

PG&E GAS R&D AND INNOVATION

Carbon Capture Technical Analysis

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1 Carbon Capture: Industrial Processes

Some commercial applications already remove CO₂ in concentrated streams as part of normal operations. For other industrial processes and electricity generation, existing systems would need to be redesigned to capture and concentrate CO₂ in one of three methods described in sections 1.1 – 1.3. The capture process is dependent on the concentration of CO₂ and the presence of impurities (acid gases, oxygen, particulates). (Center for Climate and Energy Solutions, 2018)

1.1 OXYFUEL CARBON CAPTURE

Uses fossil fuel combustion in pure oxygen (not air) to produce an exhaust gas that is CO₂ rich, to facilitate capture. The mixture of CO₂ and steam can be separated through condensation. There are no commercial applications available today due to the main challenges of high combustion temperature (as high as 3500°C) and the high cost of nitrogen separation. (Center for Climate and Energy Solutions, 2018)

1.2 PRE-COMBUSTION CARBON CAPTURE

Fuel is gasified (not combusted) to produce a syngas consisting mostly of CO and H₂. A shift reaction converts CO to CO₂, and then a physical solvent separates CO₂ from H₂. This can be combined with an integrated gasification combined cycle (IGCC) power plant to generate power from the separated H₂ in a turbine. (Center for Climate and Energy Solutions, 2018)

1.3 POST-COMBUSTION CARBON CAPTURE

Uses chemical solvents to separate CO₂ out of the flue gas from fossil fuel combustion. This is well suited towards retrofits of existing power plants. The main process is absorption/desorption with solvents. (Center for Climate and Energy Solutions, 2018)

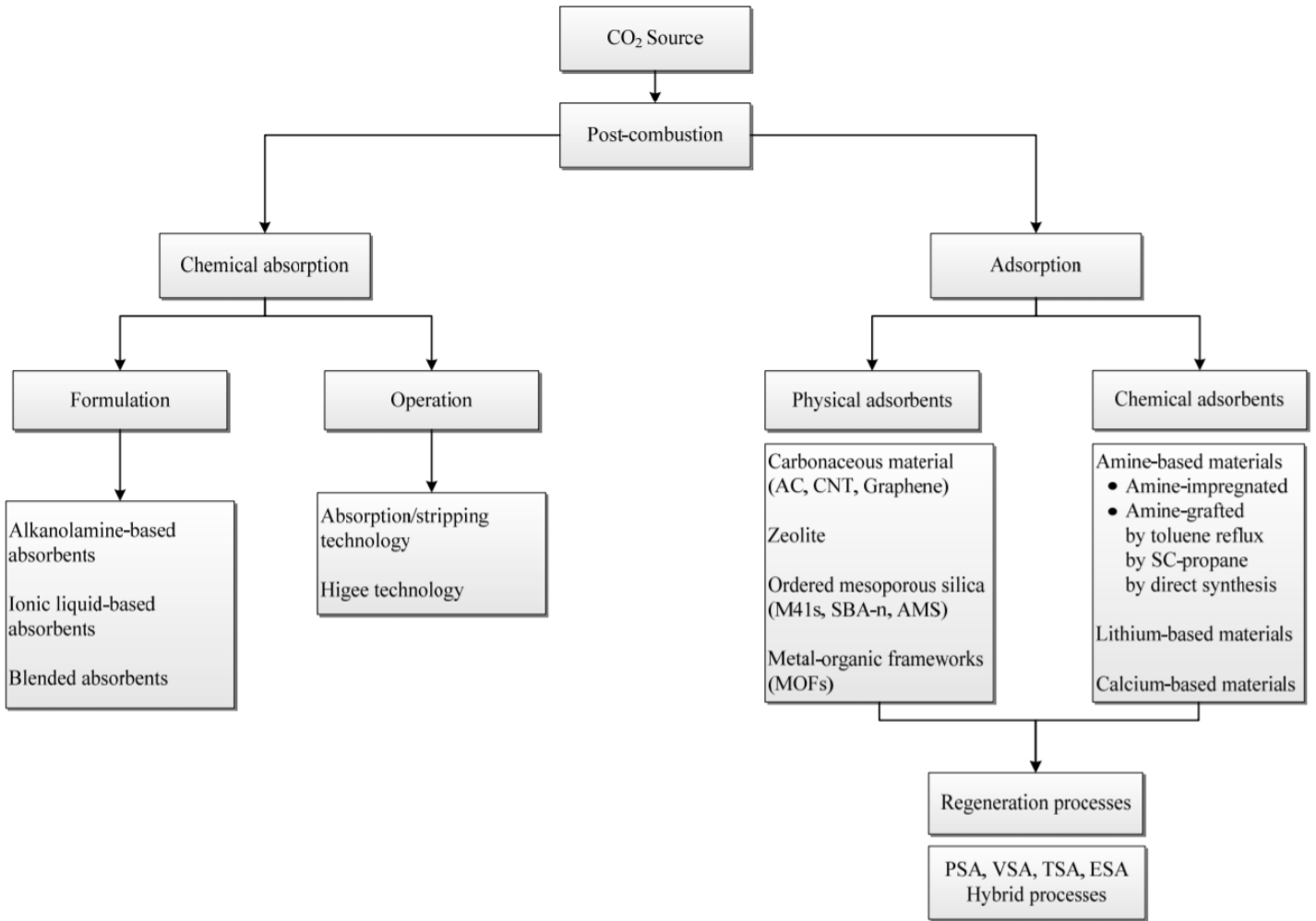


Figure 1 Flow diagram for CO₂ capture by absorption and adsorption (Yu, Huang, & Tan, 2012)

1.4 SCHEMATIC OF CARBON CAPTURE PROCESSES

The below diagram shows the different capture processes highlighted in sections 1.1 – 1.3, and how they end up with captured CO₂.

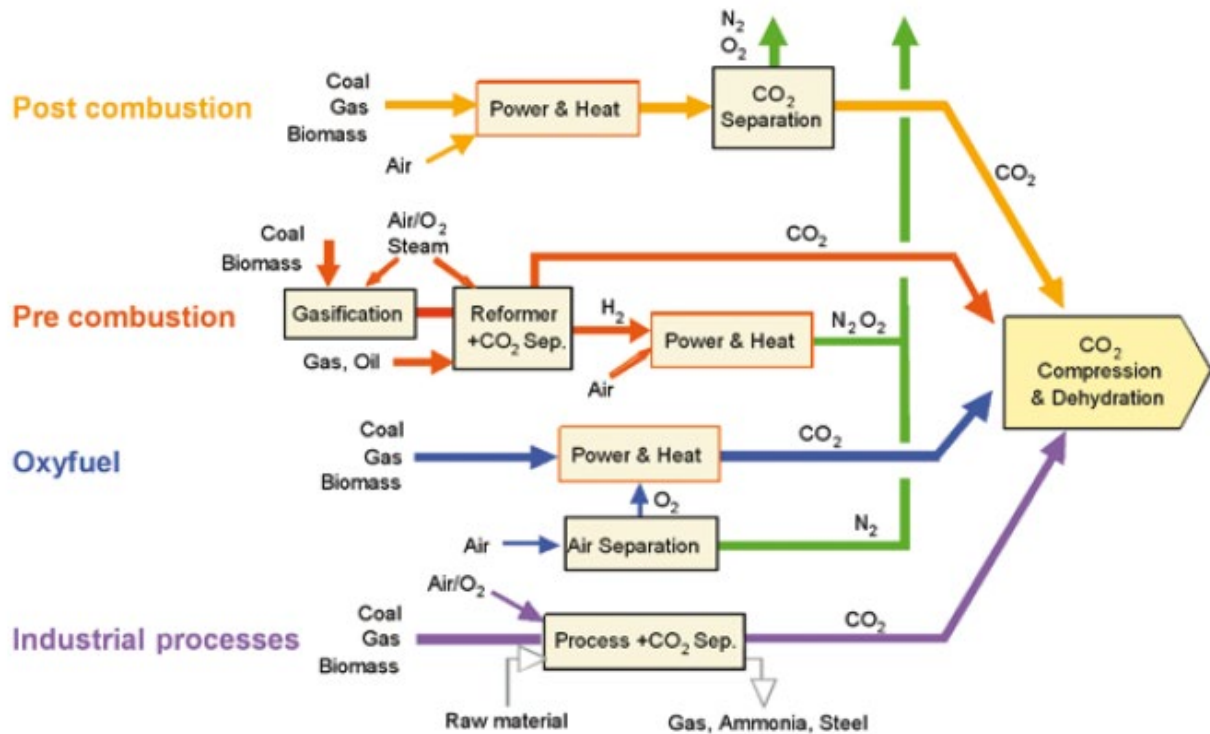


Figure 2 Pathways to produce CO₂ (Duncan & Gallant, n.d.)

1.4.1 ABSORPTION

1.4.1.1 Physical Absorption

CO₂ is absorbed under a high pressure and a low temperature, and desorbed at reduced pressure and increased temperature.

Existing commercial processes: Selexol Process, Rectisol Process, Purisol Process, Morphysorb Process, and Fluor process. The absorbents are dimethylether or propylene glycol for Selexol Process, methanol for Rectisol Process, Nmethylpyrrolidone for Purisol Process, morpholine for Morphysorb Process and propylene carbonate for Fluor Process. (Yu, Huang, & Tan, 2012)

1.4.1.2 Chemical Absorption

A typical chemical absorption process consists of an absorber and a stripper in which absorbent is thermally regenerated. In a chemical absorption process, the flue gas containing CO₂ enters a packed bed absorber

from the bottom and contacts counter-currently with a CO₂-lean absorbent. After absorption, the CO₂-rich absorbent flows into a stripper for thermal regeneration. After regeneration, the CO₂-lean absorbent is pumped back to the absorber for cyclic use. The pure CO₂ released from the stripper is compressed for the subsequent transportation and storage. The operation pressure is around 1.0 bar and the temperatures in the absorber and stripper are generally in the ranges of 40–60°C and 120–140°C, respectively. The theoretically minimum energy required for recovery of CO₂ from a flue gas and compression of CO₂ to 150 bar is 0.396 GJ/tonne CO₂. (Yu, Huang, & Tan, 2012)

1.4.1.3 Ionic Liquid

Ionic liquid (IL) has unique properties, such as very low vapor pressure, good thermal stability, high polarity, and non-toxicity. IL has been extensively used as the solvents for catalysis and synthesis. For CO₂ capture, IL can be applied to absorb CO₂ by either physical absorption or chemical absorption. (Yu, Huang, & Tan, 2012)

1.4.1.4 Higee Technology

To enhance mass transfer rate between gas and liquid, a rotating packed bed (RPB) aka Higee was created. In a RPB, liquid contacts gas on the surface of packing under high centrifugal field. With high gravity, liquid is split into small droplets and thin film during it passes through the packing, and increasing the gas-liquid contact area and mass transfer rate. RPB can be classified into 2 types, countercurrent flow and cross flow, depending on the flow directions of gas and liquid. (Yu, Huang, & Tan, 2012)

1.4.2 ADSORPTION

1.4.2.1 Physical Adsorbent

Carbonaceous adsorbents (Yu, Huang, & Tan, 2012)

- Wide availability, low cost, high thermal stability and low sensitivity to moisture, limited application to treat high pressure gases
- Weak CO₂ adsorption from 50-120°C resulting in high sensitivity in temperature and low selectivity in operation
- Improvements are needed: (1) to improve surface area and pore structure of the carbonaceous adsorbents either using different precursors or fabricating different structures such as ordered

mesoporous carbon, single-wall CNT, multi-walled CNT, graphene, etc.; (2) to increase alkalinity by chemical modification on surface.

Zeolites (Yu, Huang, & Tan, 2012)

- Adsorption efficiencies of zeolites are largely affected by their size, charge density, and chemical composition of cations in their porous structures
- CO₂ adsorption capacity and the CO₂/N₂ selectivity are relatively low
- CO₂ adsorption capacity declines in the presence of moisture due to their highly hydrophilic character, requiring a high regeneration temperature (> 300°C)
- Research is focused on: (1) highly crystalline structure, high surface area, and 3-dimensional pore structures by altering their composition as Si/Al ratio; (2) exchange with alkali and alkaline-earth cations in the structure of zeolites to enhance the CO₂ adsorption

Ordered mesoporous silica (Yu, Huang, & Tan, 2012)

- High surface area, high pore volume, tunable pore size and good thermal and mechanical stability
- Low CO₂ adsorption capacities

Metal-organic frameworks (MOFs) (Yu, Huang, & Tan, 2012)

- High surface area, controllable pore structures and tunable pore surface properties, which can be easily tuned by changing either the metallic clusters or the organic ligands
- Adsorption capacities are dramatically reduced when they are exposed to a gas mixture
- Additional research required to verify practical applications, studies completed in laboratory so far

1.4.2.2 Chemical Adsorbent: Amine-Based

Low heat of regeneration over aqueous amines due to the low heat capacity of solid supports. However, the low CO₂ adsorption capacity and high cost, however, are the major challenges to commercialize.

Improvement is needed: (1) the preparation of supports with high amine loading, (2) the use of amine with high nitrogen content; (3) effective methods for amine introduction. (Yu, Huang, & Tan, 2012)

1.4.2.3 Other Adsorbents

Porous inorganic metal oxides such as alkali metals or alkali-earth metals providing alkalinity have been widely used to incorporate or disperse in porous supports for CO₂ capture. Among metal oxides, lithium based materials have high adsorption capacity, but have significant diffusion resistance hindering industrial application. The calcium based adsorbents have high adsorption capacity, long-term durability, fast adsorption/desorption kinetic, good mechanical strength, wide availability and low cost in natural minerals. Improvements are needed by (1) reactivation by steam hydration, (2) incorporation of inert materials, and (3) modification of pore structure. (Yu, Huang, & Tan, 2012)

1.4.2.4 Adsorption Regeneration Process

Regeneration techniques include (1) pressure swing adsorption (PSA), (2) vacuum swing adsorption (VSA), (3) temperature swing adsorption (TSA), (4) electric swing adsorption (ESA), the increase of temperature by conducting electricity through the conductive adsorbents; (5) pressure and temperature hybrid process (PTSA), and (6) washing. (Yu, Huang, & Tan, 2012)

2 Carbon Capture: Direct Air Capture

2.1 WHAT IS IT?

The capture of CO₂ from ambient air was commercialized in the 1950s as a pre-treatment for cryogenic air separation. In the 1960s, capture of CO₂ from air was considered as a feedstock for production of hydrocarbon fuels using mobile nuclear power plants. In the 1990s, Klaus Lackner explored the large-scale capture of CO₂ as a tool for managing climate risk, now referred to as direct air capture (DAC). (Keith, Holmes, Angelo, & Heidel, 2018)

DAC technology takes ambient air and directs its flow over a chemical sorbent that selectively removes CO₂. The CO₂ is then released as a concentrated stream for disposal or reuse, while the sorbent is regenerated and the CO₂-depleted air is returned to the atmosphere. (Carbon Engineering, 2018)

2.2 WHY IS IT IMPORTANT?

DAC is one of a small number of strategies that might allow the world someday to lower the atmospheric concentration of CO₂. The wide-open science and engineering issues that will determine ultimate feasibility and competitiveness involve alternative strategies for moving the air and alternative chemical routes to sorption and regeneration. (Carbon Engineering, 2018)

If people choose to reduce the atmospheric CO₂ concentration gradually, DAC would compete with two terrestrial biological strategies: 1) afforestation, reforestation, and other measures that store additional carbon on the land, and 2) capture of CO₂ from bioenergy facilities, such as biomass power plants. DAC may be deployed in parallel with these biocapture strategies and other strategies for removing CO₂ from air. (Carbon Engineering, 2018)

2.3 KEY TAKEAWAYS

(Carbon Engineering, 2018)

- DAC is not currently an economically viable approach. The storage part of CCS needs to be inexpensive and feasible at huge scale for DAC to be economically viable.
- The world has centralized sources of carbon emissions, so any future deployment that relies on low-carbon energy sources for powering DAC would usually be less cost-effective than just using the low-carbon energy to displace those centralized carbon sources. Consequently, coherent CO₂ mitigation delays the deployment of DAC until large, centralized CO₂ sources have been nearly eliminated on a global scale.
- DAC may have a role to play in countering emissions from decentralized emissions of CO₂, such as from buildings and vehicles (ships, planes) that are costly to reduce by other means.
- All air capture strategies are strongly constrained by the need to remove more CO₂ from the atmosphere than one emits to the atmosphere during the capture process—the “net-carbon” problem. High-carbon energy sources are not viable options for powering DAC systems, because their CO₂ emissions may exceed the CO₂ captured.
- Given the large uncertainties in estimating the cost of DAC, century-scale economic models of global CO₂ emissions that feature “overshoot trajectories” and rely on DAC should be viewed with extreme caution.

3 Carbon Capture Technologies

3.1 NORTHWESTERN UNIVERSITY: METAL-ORGANIC FRAMEWORKS (MOFS)

(JWN Energy, 2017)

A genetic algorithm rapidly searches through a database of 55,000 MOFs to identify potential MOFs for specific applications. One key candidate, a variant of NOTT-101, has a higher capacity for CO₂ than those reported in scientific literature. MOFs have nanoscopic pores and very high surface areas, allowing them to hold high volumes of gas.

A new MOF has been designed that can capture CO₂ directly from a power plant exhaust before it enters the atmosphere.

3.2 CORNELL UNIVERSITY: NANOSPONGES

Low-toxicity, highly effective carbon-trapping “sponges” with potential to improve carbon capture economics. The design consists of a silica scaffold, the sorbent support, with nanoscale pores to maximize surface area. The scaffold is dipped into liquid amine which absorbs into the support and partially hardens. The final produce is a stable, dry white powder that captures CO₂ even in the presence of moisture. (JWN Energy, 2017)

3.3 LAWRENCE BERKELEY NATIONAL LABORATORY: HYBRID MEMBRANES

A hybrid membrane that is part polymer and part MOF. The MOFs account for 50 per cent of its weight, which is about 20 per cent more than other hybrid membranes, without compromising structural integrity. Previously, the mechanical stability of a hybrid membrane limited the amount of MOFs that could be packed in it. The hybrid membrane provides two channels for the molecules to move through (dual transport pathways). (JWN Energy, 2017)

3.4 SOGANG UNIVERSITY: CRYSTALS

A new material called SGU-29, is a copper silicate crystal, that can be used for capturing CO₂ directly (in the presence of moisture) from the atmosphere. (JWN Energy, 2017)

3.5 UNIVERSITY OF SOUTHAMPTON: TURNING CARBON TO ROCK

It has been shown for the first time that CO₂ can be permanently and rapidly locked away from the atmosphere by injecting it into volcanic bedrock. It reacts with the surrounding rock, forming environmentally benign minerals.

The gas was injected into a deep well at the study site in Iceland. As a volcanic island, Iceland is made up of 90 per cent basalt, a rock rich in elements required for carbon mineralization, such as calcium, magnesium and iron. The CO₂ is dissolved in water and carried down the well. On contact with the target storage rocks at 400–800 metres under the ground, the solution quickly reacts with the surrounding basaltic rock, forming carbonate minerals.

The next step is to upscale CO₂ storage in basalt. This is currently happening at Reykjavik Energy's Hellisheiði geothermal power plant, where up to 5,000 tonnes of CO₂ per year are captured and stored in a basaltic reservoir. (JWN Energy, 2017)

The investigation is part of the CarbFix project, a European Commission– and Department of Energy–funded program to develop ways to store anthropogenic CO₂ in basaltic rocks through field, laboratory and modelling studies.

3.6 UNIVERSITY OF SOUTHERN CALIFORNIA: TURNING CARBON INTO FUEL

Air was bubbled through an aqueous solution of pentaethylenhexamine, with a catalyst to promote hydrogen to latch onto the CO₂ under pressure. Then the solution was heated, converting 79% of the CO₂ into methanol. Though mixed with water, the resulting methanol can be easily distilled.

The system operates at around 125–165°C, minimizing the decomposition of the catalyst, which occurs at 155°C. It also uses a homogeneous catalyst. In a lab, the researchers demonstrated that they were able to run the process five times with minimal loss of the effectiveness of the catalyst. (JWN Energy, 2017)

3.7 GEORGE WASHINGTON UNIVERSITY: TURNING CARBON INTO FIBERS

A new system can turn carbon into fibers. It is a high efficiency, low-energy process, with heat and electricity produced through a hybrid solar-energy system. The system uses electrolytic syntheses to make the nanofibers. CO₂ is broken down in a high-temperature electrolytic bath of molten carbonates at 750°C. Atmospheric air is added to an electrolytic cell causing the CO₂ to dissolve when subjected to the heat and direct current through electrodes of nickel and steel. The carbon nanofibers build up on the steel electrode, where they can be removed.

The electrical energy costs of the “solar thermal electrochemical process” are estimated to be around \$1,000/ton of carbon nanofiber product, much less than the value of the product. Carbon nanofiber growth can occur at less than one volt at 750°C, which is less than the three to five volts used in the 1,000°C industrial formation of aluminum. (JWN Energy, 2017)

The next step is to ramp up the process and gain experience to make consistently sized nanofibers.

3.8 CARBON ENGINEERING (CE): DIRECT AIR CAPTURE

Carbon Engineering (CE) has been developing an aqueous DAC system since 2009. Since 2015, CE has been operating a 1 t-CO₂/day pilot plant.

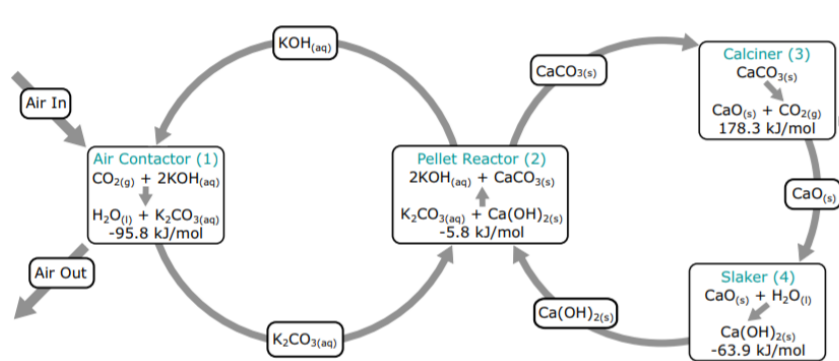
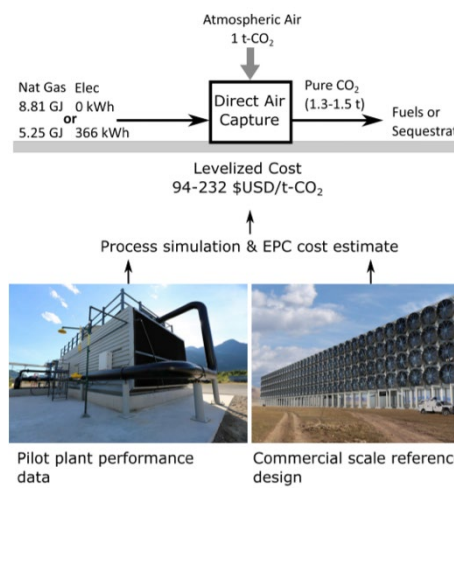


Figure 3 Process Chemistry and Thermodynamics (Keith, Holmes, Angelo, & Heidel, 2018)

The **contactor** brings ambient air in contact with the alkali capture solution. Capture of CO₂ from the air occurs at the surface of a ~50 mm film of solution flowing downward through structured plastic packing through which the air flows horizontally (cross-flow configuration). The transport of CO₂ into the fluid is limited by a reaction-diffusion process occurring in the liquid film. In the **pellet reactor**, the carbonate ion is removed from solution by causticization. In this fluidized bed reactor, CaCO₃ pellets are suspended in solution that flows upward. A slurry of 30% Ca(OH)₂ is injected into the bottom of the reactor vessel. As Ca²⁺ reacts with CO₃⁻² it drives dissolution of Ca(OH)₂ and precipitation of CaCO₃. Small seed pellets are added at the top of the bed, and as pellets grow they sink through the reactor until finished pellets are discharged at the bottom. Roughly 10% of the Ca leaves the vessel as fines that must be captured in a downstream filter. The finished pellets are roughly spherical agglomerations of calcite crystals with negligible porosity. In an oxygen fired CFB **calciner**, calcination of CaCO₃ to produce CO₂ is performed. In the **slaker**, heat from slaking is used to dry and preheat the pellets, yielding sufficient steam to sustain the slaking reaction. (Keith, Holmes, Angelo, & Heidel, 2018)

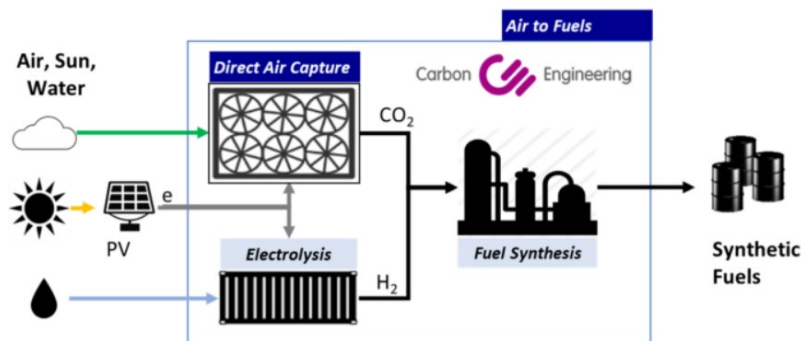


Figure 4 How Carbon Engineering's DAC Technology Works (Carbon Engineering, n.d.)

Carbon Engineering uses their DAC technology to extract and purify CO₂ from the air, and uses electrolysis to create hydrogen from water using renewable electricity. The CO₂ and hydrogen are then combined in a process called “thermo-catalysis”, where they are directly synthesized into liquid fuels such as gasoline and diesel (and in the future, jet fuel).

3.8.1 Benefits

(Keith, Holmes, Angelo, & Heidel, 2018)

- **Contactor:** Differs from commercial configuration in that the cross-flow cooling-tower components are used for a chemical gas-exchange process, rather than the counter-flow vertically oriented tower philosophy typically used for chemical processes. This design choice is a crucial enabler of cost-effective DAC, as designs using vertical packed towers are far more expensive.
- **Pellet Reactor:** Differs from traditional water treatment technology used to remove multi-valent ions (e.g. CO₃²⁻) in that it: (1) the causticization agent is the limiting reagent, (2) it uses 30% lime slurry rather than the ~2% slurries used in water treatment, and (3) the process parameters are optimized to maximize caustic flux per unit bed area rather than water flux.
- **Calciner:** Differs from the commercial configuration in that it uses a fluoseal for solids recirculation, but not for solids discharge, does not include preheat for the pellets or oxygen, and uses an air quench and baghouse prior to venting to manage off-gases. High material flux and high calcination, in conditions where reaction enthalpy is driven by in-bed combustion using oxygen and natural gas as the sole fluidizing gas.
- **Slaker:** Differs from conventional water slaking in that the slaking reaction enthalpy is released at higher temperatures which provides a thermodynamic advantage.

3.8.2 Limitations

(Keith, Holmes, Angelo, & Heidel, 2018)

- **Contactor:** Using cross-flow cooling-tower components may allow for droplets of contactor fluid to escape into the ambient air, posing a health hazard.
- **Pellet Reactor:** Energy trade-off between energy requirement and retention
- **Calciner:** Attained the specified 90 kg-CaCO₃/ hr feed rate over hundreds of hours of run time with stable bed performance, and with stable combustion with excess oxygen concentration of 20%. This is high due to the small bed diameter sized used for the pilot.
- **Calciner:** Two kinds of fouling:
 - Re-carbonization fouling occurs if temperature drops below the re-carbonation temperature allowing CaO and CO₂ to form CaCO₃, which forms a hard deposit on surfaces. It posed challenges to achieving stable operation of the pilot.
 - Alkali fouling is driven by the sticky alkali species, particularly influenced by carryover of K from the aqueous process. It poses a significant process risk.



4 CO₂ Transportation

After CO₂ is capture, it needs to be transported to the storage site. There are over 4500 miles of existing pipelines used to transport CO₂ in the United States, from use in enhanced oil recovery. However, more will be needed. (Center for Climate and Energy Solutions, 2018)

5 Carbon Sequestration

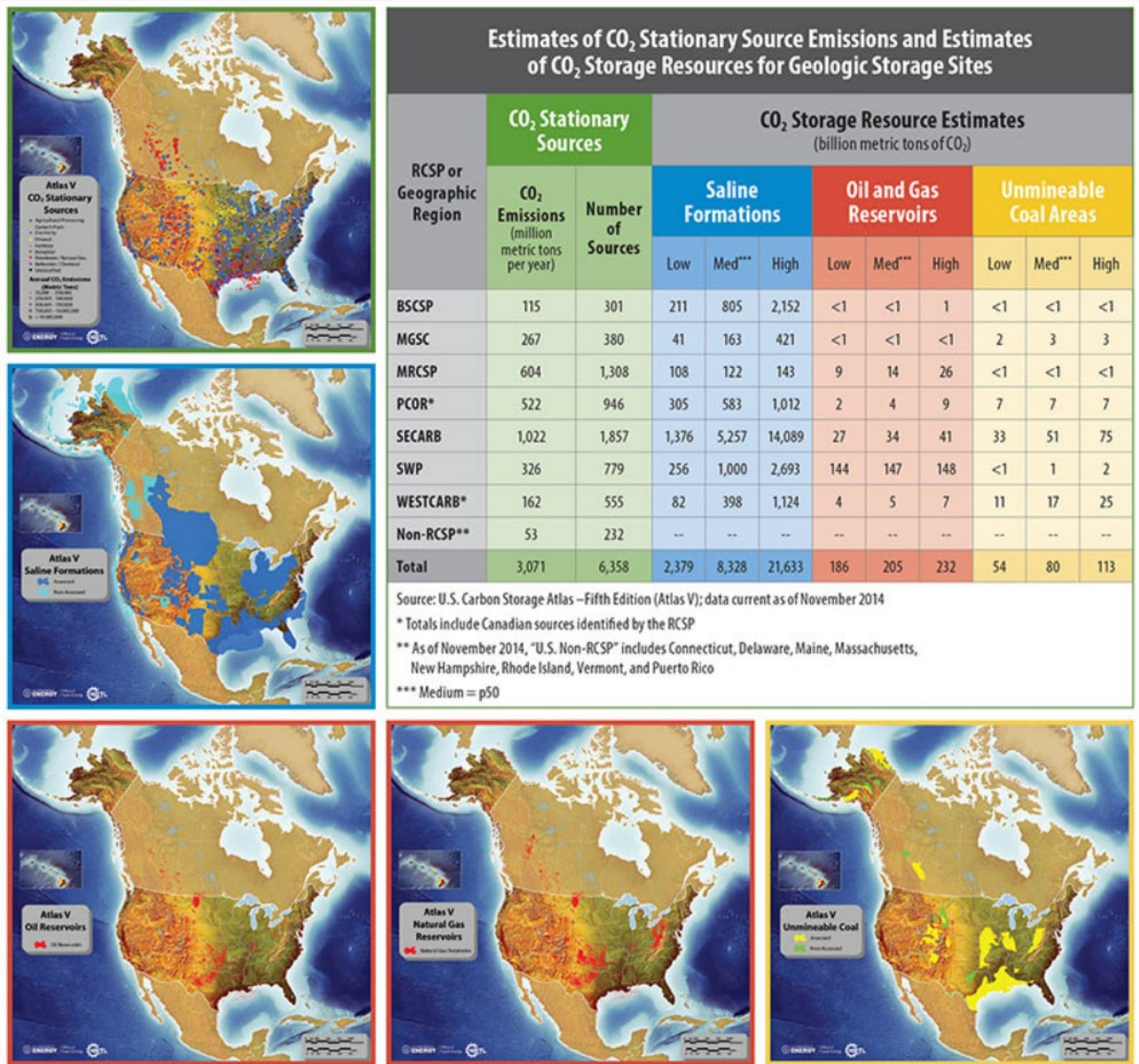


Figure 5 Estimates of CO₂ Stationary Source Emissions and Estimates of CO₂ Storage Resources for Geologic Storage Sites (Center for Climate and Energy Solutions, 2018)

CO₂ can be injected into geological formations to be stored deep underground. The CO₂ can be stored for centuries this way. Four options exist for CO₂ geologic storage (Center for Climate and Energy Solutions, 2018):

Oil and Gas Reservoirs (Enhanced Oil Recovery with Carbon Dioxide, CO₂-EOR)

In addition to storage, injecting CO₂ allows for more oil to be extracted from developed sites. Oil and gas reservoirs have held oil and gas resources for millions of years, making them good candidates for CO₂ storage. Data from prior fossil fuel exploration on subsurface areas exist that may help ensure permanent CO₂ storage. Revenue from selling capture CO₂ to EOR operators may help balance out the cost of the capture technology.

Deep Saline Formations

These are porous rock formations infused with brine. These have potential for geologic storage locations, but not have not been examined extensively.

Coal Beds

Coal beds that are too deep or thin to be cost effectively mined, could be used for CO₂ storage instead. The CO₂ may enhance coal bed methane recovery (ECBM) to extract methane gas.

Basalt Formations and Share Basins

These have potential for geologic storage locations, but not have not been examined extensively.

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