A New **Carbon Economy** Takes Shape

A Laboratory Director's Initiative responds to the unrelenting buildup of greenhouse gases in the atmosphere with new technologies and approaches aimed at "negative emissions."

THE atmospheric concentration of carbon dioxide (CO_2) has surged in the last two centuries, from 280 parts per million during the preindustrial age in the early 1800s to more than 410 parts per million today. Climate scientists calculate that even with clean electrical power sources, such as the wind and Sun, and emission-free cars and trucks, the world will need the capabilities to remove 10 billion metric tons (10 gigatons) of atmospheric CO_2 per year beginning in 2050 to avoid a significant global temperature increase. For scale, 10 gigatons of CO_2 is the amount produced by approximately 2,500 coal-fired power plants in a single year.

Without such an enormous undertaking, the United Nations Intergovernmental Panel on Climate Change warns that the average global temperature could increase by more than 2°C this century. This warning was the basis of the Paris Agreement of 2016—an international accord aimed at strengthening the global response to climate change. "About 75 percent of the goal to keep global temperature below 2°C could be met by aggressive zero carbon–technologies," says Roger Aines, chief scientist for Lawrence Livermore's Energy Program. "However, humankind has no obvious option but to also remove large amounts of CO_2 from the atmosphere to meet the remaining 25 percent of the goal."

Aines explains that global-scale atmospheric CO_2 removal (also called negative emissions) will be an unprecedented endeavor requiring enhanced scientific understanding, new technologies, collaborations, and companies dedicated to "cleaning" the atmosphere through CO_2 capture, sequestration, and conversion to useful products and fuels. The Lawrence Livermore Director's Engineering the Carbon Economy Initiative, which is overseen by Aines, was conceived in 2018 to help support global-scale CO_2 and methane removal.

(Director's Initiatives focus on important emerging national needs.) The effort comprises several research areas that include manufacturing carbon-based products from CO_2, returning carbon to CO_2-depleted soil, sequestering CO_2 deep underground, and performing systems analysis to predict the costs and benefits of different carbon management approaches.

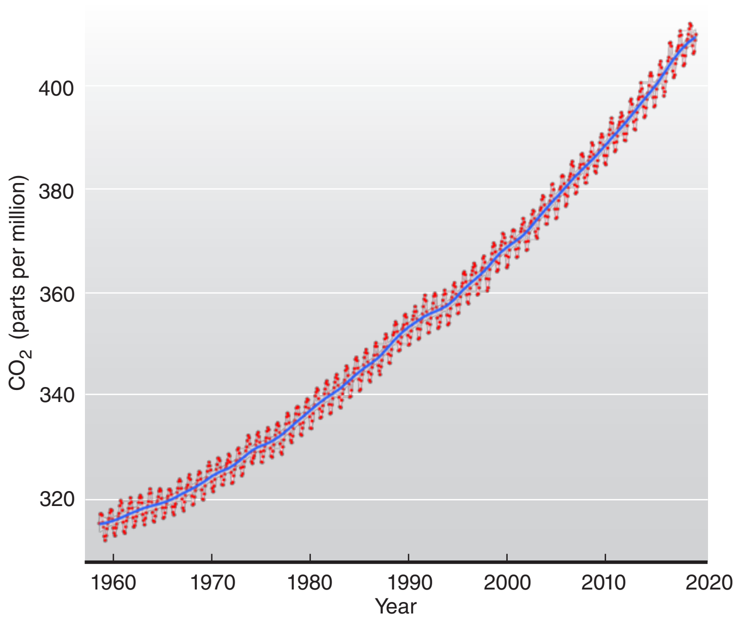
Supported by Laboratory Directed Research and Development (LDRD) funds, the Department of Energy (DOE), the ClimateWorks Foundation, and Cooperative Research and Development Agreements (CRADAs), this new carbon-reduction initiative involves approximately 50 researchers, including early career staff and postdocs. Numerous partnerships with universities, other national laboratories, California state agencies, and nongovernmental organizations have also been established. Researchers draw on Laboratory strengths in geoscience, atmospheric science, materials science, advanced manufacturing, and systems analysis and optimization.

The Engineering the Carbon Economy Initiative responds to the increasing threat presented by the buildup of greenhouse gases that trap heat within the planet and make it warmer. Aines explains that before the industrial age, the amount of CO_2 that plants and the ocean absorbed was in balance. "The extra 45 billion tons that we put into the air every year is affecting this stability. We have already put too much carbon dioxide into the atmosphere. Stopping these emissions is critically important, but it will take many years to build up the needed negative-emissions technology and infrastructure. The time is right for this research effort."

The new Director's Initiative is aligned with DOE's Rewiring the Carbon Economy strategy, which aims to use waste CO_2 as a feedstock to produce chemicals, fuels, and other products and create a sustainable carbon-based economy. Low-cost renewable electricity is at the heart of this effort, and Aines points to the nation's Midwest region, where wind and solar farms are producing remarkably cheap electricity, as the likely place where CO_2 will be harvested and repurposed.

Capture and Convert

The Engineering the Carbon Economy Initiative builds upon the Laboratory's existing research to limit atmospheric carbon by capturing emissions. Environmental scientist Joshuah Stolaroff notes that CO_2 is typically mixed with other greenhouse gases that together escape from factory smokestacks and power plants. The CO_2 must be at least 95 percent pure before it can be compressed and transported for use as a feedstock—a renewable, raw material that can be used as a fuel or converted to one—or else stored underground. (*S&TR*, December 2015, pp. 13–16.)



The Keeling curve depicts the accumulation of CO_2 in the Earth's atmosphere based on continuous measurements taken at Hawaii's Mauna Loa Observatory from 1958 to the present.

DOE's Office of Fossil Energy supports Livermore's development of new carbon-capture approaches that use three-dimensional (3D) printing, also known as additive manufacturing, to make microengineered components that are cheap to produce. For example, Livermore researchers have developed microencapsulated CO_2 sorbents—reusable capsules measuring less than 1 millimeter in diameter. The capsules comprise a highly permeable polymer shell enclosing a fluid made up of sodium carbonate. Gaseous CO_2 diffuses through the shell and reacts with the sodium carbonate solution, forming crystallized sodium bicarbonate (baking soda). The capsules could be used to capture CO_2 from power plants or from smaller industrial systems. In addition, materials scientist Jennifer Knipe is leading a DOE-funded program to demonstrate how the Laboratory's capsule materials could be used for transporting CO_2 to algae. Knipe's team is showing that algae can live on CO_2 obtained directly from the materials as opposed to traditional bubbled CO_2. This discovery may prove useful for improving algal biomass production.

Similar significant sources of CO_2 include landfills, sewage plants, steel mills, and biogas facilities. In the case of biogas facilities, removing CO_2 would leave pure methane (natural gas) as a renewable fuel or to make specialty chemicals. Chemist Sarah Baker, Stolaroff, and others are working with Southern California Gas Company to build a pilot plant at a California biogas facility to capture CO_2 for later storage and produce a steady stream of methane. Capturing and then repurposing or storing CO_2 from a biological source would effectively remove it from the air—a prime example of a negative-emissions strategy.

Researcher Will Smith holds a vial of microencapsulated CO_2 sorbents, which could be used to capture CO_2 from power plants or from smaller industrial processes. (Photo by George Kitrinos.)

A Chemical Industry Transformation

In a separate project, Baker and materials engineer Eric Duoss are leading an LDRD Strategic Initiative (SI) to transform the way chemicals are made by creating 3D-manufactured reactors that catalyze the conversion of CO_2 into valuable feedstocks. Aines points to a recently completed $18 billion petrochemical plant in Dubai that converts natural gas to various low molecular weight hydrocarbons such as ethylene (C_2H_4, the most abundant chemical feedstock). Such enormous plants use thermochemical reactors, which have high capital and operating costs. Aines says, "Chemical manufacturing today is a separations nightmare."

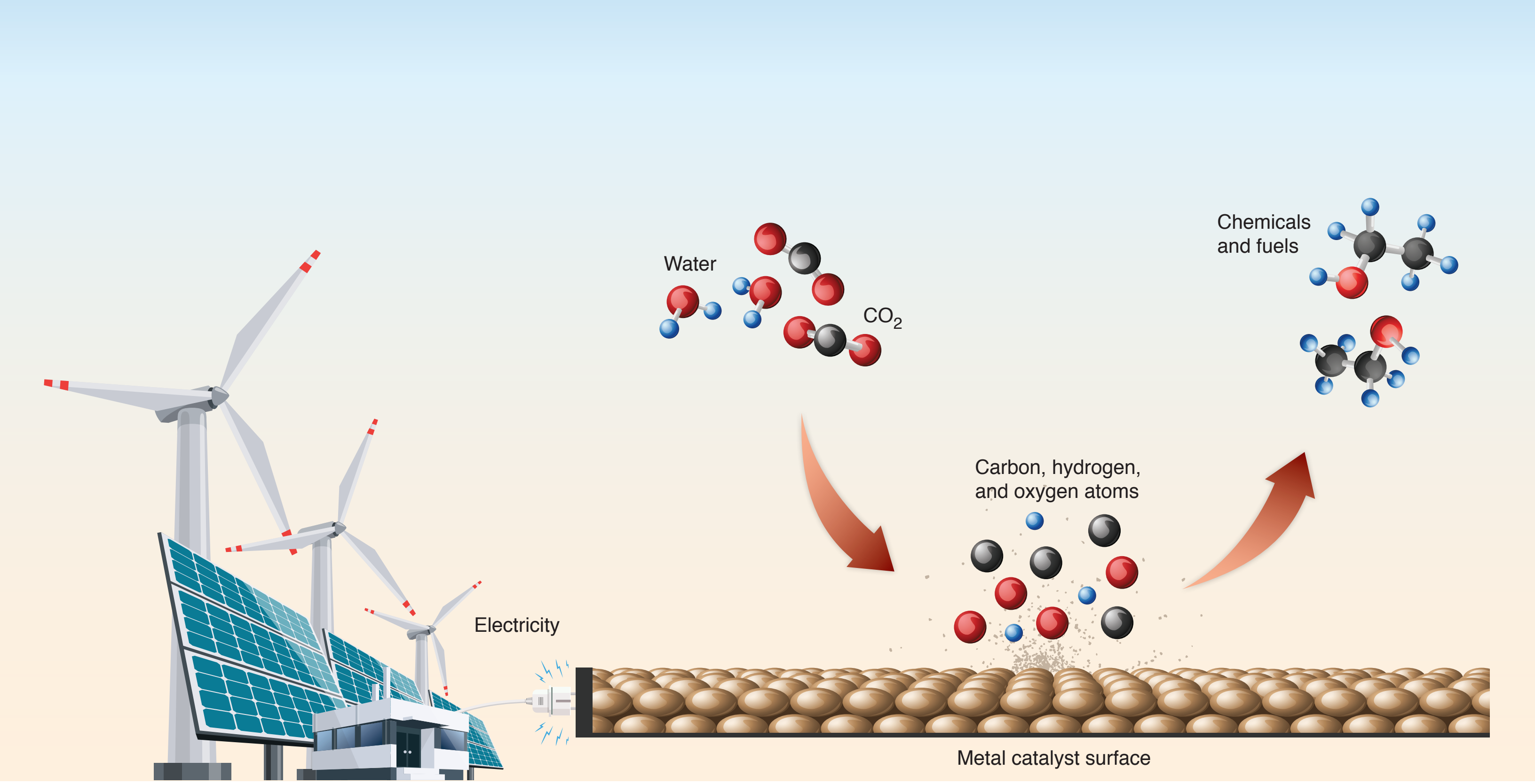
Whereas temperature is the driving force in traditional reactor and separation technologies that use oil and gas as carbon sources, Livermore prototype reactors that harness CO_2 as the carbon source use electricity (ideally produced from renewables). The SI team of more than 15 researchers is developing these modular electrochemical reactors for converting CO_2 into industrial chemicals, lubricants, and polymers while radically improving efficiency and selectivity. The reactors are designed to operate at ambient temperature and low pressure, thereby promising much lower capital and operating costs.

The team is working to control the local reaction environment (electric field, species concentration, ionic strength, pH, multiphase flow, and other factors) to an unprecedented degree. Similarly, the team is learning to control the 3D microstructure, from individual grains and crystal facets to the overall reactor system, of metal catalysts and other materials that are key to converting CO_2 to a host of organic compounds. Guided by multiscale models that span atomic to continuum levels in length and time, researchers are combining emerging computational design optimization methods with technoeconomic analyses to invent commercially viable reactors. "With these innovative designs in hand, we will use Livermore's unique additive manufacturing approaches to implement the best catalysts onto our 3D reactor platforms. In doing so, we will achieve an unprecedented level of performance," states Duoss.

Through application of these advanced manufacturing techniques, the researchers aim to shorten development cycles from what are typically months (or years) in academic settings to weeks or even days for conceptualization, construction, and testing of electrochemical cells and reactors. Ultimately, the researchers envision their reactors mimicking biological structures, such as trees and lungs, that feature 3D and hierarchal flow paths to control and speed the transport of reactants and products. The researchers are collaborating with colleagues from Stanford University, the University of California (UC) at Santa Cruz, the University of Toronto, the California Institute of Technology, Carnegie Mellon University, the University of Massachusetts Amherst, and French multinational gas and oil company Total S.A.

Bacteria Do It Better

Commercial production of methane, along with agriculture and livestock activities and landfills, results in a large volume of methane lost to the atmosphere. In fact, methane emissions contribute about one-third of present net global warming. Conventional separation technologies, such as stirred tanks, are designed to convert methane to more valuable products



As depicted in this rendering, Livermore is developing a prototype electrochemical reactor that uses electricity (ideally produced from renewable sources) to convert CO_2 to valuable feedstocks. The team is learning to control the three-dimensional (3D) microstructure of metal catalysts and other materials that are key to this conversion process.

using high temperature and pressure, and they have a low conversion efficiency.

In an LDRD-supported endeavor, Baker and materials scientist Fang Qian are working to improve methane conversion by "printing" bacteria into the polymer walls of the 3D-printed reactors. The research team has partnered with the National Renewable Energy Laboratory, which provides Livermore with genetically modified microbes called methanotrophs that convert methane to organic acids, which can be used in other products.

Using live microbes instead of inorganic catalysts has advantages of mild reaction conditions, self-regeneration, low cost, and catalytic specificity. No added electricity or heat is needed, and the reactors continuously produce organic acids from methane at room temperature and pressure. This work is the first demonstration of 3D-printing live cells to create chemical reactors. In initial tests, the printed microbes were 20 times more productive than microbes in a stirred tank.

Returning Carbon to Soils

Soils are a huge natural sink for atmospheric CO_2, making carbon uptake by soils a promising method for removing gigatons of carbon from the air. Modern agricultural practices, such as routine machine tilling, have depleted soils' natural CO_2 content, resulting in carbon oxidation and enormous losses of CO_2 from microbial respiration. "Loss of CO_2 from soil is on par with human-caused emissions," says biogeochemist Jennifer Pett-Ridge. She and other researchers are exploring approaches for returning carbon to the soil in long-lived forms, which would reduce atmospheric CO_2 and make farmland more productive. The research team is using Livermore's Center for Accelerator Mass Spectrometry and its NanoSIMS (nanometer-scale secondary ion mass spectrometer) to quantify carbon uptake in prairie soils and determine how soil microbes metabolize carbon compounds.

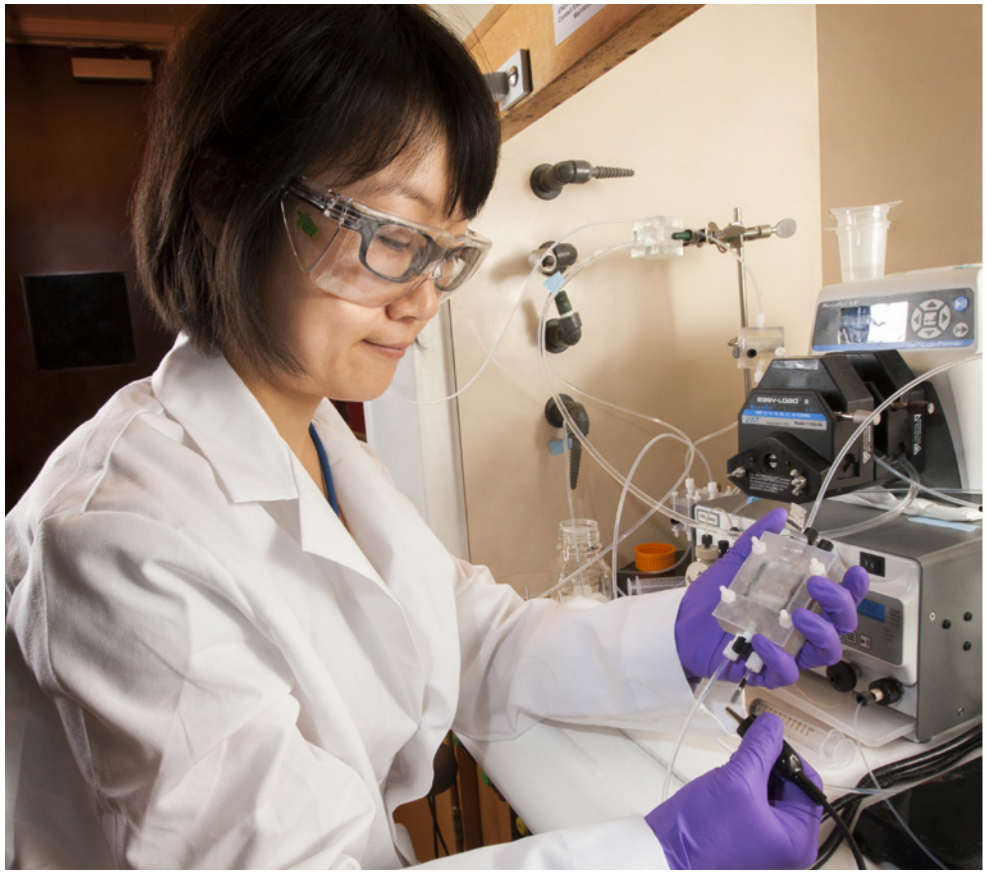
As part of this study, Livermore researchers Erin Nuccio, Pett-Ridge, and others are investigating key microbial processes in soil, such as the decomposition of root residue and turnover of soil organic matter, to identify specific minerals that seem to absorb higher levels of carbon than other materials. In doing so, they are discovering that soil organic matter may be more vulnerable to climate change than previously thought. Plants store a large portion of the carbon from photosynthesis in their roots. Much of this carbon is secreted and then taken up by soil microorganisms. However, elevated CO_2 concentrations in the atmosphere can cause plants to over-supply root-associated microbes, causing excess decomposition activity, which frees organic compounds from protective associations with minerals, resulting in a net loss of soil carbon.

The researchers are also looking at the effects of deep-rooted plants on soil carbon stocks, especially perennial grasses found in the Midwest, which form roots that can extend down to 4 meters—deeper than the reach of a plow's blades. The roots have a one- to two-year lifetime, and when they die, they are eaten by microbes. The steady breakdown of the native prairie grass roots over tens of thousands of years has yielded the Midwest's black, rich soils. Tilling the soil disrupts the root networks, causing huge amounts of CO_2 to be liberated, in particular when native perennial grasses are replaced with shallowly rooted crops. Pett-Ridge says no-till agriculture, a relatively new movement, leaves the carbon-rich roots in place, and is one approach to slowing the relentless removal of soil carbon. Together with colleagues at UC Merced and UC Berkeley, Pett-Ridge, Nuccio, and postdoc Eric Slessarev have been quantifying the carbon contribution of switchgrass located at 12 sites in areas ranging from Texas to Wisconsin and from Oklahoma to Florida.

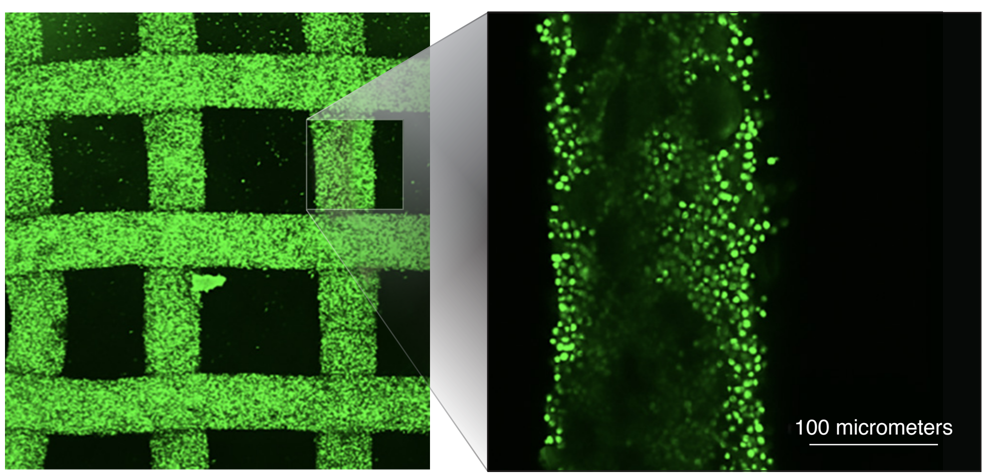
Taking Advantage of Biomass

An important part of the Engineering the Carbon Economy Initiative is performing systems analysis of how various industries contribute to CO_2 emissions. Livermore scientists are working with industry, academia, state, and federal partners to perform life-cycle and technoeconomic analyses to identify areas where carbon emissions can be drastically reduced. For example, both biomass-fired electricity and fermentation generate large amounts of CO_2 that could be stored underground or converted to useful products and fuels.

Biomass comprises waste from agricultural practices, food processing, animal manure, and even sewage treatment plants. Conventional pyrolysis, in which biomass materials are decomposed by heating them at high temperatures produced by natural gas and without oxygen, is a standard technique for turning biomass into other useful chemicals and fuels. Postdoc Wenqin Li and Laboratory scientist George Peridas are analyzing new technologies for making this process more efficient, collaborating with Iowa State University's Bioeconomy Institute to leverage autothermal pyrolysis for biomass conversion. Autothermal pyrolysis uses only air as the fluidizing gas, allowing for



Materials scientist Fang Qian checks the performance of a methane flow-through device for a 3D-printed reactor containing genetically modified microbes. The microbes, printed into the reactor's polymer walls, convert methane to organic acids.



In initial tests, "printed" microbes (green dots), shown here embedded within a reactor's polymer wall, were 20 times more productive than microbes used in a conventional stirred tank.

25 percent fewer capital costs and eliminating the heat transfer barriers of traditional methods.

In California, recent droughts and insect infestations have generated about 145 million dead and dying trees, which also pose a significant fire threat. Livermore researchers are studying how to best manage this enormous amount of biomass by applying expertise in systems design and technoeconomic and life-cycle analysis. "We're working on understanding the economics of this process," says Li. "Our goal is to mitigate CO_2 emissions by decomposing biomass in small, transportable units to produce valuable products."

Livermore researchers are working with Sierra Pacific Industries, the state's largest private landowner, to erect a modular, pilot-scale autothermal pyrolysis plant that will take dry biomass materials, grind them, and dump them into a column operating at about 500°C at atmospheric pressure. The decomposed carbon constituents would be vaporized and then condensed to liquids that can be upgraded into transportation fuels and chemicals. Autothermal pyrolysis also produces solid biochar (charcoal), which can be used as a soil amendment and thereby sequester carbon underground.

Storing CO_2 Deep Underground

Livermore researchers have been instrumental in developing ways to sequester CO_2 deep underground (more than 1,000 meters), where the pressure turns it into a liquid. The researchers are particularly interested in engaging the U.S. oil industry to make underground CO_2 storage a reality in depleted oil fields. An attractive option is using the well-established infrastructure and expertise resident in oil and gas production companies in Central California. Aines points out that Livermore researchers provide the most advanced 3D fracture mechanics modeling for managing the risk of induced seismicity associated with underground CO_2 sequestration projects.

CO_2 sequestration is not a new concept, and DOE-sponsored pilot studies for the past decade have demonstrated its utility by safely storing 16 million tons underground. Notably, since 1996, the Sleipner oil platform off Norway's coast in the North Sea has been putting nearly 1 million metric tons of CO_2 underground per year, the first large-scale carbon removal plant in the world. Livermore researchers are working with an independent oil producer in California to determine if CO_2 storage under its oil fields is a safe and economical approach for the company.

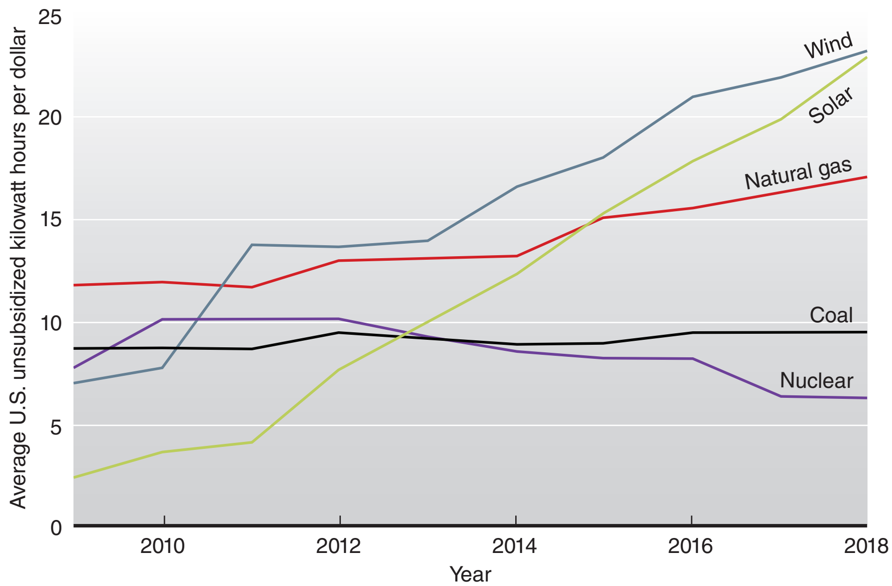
Using a Geoprobe 54LT coring device, researcher Eric Slessarev takes a 2.5-meter-long core sample to determine whether the deep rooting system of Texas switchgrass retains more soil carbon than annual crops. (Photo by Erin Nuccio.)

Toward a New Carbon Economy

According to Aines, the United States is poised to become the world leader in negative emissions largely through CO_2 sequestration and production of carbon-based materials and fuels from atmospheric waste products. Development and demonstration of innovative technologies will be key to this new carbon economy, which could surpass today's agriculture, oil and gas, or electrical power sectors in size. In many parts of the country, infrastructure exists for such a transformation. For example, California's Central Valley has 100,000 trained oil workers, whose skills could be applied to putting large amounts of CO_2 under existing oil fields. "The technology, people, and jobs are comparable for both oil production and underground CO_2 sequestration. Today's oil jobs could be converted to tomorrow's carbon reduction jobs."

New technologies for converting CO_2 into everyday materials and fuels will provide opportunities for commercial enterprises, especially where CO_2 and natural gas are readily available, and electricity is inexpensive. In the Texas to Iowa corridor, for example, CO_2 is an abundant feedstock, and new wind turbines and solar farms routinely sell power on the wholesale market for less than 2 cents a kilowatt hour, much cheaper than power from natural gas, coal, and nuclear power plants. Industries could use that electricity and CO_2 to make chemical products in high yields without much of the expensive separation equipment required in today's refineries and chemical plants. Moreover, this new economy would improve national security through energy self-sufficiency, as well as promote climate and economic security.

Aines reports that interest is high among U.S. businesses for the new Livermore technologies. In June 2018, Lawrence Livermore held a workshop for 20 companies, including ExxonMobil, 3M, and Nike, all interested in how their products can be produced with materials fabricated from CO_2. Aines says oil companies in particular are aware of shifting public attitudes about global warming and the industries responsible for generating large amounts of CO_2. The major oil and gas companies are looking at ways to supply the same products but with CO_2 and methane as the starting ingredients.



A new carbon-based economy would make use of electricity produced from renewable sources over more expensive natural gas, coal, and nuclear power plants. This graph shows the amount of electricity that would be generated per dollar invested in a new power plant, based on U.S. average costs for the full lifetime, using data from the investment firm Lazard.

Partnerships Are Critical

French oil producer Total S.A. has two five-year CRADAs in operation with Livermore and Stanford University. One focuses on underground CO_2 sequestration and the other on reactors for conversion of CO_2 into useful products. Aines says, "Total S.A. wants to create its entire suite of products from CO_2 and methane."

Lawrence Livermore was a founding member of the New Carbon Economy Consortium, an alliance of universities, national laboratories, and nongovernmental organizations working to build a carbon-conscious world. The Laboratory was also a founding member of DOE's Joint Bioenergy Institute to accelerate research in biofuels. The institute combines the scientific expertise of four national laboratories, five academic institutions, and one industry partner.

Livermore researchers who are part of the Engineering the Carbon Economy Initiative have developed strong partnerships with California state agencies to create solutions to address climate change challenges. For example, the state's low carbon fuel standard attempts to combat the steady growth of transportation-related CO_2—half of California's yearly total. A 2018 executive order by former California Governor Jerry Brown declared a statewide goal to achieve carbon neutrality no later than 2045, and to achieve and maintain net negative emissions thereafter. In addition, a recent state law calls for renewable energy resources and zero-carbon resources to supply 100 percent of electricity retail sales to California end-use customers and 100 percent of electricity procured to serve state agencies by 2045. Another law requires statewide greenhouse gas emissions to be reduced to 40 percent below 1990 levels by 2030. Aines remarks that as the world's fifth-largest economy, California's actions cannot be ignored.

Meeting the former governor's executive order will require 100 to 150 metric tons of negative emissions per year. Aines asks the tough questions: "Can we really clean up the atmosphere? Can we create a negative-emissions infrastructure twice as big as today's oil industry?" His answer is equally direct. He states, "By engaging science, engineering, and most importantly, partnerships, we can help address one of the greatest challenges of this century. Lawrence Livermore is proud to be a part of finding the necessary solutions."

—Arnie Heller

Key Words: Bioeconomy Institute, carbon dioxide (CO_2), CO_2 sequestration, Cooperative Research and Development Agreement (CRADA), electrochemical reactor, Engineering the Carbon Economy Initiative, greenhouse gas, Intergovernmental Panel on Climate Change, Joint Bioenergy Institute, Laboratory Directed Research and Development (LDRD) Program, methane, microencapsulated CO_2 sorbent, National Renewable Energy Laboratory, negative emissions, pyrolysis, switchgrass, Total S.A.

For further information contact Roger Aines (925) 423-7184 (aines1@llnl.gov).