FEATURES

RENEWABLE BONDS

With solar and wind booming, the chemical industry dabbles with forgoing petroleum as its feedstock

By **Robert F. Service**

Black, gooey, greasy oil is the starting material for more than just transportation fuel. It's also the source of dozens of petrochemicals that companies transform into versatile and valued materials for modern life: gleaming paints, tough and moldable plastics, pesticides, and detergents. Industrial processes produce something like beauty out of the ooze. By breaking the hydrocarbons in oil and natural gas into simpler compounds and then assembling those building blocks, scientists long ago learned to construct molecules of exquisite complexity.

Fossil fuels aren't just the feedstock for those reactions; they also provide the heat and pressure that drive them. As a result, industrial chemistry's use of petroleum accounts for 14% of all greenhouse gas emissions. Now, growing numbers of scientists and, more important, companies think the same final compounds could be made by harnessing renewable energy instead of digging up and rearranging hydrocarbons and spewing waste carbon dioxide (CO_2) into the air. First, renewable electricity would split abundant molecules such as CO_2, water, oxygen (O_2), and nitrogen into reactive fragments. Then, more renewable electricity would help stitch those chemical pieces together to create the products that modern society relies on and is unlikely to give up.

"This is very much a topic at the forefront right now," says Daniel Kammen, a physicist at the University of California, Berkeley.

Chemists in academia, at startups, and even at industrial giants are testing processes—even prototype plants—that use solar and wind energy, plus air and water, as feedstocks. "We're turning electrons into chemicals," says Nicholas Flanders, CEO of one contender, a startup called Opus 12. The company, located in a low-slung office park in Berkeley, has designed a washing machine–size device that uses electricity to convert water and CO_2 from the air into fuels and other molecules, with no need for oil. At the other end of the commercial scale is Siemens, the manufacturing conglomerate based in Munich, Germany. That company is selling large-scale electrolyzers that use electricity to split water into O_2 and hydrogen (H_2), which can serve as a fuel or chemical feedstock. Even petroleum companies such as Shell and Chevron are looking for ways to turn renewable power into fuels.

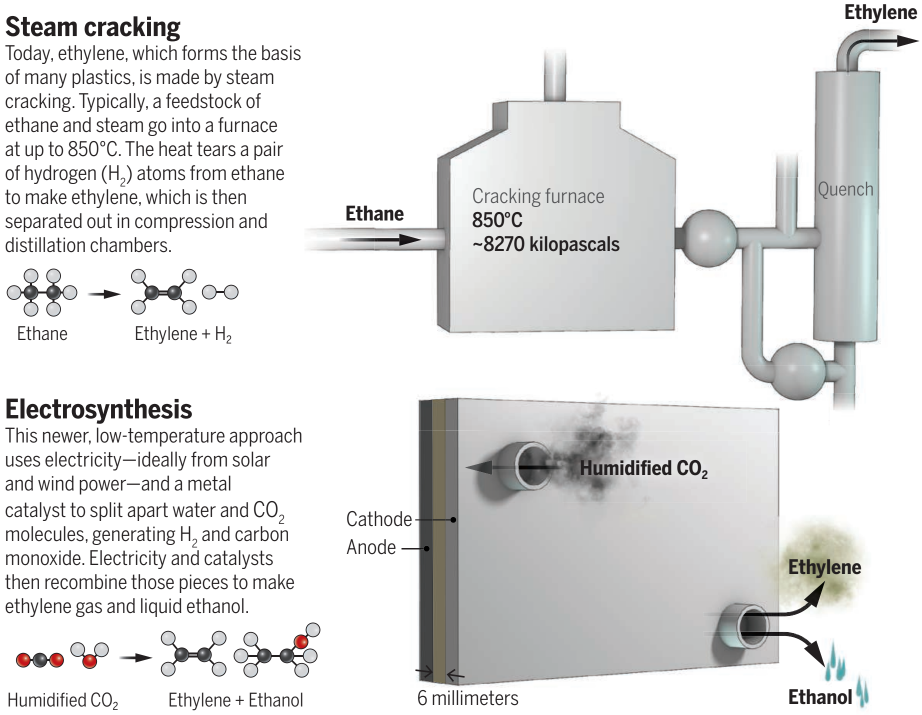
Changing the lifeblood of industrial chemistry from fossil fuels to renewable electricity "will not happen in 1 to 2 years," says Maximilian Fleischer, chief expert in energy technology at Siemens. Renewable energy is still too scarce and intermittent for now. However, he adds, "It's a general trend that is accepted by everybody" in the chemical industry.

A SHARP RISE in supplies of solar, wind, and other forms of renewable electricity lies behind the trend. In 2018, the world surpassed 1 terawatt (TW) of installed solar and wind capacity. The second TW is expected by mid-2023, at just half the cost of the first, and the pace is likely to accelerate. One recent analysis suggests lower prices for renewable generation could prompt the development of 30 to 70 TW of solar energy capacity alone by 2050, enough to cover a majority of global energy needs (*Science*, 31 May, p. 836). "In the near future there will be a bunch of renewable electrons around," says Edward Sargent, a chemist at the University of Toronto in Canada. "And a lot of them are going to be cheap." According to the National Renewable Energy Laboratory, the cost of utility-scale solar power should drop by 50% by 2050 and the cost of wind power by 30%.

That surge in renewables has already led to brief periods when electricity supplies exceed demand, such as midday in sunny Southern California. The result is dramatic price drops. At times, utilities even pay customers to take electricity so that excess supply doesn't melt transmission lines. "This gives us an opportunity to make something valuable with these electrons," Sargent says.

Better living through renewables

Industrial chemists make most molecules by breaking down and refining hydrocarbons in oil and natural gas into smaller compounds. Researchers now want to use renewable electricity to energize simple starting materials such as water and carbon dioxide (CO_2) and stitch the pieces together into the same compounds.



Steam cracking

Today, ethylene, which forms the basis of many plastics, is made by steam cracking. Typically, a feedstock of ethane and steam go into a furnace at up to 850°C. The heat tears a pair of hydrogen (H_2) atoms from ethane to make ethylene, which is then separated out in compression and distillation chambers.

Electrosynthesis

This newer, low-temperature approach uses electricity—ideally from solar and wind power—and a metal catalyst to split apart water and CO_2 molecules, generating H_2 and carbon monoxide. Electricity and catalysts then recombine those pieces to make ethylene gas and liquid ethanol.

One potential role for those electrons is to displace the fossil fuels that now provide the heat needed to drive industrial reactions. In the 24 May issue of *Science* (p. 756), Sebastian Wismann and Ib Chorkendorff of the Technical University of Denmark in Kongens Lyngby and colleagues reported redesigning a conventional fossil fuel–powered reactor that makes H_2 from methane and steam to run on electricity. In their new reactor, electricity flowing through an iron alloy tube encounters resistance, pushing temperatures as high as 800°C. The heat causes methane and steam flowing though the tube to react, stripping H_2 from methane more efficiently than traditional methods and potentially offering both cost savings and reduced climate impact.

But even if the heat comes from electricity, reactions such as those that generate fuel from methane still emit waste CO_2. Chemists want to go further, harnessing electrons not just as a source of heat, but as a direct input to the reactions. Industrial chemists already use electricity to smelt aluminum from bauxite ore and generate chlorine from salt—electron-adding reactions for which electrically driven chemistry is ideally suited. But as with H_2, most

CREDITS: (GRAPHIC) V. ALTOUNIAN/SCIENCE; (ILLUSTRATION, OPPOSITE PAGE) BENEDETTO CRISTOFANI/SALZMANART

commodity chemicals are made from fossil fuels, transformed with heat and pressure generated by more fossil fuels.

Giving up those fuels doesn't involve chemical magic. Key industrial chemicals such as carbon monoxide (CO) and ethylene can already be made by adding electrons to abundant starting materials such as CO_2 and water, if efficiency is no object. The trick is to do so economically.

That process requires a cheap source of renewable electricity. But according to an analysis in the 26 April issue of *Science* led by Sargent and Thomas Jaramillo, a chemical engineer at Stanford University in Palo Alto, California, that's not the only prerequisite. Sargent, Jaramillo, and colleagues compared the costs of making a variety of simple industrial compounds with fossil fuels or renewable electricity. They found that electrosynthesis would be competitive for producing chemical staples such as CO, H_2, ethanol, and ethylene if electricity cost 4 cents per kilowatt hour (kWh) or less—and if the conversion of electrical energy to energy stored in chemical bonds was at least 60% efficient.

If electricity's cost fell further, more compounds would be within reach. In a May 2018 analysis in *Joule*, Sargent and colleagues found that under stricter market assumptions, including an electricity price of 2 cents/kWh, synthesizing formic acid, ethylene glycol, and propanol would all be feasible. "This gives us a clear set of targets," says chemist Phil De Luna, a Sargent collaborator at National Research Council Canada in Toronto.

Sargent's papers are "right on the mark," says Harry Gray, a chemist at the California Institute of Technology (Caltech) in Pasadena, who has analyzed what's needed to displace fossil fuels with electrosynthesis. Of making commodities by electrosynthesis, he says, "I think we'll be there within 10 years."

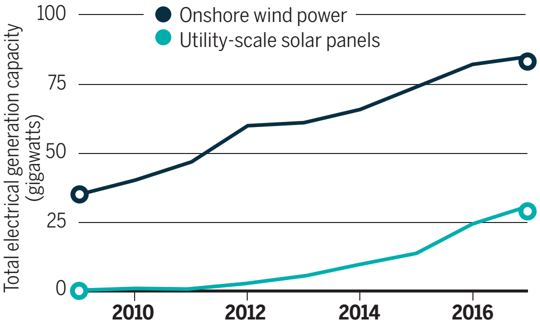
Kammen notes that several utility-scale solar and wind projects already meet one benchmark, delivering power at or below 4 cents/kWh, and the cost of renewables continues to decline (*Science*, 12 July, p. 108). But reaching 60% conversion efficiency of electrical to chemical energy is a bigger challenge, and that's where researchers are focusing their efforts.

The simplest processes, those that make H_2 and CO, are already reaching that second benchmark. According to Fleischer, commercial electrolyzers from Siemens and other companies already do better than 60% efficiency in splitting water to produce H_2. Siemens uses an established technology called proton-exchange membrane (PEM) electrolyzers, which apply a voltage between two electrodes, one on each side of a polymer membrane. The voltage splits water molecules at a catalyst-coated anode into O_2, hydrogen ions, and electrons. The membrane only allows hydrogen ions to pass to the other catalyst-coated electrode, the cathode, where they meet up with electrons to generate H_2 gas. The cost of the H_2 produced has fallen dramatically in recent years as the size of electrolyzers has increased to industrial scale. Still, Bill Tumas, an associate lab director at the National Renewable Energy Laboratory in Golden, Colorado, noted last month at a meeting of the American Chemical Society that the cost of the electrolyzers, as well as their component electrode materials and catalysts, needs to drop further to generate H_2 at a price competitive with massive thermal plants that break apart methane.

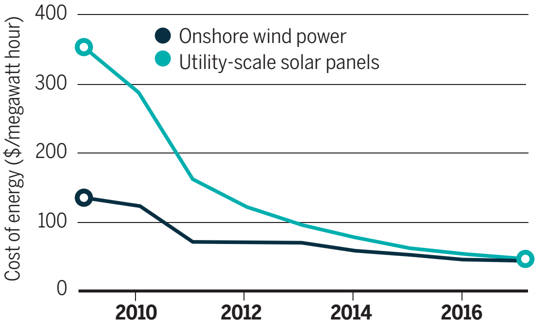
Rise and fall

As the deployment of utility-scale wind and solar power has increased over the past decade, the cost of electricity from those sources has plummeted. Both trends should continue in the coming decades, adding to the appeal of powering industrial chemistry with green electrons.

U.S. deployment of renewable energy



U.S. cost of renewable energy



CREDITS: (GRAPHIC) N. DESAI/SCIENCE; (DATA) ENERGY INNOVATION

Opus 12 and other companies also rely on PEM electrolyzers but add a supplementary catalyst to the cathode to split piped-in CO_2 into CO and O_2. The CO can be captured and sold for use in chemical manufacturing. Or it can be combined with hydrogen ions and electrons generated at the anode to construct a range of other building blocks for industrial chemistry, including gases such as ethylene—the raw material for certain plastics—and liquids such as ethanol and methanol. According to Etosha Cave, Opus 12's chief scientific officer, the company has already produced 16 commodity chemicals. And it is working to scale up its reactors over the next few years to process tons of CO_2 per day, most likely captured from flue gas from power plants and other industrial sources.

The growing supply of renewable energy has some chemists thinking about ways to generate carbon-neutral fuels (*Science*, 5 July, p. 18). Last month, in Dresden, Germany, a company called Sunfire completed a test run of a high-temperature electrolysis reactor, known as a solid-oxide fuel cell, that promises even higher efficiency than PEM electrolyzers. The reactor is at the heart of a four-stage test plant that generates fuel from water, CO_2, and electricity. The first stage of the boxcar-size plant separates CO_2 from air and then feeds the CO_2 to Sunfire's fuel cell. It works a bit differently from its PEM counterparts: It uses electricity to split both water and CO_2 at the cathode, generating a mix of CO, H_2, and negatively charged oxygen atoms, or oxide ions. Those ions travel through an oxygen-permeable solid membrane to the anode, where they give up electrons and combine to produce O_2. The mix of CO and H_2, known as synthesis gas, then moves to a third reactor, which assembles them into more complex hydrocarbons. At the fourth stage, those hydrocarbons are combined with more H_2 and refashioned into the mix of hydrocarbons in gasoline, diesel, and jet fuel. Because the plant works at high temperatures, the water- and CO_2-splitting reactions convert electrical energy to chemical bonds at nearly 80% efficiency, the company says.

Sunfire's test plant now makes about 10 liters of fuel per day. The company is already scaling up the technology and plans to open its first commercial plant, in Norway, next year. The setup will be part of a larger plant that will use 20 megawatts of hydropower to produce 8000 tons of transportation fuel per year, enough to supply 13,000 cars. Its method will avoid producing 28,600 tons of CO_2 annually from fossil fuels.

Another advance could also boost efficiency: using industrial waste as the source of electrons needed to split off CO from CO_2. Oxygen's formation at the anode, producing electrons, is normally so sluggish that 90%

of the overall process's electrical energy goes to this reaction. In the 22 April issue of *Nature Energy*, chemist Paul Kenis of the University of Illinois in Urbana and colleagues reported spiking the anode with glycerol—a clear, viscous liquid that's a byproduct of biodiesel production—which gives up its electrons more readily. By doing so, the technique could reduce the energy requirement for splitting CO_2 by 53%. And as a bonus, when glycerol loses electrons, it produces a combination of formic acid and lactic acid, two common industrial compounds used as preservatives and in cleaning products and cosmetics. "You take a waste and turn it into something of value," Kenis says.

ILLUSTRATION: BENDETTO CRISTOFANI/SALZMANART

THOUGH SIMPLE INDUSTRIAL chemicals may be poised for greening, directly synthesizing most complex hydrocarbons with electricity remains too inefficient and costly. Even making compounds with just two carbons, such as ethylene and ethanol, typically captures only about 35% of the input of electrical energy in the final compound. With three-carbon compounds and beyond, the efficiency can drop below 10%. The problems are twofold: First, every time new bonds are forged, some energy is lost. And generating more-complex hydrocarbons inevitably means making more side products. That outcome forces producers to separate their desired compound, at extra cost.

But innovations are starting to help there, too, including better catalysts. In the 21 August online issue of *Joule*, for example, Sargent and his colleagues report creating a device that uses a membrane coated with a copper catalyst to convert CO_2 and steam to a mix of two-carbon compounds, including ethylene and ethanol, with 80% efficiency. They achieved that efficiency by pressing one electrode directly onto the membrane, thereby eliminating a fluid-filled gap that was sapping energy and was causing the device to break down quickly.

One class of complex molecules that could prove easier to make with electricity is carbon nanotubes. Those long, hollow, strawlike molecules—prized for their strength and electronic capabilities—are commonly made through chemical vapor deposition: In a heated quartz tube, cobalt and iron catalysts strip away carbon atoms from pumped-in acetylene gas and add them to growing nanotubes that take seed on the metal particles. That process is energy intensive and expensive, typically costing about $100,000 to produce 1 ton of nanotubes. But in 2015 in *Nano Letters*, Stuart Licht, a chemist at George Washington University in Washington, D.C., and colleagues reported an electrolysis approach calculated to cost one-100th as much.

Licht's setup starts with molten lithium carbonate spiked with metal catalysts. An electric current strips carbon atoms from the lithium carbonate and adds heat that sustains the reaction. The catalysts pick up the carbons and insert them into growing nanotubes. Bubbling CO_2 into the mix then regenerates the lithium carbonate. The process is 97.5% efficient. Because it uses waste CO_2, Licht notes it is carbon negative: Making each ton of carbon nanotubes uses 4 tons of CO_2.

The nanotubes can then be mixed into cement to create a high-strength composite that sequesters the carbon, keeping it from oxidizing and returning to the atmosphere. The tubes can also be mixed with metals such as aluminum, titanium, and stainless steel to strengthen them. C2CNT, a company Licht formed to commercialize the technology, is one of 10 finalists for the Carbon XPrize, which will award $20 million for successful technologies for turning CO_2 into products.

HOW QUICKLY THE VAST chemical plants sprawling over the world's industrial zones will shift from fossil fuels to green power is a matter of debate. Nate Lewis, a chemical engineer at Caltech, says the transition will be slow. One major hurdle, he notes, is that renewables are intermittent, meaning chemical plants relying on them will be inefficient. Economists capture the idea with a measure called the capacity factor, a ratio of a plant's output over time compared with what's theoretically possible. Fossil fuel–powered chemical plants can run around the clock, although downtime for maintenance and for other issues typically reduces their capacity factor to about 60%. But the inputs to a plant powered by renewables themselves have low capacity factors: Wind and hydropower typically come in just under 50%, and solar drops to below 25% because of nighttime and cloudy days. "Your full capacity is only being used for a few hours a day," says Harry Atwater, a chemist at Caltech and head of the Joint Center for Artificial Photosynthesis, a solar fuel collaboration among Caltech, Lawrence Berkeley National Laboratory, and other institutions. The upshot, Lewis notes, is that any plant powered by renewables would take longer to make a profit, making investors reluctant to back such projects.

Plants driven by renewables could stay online longer if they drew on multiple power sources or had a steadier power supply thanks to batteries or another form of energy storage, Kammen notes. But those solutions can add cost, Lewis says. "We're still a long way away" from generating most commodity chemicals profitably from renewables. Producing enough renewable electricity to remake the chemical industry is also a challenge. In an analysis in the 4 June issue of the *Proceedings of the National Academy of Sciences*, for example, researchers concluded that running the global chemical industry on renewables would require more than 18 petawatt hours of electricity, or 18,000 terawatt hours, every year. That's 55% of the total global electricity production expected from all sources in 2030.

Perhaps the most likely outlook for industrial chemistry is a gradual greening. Until chemists can find catalysts able to make complex hydrocarbons with high efficiency, companies may use renewable electricity to produce simple molecules such as H_2 and CO and then fall back on fossil fuels to drive the reactions to stitch those together into more complex hydrocarbons.

But as chemists develop new reactors and find ever-more-charmed combinations of catalysts—and as renewable energy continues to surge—the plants that churn out chemical staples will inevitably become more like the green variety, fully sustained by sun, air, and water. ■

Science

Renewable bonds

Robert F. Service

Science **365** (6459), 1236-1239.
DOI: 10.1126/science.365.6459.1236

Science (print ISSN 0036-8075; online ISSN 1095-9203) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. The title *Science* is a registered trademark of AAAS.