Direct Air Capture of Carbon Dioxide

By John Benson

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1. Introduction

It hasn't been that long since I wrote about the title subject, but the current issue of Scientific American had an excellent article in September's issue and I needed to share some excerpts from this with my readers, plus drill a bit deeper. Also, when I had basically completed this article, I discovered a major advance in a material that captures carbon dioxide. That is reported in the last section of this paper.

My last article on this subject is summarized and linked below.

Two New Processes for Carbon Removal and a Monitor: *Virtually all experts on climate change mitigation agree that, in order to do this rapidly enough to avoid really major repercussions (like many current coastal areas under water, mainly from melting Greenland and Antarctic Ice Sheets), we need to actively remove greenhouse gasses from the atmosphere. The main key for developing a viable technology it to reduce the net cost of doing this below $100 per ton of CO_2 removed…*

https://energycentral.com/c/cp/two-new-processes-carbon-removal-and-monitor

2. The Need

Scientists had known since the 1950s how to strip CO_2 from the air inside submarines and spaceships to keep the crews from suffocating. However, Klaus Lackner, a physicist working on nuclear fusion at Los Alamos National Laboratory, published a paper arguing that extracting CO_2 from air "has a reasonable probability of success" at reducing global warming. Lackner's paper was the first to argue that we could strip it from the atmosphere to keep Spaceship Earth livable…"[1]

Several years later Lackner co-founded a company called Global Research Technologies, and in 2007 it staged the first demonstration of a technology to extract CO_2 from the ambient air, an approach now called direct air capture (DAC). The device was a tall plexiglass box containing plastic sheets that had been coated with a dry CO_2-absorbing resin. The box door opened like a wardrobe's to let air flow across the plastic. When the door shut, the sheets were misted with water, releasing the CO_2, which was captured in a tank to be used in industry or stashed away underground. That same year Virgin Atlantic airline owner Richard Branson announced a $25-million prize for a "commercially viable" technology to remove greenhouse gases from the atmosphere.

Although the chemistry may not be "all that hard," DAC requires a lot of equipment and a lot of energy—and therefore a lot of money. After the 2008 financial crisis hit, Global Research Technologies ran out of funding. Branson never awarded his prize; a spokesperson said in 2010 that none of the 2,500 entries were ready to draw down any significant quantity of CO_2, and he also acknowledged a growing public "un-ease" about messing with the atmosphere. Although a few start-ups continued developing their technologies and opened small facilities, DAC fell out of the spotlight.

[1] Alec Luhn, Scientific American, "Can Pulling Carbon from Thin Air Slow Climate Change?" August 20, 2024, https://www.scientificamerican.com/article/can-thousands-of-huge-machines-capture-enough-carbon-to-slow-climate-change/ Note that direct Internet access is limited to subscribers of this service.

Since the 2000s global emissions have only continued to rise, however, and Earth has gotten hotter. Scientists increasingly recognize that limiting warming to the Paris Climate Agreement goal of 1.5 degrees Celsius above preindustrial temperatures will require more than drastically cutting emissions—it will involve pulling hundreds of billions of tons of CO_2 out of the atmosphere this century. The most obvious way is planting trees. But even a trillion trees would not be nearly enough, and trees can burn or die of disease, emitting most of the carbon they've stored. In the 2000s the world wasn't ready for DAC, Lackner says. "Now I think we are too late to do without it."

For its goal of the Biden administration is trying to slash carbon pollution by building renewables, electrifying everything from cars to home heating, and encouraging carbon capture and sequestration at power plants. But emissions that are difficult to eliminate, such as those from long-distance air travel, shipping, agriculture, and cement and steel production, will probably have to be removed from the atmosphere, so the government is trying to ramp up DAC. Humans built machines that made a mess; now we'll build more machines to clean it up. And if the world could start taking more emissions out than it's putting in—so-called negative emissions—carbon removal could even begin lowering the global temperature slightly.[2]

The U.S. plans to draw down and store more than a billion tons of CO_2 annually by 2050, more than one fifth of what it currently emits. For that to be possible, carbon removal would have to become one of the world's largest industries in just a few decades, expanding by more than 40 percent each year. That's far faster than most technologies develop—although it is comparable to the pace of solar panels and electric vehicles. "It'd be one of the biggest things humans have ever done," says Gregory F. Nemet, a professor of public policy at the University of Wisconsin–Madison…

3. Federal Assistance and Corporate Demand

Key climate laws in 2021 and 2022 included a major tax break for DAC and $3.5 billion in funding to build several regional DAC hubs. Meanwhile, big companies started looking to purchase carbon removal credits to offset their carbon footprint. A business can buy a credit for one metric ton of CO_2 that a DAC firm sequestered instead of reducing its own emissions by that amount. To this end, more than 130 commercial DAC plants have been proposed in the U.S. Almost all those plants, however, are planned by an oil company that injects CO_2 underground to squeeze out more crude oil from old deposits. U.S. Secretary of Energy Jennifer Granholm has described DAC as "giant vacuums that can suck decades of old carbon pollution straight out of the sky." But now the question is, could it also end up putting new carbon pollution into the atmosphere?

Author's comment: The last question in the above paragraph prompted this response, because it's really two questions. (1) Will using CO_2 to help extract underground crude oil result in more CO_2 emissions? (2) Will DAC+sequestration result in more emissions?

[2] Albeit not anytime soon. Although "…reaching net-zero emissions by 2050." Is a laudable and ambitious goal, I expect the amount of inertia in our climate will delay any "…lowering the global temperature…" until well after the year 2100, and most likely 2200. Read the next paragraph after the one where this footnote is.

(1) Probably the reason drillers are using CO_2 is to ease extraction or allow them to extract more crude, which equates to lower cost when the crude gets to the refinery. This might result in slightly lower cost of petroleum products (mainly burned gasoline and natural gas emit huge amounts of CO_2) to consumers. Although lower cost generally results in higher purchase volumes, I don't believe the any tiny reduction would result in a significant increase in volume.

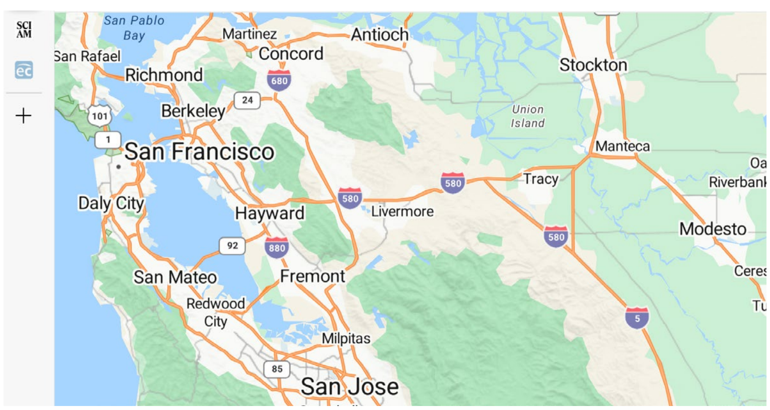
(2) The only scenario where DAC + sequestration would result in more emissions is if this process consumed energy or other resources, and that the process that produced that energy and/or resources produced more emissions. If the energy consumed by the primary processes were renewable (or zero-carbon). There might be some small amounts of grid-energy used for secondary or tertiary processes. Reasonably careful accounting should make sure the DAC + sequestration process is strongly positive (CO_2 emissions by the total process are only a small percentage of the CO_2 captured and sequestered).

4. Specific Process

Earlier this year I drove an hour east of San Francisco to visit America's first commercial DAC plant, which Silicon Valley start-up Heirloom Carbon had inaugurated with Secretary Granholm in the farm fields outside Tracy, Calif. After I listened to a safety briefing and put on a hard hat, Heirloom CEO Shashank Samala, a trim, bearded man with a quick grin, took me behind the white mesh netting that surrounded the plant.

Above paragraph raises the question: why did Heirloom put their DAC Plant in Tracy?

First of all, Heirloom's HQ just east of Daly City and south of San Francisco in the map below. Second, I grabbed a picture from their website of the inside of their plant and it is on the next page.[3] From the map below, note that Tracy and Livermore (my home town) are on I-580 east of SF. I-580 between Livermore and Tracy goes through the Altamont Wind Resource Area. Yes, it's quite windy in Tracy. Also, property cost is reasonable.



Back to the pic on the next page. Note that there are a bunch of fans on the wall in front of their racks. Also, the whole wall is permeable to wind, and they only run the fans when there is little or no wind. With normally much wind, they need less energy for the capture process.

[3] https://www.heirloomcarbon.com/

Inside, the operation resembled an oversized industrial kitchen. Hundreds of plastic trays holding what looked like white flour were stacked in 12-meter towers. Rectangular robots moved up and down vertical girders between the towers, checking the flour, which was actually pulverized lime. The lime absorbs CO_2 from air passing over the tray, forming calcium carbonate—limestone powder—over the course of about three days.

Then a larger, wheeled robot with a forklift pulls trays from the bottom of a stack and dumps the powder into a duct leading to a 900-degree-C kiln outside. When heated, the limestone releases CO_2 and turns back into lime. The CO_2 is compressed and pumped into a big tank. Later it will be injected underground or mixed into wet concrete, locking the carbon away for centuries. The lime goes back onto the trays to soak up more CO_2

Samala[4] grew up in an 18-square-meter (194 square-foot) house in Hyderabad, India… His father worked in the U.S., and he brought the family to Maine when Samala was 12. After studying economics and robotics at Cornell University and working at the payment company Square, Samala co-founded a company in San Francisco in 2013 that built and delivered custom circuit boards within days.

But Samala was growing concerned about climate disasters, including in India. The 2018 report by the Intergovernmental Panel on Climate Change (IPCC), which for the first time said carbon removal would probably be required to keep global warming to 1.5 degrees C, convinced him that "there is no future of the planet" without the technology. Two years later he founded Heirloom with Noah McQueen, a chemical engineering Ph.D. student. They developed an approach they could scale up to hundreds of plants, ditching the chemical solvents, intricate filters and high-powered fans of other DAC start-ups in favor of cheap limestone and a breeze.

[4] Heirloom CEO Shashank Samala

Around the same time, big tech firms were starting to invest in carbon removal, sometimes with the goal of offsetting their own considerable emissions. Within months after Heirloom announced its technology on paper, online retail-services companies Stripe and Shopify committed to pay it hundreds of thousands of dollars for future CO_2 credits, their own effort to help kick-start the demand for carbon removal.

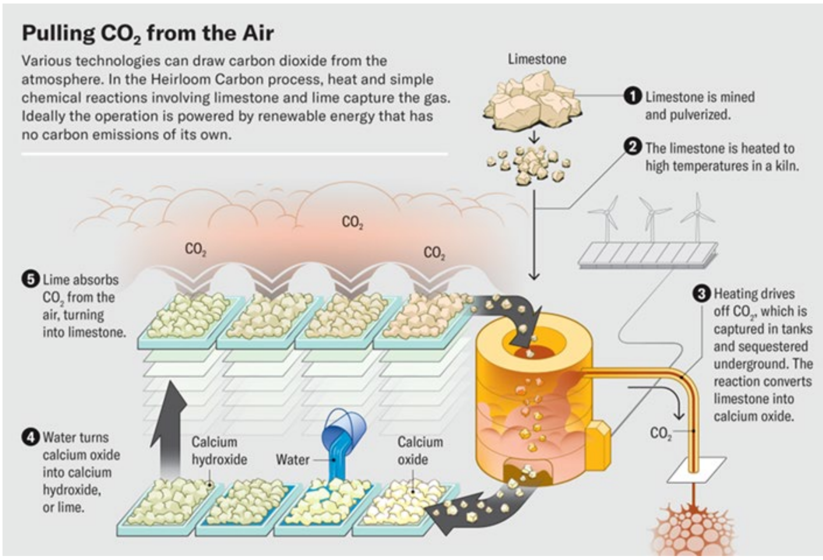
The next year Heirloom raised $53 million from a group of investors that included Bill Gates's Breakthrough Energy Ventures, and it won a $1-million preliminary award in Elon Musk's $100-million XPRIZE competition to remove 1,000 metric tons of CO_2 a year and "show a pathway" to billions more. The start-up began building the Tracy facility. In August 2023 the U.S. Department of Energy awarded Heirloom and Climeworks—which operates the world's only other CO_2-sequestering commercial DAC facility, on a mountain plateau in Iceland—up to $600 million to build a DAC hub in western Louisiana, along with project manager Battelle. Called Project Cypress, the joint hub is meant to capture a million metric tons of CO_2 a year and inject it underground.

The goal of both the DOE and tech firms, several of which have now pooled $1 billion to invest in carbon removal, is to bring down the price of DAC by bringing up capacity. Right now, a credit for removing a metric ton of CO_2 via DAC costs around $1,000, many times more than the equivalent tree planting. But economies of scale can reduce that, according to Samala. "This will come down the cost curve very quickly," he said. "You're just putting rocks on trays."

After California I went to the future site of Project Cypress at Gray Ranch, 400 square kilometers of marshy rangeland on the Louisiana coast, just across the state line from Texas. Driving from Houston to Lake Charles, La., I passed Spindletop Hill, where a 60-meter gusher kicked off the Texas oil boom in 1901. About half of Gray Ranch's income still comes from leasing land for timber, ranching and oil extraction, says family scion Gray Stream, a wiry, blond man who was waiting for me at his colonnaded historic mansion in boots and jeans. But he hopes that carbon sequestration will be its next big business, starting with Project Cypress.

I climbed into a black Cadillac Escalade with Stream and four employees for the 50-kilometer drive to the site. We got out on a gravel road next to a grassy field, with an oil well not far in the distance. As we talked, mosquitoes and turkey vultures began to circle. Within three years this spot will look more like a science-fiction movie set than a cow pasture. Climeworks's latest technology is a cube 23 meters on edge with mesh sides, rounded corners and 16 fan nozzles sticking out of the top, lifted off the ground by massive concrete feet. Some 60 cubes will stand in rows, connected by compressors and pipes. Inside each cube 16 vented boxes will contain filters coated with an ammonia-derived sorbent, which will capture CO_2 from air pulled through the mesh walls by the fans. When the boxes are closed and filled with 100-degree steam, the CO_2 will be released into pipes for sequestration. From the pasture the captured CO_2 will be pumped about 11 kilometers to another part of the ranch, where Stream's team will inject it deep underground.

Heirloom was going to build a plant here next to Climeworks, but after I visited, it moved its part of Project Cypress north to be near another facility it is developing in Shreveport, La., which will sequester CO_2 under a timber plantation in central Louisiana.



5. Major Breakthrough in CO_2 Capture Material

A new type of absorbing material developed by chemists at the University of California, Berkeley, could help get the world to negative emissions. The porous material—a covalent organic framework (COF)—captures CO_2 from ambient air without degradation by water or other contaminants, one of the limitations of existing direct air capture (DAC) technologies.[5]

"We took a powder of this material, put it in a tube, and we passed Berkeley air—just outdoor air—into the material to see how it would perform, and it was beautiful. It cleaned the air entirely of CO_2. Everything," said Omar Yaghi, the James and Neeltje Tretter Professor of Chemistry at UC Berkeley and senior author of a paper that appeared online Oct. 23 in the journal Nature.

"I am excited about it because there's nothing like it out there in terms of performance. It breaks new ground in our efforts to address the climate problem," he added.

According to Yaghi, the new material could be substituted easily into carbon capture systems already deployed or being piloted to remove CO_2 from refinery emissions and capture atmospheric CO_2 for storage underground.

UC Berkeley graduate student Zihui Zhou, the paper's first author, said that a mere 200 grams of the material, a bit less than half a pound, can take up as much CO_2 in a year—20 kilograms (44 pounds)—as a tree.

Author's comment: I expect the above amount will need multiple cycles of adsorption.

[5] Science X via MSN, "Novel covalent organic framework quickly captures CO_2 from ambient air," Oct 23, 2024, https://www.msn.com/en-us/weather/topstories/novel-covalent-organic-framework-quickly-captures-co-from-ambient-air/ar-AA1sN6t9?ocid=BingNewsSerp

"Flue gas capture is a way to slow down climate change because you are trying not to release CO_2 to the air. Direct air capture is a method to take us back to like it was 100 or more years ago," Zhou said.

"Currently, the CO_2 concentration in the atmosphere is more than 420 ppm, but that will increase to maybe 500 or 550 before we fully develop and employ flue gas capture. So, if we want to decrease the concentration and go back to maybe 400 or 300 ppm, we have to use direct air capture."

Yaghi is the inventor of COFs and MOFs (metal-organic frameworks), both of which are rigid crystalline structures with regularly spaced internal pores that provide a large surface area for gases to stick or adsorb…

Two years ago, his lab created a very promising material, MOF-808, that adsorbs CO_2, but the researchers found that after hundreds of cycles of adsorption and desorption, the MOFs broke down. These MOFs were decorated inside with amines (NH_2 groups), which efficiently bind CO_2 and are a common component of carbon capture materials…

Working with colleagues, Yaghi discovered why some MOFs degrade for DAC applications—they are unstable under basic, as opposed to acidic, conditions, and amines are bases. He and Zhou worked with colleagues in Germany and Chicago to design a stronger material, which they call COF-999.

Whereas MOFs are held together by metal atoms, COFs are held together by covalent carbon-carbon and carbon-nitrogen double bonds, among the strongest chemical bonds in nature.

As with MOF-808, the pores of COF-999 are decorated inside with amines, allowing uptake of more CO_2 molecules.

"Trapping CO_2 from air is a very challenging problem," Yaghi said.

"It's energetically demanding, you need a material that has high carbon dioxide capacity, that's highly selective, that's water stable, oxidatively stable, recyclable. It needs to have a low regeneration temperature and needs to be scalable. It's a tall order for a material. And in general, what has been deployed as of today are amine solutions, which are energy intensive because they're based on having amines in water, and water requires a lot of energy to heat up, or solid materials that ultimately degrade with time."

Yaghi and his team have spent the last 20 years developing COFs that have a strong enough backbone to withstand contaminants, ranging from acids and bases to water, sulfur and nitrogen, that degrade other porous solid materials.

The COF-999 is assembled from a backbone of olefin polymers with an amine group attached. Once the porous material has formed, it is flushed with more amines that attach to NH_2 and form short amine polymers inside the pores. Each amine can capture about one CO_2 molecule.

When 400 ppm CO_2 air is pumped through the COF at room temperature (25 °C) and 50% humidity, it reaches half capacity in about 18 minutes and is filled in about two hours. However, this depends on the sample form and could be speeded up to a fraction a minute when optimized.

Heating to a relatively low temperature—60 °C, or 140 °F—releases the CO_2, and the COF is ready to adsorb CO_2 again. It can hold enough CO_2 to stand out from other solid sorbents.

Yaghi noted that not all the amines in the internal polyamine chains currently capture CO_2, so it may be possible to enlarge the pores to bind more than twice as much.

"This COF has a strong chemically and thermally stable backbone, it requires less energy, and we have shown it can withstand 100 cycles with no loss of capacity. No other material has been shown to perform like that," Yaghi said. "It's basically the best material out there for direct air capture."

Yaghi is optimistic that artificial intelligence can help speed up the design of even better COFs and MOFs for carbon capture or other purposes, specifically by identifying the chemical conditions required to synthesize their crystalline structures.

He is scientific director of a research center at UC Berkeley, the Bakar Institute of Digital Materials for the Planet (BIDMaP), which employs AI to develop cost-efficient, easily deployable versions of MOFs and COFs to help limit and address the impacts of climate change.

"We're very, very excited about blending AI with the chemistry that we've been doing," he said.