

Biology leads the race to turn sunlight into fuels

A bacterium can be harnessed to do the job, but can that process be scaled up?

Now in its seventh year, a Department of Energy-funded effort to produce liquid fuels from sunlight, water, and carbon dioxide continues to hinge on finding an inexpensive and abundant catalyst. Meanwhile, a separate project led by Harvard University's Daniel Nocera already has produced isobutanol and isopentanol fuels using a hybrid chemical-biological process.

Founded in 2010 by former energy secretary Steven Chu and managed by Caltech, the Joint Center for Artificial Photosynthesis (JCAP) is the largest of many initiatives that aim to convert sunlight's energy into chemical fuel. Others include Nocera's project, a collaboration based at Sweden's Uppsala University, and a collaboration led by scientists from Technion-Israel Institute of Technology. All begin by splitting water into hydrogen and oxygen in photoelectrochemical cells. The next and far more difficult step is to reduce carbon dioxide to end up with hydrocarbon fuels.

Supported at \$15 million annually, JCAP in 2015 achieved its initial five-year goal: producing compact prototype cells that split water using inorganic catalysts and have better than 10% efficiency. Harry Atwater, JCAP's director, expects efficiency will approach the 20% attained by today's best commercial solar panels in five years or so. Now JCAP has moved on to the CO₂ reduction challenge set forth by the five-year grant extension that began in 2015. JCAP brings together more than 100 graduate students, post-docs, and faculty members at Caltech, Lawrence Berkeley National Laboratory (LBNL), SLAC, and the University of California's Irvine and San Diego campuses.

Although reducing CO₂ counts as a success, the type of fuel produced is not fixed. Compounds could range from



DANIEL NOCERA OF HARVARD UNIVERSITY has produced multiple-carbon alcohol fuels from sunlight using a hybrid chemical-biological process.

ROSE LINCOLN, STAFF PHOTOGRAPHER, HARVARD UNIVERSITY

one-carbon molecules such as methanol or even carbon monoxide to the more energy-dense multiple-carbon alcohols such as ethanol or isobutanol.

The most basic fuel from CO₂ reduction is CO. It has a low energy density and is toxic but can be converted to liquid fuels via the well-established Fischer-Tropsch process. Methanol is more energy-dense and could be used directly as a fuel or converted to gasoline via another well-known chemical pathway. But Atwater notes that JCAP's premise is building compact fuel generators that don't require refineries to produce finished fuels.

The hydrogen from water splitting could be used in fuel-cell vehicles. But despite their efficiency, Atwater says, JCAP's solar devices can't compete economically today with the CO₂-emitting commercial plants that convert methane into the hydrogen being sold at California filling stations.

The hybrid artificial photosynthetic method developed by Nocera and his fellow Harvard researcher Pamela Silver combines an inorganic catalyst for water splitting with the hydrogen-feeding bacterium, *Ralstonia eutropha*, for CO₂ reduction. Nocera says that if he uses pure CO₂, the process yields a general solar-to-fuel conversion efficiency of 5–7% for liquid fuels. Even with CO₂ from ambi-

ent air, the process beats the 1% efficiency of natural photosynthesis.

Using inorganic catalysts rather than a bacterium, JCAP has so far succeeded, with 10% efficiency, in reducing CO₂ to formic acid (HCOOH) in a device similar to a solar cell, says Atwater. Although formic acid isn't combustible, it is used in fuel cells. And the ability to selectively produce it is an early indicator that with the right catalysts it should be possible to direct the CO₂ and hydrogen to form a single compound while preventing formation of diatomic hydrogen and other potential reduction byproducts.

String of pearls

Most CO₂ reduction schemes produce compounds containing a single carbon atom. "What's hard to do is stringing a bunch of carbon atoms together to make C₂, C₃, C₄ molecules, like pearls on a necklace," says Nocera. Compounding the challenge of making carbon-carbon bonds is the large number of transferable protons and electrons that need to be managed lest they participate in competing hydrogen-producing reactions.

Biology manages that process "beautifully," says Nocera. "It knows how to make carbon-carbon bonds and not make hydrogen and do it selectively. And it can manage lots of protons and electrons." The other advantage to the

bacterial reduction process is that it requires no sunlight; only the water-splitting reaction requires the sun. That separation eases the design constraints on scaling up the process, he says. Last year, he and Silver announced an improvement to their process—a water-splitting catalyst that doesn't produce reactive oxygen species toxic to the bacterium.

Each of Nocera's bench-scale 1-liter reactors can produce fuel from 1200 liters of air at ambient conditions per day. He has granted the rights to use the proprietary process to India's Institute of Chemical Technology, which is scaling up the technology for use in the developing world. Neither he nor Atwater expects any artificial photosynthesis technology to compete against fossil fuels—at least absent a carbon tax. But Nocera says his method could make sense in the developing world, where refineries, chemical plants, and other infrastructure are scarce and where solar fuel plants could be sized to fit in a backyard.

Although the biological approach offers reduction-product selectivity, it's difficult to speed up the management of copious protons and the formation of carbon-carbon bonds. Speed is the potential selling point of the chemical approach, provided that it can meet the challenges biology has already tackled.

Atwater is careful not to oversell expectations for JCAP. "The most important thing we'll have at the end of five years is an understanding of the criteria for activity and selectivity for catalysts for carbon dioxide, informed by theory and validated by experiment," he says. "It's not wise or appropriate to claim that we're within a couple years going to have a complete manufacturable device that works with high activity and high selectivity."

Caltech performs high-throughput screening of potential catalyst compounds using combinatorial synthesis in ways analogous to the pharmaceutical industry's screening of small molecules for new drug candidates. A parallel theory effort uses the high-performance computing assets at LBNL's National Energy Research Supercomputing Center to rule out most of the millions of potential candidate compounds and thus dramatically lower the need for synthesis and testing.

Ian Sharp, a JCAP researcher at LBNL,

says the center draws on expertise at the lab's Molecular Foundry to find catalysts and materials for thin-film semiconductors used in the photovoltaic part of the cells. "We are at a stage now where materials prediction is sufficiently good that we can use that with some degree of reliability for targeting the compounds we want to use."

But trying to fabricate devices that will both oxidize water and reduce CO₂ won't be easy. "The problem is that in terms of semiconductors, there are no materials that can all at the same time exploit high efficiency and [that] are chemically stable in reaction environments and are composed of elements that can be scalably deposited," he says. So while the search for materials with the necessary properties continues, researchers are taking a parallel path in seeking ways to protect traditional semiconductor materials such as silicon, gallium arsenide, and indium gallium phosphide from the corrosive environment.

The theorist contingent at JCAP has increased from about 5% of staff in the initial five years to 25% today; that switch reflects the difficulty facing CO₂ reduction. The influx of theorists has improved the understanding of catalytic mechanisms. Although it was known that there were heterogeneous or inorganic metal catalysts such as silver or gold that could produce CO, for example, the mechanism by which, say, copper could produce more complex fuels remained a mystery. "We have developed a lot more understanding of that," Atwater says.

A secret (so far) process

Among other solar fuels research projects is an Israeli collaboration that envisions hydrogen as the end product. Avner Rothschild of the Technion favors combining the hydrogen from water splitting with plentiful atmospheric nitrogen to produce ammonia for fertilizer or fuels. He notes that extracting sufficient amounts of CO₂ at its atmospheric concentration of 400 ppm for reduction to fuels will be very challenging. Ammonia can't be produced in a photoelectrochemical cell, however; that requires a chemical plant.

Rothschild and Technion chemical engineer Gideon Grader are working with metal oxide catalysts to develop efficient photoelectrochemical water-splitting

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SCIENTIST ANIKETA SHINDE works on the rapid screening of materials for solar-fuels generators in the high-throughput experimentation laboratory at Caltech.

cells. “Most of us realize we’re not going to split water with some simple material like metal oxide powder in a solution,” Grader admits. Why not just use well-established photovoltaic-powered electrolysis? Grader and Rothschild’s analysis finds that the photoelectrochemical process has the potential to increase water-splitting efficiency by 30–40% relative to PV electrolysis. And the catalysts that are developed will be less costly than the rare earths and platinum group metals currently used in electrolysis.

As *PHYSICS TODAY* went to press, the Technion team was days from publishing its novel approach for generating hydrogen from the millions of photoelectrochemical cells that would be needed to produce large quantities of hydrogen. They would not describe the concept in detail pending its publication, except to say that the hydrogen would be generated at a central location.

The Swedish collaboration’s investigation of catalysts draws on resident expertise in the mechanisms for proton-coupled

electron-transfer reactions that occur in inorganic catalysts and in enzymes such as photosystem II, which participates in photosynthesis in cyanobacteria, algae, and plants. “We make cells but we don’t promise to solve the world’s problems within the next granting period,” says Stenbjörn Styring, the Uppsala University chemist who heads the 75-person consortium. “We study how protons and electrons couple in the very complicated reactions, and we drive the idea that molecular systems have a future in the field.”

The consortium has focused on developing water-splitting catalysis based on ruthenium, cobalt oxide, and cobalt-containing molecular complexes. Although ruthenium is expensive, it is “amazingly efficient,” Styring says. Citing Nocera’s approach, he favors biological pathways for reducing CO_2 to long-carbon-chain fuels. Photosynthetic algae and bacteria can make almost any compound from CO_2 , water-derived electrons, and solar energy, he notes.

Atwater mentions another challenge: durability. Rooftop solar panels make economic sense because they will last 25 years. “To date we don’t have any demonstration that these relatively efficient water-splitting devices are able to last for more than a few hundred hours.” Efforts to improve device lifetimes are under way at JCAP. **David Kramer**

Theory institute opens residence hall for visitors

The aim is for informal interactions to stimulate creativity and collaborations.

Visitors to the Kavli Institute for Theoretical Physics (KITP) at the University of California, Santa Barbara, can now lodge together in a sleek new residence hall. Before the hall opened in January, visitors were scattered across town in hotels, rental quarters, and campus housing. The new building is named for Charles T. Munger, who gave \$65 million for its construction. Munger is the vice chairman of Berkshire Hathaway, the



PATRICK PRICE

NEW GUEST HOUSING opened in January at the Kavli Institute for Theoretical Physics at the University of California, Santa Barbara.

conglomerate founded by Warren Buffett.

Some 700 visitors come to KITP each year for three weeks or longer, and another 600 come for shorter visits. Roughly

half of the visitors come from outside the US. The institute hosts about 10 topical programs each year, on everything from the mysteries of massive stars to the