

## Carbon Capture, How and then What?

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CO<sub>2</sub> emissions have been rising over the last decades following world's development and industrialization. Recently a level of 400 ppm in the atmosphere has been surpassed and over 32 GtCO<sub>2</sub> are emitted every year. The effect of greenhouse gas emissions on the Earth is unquestionable and has become a huge concern for society who leads the plea for measurements to mitigate its emission. If we are to control the emissions of CO<sub>2</sub>, we have to bear in mind that there are two different sources, *static ones* such as power facilities, representing 38% of US CO<sub>2</sub> emissions and industry, accounting for 14% of the CO<sub>2</sub> emitted, and *mobile ones*, the transportation sector, representing 32% of the total [1,2]. The approach to mitigate the emissions from the different type of source depends on its characteristics. Apart from social support, the question is whether we can make CO<sub>2</sub> capture attractive for industry via its utilization.

The technologies for CO<sub>2</sub> capture from static sources have been known for long in industry. It is possible to capture it either post combustion, from an expanded gas, or precombustion, from a compressed raw syngas with a larger concentration of CO<sub>2</sub>. We can distinguish between chemical absorption, physical absorption, physical adsorption, membrane technologies, cryogenic separation, mineral capture and oxy-fuel combustion [3]. *Chemical absorption* uses alkali solutions of amines that remove sour gases, CO<sub>2</sub> and H<sub>2</sub>S, by chemical reaction between the sour gas and the amine. The reaction is exothermic and takes place at low temperature and medium pressure. There are some important drawbacks such as the high energy requirement to regenerate the amines due to the strong binding between the sorbent and the sour gas, the effect of the impurities of the gas on the amines that degrade them and the corrosivity of the solutions. *Physical absorption* uses various sorbents giving rise to different patented processes such as Retisol, which uses methanol as solvent, Selexol, which uses dimethyl ether of polyethylene glycol (DMPEG), Sepsolv that uses n-oligoethylene glycol methyl isopropyl ethers (MPE), Purisol that uses N-methyl-2-pyrrolidone (NMP), and Gaselan that uses N-methylcaprolactam (NMC). The binding between the CO<sub>2</sub> and the solvent is electrostatic or Van der Waals' type, no chemical reaction takes place, and the amount of gas absorbed is directly proportional to the CO<sub>2</sub> partial pressure resulting in the need to operate at high pressures, 20-140 bar, and low temperatures, even cryogenic ones [4,5]. We can regenerate the solvent by reducing the pressure or heating it up. In Figure 1 we see the comparison between physical and chemical adsorbents where for high partial pressure physical absorption is favored. *Physical adsorption* consists of using a bed of different materials such as activated carbon, silica gel or zeolites that remove the CO<sub>2</sub> from the flue gases based on the difference in the size of the molecules (steric effect) or difference binding forces (equilibrium effect). The bonding between the CO<sub>2</sub> and the surface is due to Van der Waals forces. We can use two alternatives, pressure swing adsorption (PSA) and temperature swing adsorption (TSA). In the first case, we use low temperature and moderate pressure to adsorb the CO<sub>2</sub> on the surface of the bed and the bed is regenerated by expansion. In the second case, the adsorption - desorption process is driven by a temperature difference. This technology has lower capacity compared to chemical absorption and the selectivity of the removal is lower. *Membrane technologies* are based on the different diffusion of the gases through the membranes under a certain applied pressure. The materials of the membranes are

typically the same as those used as physical adsorbents. There are two types of membranes, gas separation membranes, which operate under an applied pressure so that the permeability of the different gases, and gas absorption membranes, where a carrier is used to eliminate the CO<sub>2</sub> molecules that diffuse through them and no hydrostatic pressure is required. The first class is not recommended for CO<sub>2</sub> capture due to the large volume of gas. The second requires the regeneration of the sorbent resulting in high energy consumptions as in the chemical absorption processes. Membrane technologies can be combined with physical absorption to improve the selectivity. *Cryogenic separation* is based on the differences in the boiling point of the species that allow CO<sub>2</sub> liquefaction by compression and cooling representing major costs and energy consumption due to the amount of other gases that are compressed and cooled together with the CO<sub>2</sub>, even higher than those in case of using chemical absorption. It is recommended for streams with concentrations over 60% in CO<sub>2</sub>. *Oxy-combustion* configurations consist of using pure oxygen instead of air, in which case the flue gas is mainly CO<sub>2</sub> and water vapor. In order to avoid high combustion temperatures part of this case is reinjected into the combustion chamber. They are recently being implemented so that we highly increase the concentration of CO<sub>2</sub> in the gas phase but the high costs and energy consumption related to O<sub>2</sub> production are the main drawback. The advantage is the more efficient combustion and the use of the CO<sub>2</sub> in a closed cycle to control the combustion temperature reduced 90% of the CO<sub>2</sub> that would have been emitted [4]. *Mineral storage and capture* is a process by which the CO<sub>2</sub> reacts exothermically with metal oxides to produce carbonates. In particular the use of CaO is interesting because we no longer talk about mineral storage but we can coin the term mineral capture, since the decomposition of the CaCO<sub>3</sub> is actually an equilibrium that we can drive onwards and backwards to capture the CO<sub>2</sub> by reversing the decomposition of CaCO<sub>3</sub> [6]. There are few optimization studies to compare these technologies. They select the use of PSA for precombustion CO<sub>2</sub> capture [7], while for post combustion the studies [8,9] show that the composition of the gas to be treated and its source determines the best technology. Thus, for concentrations above 30% membranes are an interesting alternative [8] while PSA is interesting for lower compositions [7,9]. However, in all the cases, the efficiency of the system due to the use of carbon capture technologies is reduced up to 20% [10]. Can CO<sub>2</sub> capture, that reduces the efficiency of the process, become attractive for industry?

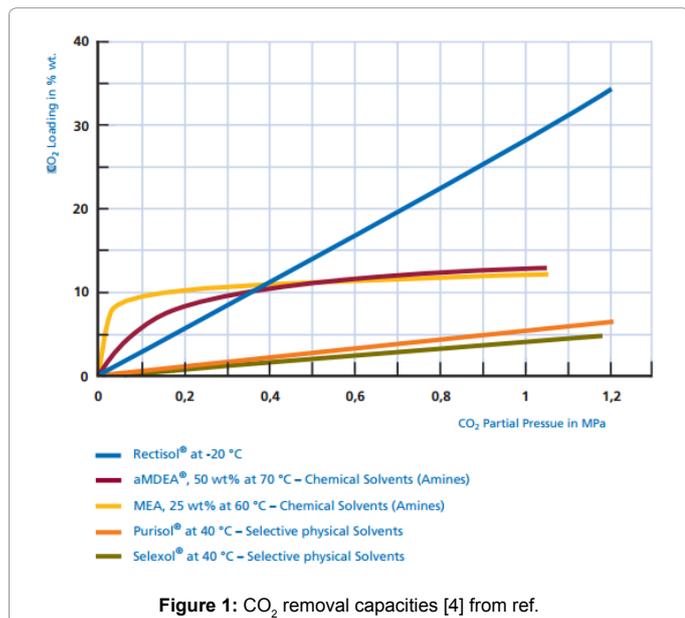
Once the CO<sub>2</sub> has been captured, the next question is what to do with it. Actually the idea of capturing CO<sub>2</sub> was not as a result of an environmental concern, but to be used for enhanced

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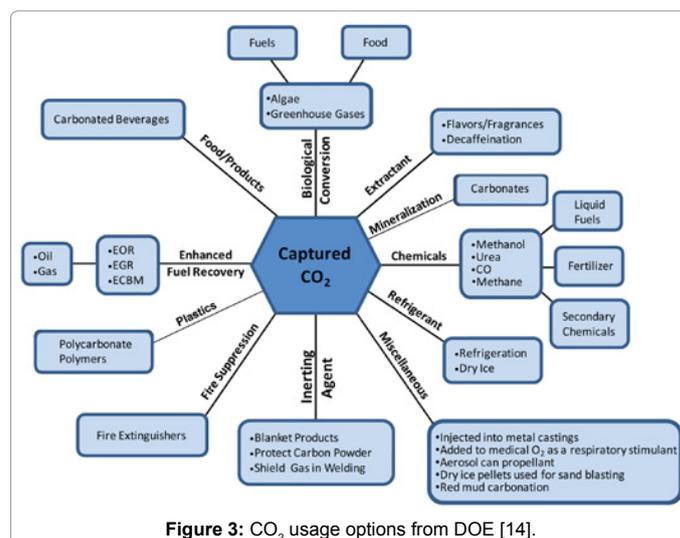
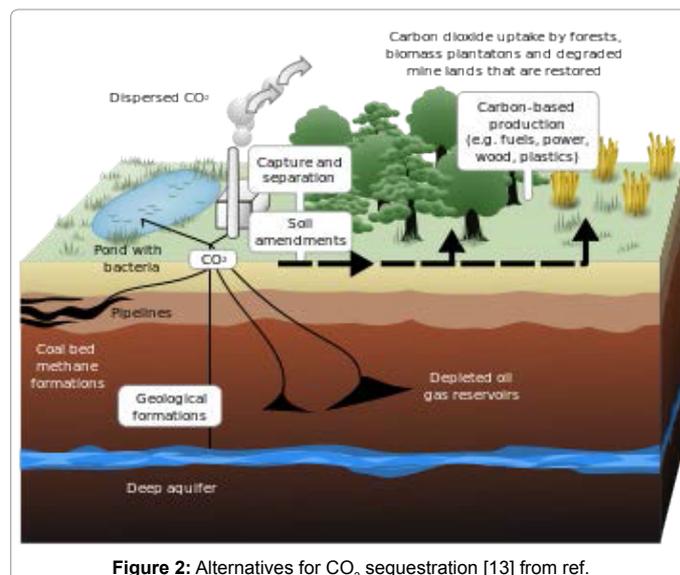


oil recovery (EOR) by injecting it into an oil reservoir so that it improves its productivity. A number of facilities were built in the US during the late 1970s and early 1980s in the US [11]. Lately Carbon Capture has been linked to the word “Sequestration” (CCS) where the CO<sub>2</sub> is injected into geological formations, into the ocean, used as source for biomass, or solid storage by reaction with metal oxides producing stable carbonates, mineral storage [11] (Figure 2). The idea of storing the CO<sub>2</sub> is related to removing it from circulation. The option of sequestration presents major concerns related to the leakage of CO<sub>2</sub> over time from the storage points such as depleted reservoirs, saline formations, unmineable coal seams and saline filled basalt. Apart from this general problem, the use of the various sinks of CO<sub>2</sub> present their own challenges. For instance, the use of *oil fields* as sink is limited by their capacity and presents the disadvantage of their geographical distribution. For coal seams, the injection of CO<sub>2</sub> may result in the release of the methane. Saline formations allow large storage volume, but their behavior over time is still unknown. Ocean storage can lead up to its acidification. However, is this an efficient way to deal with the problem? For how long can we store the current production rate of CO<sub>2</sub>? Why would we be interested in burying a chemical that can be used as carbon source for fuels or a raw material for other products? Alternatively, we can actively use it [12,13].

There are a number of alternative uses for the captured CO<sub>2</sub> that can become promising alternatives to storage (Figure 3) [14]. We can use it as carbon source for fuels, food and chemicals not only via biomass and biochemical sequestration such as algae growing [14,15] but lately CO<sub>2</sub> has been hydrogenised to produce methane and store renewable energy in a handy form [16]. One of the main issues for using CO<sub>2</sub> to produce fuels is the economics of such processes. Algae production for fuels has long been deemed uneconomical since the early studies by the DOE in the 1970’s [17]. Recently new processes and technologies for algae harvesting are providing interesting values but are yet to be scaled up [15]. Chemical synthesis of methane is being studied at laboratory scale and only recently novel processes and pilot plants are being designed with promising technical feasibility but limited economic viability until renewable production of hydrogen becomes cheaper [16]. The low prices for natural gas [18] and the easy availability of shale gas

across the globe [19] has reduced the development of this process. Apart from low value products such as fuels, it is possible to pursue higher value ones such as polymers, where traditional monomers, such as ethylene and propylene, can be combined with CO<sub>2</sub> to produce polycarbonates (i.e. polyethylene carbonate, polypropylene carbonate). The advantage of these processes is that CO<sub>2</sub> copolymerizes directly with other monomers without having to convert it to CO or to other species. Other high value products that can be obtained are refrigerants, beverages, flavors or fragrances as well as it can be used in decaffeination or fire extinguishers to mention a few[14]. In this case a trade-off between the required purity and the price will determine their profitability. Higher value products seem a more interesting alternative but the large availability of CO<sub>2</sub> together with the need to maintain the prices for these specialized products and the need to avoid its emission opens the field to many opportunities. Therefore, in order to make CO<sub>2</sub> attractive as raw material, the economy of the processes using it must be improved in a way that the use of CO<sub>2</sub> pays for its capture.

Even if we can deal with CO<sub>2</sub> from static sources in any of the ways presented along this paper, we have to realize that the transport section still contributes 30% to the total CO<sub>2</sub> emissions. Thus, a different



approach is needed since the existing technologies are difficult to be implemented in automobiles. It is possible to consider two alternatives, either the development of novel technologies or the use of carbon neutral fuels or energy (i.e. biofuels, electricity from renewables or fossil fuels with carbon capture). The use of biofuels is the easiest alternative to date, since we can substitute current gasoline or diesel by its renewable counterparts with no or just few modifications to the engines. Furthermore, the current infrastructure can be used for biofuels distribution. However, at this point with the price of crude oil and the lack of development of the biofuel production processes, they are not economically competitive with crude based diesel or gasoline. On the other hand, the move from the current automobile system based on liquid fuels to electric cars is a more profound challenge. Even though a number of car makers are already producing electric vehicles or hybrid ones, there are still a few drawbacks related to the production of electricity from renewables, due to the limited autonomy of those vehicles and the lack of infrastructure to maintain the new fleet of vehicles including batteries, charging stations etc. Graphene is considered to be the next technological breakthrough for, among others, energy storage and quicker recharging times [20] which could potentially eliminate this drawback. Furthermore, when the electricity is produced using fossil based fuels with carbon capture, it is possible to extend and use the CO<sub>2</sub> capture to produce methane as commented above [16]. Can carbon neutral fuels and energy become competitive? Eventually they will, but no without further research and development.

We can foresee much work on the technologies to mitigate CO<sub>2</sub> emissions and to find profitable uses. One important point of this particular research is who should fund the research on carbon capture technologies or even whether we should go for them. On the one hand, from the economic point of after view no company is interested in a technology that reduces the efficiency of the whole process and which is expensive on its own. On the other hand, if instead of storing the captured CO<sub>2</sub>, further usage is developed and economic incentives are obtained, there is a real opportunity to change the wind in this topic. So far, most of the times CO<sub>2</sub> capture has been implemented within a process were related to its poisonous effect on the downstream process and not because of the benefits to the environment. Thus, once the CO<sub>2</sub> is captured, instead of just storing it away hiding the problem, further usage is to be encouraged. The large availability makes it an interesting raw material not only to become a source of carbon for fuels and chemicals but to store solar or wind energy [16] and for higher value products. The way the use of CO<sub>2</sub> as a raw material is going to affect current processes and its economy is still unknown, since the market may turn depending on the benefit that the current production facilities may obtain from our nowadays best known waste. Furthermore, there is a responsibility to the society to produce in a sustainable way.

Regulations on the emissions can force the companies to be more involved in the development of such technologies. This requires the compromise from countries all over since those not involved can get in the short term enough advantage that discourages or lead to bad economic situations to those working on it.

## References

1. EPA (2014) Overview of Greenhouse gases.
2. EIA (2014). International energy statistics.
3. USDOE, Chen ZY, Review of CO<sub>2</sub> capture technologies and some improvement opportunities.
4. Lurgi (2014) The Rectisol Process.
5. GPSA Engineering Data Book (2004) FPS VERSION 21-10.
6. Grasa GS, Abanades JC (2006) CO<sub>2</sub> Capture Capacity of CaO in Long Series of Carbonation/Calcination Cycles. *Ind Eng Chem Res* 45: 8846-8851.
7. Martín M, Grossmann IE (2011) Energy Optimization of Bioethanol Production via Gasification of Switchgrass *AIChE J* 57: 3408-3428.
8. Hasan MMF, Baliban RC, Elia JA, Floudas CA (2012) Modeling, Simulation, and Optimization of Postcombustion CO<sub>2</sub> Capture for Variable Feed Concentration and Flow Rate. 1. Chemical Absorption and Membrane Processes. *Ind Eng Chem Res*, 51: 15642-15664.
9. Hasan MMF, Baliban RC, Elia JA, Floudas CA (2012) Modeling, Simulation, and Optimization of Postcombustion CO<sub>2</sub> Capture for Variable Feed Concentration and Flow Rate. 2. Pressure Swing Adsorption and Vacuum Swing Adsorption Processes. *Ind Eng Chem Res* 51: 15665-15682.
10. USDOE (2014) Postcombustion carbon capture research.
11. Herzog H (1999) An introduction to CO<sub>2</sub> separation and capture technologies.
12. Kondratenko EV, Mul G, Baltrusaitis J, Larrazábal GO, Pérez-Ramírez J (2013) Status and perspectives of CO<sub>2</sub> conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes. *Energy Environ Sci* 6: 3112-3135.
13. Wikipedia (2014) Carbon Capture and storage.
14. NETL (2014) CO<sub>2</sub> utilization focus area.
15. Martín M, Grossmann IE (2013) Optimal engineered algae composition for the integrated simultaneous production of bioethanol and biodiesel. *AIChE J* 59: 2872-2883.
16. Davis W, Martín M (2014) Optimal year-round operation for methane production from CO<sub>2</sub> and Water using wind energy. *Energy* 69: 497-505.
17. Sheehan JM, Dunahay T, Benemann J, Roessler P (1998) A Look Back at the U.S. Department of Energy's Aquatic Species Program: Biodiesel from Algae. National Renewable Energy Laboratory.
18. EIA (2014) Natural Gas Prices.
19. EIA (2013) Technically Recoverable Shale Oil and Shale Gas Resources: An Assessment of 137 Shale Formations in 41 Countries outside the United States.
20. Chandler DL (2014) Crumpled graphene could provide an unconventional energy storage.