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WHITEPAPER

Carbon Capture and Sequestration / Alternative Carbon Markets

9/19/2018

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Carbon Capture: Industrial Process

Some commercial applications already remove CO_2 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 CO_2 in one of three methods described in below sections. The capture process is dependent on the concentration of CO_2 and the presence of impurities (acid gases, oxygen, particulates).

OXYFUEL CARBON CAPTURE

Uses fossil fuel combustion in pure oxygen (not air) to produce an exhaust gas that is CO_2 rich, to facilitate capture. The mixture of CO_2 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.

PRE-COMBUSTION CARBON CAPTURE

Fuel is gasified (not combusted) to produce a syngas consisting mostly of CO and H_2. A shift reaction converts CO to CO_2, and then a physical solvent separates CO_2 from H_2. This can be combined with an integrated gasification combined cycle (IGCC) power plant to generate power from the separated H_2 in a turbine.

POST-COMBUSTION CARBON CAPTURE

Uses chemical solvents to separate CO_2 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.

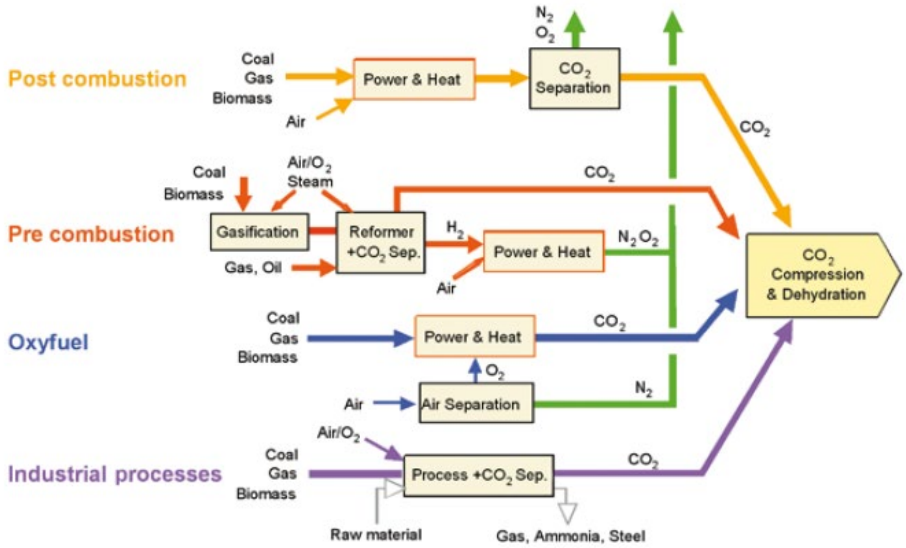


Figure 1 Schematic of carbon capture processes (R&D and Innovation, 2018)

Carbon Capture: Direct Air Capture

WHAT IS IT?

The capture of CO_2 from ambient air was commercialized in the 1950s as a pre-treatment for cryogenic air separation. In the 1960s, capture of CO_2 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 CO_2 as a tool for managing climate risk, now referred to as direct air capture (DAC). (Keith, 2018)

DAC technology takes ambient air and directs its flow over a chemical sorbent that selectively removes CO_2. The CO_2 is then released as a concentrated stream for disposal or reuse, while the sorbent is regenerated and the CO_2-depleted air is returned to the atmosphere. (Socolow, 2011)

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. (Socolow, 2011)

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.

KEY TAKEAWAYS

(Socolow, 2011)

- 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 CO_2 mitigation delays the deployment of DAC until large, centralized CO_2 sources have been nearly eliminated on a global scale.
- DAC may have a role to play in countering emissions from decentralized emissions of CO_2, 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 CO_2 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 CO_2 emissions may exceed the CO_2 captured.
- Given the large uncertainties in estimating the cost of DAC, century-scale economic models of global CO_2 emissions that feature “overshoot trajectories” and rely on DAC should be viewed with extreme caution.

Carbon Capture Technologies

METAL-ORGANIC FRAMEWORKS (MOFS) BY NORTHWESTERN UNIVERSITY

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 CO_2 than those reported in scientific literature. MOFs have nanoscopic pores and very high surface areas, allowing them to hold high volumes of gas. (JWN Energy, 2017)

A new MOF has been designed that can capture CO_2 directly from a power plant exhaust before it enters the atmosphere.

NANOSPONGES BY CORNELL UNIVERSITY

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 CO_2 even in the presence of moisture. (JWN Energy, 2017)

HYBRID MEMBRANES BY LAWRENCE BERKELEY NATIONAL LABORATORY

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)

CRYSTALS BY SOGANG UNIVERSITY

A new material called SGU-29, is a copper silicate crystal, that can be used for capturing CO_2 directly (in the presence of moisture) from the atmosphere. (JWN Energy, 2017)

TURNING CARBON TO ROCK BY UNIVERSITY OF SOUTHAMPTON

It has been shown for the first time that CO_2 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 CO_2 is dissolved in water and carried down the well. On contact with the target storage rocks at 400–800 meters under the ground, the solution quickly reacts with the surrounding basaltic rock, forming carbonate minerals. (JWN Energy, 2017)

The next step is to upscale CO_2 storage in basalt. This is currently happening at Reykjavik Energy's Hellisheiđi geothermal power plant, where up to 5,000 tonnes of CO_2 per year are captured and stored in a basaltic reservoir.

The investigation is part of the CarbFix project, a European Commission– and Department of Energy–funded program to develop ways to store anthropogenic CO_2 in basaltic rocks through field, laboratory and modelling studies.

TURNING CARBON INTO FUEL BY:

University of Southern California

Air was bubbled through an aqueous solution of pentaethylenehexamine, with a catalyst to promote hydrogen to latch onto the CO_2 under pressure. Then the solution was heated, converting 79% of the CO_2 into methanol. Though mixed with water, the resulting methanol can be easily distilled.
The system operates at around 125–165ºC, minimizing the decomposition of the catalyst, which occurs at 155ºC. 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)

Carbon Recycling International (CRI)

CO_2 and H_2 are mixed together and put through a catalytic conversion unit to produce crude methanol (mixture of methanol and water) at elevated temperature and pressure. The reaction is exothermic. In the distillation unit, the crude methanol is separate into methanol (at designed purity/quality) and water for re-use or disposal. (Carbon recycling international) A first of its kind emissions-to-liquids facility was commissioned in Iceland in 2012, with a production capacity of 4000 ton/year of methanol (Stefannsson, 2017).

Turning Carbon into Fibers by George Washington University

A new system can turn carbon info 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. CO_2 is broken down in a high-temperature electrolytic bath of molten carbonates at 750^oC. Atmospheric air is added to an electrolytic cell causing the CO_2 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. (JWN Energy, 2017)

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^oC, which is less than the three to five volts used in the 1,000^oC industrial formation of aluminum.

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

Direct Air Capture by Carbon Engineering (CE)

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. (Keith, 2018)

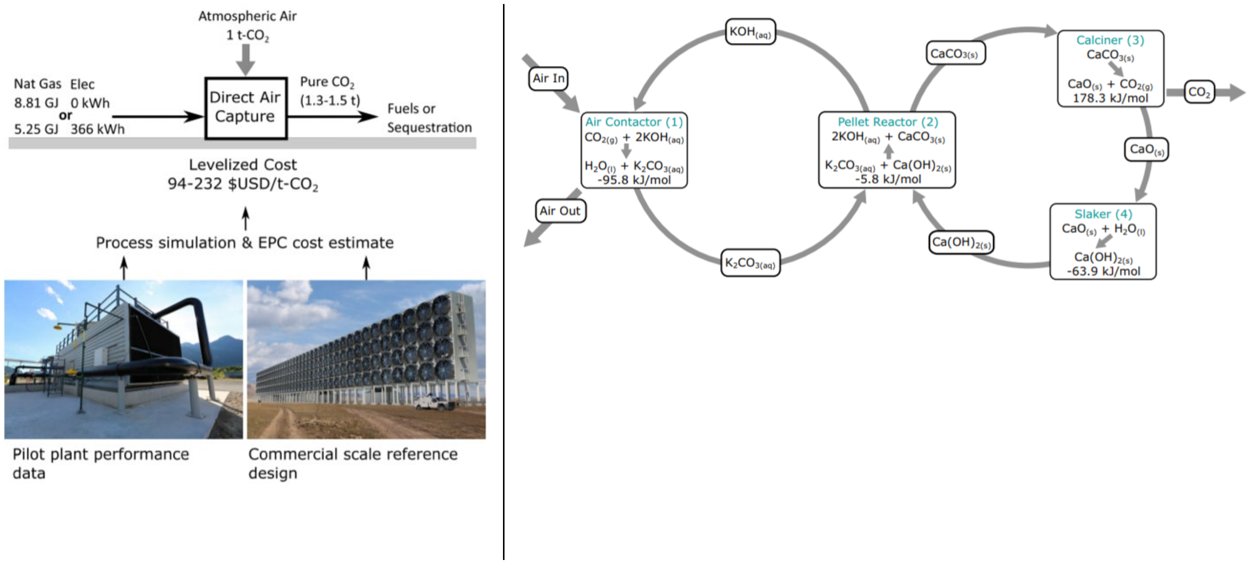


Figure 2 Process Chemistry and Thermodynamics (Socolow, 2011)

The **contactor** brings ambient air in contact with the alkali capture solution. Capture of CO_2 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 CO_2 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, $CaCO_3$ 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 Ca^{2+} reacts with CO_3^{-2} it drives dissolution of $Ca(OH)_2$ and precipitation of $CaCO_3$. 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 $CaCO_3$ to produce CO_2 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, 2018)

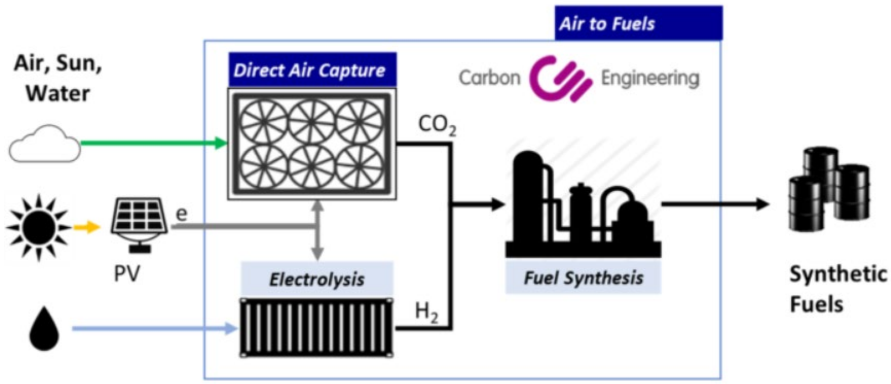
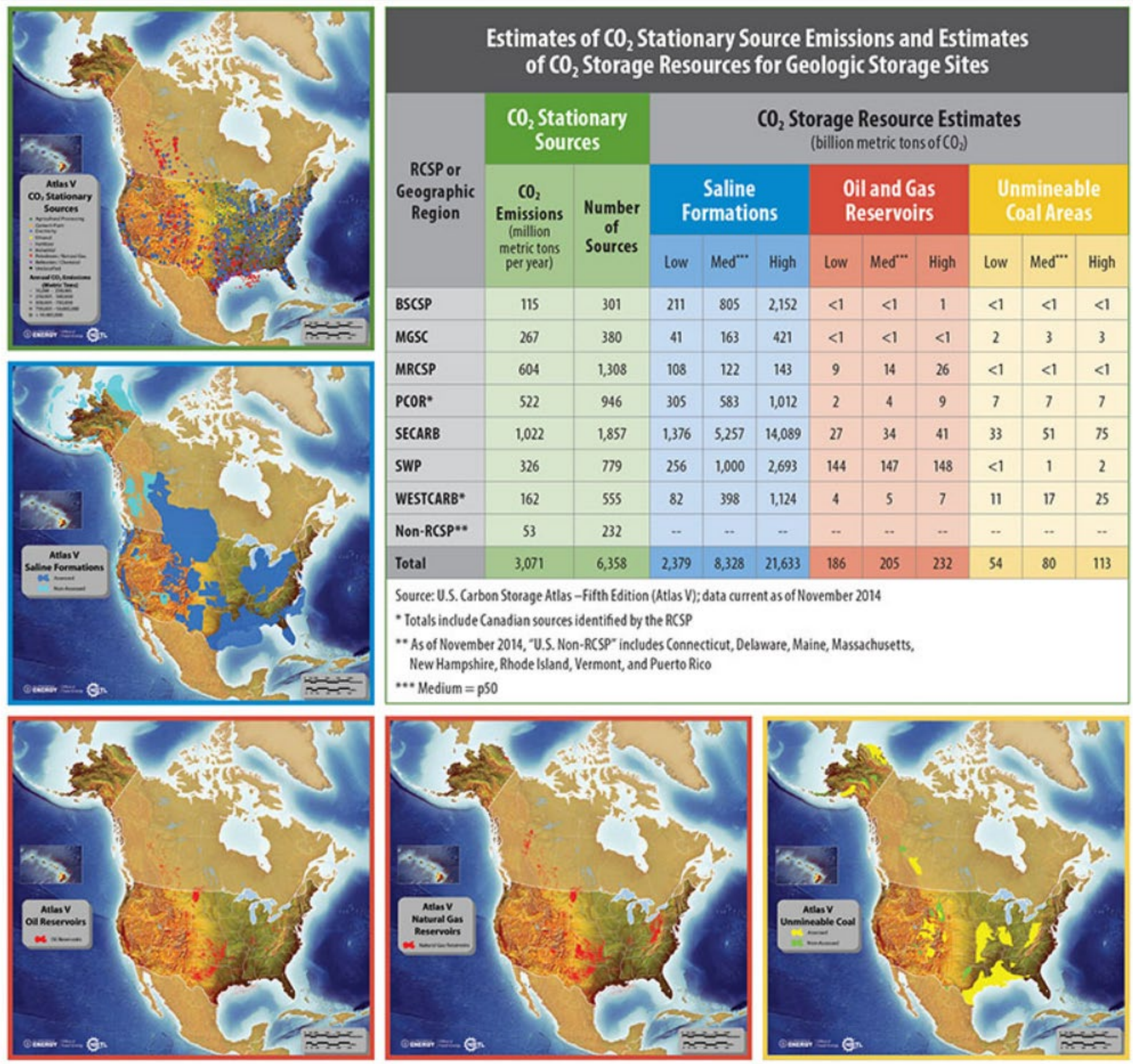


Figure 3 Carbon Engineering's Process Flow Chart (Carbon Engineering Ltd., n.d.)

Carbon Engineering uses their DAC technology to extract and purify CO_2 from the air, and uses electrolysis to create hydrogen from water using renewable electricity. The CO_2 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).

Carbon Sequestration



Estimates of CO_2 Stationary Source Emissions and Estimates of CO_2 Storage Resources for Geologic Storage Sites

RCSP or Geographic Region	CO_2 Stationary Sources: CO_2 Emissions (million metric tons per year)	CO_2 Stationary Sources: Number of Sources	CO_2 Storage Resource Estimates (billion metric tons of CO_2) — Saline Formations: Low	Saline Formations: Med***	Saline Formations: High	Oil and Gas Reservoirs: Low	Oil and Gas Reservoirs: Med***	Oil and Gas Reservoirs: High	Unmineable Coal Areas: Low	Unmineable Coal Areas: Med***	Unmineable Coal Areas: High
BSCSP	115	301	211	805	2,152	<1	<1	1	<1	<1	<1
MGSC	267	380	41	163	421	<1	<1	<1	2	3	3
MRCSP	604	1,308	108	122	143	9	14	26	<1	<1	<1
PCOR*	522	946	305	583	1,012	2	4	9	7	7	7
SECARB	1,022	1,857	1,376	5,257	14,089	27	34	41	33	51	75
SWP	326	779	256	1,000	2,693	144	147	148	<1	1	2
WESTCARB*	162	555	82	398	1,124	4	5	7	11	17	25
Non-RCSP**	53	232	--	--	--	--	--	--	--	--	--
Total	3,071	6,358	2,379	8,328	21,633	186	205	232	54	80	113

Source: U.S. Carbon Storage Atlas –Fifth Edition (Atlas V); data current as of November 2014

* Totals include Canadian sources identified by the RCSP

** As of November 2014, "U.S. Non-RCSP" includes Connecticut, Delaware, Maine, Massachusetts, New Hampshire, Rhode Island, Vermont, and Puerto Rico

*** Medium = p50

Figure 4 Estimated CO2 Storage Resources for Geologic Storage Sites (Center for Climate and Energy Solutions, 2018)

CO_2 can be injected into geological formations to be stored deep underground. The CO_2 can be stored for centuries this way. Four options exist for CO_2 geologic storage:

OIL AND GAS RESERVOIRS (ENHANCED OIL RECOVERY WITH CARBON DIOXIDE, CO_2-EOR)

In addition to storage, injecting CO_2 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 CO_2 storage. Data from prior fossil fuel exploration on subsurface areas exist that may help ensure permanent CO_2 storage. Revenue from selling capture CO_2 to EOR operators may help balance out the cost of the capture technology.

As an example, the Hydrogen Energy California (HECA) project proposed to do just that – capture CO_2 emitted during the conversion of coal / petroleum coke to hydrogen, permanently store it safely underground in a nearby oil field, and enhance oil recovery to increase domestic oil production by 5 million barrels per year (Hyodrgen Energy California, 2010). However, the project was later cancelled in 2016, due to opposition and other hurdles (Trihey, 2016).

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 CO_2 storage instead. The CO_2 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.

Alternative Carbon Markets

Carbon, capture, and storage (CCS) has been one method to significantly reduce greenhouse gas (GHG) emissions by storing the CO_2 underground. However, CCS is an expensive process, so it is not prevalent today.

Table 1 Average cost and performance impact of adding CO2 capture in OECD countries (International Energy Agency, 2013)

	Coal			*Natural gas*
Capture route	**Post-combustion**	**Pre-combustion**	**Oxy-combustion**	**Post-combustion**
Reference plant without capture	PC	IGCC (PC)	PC	NGCC
Net efficiency with capture (LHV, %)	30.9	33.1	31.9	48.4
Net efficiency penalty (LHV, percentage points)	10.5	7.5	9.6	8.3
Relative net efficiency penalty	25%	20%	23%	15%
Overnight cost with capture (USD/kW)	3 808	3 714	3 959	1 715
Overnight cost increase (USD/kW)	1 647	1 128 (0)	1 696	754
Relative overnight cost increase	75%	44% (0%)	74%	82%
LCOE with capture (USD/MWh)	107	104	102	102
LCOE increase (USD/MWh)	41	29 (0)	40	25
Relative LCOE increase	63%	39% (0%)	64%	33%
Cost of CO_2 avoided (USD/tCO_2)	58	43 (55)	52	80

Notes: average figures for OECD member countries do not include cost of CO_2 transportation and storage.

LHV = low heating value; kW = kilowatt; MWh = megawatt hour; tCO_2 = tonne of carbon dioxide.

The accuracy of capital cost estimates from conceptual design studies is on average ± 30%; hence, for coal the variation in average overnight costs, LCOE and cost of CO_2 avoided between capture routes is within the uncertainty of the study.

Underlying oxy-combustion data include some cases with CO_2 purities < 97%. Overnight costs include owners', engineering procurement construction (EPC) and contingency costs, but not interest during construction (IDC).

A 15% contingency based on EPC cost is added for unforeseen technical or regulatory difficulties for CCS cases, compared with a 5% contingency applied for non-CCS cases. IDC is included in LCOE calculations.

The cost profile of captured carbon could be altered by finding an industrial or commercial use for the CO_2 resulting in revenue generation. It has been estimated that the top three reuse applications for CO_2

(fuel production, concrete enrichment, and power generation) could result in as much as one billion metric tons in 2030 (Biniek, 2018).

There is a $20 million challenge through XPrize called "Carbon XPrize" which is a global competition to develop breakthrough technologies that convert CO_2 into valuable products that we use every day (X Prize, 2018).

CHALLENGES

In order for the use of captured carbon to be cost effective and to make an appreciable dent in global GHG emissions, a large amount of CO_2 is needed to reach the necessary economies of scale. Another challenge is that CO_2 is a highly inert molecule (U.S. Environmental Protection Agency, 2018). For this reason, transforming CO_2 into industrial products requires a lot of energy.

The cost of capturing carbon can be as high as $80 per metric ton (Biniek, 2018). Firms working in this area expect to cut this number in half in the near future. Fossil fuels, which are the existing feedstock to most of the applications listed below are low cost, so the cost (including subsidies) will need to be improved in order to be competitive.

ALTERNATE USES FOR CAPTURED CARBON DIOXIDE

Much research has been performed on how to repurpose CO_2 and produce valuable products. Table 1 below shows alternative uses that large market potential based on the volume of CO_2 needed including key limitations and who is currently working on these markets.

Table 2 Alternative Uses for Captured Carbon Dioxide (Global CCS Institute, 2018)

Application	Description	Limitations	Who is working on this?
Fuel Production	Break down CO_2 to carbon monoxide. Hydrogen and carbon monoxide can be chemically reacted to create hydrocarbon chains that make up liquid fuels.	Energy intensive (equivalent to combustion)	- Carbon Engineering - Harvard University

	Develop methanol using an artificial photosynthesis process.	Works best when using excess renewable electricity	- California Institute of Technology - Breathe - Stanford University
Building Materials/Concrete Enrichment	CO_2 can be combined with waste products, such as fly ash, and produce an additive to concrete mixtures. The captured carbon would sequester the gas in the concrete, allowing the material to serve as a major carbon sink. A process called "Carbon Curing" allows for CO_2 to be injected into wet concrete, up to 4% by mass. This forms carbonate ions that turn into solid calcium carbonate. The process shortens curing time, increases water resistance, and overall strength. (Biniek, 2018)	Still in the early stages, so scaling of the technology needs to be improved.	- Carbon8 (Williams, 2017) - Mineral Carbonation International - Carbon Upcycling Technologies
Power Generation	Use CO_2 to make turbines run more efficiently. Although not a reuse, this process will prevent large amounts of CO_2 from being released. In this process, CO_2 is heated and pressurized into a supercritical fluid. By taking less energy to compress compared to steam, this process is more energy	Still in the early stages of the technology.	- Sandia National Lab - GE - Net Power

	efficient. Up to 49% efficiency to electricity generation. (Stockton, 2017)		
Oil and Gas Operations	**Enhanced Oil Recovery:** CO_2 is a common injection gas for enhanced oil recovery (EOR) to either increase pressure at the bottom of the reservoir or to reduce viscosity of heavy crude oil, which is prevalent in the Bakersfield area. When the reservoir is depleted of oil following the injection, the CO_2, will remain stored underground in the reservoir. **Fracking:** CO_2 can be added to fracking fluid to increase stimulation of the oil and gas fields.	The hydrocarbons produced using the CO_2 are likely to result in carbon emissions, which can negate the GHG advantages.	- NRG (Petra Nova Project) - Numerous oil and gas operators use this technique for EOR
Carbon Nanotubes/ Carbon Fiber	Convert CO_2 to carbon fibers or nanotubes using a molten electrolysis process. Use CO_2 and electricity to produce a strong, light-weight alternative to metal. This process costs less than traditional carbon nanotube manufacturing. (Grossman, Scientists Discover How to Make Carbon Nanotubes Out of Carbon Dioxide, 2018) Another method involves separating carbon from the CO_2 and reacting it with an iron catalyst to create carbon nanotubes.	The iron catalysts are not very stable and depending on how long it is in use, it can create irregularly sized carbon nanotubes.	- C2CNT (Sweet, 2018) - Vanderbilt University

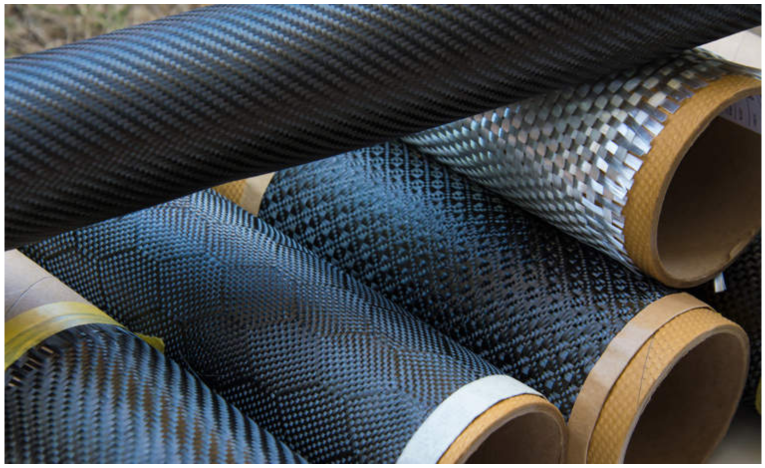


Figure 5 A material made of thin yet strong crystalline filaments from carbon (Allied Market Research, 2018)

OTHER APPLICATIONS (THAT DO NOT REQUIRE AS MUCH INPUT CO_2)

There are a few applications for carbon capture that do not require as much CO_2 (Global CCS Institute, 2018).

- **Food Processing –** CO_2 can be used in cooling while grinding powders and in modified atmosphere packaging (MAP) to extend shelf life by inhibiting growth of bacteria that cause spoilage.
- **Paper Processing** – Used to reduce pH during pulp washing operations
- **Refrigerant Gas** – CO_2 can be used as the working fluid in a refrigerant plant, specifically larger industrial air conditioning and refrigeration systems. The CO_2 would replace other toxic gases that have larger global warming potential.
- **Fertilizer –** CO_2 can be combined with waste straw and methane from landfill sites to create a crumbly soil enriching fertilizer.

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