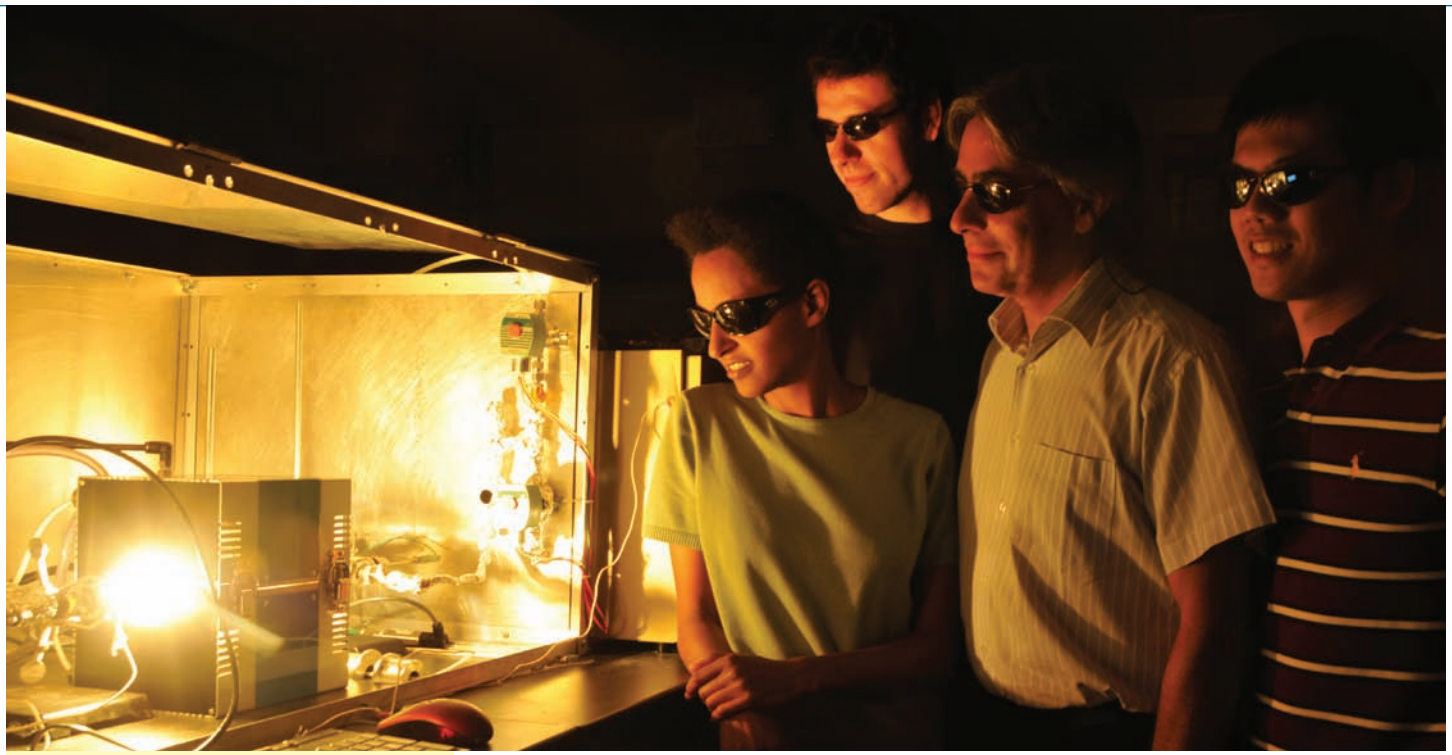
Put Some Sunlight in Your Tank

by Douglas L. Smith

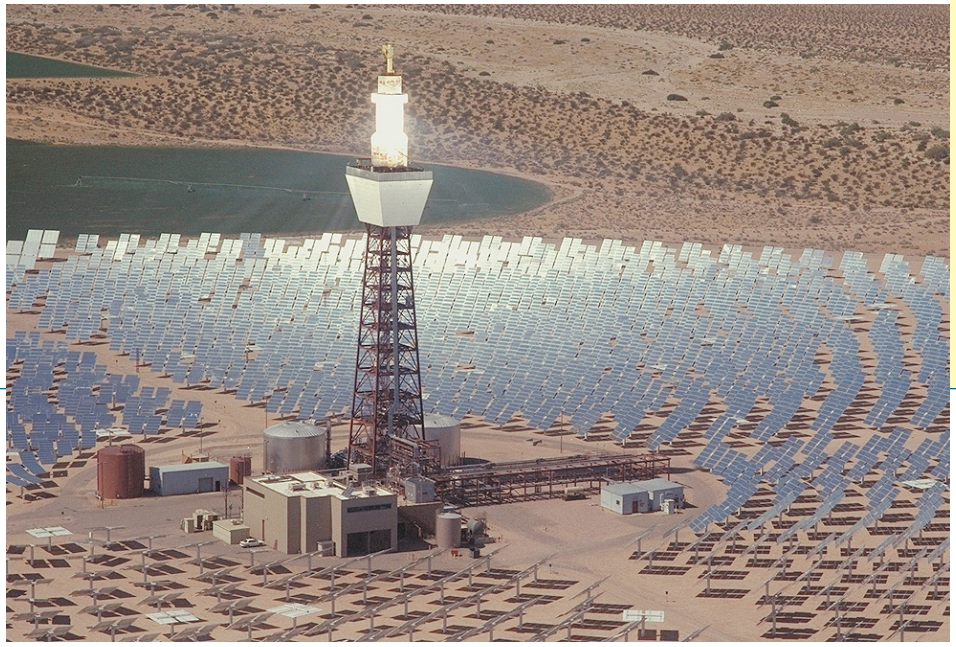


Carbon-neutral doesn't need to be carbon-free. Green plants make fuel from sunlight and carbon dioxide—can we make gasoline the same way? It would certainly be a lot simpler than replumbing the planet to run on compressed hydrogen.

You know what would be really cool? A gadget that turns carbon dioxide into gasoline. And while we're at it, let's make this gizmo solar powered. It's a great daydream, and grad student William Chueh (BS '05, MS '06), in Professor of Materials Science and Chemical Engineering Sossina Haile's lab, has taken the first steps toward making it happen.

As you may have heard, humanity's reliance on burning coal, oil, and other fossil fuels has helped raise atmospheric carbon dioxide levels from 285 to 385 parts per million by volume over the last century, with no end in sight. The alterations to the world's climate likely to result are widely considered to be a bad thing, except perhaps in Alaska. As a civilization, we currently consume 16 trillion watts, or terawatts, of energy. If we are to rein in CO_2 at 550 parts per million, which is thought to be the prudent upper limit to avoid irreparable harm, we are going to need 20 terawatts of carbon-neutral energy by the year 2050. But being carbon neutral doesn't necessarily mean we have to be completely carbon-free. If we could use

The future's so bright they have to wear shades. . . . From left: Sossina Haile, Christoph Falter, Aldo Steinfeld, and William Chueh bask in the glow of the high-temperature furnace that simulates concentrated sunlight for the CO_2-to-solar-fuel studies.



The Department of Energy's Solar Two demonstration plant, just east of Barstow on the outskirts of Daggett, California, used motorized mirrors called heliostats to focus sunlight on a collector atop a 90-meter tower. Fourteen hundred tons of molten salt were pumped through the collector, heated to 565°C, and stored in an insulated tank at the tower's base. The hot salt was used to make steam that ran a turbine, producing enough electricity to power 10,000 homes for as long as three hours after sunset. The project ran from 1996 to 1999. Plants now under development can store enough salt for up to 15 hours of power.

the same carbon atoms over and over again, turning the CO_2 from burning hydrocarbons back into hydrocarbons that we could burn again, we would come out even in the global sense.

Unfortunately, turning carbon dioxide back into hydrocarbons is very, very hard. The world's worth of energy that we get out of hydrocarbons comes from forming carbon-oxygen bonds, and we'd need to pump all that energy back into the bonds in order to break them. That's why carbon dioxide doesn't go away by itself once it's been released into the atmosphere. "Breaking CO_2 apart is an uphill struggle," says Haile. "It's like hiking from Pasadena up into the San Gabriel Mountains to Charlton Flats. And worse, if you make a beeline for Charlton, you have to climb Mount Harvard and Mount Wilson in the process. It takes a top-notch catalyst to insert the necessary energy into the bonds, especially at room temperature, or in other words to find a trail that goes around the mountain peaks."

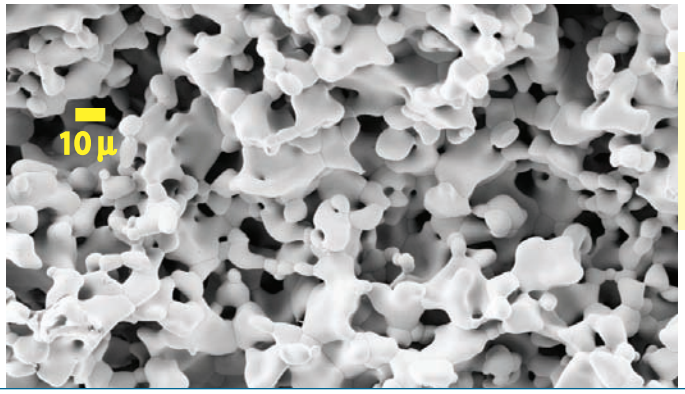
While green plants use cheap, readily available materials to make a woefully fragile but marvelously efficient manganese catalyst, we humans have had less luck at using sunlight to convert CO_2 into fuel. It is so hard, in fact, that most scientists have opted to take another approach to the solar-fuel problem, focusing on splitting water to make H_2. The hydrogen-oxygen bond is easier to break, but even that requires rare, expensive metals such as platinum. (See *E&S* 2008, No. 2, and 1997, No. 3.) Says Haile, "So we asked ourselves, if inserting the energy from sunlight into the chemical bonds of CO_2 is so hard, is there another route? And the answer is to use the sun's heat. The heat lets the reaction take an easier path around the mountains, and because everything moves faster at higher temperatures, we get the added bonus of producing the fuel very quickly."

The catch is that when Haile says "higher temperatures," she means *really* higher temperatures—an incendiary 1,500°C, hot enough to melt steel. This doesn't bode well for designing a device that you can bolt to the muffler under your minivan.

The work was inspired by tailpipe technology, however. For the last eight years, Haile's lab has been working with cerium oxide, CeO_2, or "ceria," which is the key ingredient in the lab's family of solid-oxide fuel cells. (See *E&S*, 2008, No. 2 and 2003, No. 1.) To the rest of us, however, ceria is best known—if we've heard of it at all—as the main ingredient in our cars' catalytic converters. There, CeO_2 acts as an oxygen-transfer system. It grabs the oxygen atoms from the smog-causing NO_x molecules in the exhaust, reducing them to harmless nitrogen gas, and then turns around and donates the seized oxygen atoms to passing carbon monoxide molecules, transforming deadly CO into CO_2.

Chueh's project goes the other way, converting carbon dioxide and steam to a mixture of H_2 and CO known as "synthesis gas," or "syngas" for short. From there, you can make pretty much any hydrocarbon—including gasoline, diesel oil, and jet fuel—via the Fischer-Tropsch process, which was invented by Franz Fischer and Hans Tropsch at the Kaiser Wilhelm Institute in Berlin in the 1920s. Nazi Germany, cut off from most of the world's petroleum reserves, used the process to convert its abundant coal supplies into liquid fuels during World War II; South Africa got around the oil embargo of the apartheid years in the same way. It would be ironic indeed if a technology with roots in such evil empires wound up doing a world of good, but history is a notorious practial joker.

Today, South Africa still makes most of its diesel fuel using the Fischer-Tropsch process. And, concerned about future fuel supplies, the Department of Defense is working with a firm called Syntroleum to have every plane in the Air Force certified



The ceria powder used in these experiments is extremely porous on the microscale, providing plenty of surface area for the reactions to occur. The scale bar is 10 microns, or millionths of a meter, in length.

to fly on a 50-50 mixture of jet fuel and a Fischer-Tropsch product by 2011.

Getting 1,500-degree temperatures from concentrated sunlight is not a cakewalk, but it has been done. Solar-thermal electric-power plants use arrays of pivoting mirrors to track the sun and focus its light on fluid-filled tubes. The superheated fluid can be piped to the turbine room to make electricity straight away, or it can be stored in insulated tanks for use after dark. A handful of commercial plants are already online in sun-drenched parts of the world, most notably the Nevada Solar One project near Boulder City and the Solúcar complex near Seville, Spain. And huge plants are planned for the Mojave Desert as California's utility companies scramble to meet the state's 20 percent renewable-energy standard that kicks in in 2010. These solar-electric plants operate at somewhat lower temperatures than are needed for the ceria-based process, but with some tweaking the concentrator technology could be adapted.

But there's no need to get riled up about the potential environmental impacts of installing square miles of mirrors in the desert. The ceria system can make syngas from the stuff that goes up the boiler-house smokestacks at coal-fired power plants. This flue gas is about 20 percent CO_2 and 10 percent H_2O, with the rest being N_2 from the air. Says Haile, "In a coal-fired power plant, the biggest cost when people think about sequestering the CO_2 is separating it from the N_2. But we don't have that worry. The nitrogen does not affect our process."

So if we continue to make electricity from coal—which is cheap and abundant, and we're therefore probably not going to stop any time soon—and then we make gasoline or jet fuel from the flue gas, we'll at least be using each carbon atom twice. At 2006 emission rates, this translates into preventing some two billion metric tons of carbon dioxide from escaping into the atmosphere from the United States alone. Converting that CO_2 back into hydrocarbons would meet the nation's petroleum needs of 14,000,000 barrels per day and "essentially eliminate the transportation sector as a CO_2 source," says Haile.

BREATHING DEEPLY

The carbon-dioxide-to-fuel conversion process hinges on bulk ceria's ability to lose lots of oxygen atoms without altering its crystal structure. When heated to 1,500°C under an inert flow of nitrogen gas, CeO_2 can surrender as much as 2.5 percent of its oxygen content, a process Haile and Chueh call exhaling. "Everyone needs to say they do something with biology these days," Haile laughs. "This is as close as I get. I have metal oxides that breathe. And like biology, we're making carbon-containing compounds from the sun." At such high temperatures, most metal oxides would collapse into other crystal forms that filled the vacated spots; keeping the voids open allows the oxygen-depleted ceria to hold its breath while it gets cooled to a mere 900°C. Then the flue gas is piped in, and the suffocating ceria gulps down all the oxygen it lost, stripping CO_2 to CO and H_2O to H_2—syngas!

Experiments done in a benchtop furnace the size of a toaster oven show that both of these steps work quite well. The finely powdered, highly porous ceria is placed in an alumina tube through which a test gas mixture is blown. The gas coming out of the tube's far end is analyzed in a mass spectrometer and a gas chromatograph, which identify the molecules in the gas stream and measure their concentrations.

In the first step of the process, where the ceria exhales, the oxygen release "is very close to our thermodynamic prediction of around 3.5 milliliters per gram of ceria," says Haile. "And because our furnace gets to high temperatures almost instantaneously and the ceria has such a phenomenal response, we see that 90 percent of that oxygen is released in less than two minutes."

On the other half of the cycle, the fuel-production end, Chueh started by testing water vapor and carbon dioxide separately, by letting the ceria exhale and cool before piping one of the two gases into the 900°C furnace. He found that he got all the hydrogen out of the water—the theoretical maximum of about seven milliliters per gram of ceria—in the same two to three minutes. Ditto for the CO. Says Haile, "We are now able to produce CO from CO_2. And by the way, that means we have a lot of good carbon-monoxide sensors in our lab."

Chueh then tried a flue-gas stand-in, a 2:1 mixture of dilute H_2O and CO_2 in nitrogen, on the blue-faced ceria. He got 100

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Opposite: The solar furnace at the Paul Scherrer Institute. The heliostat, seen from the rear, directs sunlight onto the parabolic mirror in the building in the background. The front of the building is a giant set of venetian blinds used to regulate the intensity of the solar flux. The furnace is capable of generating temperatures in excess of 3,000 kelvins at heating rates of more than 1,000 kelvins per second.

percent conversion to syngas—a 2:1 mixture of H_2 and CO out the other side—again, in under two minutes. This equates to 0.2 liters of the mixture per gram of ceria per hour. Says Chueh, "The record production rate for hydrogen is on the order of 10,000 microliters [0.01 liters] per hour per gram, whereas for CO_2, the highest is only on the order of 160 microliters, using platinum and copper catalysts on titania." Says Haile, "Our fuel production rate is 200,000 microliters per hour per gram of material. We have to convert into units of microliters, because this is what other groups typically report, and we are at *liters* per gram per hour. So that's the benefit of being at a high temperature. Things just proceed much more quickly."

FROM SYNGAS TO NATURAL GAS

Chueh didn't need nickel to get phenomenal reaction rates, but since nickel is known to catalyze the breakdown of CO_2, he decided to try adding some to see if he could manipulate the outcome of the dissociation reaction. Normally, he explains, "When you break the carbon-oxygen bond, the carbon does not like to reside on the ceria. It absolutely hates it. So that means that we cannot split CO_2 to the thermodynamic limit, which is pure carbon, and we get CO instead. We can't break the carbon's triple bond to the oxygen in carbon monoxide. Energetically, forming solid carbon is favored, but we just can't get there kinetically." As Haile is fond of saying, "Thermodynamics tells you what *can* happen, not what *will* happen." In terms of the cross-country hike to Charlton Flats, the kinetic route is the one that takes you over the summit of Mount Wilson. If you don't have a catalyst that knows the thermodynamic trail that winds along the lower elevations of the canyon floors, and you don't feel energetic enough to tackle the steep slopes, you'll say the heck with it and stay home.

After Chueh added nickel particles to the powdered ceria, "when we put pure CO_2 in, *nothing* came out. Nothing. When the ceria inhaled the oxygen, all that was left of the CO_2 was some solid carbonaceous species. When we took the powder out of the tube to look at it, it was just coated with graphite. You could write with it. We found that if you add nickel, all the carbon resides on the nickel. The ceria still can't take any carbon, but the nickel can." With elemental carbon now available on the nickel, a whole new set of possible reactions opens up. If you add water vapor, you can make methane, CH_4, aka natural gas—another fuel that's pipeline-ready. And indeed, blowing the mock flue gas through the nickel-ceria mixture produced methane.

Better still, with the nickel catalyst you can tune the system to choose your product. When you process flue gas at lower temperatures, around 400°C, the nickel catalyst enables the thermodynamic pathway to compete with the kinetic one, and methane production predominates—up to 80 percent methane under the right conditions. As the temperature increases, the kinetically favored reaction takes over, and by 700°C the methane is gone and you're back to pure syngas. "We're not making policy choices," Haile says. "We're giving the policy makers technological options."

With making natural gas now an option, a solar-thermal ceria plant could be operated the way that windmill farms are, Haile says. "Many wind farms are co-sited with natural-gas-fired power plants. During the daytime, a solar farm would provide electricity, but we'd simultaneously generate natural gas. The co-sited natural-gas plant—or better yet, a fuel-cell power plant—would operate on rainy days and at night, or to compensate for variations in demand, and we'd cycle the waste CO_2 back into the solar-thermal plant."

TAKING IT OUTDOORS

By Haile's calculations of how much sunlight it would take to get the ceria up to 1,500°C, "we end up with about 13 percent efficiency. Photovoltaics started off with a fraction of a percent, and now you can go out and buy ones that are on the order of 13 percent efficient in producing electricity. So this is not bad." And there is plenty of room for improvement—as the ceria breathes, there's a temperature swing of 600°C to 1,100°C, depending on which fuel you're making. That's an awful lot of waste heat to get rid of during each cooling cycle, so any practical system would need to capture and reuse as much of that energy as possible. "If we could come up with some scheme to recover half of that heat, then we would

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increase the overall efficiency to about 23 percent," Haile says. "And that gets to be really quite attractive."

Haile's lab is collaborating with Aldo Steinfeld, a professor at the Swiss Federal Institute of Technology (ETH) in Zürich and head of the Solar Technology Laboratory at the Paul Scherrer Institute. Steinfeld, who is on campus through December as part of a sabbatical in the States, has been in the high-temperature solar-fuel hunt since the early '90s. In 1997, his lab fired up a solar furnace capable of producing 5,000 kilowatts per square meter, that is, the flux intensity of 5,000 suns. The unit looks rather like a giant headlight aimed across a grassy lawn at a drive-in movie screen. The movie screen is a rectangular heliostat—a pivoting 12-by-10-meter mirror that tracks the sun and throws its light onto an 8.5-meter-diameter parabolic reflector that in turn is focused on a reaction vessel roughly the size of an oil drum.

The reactor now occupying the focal point splits water into H_2 and O_2 in a two-step thermochemical cycle based on a zinc catalyst. Steinfeld and his grad student Christoph Falter, who came to Caltech with him, are designing a three-kilowatt apparatus for the ceria process. "In contrast to the zinc-based system, where zinc oxide thermally dissociates into zinc vapor and oxygen, the ceria remains in solid form throughout. So we need an entirely different reactor concept," says Steinfeld. The prototype will be a cylinder about 20 centimeters in diameter by 20 centimeters long, or somewhat larger than a gallon milk jug. The concentrated sunlight will be focused on a quartz or sapphire window in one end of the reactor's cavity. The cavity will act as a black-body absorber, soaking up all the energy and transferring it to the porous ceria monoliths—a fancy word for bricks—within.

The plan is to ship the setup to Zürich in December. "The goal is to demonstrate an integrated solar-reactor technology with the ceria-based thermochemical cycle," says Steinfeld. "It's an ambitious goal—we basically need to operate a mini thermochemical plant with concentrated solar energy." Haile adds, "We need to maintain very high temperatures in the cavity while keeping everything gas-tight. We also have to cycle

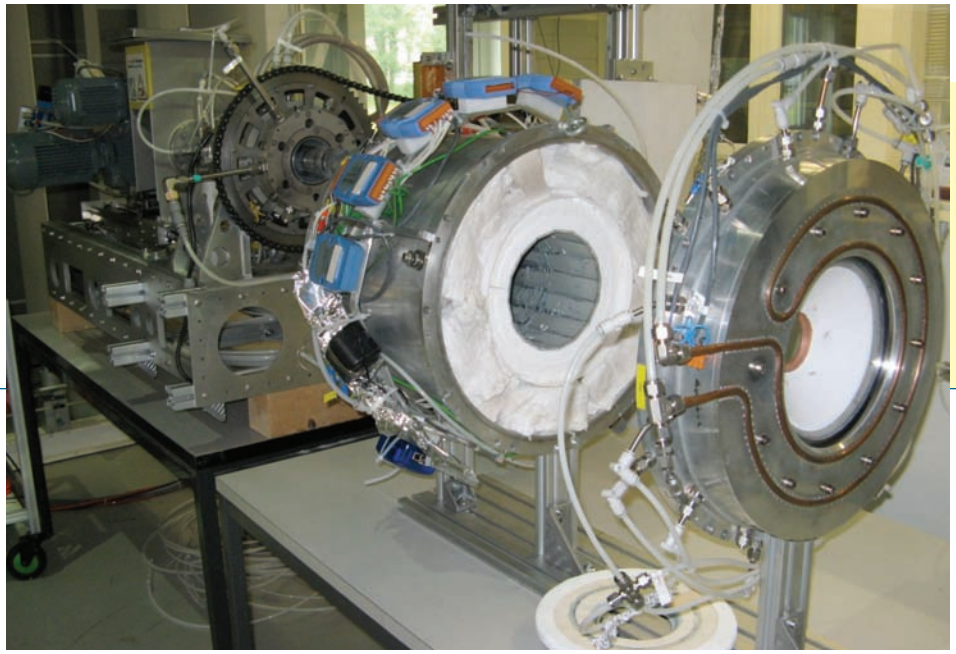
THERE'S PLENTY OF ROOM UNDER THE SUN

Solar-thermochemical fuel production is a hot research topic. The Sandia National Laboratory in Albuquerque, New Mexico, has a solar reactor designed to turn CO_2 into CO, while the University of Colorado at Boulder is working on a project to turn biomass, such as corn stalks, into syngas.

On the water front, Jane Davidson of the University of Minnesota is collaborating with Steinfeld on the zinc-based water splitter. The Weizmann Institute of Science in Rehovot, Israel, has a zinc system of its own, while the DLR, the German space agency, is developing a system based on iron oxides. And in Japan, Niigata University and the Tokyo Institute of Technology are working on mixed metal oxides based on iron, nickel, and cobalt.

The French national research agency, CNRS, has a one-megawatt solar furnace at Odeillo, a ski resort in the Pyrenees; across the border in Spain, CIEMAT, the Spanish national energy reseach institute, has a solar tower at Almería, on the Mediterranean.

"Solar-thermochemical fuel systems can use the concentrator technologies now being deployed for large-scale solar-thermal power production, and thus have the potential to be economically competitive," says Steinfeld. E&S



Steinfeld's 10-kilowatt zinc reactor operates at 2,000 kelvins. In the middle of the picture is the rotating reaction cavity, where the zinc oxide particles are held against the heavily insulated chamber wall by centrifugal force. The concentrated sunlight enters through the quartz window on the right, inside the copper C of cooling-water lines.

the system between the two temperatures very rapidly, and we have to guard against solar leakage, so that we focus the sunlight where we want it, and not where we don't. There are a lot of things that have to happen correctly, and we are really relying on Aldo's experience to help guide us through the design and construction."

Chueh will accompany Falter back to Switzerland for the reactor studies. Chueh did an exhaustive kinetic and thermodynamic analysis as part of his PhD. As part of his own thesis, Falter is developing a comprehensive heat- and mass-transfer model of the entire process in parallel with working on the reactor design. If the experiments are successful, and the model measures up, the next step will be to use it to optimize the reactor configuration for maximum solar-energy-to-fuel conversion efficiency. Then, says Steinfeld, "We would like to scale it up from kilowatts to megawatts."

"Certainly many challenges remain," says Haile. "We're just getting started. We'd like better lungs on our ceria, which would give us higher efficiency, higher fuel productivity, and lower cost. But precious-metal catalysts have really been the stumbling block for most of the ways of generating fuels from the sun. Cerium is as abundant as copper. The total world reserves are on the order of 40 megatons—some 15 percent of it right here in California—and we estimate that if we had 100 cycles a day running under optimal conditions, and we produced enough fuel to operate for six more hours after dark, there's enough ceria to run about 140,000 one-hundred-megawatt power plants. That's not bad. It's 14 terawatts at nighttime or, in terms of total energy consumption in terawatt-hours, it's nearly 20 percent of the clean energy that we're going to need by 2050. Making gasoline from sunlight is all very well, but what I find personally much more exciting is using our process to store solar energy at a power plant, for generating electricity when the sun isn't shining. Right now, a national consensus is building that we can't provide more than about 20 percent of our electricity from renewable sources until we have solved the storage problem. Maybe, just maybe, this will be the key to getting us to 100 percent." E&S

Sossina Haile got her BS and PhD from MIT (the latter in 1992), with a side trip out west for an MS at UC Berkeley. She came to Caltech in 1996, after three years as an assistant professor at the University of Washington in Seattle.

A paper describing this work appeared online in ChemSusChem, the journal of chemistry and sustainability, on July 27. (See.)

Chueh presented his results at the first annual $30,000 Lemelson-Caltech Student Prize competition, awarded to an undergrad or graduate student "to recognize and inspire . . . burgeoning innovators and inventors," and funded by the Lemelson-MIT Program and Michael W. Hunkapiller (PhD '74). Chueh won $10,000 as runner-up to Ophir Vermesh, a grad student of Gilloon Professor and Professor of Chemistry James Heath. Vermesh's work was described in the Winter 2008 issue of E&S.

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PICTURE CREDITS
21 — Bob Paz; 22 — Department of Energy; 23 — William Chueh; 25, 26 — PSI/ETH

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