA design was scaled up to an industrial size, the hydrogen output would be significant. This hydrogen can be used as a fuel for the plant to generate more power.

This design for SSA carbon capture could potentially function on an industrial scale,[27] but currently, capturing carbon using SSA is much less efficient than standard amine-based capture. In fact, the energy cost of capturing one ton of carbon using SSA is about four times higher than conventional amine absorption.[28] This estimation does not account for the energy that can be extracted from the hydrogen produced during SSA, so the net energy cost for SSA carbon capture is somewhat smaller. Being an emerging technology, there is significant optimization potential, and the energy extracted by burning the hydrogen could potentially offset a significant portion of the energy used during carbon capture.[29] One advantage of this method is that, for the most part, it uses cheap, non toxic materials like Al scrap metal and solid carbon. SSA carbon capture produces large amounts of metallic carbonates, which could be sold as a product. Even if there is no demand for these carbonates, sequestering carbon dioxide in a carbonate compound appears to be a much safer and more stable method than underground geological sequestration of pure CO_2.[30] What to do with the waste solution of $NaHCO_3$ remains unanswered. As a whole, SSA is a sustainable method of carbon capture that has the intriguing possibility of generating more electricity than it uses.

Metal-Organic Frameworks (MOFs)

Metal-organic frameworks are a type of polymer consisting of metal ions bonded to organic ligands. MOFs have a crystalline structure, often with gaps large enough for gas molecules to enter the structure.[31] This porous structure vastly increases its effective surface area. In the context of carbon capture, a high surface area means that MOFs have the potential to adsorb high volumes of CO_2 per unit mass of MOF.[32]

MOFs have the advantage of requiring very little heat to release trapped carbon dioxide.[33] This is because the intermolecular forces that hold the CO_2 in place are relatively weak forces that can be overcome by a small amount of molecular kinetic energy. One of the current roadblocks in using MOFs for carbon capture is finding a MOF that will selectively adsorb CO_2 over N_2 and any trace contaminants in a stream of flue gas.[34] Two MOFs that are promising candidates for carbon capture due to their high CO_2 selectivity were analyzed by Yu et al. to determine the impact of trace flue contaminants such as SO_2, SO_3, NO, and NO_2 on the ability of these MOFs to adsorb carbon dioxide.[35] It was determined that these particular MOFs, MG/MOF-74 and MIL-101, exhibit a preference for sulfur oxides and nitrogen oxides over carbon dioxide. When used to separate CO_2 from N_2 and trace contaminants, these MOFs became less efficient at adsorbing CO_2 because the contaminant gases begin occupying the bonding sites used by CO_2 molecules. Simulations run by Yu et al. suggested that this is likely a widespread phenomenon among MOFs. Purging MOFs of these adsorbed contaminants would likely be prohibitively difficult.[36] To make MOFs a viable method of carbon capture in a fossil fuel power plant, a paradigm shift in MOF technology is likely required.

Conclusion

The continued emission of CO_2 as a byproduct of fossil fuel combustion is having a noticeable effect on the composition of earth’s atmosphere, which in turn is changing earth’s climate. Effects of climate change, among other things, include ocean acidification, increased temperatures on earth’s surface, more frequent and violent storms, and extinction of many species who are unable to adapt to their changing ecosystems. Unless carbon emissions are curbed, either via CCS or a global paradigm shift towards alternative energy, the consequences of climate change will be dire.

In order to combat climate change and minimize the damage done by CO_2 emissions, much research has been done with the goal of creating an efficient way to capture carbon dioxide at its largest source, fossil fuel burning power plants, and store it permanently, generally underground. There are several methods of carbon capture and storage ready to implement. Other methods of carbon capture such as metal-organic framework (MOF) adsorption and supercapacitive swing adsorption (SSA) are currently being investigated. Future research is likely headed towards creating new MOFs and integrating them into polymer membranes to create a membrane with high CO_2 selectivity. There is also significant potential for efficient carbon capture in the field of SSA, in part due to the fact that hydrogen gas, a valuable fuel unto itself, is a byproduct of SSA carbon capture.

Currently, no methods of CCS are profitable for a fossil fuel burning power plant in the US, even with the tax credits offered by the federal government for CO_2 sequestration. In order for CCS to be implemented on a large scale, there must be a breakthrough in CCS technology, large increases in tax credits, or new regulations that require power plants to use CCS.

Arguably, a better solution for curbing climate change lies in alternative energy. Photovoltaic cells are becoming cheaper and more efficient, and if funding is dedicated to this field, PV cells could become a cheaper source of electricity than fossil fuels,[37] eliminating the need for CCS altogether.

References

(1) Atmosphere of Earth. (2018). Retrieved November 9, 2018, from http://en.wikipedia.org/w/index.php?title=Atmosphere_of_Earth&oldid=572498976.

(2) Atmosphere of Earth. (2018). Retrieved November 9, 2018, from http://en.wikipedia.org/w/index.php?title=Atmosphere_of_Earth&oldid=572498976.

(3) Azevedo, L. B., De Schryver, A. M., Hendriks, A. J., & Huijbregts, M. A. J. (2015). Calcifying species sensitivity distributions for ocean acidification. *Environmental Science and Technology*, *49*(3), 1495–1500. https://doi.org/10.1021/es505485m.

(4) Hsiang, S., Kopp, R., Jina, A., Rising, J., Delgado, M., Mohan, S., … Houser, T. (2017). Estimating Economic Damage from Climate Change in the United States, *1369*(June), 1362–1369. Retrieved from http://www.impactlab.org/research/estimating-economic-damage-from-climate-change-in-the-united-states/.

(5) Hsiang, S., Kopp, R., Jina, A., Rising, J., Delgado, M., Mohan, S., … Houser, T. (2017). Estimating Economic Damage from Climate Change in the United States, *1369*(June), 1362–1369. Retrieved from http://www.impactlab.org/research/estimating-economic-damage-from-climate-change-in-the-united-states/.

(6) Fanchi, John R; Fanchi, Christopher J (2016). *Energy in the 21st Century*. World Scientific Publishing Co Inc. p. 350. ISBN 9789813144804.

(7) Zhao, L., Riensche, E., Blum, L., & Stolten, D. (2010). Multi-stage gas separation membrane processes used in post-combustion capture: Energetic and economic analyses. *Journal of Membrane Science*, *359*(1–2), 160–172. https://doi.org/10.1016/j.memsci.2010.02.003.

(8) Service, R. F. (2016). Cost of carbon capture drops, but does anyone want it? Science, 354(6318), 1362–1363. https://doi.org/10.1126/science.354.6318.1362.

(9) Landskron, K. (2018). Capacitance for Carbon Capture. *Angewandte Chemie - International Edition*, *57*(14), 3548–3550. https://doi.org/10.1002/anie.201800941.

(10)Service, R. F. (2016). Cost of carbon capture drops, but does anyone want it? *Science*, *354*(6318), 1362–1363. https://doi.org/10.1126/science.354.6318.1362.

*(11)*Service, R. F. (2016). Cost of carbon capture drops, but does anyone want it? *Science*, *354*(6318), 1362–1363. https://doi.org/10.1126/science.354.6318.1362.

(12)Service, R. F. (2016). Cost of carbon capture drops, but does anyone want it? Science, 354(6318), 1362–1363. https://doi.org/10.1126/science.354.6318.1362.

*(13)*Service, R. F. (2016). Cost of carbon capture drops, but does anyone want it? *Science*, *354*(6318), 1362–1363. https://doi.org/10.1126/science.354.6318.1362.

*(14)*Service, R. F. (2016). Cost of carbon capture drops, but does anyone want it? *Science*, *354*(6318), 1362–1363. https://doi.org/10.1126/science.354.6318.1362.

(15)Zhao, L., Riensche, E., Blum, L., & Stolten, D. (2010). Multi-stage gas separation membrane processes used in post-combustion capture: Energetic and economic analyses. *Journal of Membrane Science*, *359*(1–2), 160–172. https://doi.org/10.1016/j.memsci.2010.02.003.

(16)*Service, R. F. (2016). Cost of carbon capture drops, but does anyone want it? Science, 354(6318), 1362–1363. https://doi.org/10.1126/science.354.6318.1362.*

*(17)*Service, R. F. (2016). Cost of carbon capture drops, but does anyone want it? *Science*, *354*(6318), 1362–1363. https://doi.org/10.1126/science.354.6318.1362.

*(18)*Service, R. F. (2016). Cost of carbon capture drops, but does anyone want it? *Science*, *354*(6318), 1362–1363. https://doi.org/10.1126/science.354.6318.1362.

*(19)*Zhao, L., Riensche, E., Blum, L., & Stolten, D. (2010). Multi-stage gas separation membrane processes used in post-combustion capture: Energetic and economic analyses. *Journal of Membrane Science*, *359*(1–2), 160–172. https://doi.org/10.1016/j.memsci.2010.02.003.

(20)Cormos, C. C. (2011). Evaluation of power generation schemes based on hydrogen-fuelled combined cycle with carbon capture and storage (CCS). *International Journal of Hydrogen Energy*, *36*(5), 3726–3738. https://doi.org/10.1016/j.ijhydene.2010.12.042.

*(21)*Cormos, C. C. (2011). Evaluation of power generation schemes based on hydrogen-fuelled combined cycle with carbon capture and storage (CCS). *International Journal of Hydrogen Energy*, *36*(5), 3726–3738. https://doi.org/10.1016/j.ijhydene.2010.12.042.

(22)Boretti, A. (2013). Is there any real chance for carbon capture to be beneficial to the environment? *Energy Policy*, *57*, 107–108. https://doi.org/10.1016/j.enpol.2013.02.010.

(23)Chen, W., van der Ham, L., Nijmeijer, A., & Winnubst, L. (2015). Membrane-integrated oxy-fuel combustion of coal: Process design and simulation. *Journal of Membrane Science*, *492*, 461–470. https://doi.org/10.1016/j.memsci.2015.05.062.

(24)Chen, W., van der Ham, L., Nijmeijer, A., & Winnubst, L. (2015). Membrane-integrated oxy-fuel combustion of coal: Process design and simulation. Journal of Membrane Science, 492, 461–470. https://doi.org/10.1016/j.memsci.2015.05.062.

(25)Boretti, A. (2013). Is there any real chance for carbon capture to be beneficial to the environment? *Energy Policy*, *57*, 107–108. https://doi.org/10.1016/j.enpol.2013.02.010.

(26)Landskron, K. (2018). Capacitance for Carbon Capture. *Angewandte Chemie - International Edition*, *57*(14), 3548–3550. https://doi.org/10.1002/anie.201800941.

(27)Landskron, K. (2018). Capacitance for Carbon Capture. *Angewandte Chemie - International Edition*, *57*(14), 3548–3550. https://doi.org/10.1002/anie.201800941.

(28)Landskron, K. (2018). Capacitance for Carbon Capture. *Angewandte Chemie - International Edition*, *57*(14), 3548–3550. https://doi.org/10.1002/anie.201800941.

(29)Landskron, K. (2018). Capacitance for Carbon Capture. *Angewandte Chemie - International Edition*, *57*(14), 3548–3550. https://doi.org/10.1002/anie.201800941.

(30)*Landskron, K. (2018). Capacitance for Carbon Capture. Angewandte Chemie - International Edition, 57(14), 3548–3550. https://doi.org/10.1002/anie.201800941.*

(31)Sumida, K., Rogow, D. L., Mason, J. A., McDonald, T. M., Bloch, E. D., Herm, Z. R., & Tae-Hyun Bae, and J. R. L. (2012). Carbon dioxide capture by metal organic frameworks. *Chemical Reviews*, *112*(Special Issue: Metal-Organic Frameworks), 734–781. https://doi.org/10.1021/cr2003272.

(32)Sumida, K., Rogow, D. L., Mason, J. A., McDonald, T. M., Bloch, E. D., Herm, Z. R., & Tae-Hyun Bae, and J. R. L. (2012). Carbon dioxide capture by metal organic frameworks. *Chemical Reviews*, *112*(Special Issue: Metal-Organic Frameworks), 734–781. https://doi.org/10.1021/cr2003272.

(33)Service, R. F. (2016). Cost of carbon capture drops, but does anyone want it? *Science*, *354*(6318), 1362–1363. https://doi.org/10.1126/science.354.6318.1362.

(34)Yu, K., Kiesling, K., & Schmidt, J. R. (2012). Trace flue gas contaminants poison coordinatively unsaturated metal-organic frameworks: Implications for CO2adsorption and separation. *Journal of Physical Chemistry C*, *116*(38), 20480–20488. https://doi.org/10.1021/jp307894e.

*(35)*Yu, K., Kiesling, K., & Schmidt, J. R. (2012). Trace flue gas contaminants poison coordinatively unsaturated metal-organic frameworks: Implications for CO2adsorption and separation. *Journal of Physical Chemistry C*, *116*(38), 20480–20488. https://doi.org/10.1021/jp307894e.

*(36)*Yu, K., Kiesling, K., & Schmidt, J. R. (2012). Trace flue gas contaminants poison coordinatively unsaturated metal-organic frameworks: Implications for CO2adsorption and separation. *Journal of Physical Chemistry C*, *116*(38), 20480–20488. https://doi.org/10.1021/jp307894e.

(37)Hsiang, S., Kopp, R., Jina, A., Rising, J., Delgado, M., Mohan, S., … Houser, T. (2017). Estimating Economic Damage from Climate Change in the United States, *1369*(June), 1362–1369. Retrieved from http://www.impactlab.org/research/estimating-economic-damage-from-climate-change-in-the-united-states/.

Abstract

The impact of CO_2 emissions on climate change is real and severe. In order to reduce CO_2 emissions many methods of carbon capture and sequestration (CCS) have been suggested. Generally in CCS, CO_2 is extracted from the exhaust stream of fossil fuel burning power plant via absorption or adsorption of the CO_2. A handful of CCS techniques are ready for implementation in the near future, and many more are in the early stages of development. This paper will delve into the chemistry behind some of these techniques. Analysis of the benefits and detriments of each will be provided, as will a prediction as to the future direction of CCS research