GRASSOLINE at the Pump

Scientists are turning agricultural leftovers, wood and fast-growing grasses into a huge variety of biofuels—even jet fuel. But before these next-generation biofuels go mainstream, they have to compete with oil at $60 a barrel

By George W. Huber and Bruce E. Dale

KEY CONCEPTS

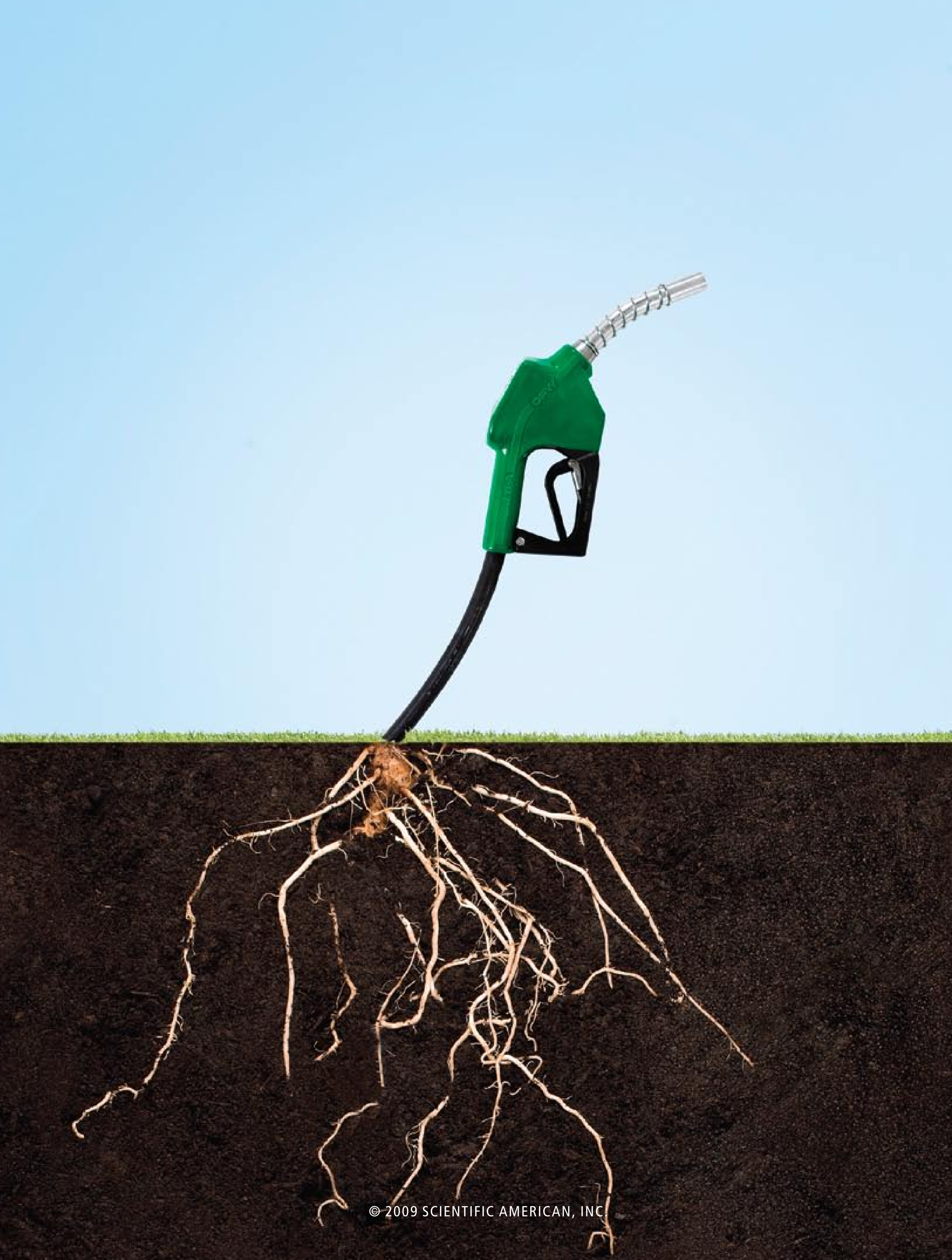
- Second-generation biofuels made from the inedible parts of plants are the most environmentally friendly and technologically promising near-term alternatives to oil.
- Most of this "grassoline" will come from agricultural residues such as cornstalks, weedlike energy crops and wood waste.
- The U.S. can grow enough of these feedstocks to replace about half the country's total consumption of oil without affecting food supplies. *—The Editors*

By now it ought to be clear that the U.S. must get off oil. We can no longer afford the dangers that our dependence on petroleum poses for our national security, our economic security or our environmental security. Yet civilization is not about to stop moving, and so we must invent a new way to power the world's transportation fleet. Cellulosic biofuels—liquid fuels made from inedible parts of plants—offer the most environmentally attractive and technologically feasible near-term alternative to oil.

Biofuels can be made from anything that is, or ever was, a plant. First-generation biofuels derive from edible biomass, primarily corn and soybeans (in the U.S.) and sugarcane (in Brazil). They are the low-hanging fruits in a forest of possible biofuels, given that the technology to convert these feedstocks into fuels already exists (180 refineries currently process corn into ethanol in the U.S.). Yet first-generation biofuels are not a long-term solution. There is simply not enough available farmland to provide more than about 10 percent of developed countries' liquid-fuel needs with first-generation biofuels. The additional crop demand raises the price of animal feed and thus makes some food items more expensive—though not nearly as much as the media hysteria last year would indicate. And once the total emissions of growing, harvesting and processing corn are factored into the ledger, it becomes clear that first-generation biofuels are not as environmentally friendly as we would like them to be.

Second-generation biofuels made from cellu-

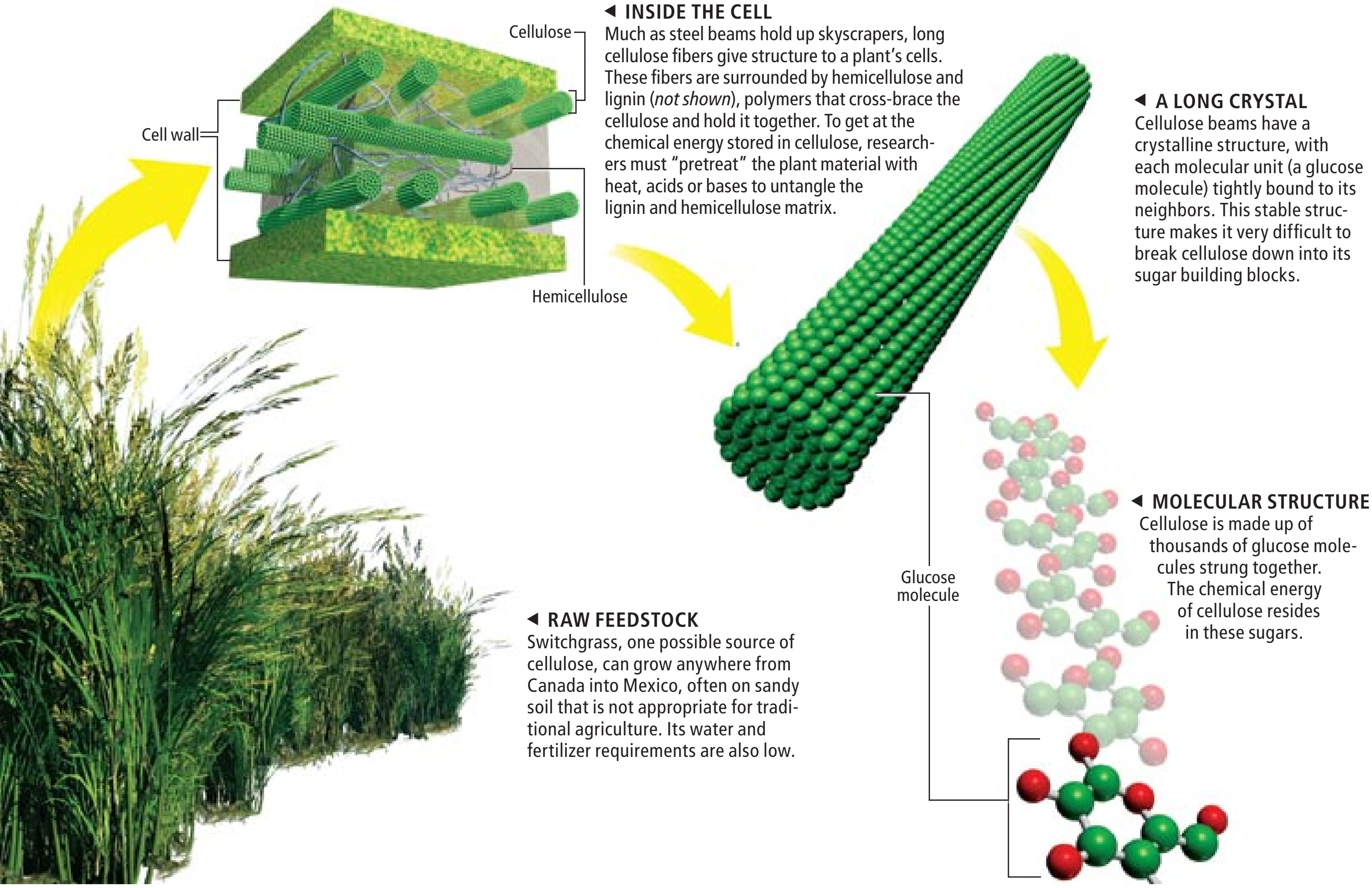
GETTY IMAGES



[BASICS]

Cellulose Scaffolding

In nature, cellulose supports a plant's vertical growth. It has a crystalline molecular structure that is both rigid and highly resistant to decomposition. Those features lend the plant stiffness but pose difficulties for those who would convert it into useful fuel.



losic material—colloquially, "grassoline"—can avoid these pitfalls. Grassoline can be made from dozens, if not hundreds, of sources: from wood residues such as sawdust and construction debris, to agricultural residues such as cornstalks and wheat straw, to "energy crops"—fast-growing grasses and woody materials that are grown expressly to serve as feedstocks for grassoline [*see box on page 57*]. The feedstocks are cheap (about $10 to $40 per barrel of oil energy equivalent), abundant and do not interfere with food production. Most energy crops can grow on marginal lands that would not otherwise be used as farmland. Some, such as the short-rotation willow coppice, will decontaminate soil that has been polluted with wastewater or heavy metals as it grows.

Huge amounts of cellulosic biomass can be sustainably harvested to produce fuel. According to a study by the U.S. Department of Agriculture and the Department of Energy, the U.S. can produce at least 1.3 billion dry tons of cellulosic biomass every year without decreasing the amount of biomass available for our food, animal feed or exports. This much biomass could produce more than 100 billion gallons of grassoline a year—about half the current annual consumption of gasoline and diesel in the U.S. [*see bottom left graph on page 57*]. Similar projections estimate that the global supply of cellulosic biomass has an energy content equivalent to between 34 billion to 160 billion barrels of oil a year, numbers that exceed the world's current annual consumption of 30 billion barrels of oil. Cellulosic biomass can also be converted to any type of fuel—ethanol, ordinary gasoline, diesel, even jet fuel.

Scientists are still much better at fermenting corn kernels than they are at breaking down

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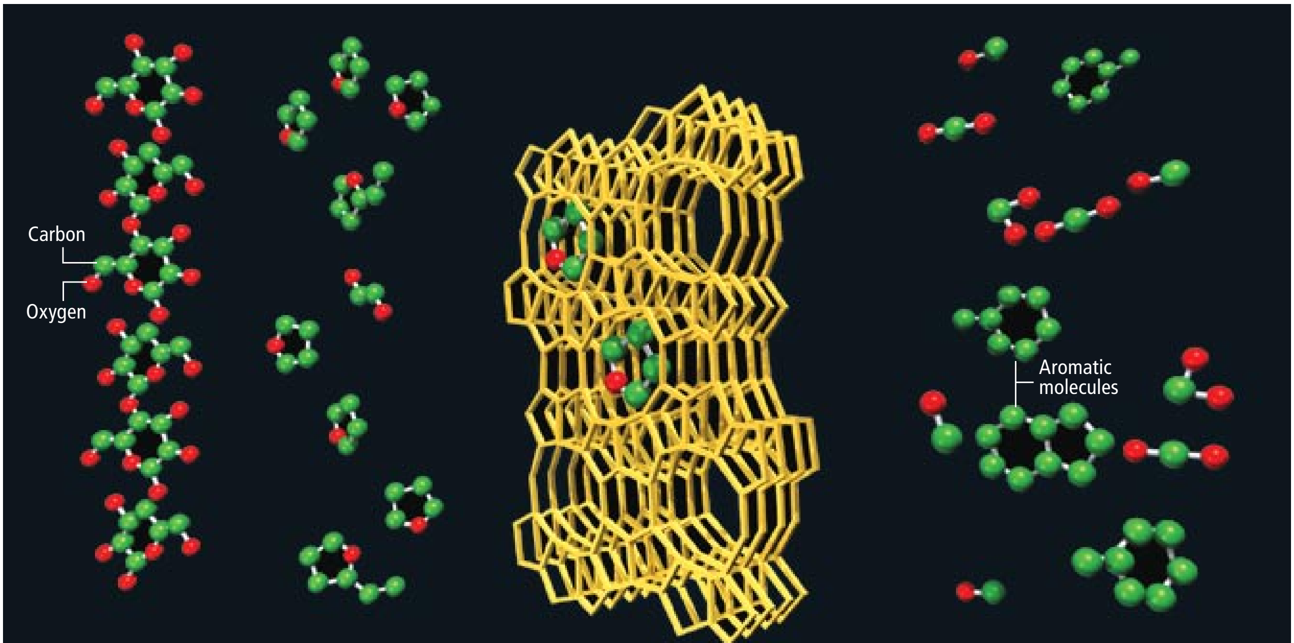
[HOW-TO #1]

TURNING CELLULOSE DIRECTLY INTO FUEL

Cellulose consists of carbon, oxygen and hydrogen atoms (*hydrogen not shown*). Gasoline is made of carbon and hydrogen. Thus, turning cellulose into grassoline is a matter of removing the oxygen from the cellulose to make high-energy-density molecules that contain only carbon and hydrogen. In the catalytic fast pyrolysis approach shown, the cellulose decomposes and is converted to gasoline in a single step.



FIRST BREAK
Cellulose entering the chamber is heated to 500 degrees Celsius in less than a second, breaking it apart into smaller, oxygen-rich molecules.

THE CATALYST
These broken fragments then fit into an intricate three-dimensional catalyst. This catalyst encourages chemical reactions that remove the oxygen from the cellulose fragments and create carbon rings. The detailed chemical process is not yet well understood.

FINAL PRODUCTS
After the reaction—which takes only a few seconds—the cellulose has been transformed into aromatic components of gasoline. By-products of the reaction include water (*not shown*), carbon dioxide and carbon monoxide.

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tough stalks of cellulose, but they have recently enjoyed an explosion of progress. Powerful tools such as quantum-chemical computational models allow chemical engineers to build structures that can control reactions at the atomic level. Research is done with an eye toward quickly scaling conversion technologies up to refinery scales. And although the field is still young, a number of demonstration plants are already online, and the first commercial refineries are scheduled for completion in 2011. The age of grassoline may soon be at hand.

The Energy Lock

Blame evolution. Nature designed cellulose to give structure to a plant. The material is made out of rigid scaffolds of interlocking molecules that provide support for vertical growth [*see box on opposite page*] and stubbornly resist biological breakdown. To release the energy inside it, scientists must first untangle the molecular knot that evolution has created.

In general, this process involves first deconstructing the solid biomass into smaller molecules, then refining these products into fuels. Engineers generally classify deconstruction methods by temperature. The low-temperature method (50 to 200 degrees Celsius) produces sugars that can be fermented into ethanol and other fuels in much the same way that corn or sugar crops are now processed. Deconstruction at higher temperatures (300 to 600 degrees C) produces a biocrude, or bio-oil, that can be refined into gasoline or diesel. Extremely high temperature deconstruction (above 700 degrees C) produces gas that can be converted into liquid fuel.

So far no one knows which approach will convert the maximum amount of the stored energy into liquid biofuels at the lowest costs. Perhaps different pathways will be needed for different cellulosic biomass materials. High-temperature processing might be best for wood, say, whereas low temperatures might work better for grasses.

INSECT POWER: **Termites are model biofuel factories. Microbes living inside the gut of a termite break cellulose down into sugars. Biological engineers are attempting to replicate this process on an industrial scale.**

Hot Fuel

The high-temperature syngas approach is the most technically developed way to generate biofuels. Syngas—a mixture of carbon monoxide and hydrogen—can be made from any carbon-containing material. It is typically transformed into diesel fuel, gasoline or ethanol through a process called Fischer-Tropsch synthesis (FTS), developed by German scientists in the 1920s. During World War II the Third Reich used FTS to create liquid fuel out of Germany's coal reserves. Most of the major oil companies still have a syngas conversion technology that they may introduce if gasoline becomes prohibitively expensive.

The first step in creating a syngas is called gasification. Biomass is fed into a reactor and heated to temperatures above 700 degrees C. It is then mixed with steam or oxygen to produce a gas containing carbon monoxide, hydrogen gas and tars. The tars must be cleaned out and the gas compressed to 20 to 70 atmospheres of pressure. The compressed syngas then flows over a specially designed catalyst—a solid material that holds the individual reactant molecules and preferentially encourages particular chemical reactions. Syngas conversion catalysts have been developed by the petroleum chemistry primarily for converting natural gas and coal-derived syngas into fuels, but they work just as well for biomass.

Although the technology is well understood, the reactors are expensive. An FTS plant built in Qatar in 2006 to convert natural gas into 34,000 barrels a day of liquid fuels cost $1.6 billion. If a biomass plant were to cost this much, it would have to consume around 5,000 tons of biomass a day, every day, for a period of 15 to 30 years to produce enough fuel to repay the investment. Because significant logistic and economic challenges exist with getting this amount of biomass to a single location, research in syngas technology focuses on ways to reduce the capital costs.

Bio-Oil

Eons of subterranean pressure and heat transformed Cambrian zooplankton and algae into present-day petroleum fields. A similar trick—on a much reduced timescale—could convert cellulosic biomass into a biocrude. In this scenario, a refinery heats up biomass to anywhere from 300 to 600 degrees C in an oxygen-free environment. The heat breaks the biomass down into a charcoal-like solid and the bio-oil, giving off some gas in the process. The bio-oil that is produced by this method is the cheapest liquid biofuel on the market today, perhaps $0.50 per gallon of gasoline energy equivalent (in addition to the cost of the raw biomass).

The process can also be carried out in relatively small factories that are close to where biomass is harvested, thus limiting the expense of biomass transport. Unfortunately, this crude is highly acidic, is insoluble with petroleum-based fuels and contains only half the energy content of gasoline. Although you can burn biocrude directly in a diesel engine, you should attempt it only if you no longer have a need for the engine.

Oil refineries could convert this biocrude into a usable fuel, however, and many companies are studying how they could adapt their existing hardware to the task. Some are already producing a different form of green diesel fuel, suggesting that refineries could handle cellulosic biocrude as well. At the moment, the facilities co-feed vegetable oils and animal fats with petroleum oil directly into their refinery. ConocoPhillips recently demonstrated this approach at a refinery in Borger, Tex., creating more than 12,000 gallons of biodiesel a day out of beef fat shipped from a nearby Tyson Foods slaughterhouse [*see box on page 59*].

Researchers are also figuring out ways to carry out the two-stage process using the chemical engineering equivalent of one-pot cooking—

[THE AUTHORS]


George W. Huber is a professor of chemical engineering at the University of Massachusetts Amherst. In 2003 *Scientific American* cited his work on hydrogen production from biomass feedstocks as one of the top 50 breakthroughs of the year. He is the founder of Anellotech, a biofuel startup, and serves as an occasional consultant for various oil and biofuel companies. Bruce E. Dale is a professor and former chair of the chemical engineering department at Michigan State University and one of the leaders of the Great Lakes Bioenergy Research Center (greatlakesbioenergy.org). He also occasionally serves as a biofuel industry consultant.

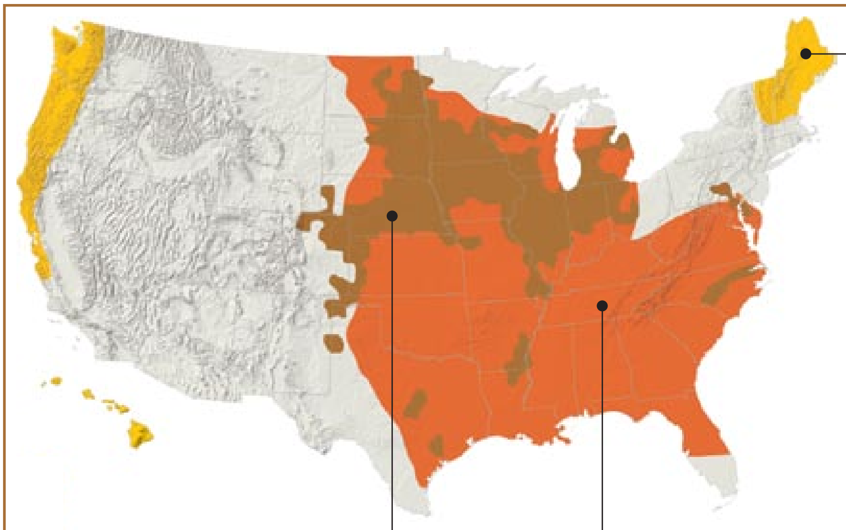
KURT STEPNITZ *Michigan State University (Dale)*; COURTESY OF GEORGE W. HUBER *(Huber)*; PHOTO RESEARCHERS, INC. *(termites)*

[PROSPECTS]

Cellulosic Feedstock Options across the U.S.

Once scientists are able to efficiently turn cellulosic material into fuel, they will find no shortage of available feedstocks to supply the necessary plant material. A study by the U.S. Department of Agriculture and the Department of Energy earlier this decade concluded that the U.S. could produce more than 1.3 billion tons of cellulosic feedstocks annually without affecting exports or the food supply (an updated version of the "Billion-Ton Vision" study will be released this fall). In addition to energy crops that could be grown over much of the U.S.—especially on land that is not fertile enough to support traditional food crops—the Northeast and Northwest could contribute waste material from logging, and leftover residues from the corn and soy harvest—including cornstalks and cobs—could power much of the Midwest.

FERTILE LAND FOR BIOFUELS

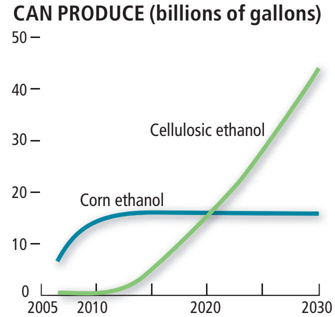


FOREST PRODUCTS
The wood supply would come from two main sources: residues that are currently left over from industries, such as logging and paper, and excess small-diameter trees that the U.S. Forest Service has identified as needing to be removed to improve forest health.

AGRICULTURAL RESIDUES
Leftover stalks, leaves and cobs from corn farming make up about half of the total crop yield. Some of these residues must be left on the field to replenish the soil, but most currently go to waste.

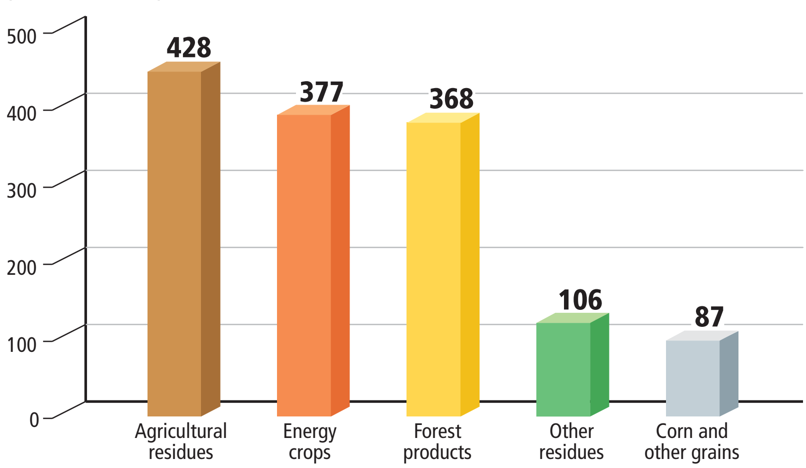
ENERGY CROPS
These plants can grow quickly with minimal fertilizer and water needs. Common examples include switchgrass, sorghum, miscanthus and energycane. Some, such as the short-rotation willow coppice, will not only grow on soil contaminated with wastewater or heavy metals, they will clean it up as they do so.

AMOUNT OF ETHANOL THE U.S. CAN PRODUCE (billions of gallons)

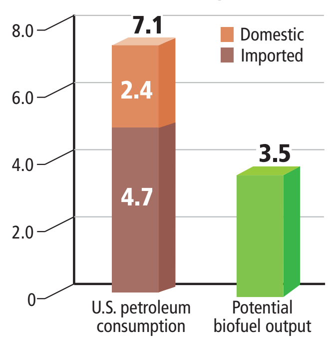


The U.S. has nearly capped its ability to produce ethanol from corn, according to a study published this year by Sandia National Laboratories. Yet the amount of ethanol the U.S. can derive from cellulose can increase for decades.

AMOUNT OF BIOFUEL FEEDSTOCK THE U.S. CAN SUSTAINABLY PRODUCE (millions of tons)



CURRENT OIL CONSUMPTION AND POTENTIAL BIOFUEL PRODUCTION (billion barrels of oil equivalent)



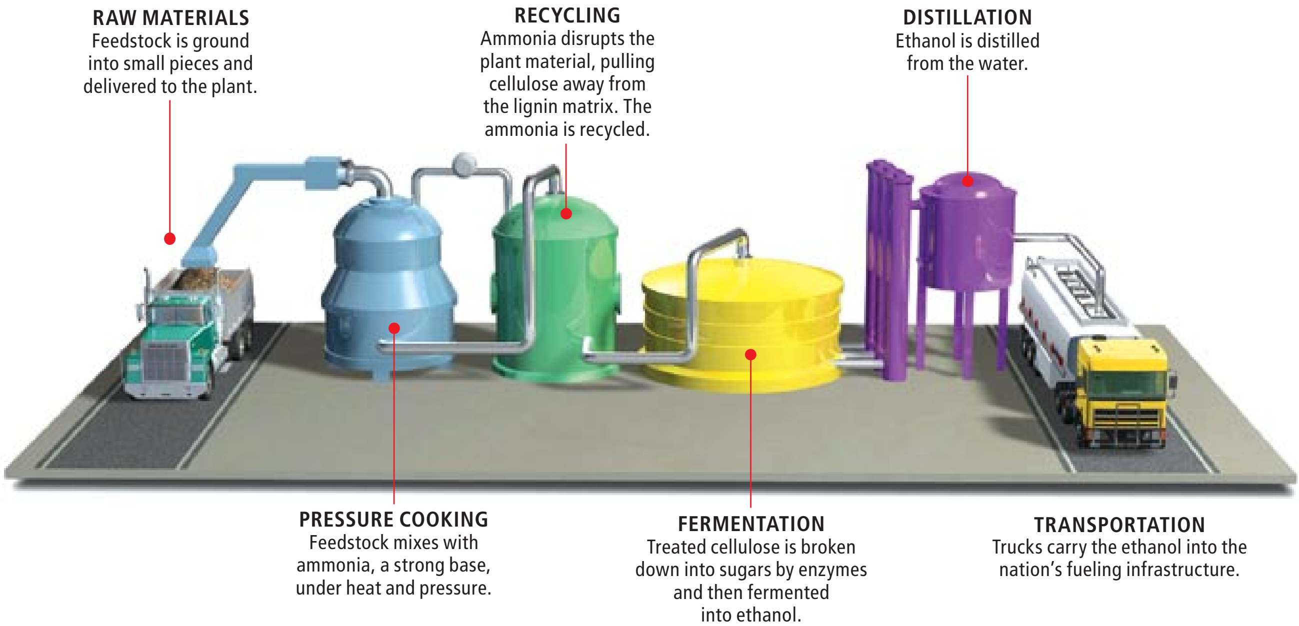
The potential biofuel output equals the peak U.S. oil production, which the country hit in 1970.

LAURIE GRACE; PETER ESSICK *Getty Images (forest)*; VAST PHOTOGRAPHY *Getty Images (cornstalks)*; WALLY EBERHART *Getty Images (switchgrass)*

[HOW-TO #2]

BREAKING DOWN CELLULOSE WITH AMMONIA

Although there are many possible ways to pretreat plant fibers to get at the cellulose—acids and heat are most commonly mentioned—the ammonia fiber expansion (AFEX) process offers a unique combination of low energy requirements, low costs and high efficiency.



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converting the solid biomass to oil and then the oil into fuel inside a single reactor. One of us (Huber) and his colleagues are developing an approach called catalytic fast pyrolysis. The "fast" in the name comes from the initial heating—once biomass enters the reactor, it is cooked to 500 degrees C in a second, which breaks down the large molecules into smaller ones. Like eggs in an egg carton, these small molecules are now the perfect size and shape to fit into the surface of a catalyst.

Once ensconced inside the catalyst's pores, the molecules go through a series of reactions that change them into gasoline—specifically, the high-value aromatic components of gasoline that increase the octane [*see box on page 55*]. (High-octane fuels allow engines to run at higher internal pressures, which increases efficiency.) The entire process takes just two to 10 seconds. Already the start-up company Anellotech is attempting to scale up this process from the laboratory to the commercial level. It expects to have a commercial facility in operation by 2014.

Sugar Solution

The route that has attracted most of the public and private investment thus far relies on a more traditional mechanism—unlock the sugars in plants, then ferment these sugars into ethanol or other biofuels. Scientists have studied literally dozens of possible ways to break down the digestion-resistant cellulose and hemicellulose—the fibers that bind cellulose together inside the cells [*see box on page 54*]—to their constituent sugars. You can heat the biomass, irradiate it with gamma rays, grind it into a fine slurry, or subject it to high-temperature steam. You can douse it with concentrated acids or bases or bathe it in solvents. You can even genetically engineer microbes that will eat and degrade the cellulose.

Unfortunately, many techniques that work in the lab have no chance of succeeding in commercial practice. To be commercially viable, the pretreatments must generate easily fermentable sugars at high yields and concentrations and be implemented with modest capital costs. They should not use toxic materials or require too much energy input to work. They must also be able to produce grassoline at a price that can compete with gasoline.

The most promising approaches involve subjecting the biomass to extremes of pH and temperature. We are developing a strategy that uses ammonia—a strong base—in one of our laboratories (Dale's). In this ammonia fiber expansion (AFEX) process, cellulosic biomass is cooked at

100 degrees C with concentrated ammonia under pressure. When the pressure is released, the ammonia evaporates and is recycled. Subsequently, enzymes convert 90 percent or more of the treated cellulose and hemicellulose to sugars. The yield is so high in part because the approach minimizes the sugar degradation that often occurs in acidic or high-temperature environments. The AFEX process is “dry to dry”: biomass starts as a mostly dry solid and is left dry after treatment, undiluted with water. It thus can provide large amounts of highly concentrated, high-proof ethanol.

AFEX also has the potential to be very inexpensive: a recent economic analysis showed that, assuming biomass can be delivered to the plant for around $50 a ton, AFEX pretreatment, combined with an advanced fermentation process called consolidated bioprocessing, can produce cellulosic ethanol for approximately $1 per gallon of equivalent gasoline energy content, probably selling for less than $2 at the pump.

The Cost of Change

Cost, of course, will be the primary determinant of how fast the use of grassoline will grow. Its main competitor is petroleum, and the petroleum industry has been reaping the technological benefits of dedicated research programs for more than a century. Moreover, most petroleum refineries now in use have already paid off their initial capital costs; grassoline refineries will require investments of hundreds of millions of dollars, a cost that will have to be integrated into the price of the fuel it produces through the years.

Grassoline, on the other hand, enjoys several major advantages over fuels from petroleum and other petroleum alternatives such as oil sands and liquefied coal. First, the raw feedstocks are far less expensive than raw crude, which should help keep costs down once the industry gets up and running. Grassoline will be domestically produced, with the national security benefits that confers. And it is far better for the environment than any fossil fuel–based alternative.

In addition, new analytical tools and computer-modeling techniques will let researchers build better, more efficient biorefinery operations at a rate that would have been unattainable to petroleum engineers just a decade ago. We are gaining a deeper understanding of the properties of our raw feedstocks and the processes we can use to convert them into fuel at an ever increasing pace. The U.S. government’s support for research into alternative forms of energy should help this process to accelerate even further. The stimulus bill signed into law by President Barack Obama earlier this year contained $800 million in funding for the Department of Energy’s Biomass Program, which will accelerate advanced biofuels research and development and provide funding for commercial-scale biorefinery projects. In addition, the bill contained $6 billion in loan guarantees for “leading edge biofuel projects” that will commence construction by October 2011.

Indeed, if the U.S. maintains its current commitment to biofuels, the logistical and conversion challenges the industry now faces should be readily overcome. Over the next five to 15 years, biomass conversion technologies will move from the laboratory to the market, and the number of vehicles powered by cellulosic biofuels will grow dramatically. This move toward grassoline can fundamentally change the world. It is a move that is now long overdue. ■

[ALTERNATIVE SOURCES]

The Fat of the Matter

There is a new drive to make fuel off the fat of the land. In April, High Plains Bioenergy opened a biorefinery next to a pork-processing plant in Guymon, Okla. The refinery takes pork fat—an abundant, low-value by-product of the industrial butchering process—and converts it, along with vegetable oil, into biodiesel. The plant is expected to turn 30 million pounds of lard into 30 million gallons of biodiesel a year. In 2010 the High Plains facility will be joined by a plant in Geismar, La., that will be run by Dynamic Fuels, a joint venture between Tyson Foods and energy company Syntroleum. That plant will use the fat from Tyson’s beef, chicken and pork operations to create 75 million gallons of biodiesel and jet fuel annually.

PETER CADE *Getty Images*

Yet the biodiesel industry has been battered recently, with many plants sitting idle for lack of demand. Low oil prices have made petroleum-based diesel fuel less expensive than biodiesel, which in the U.S. is typically made from soy and vegetable oils. A $1 per gallon federal tax credit for biodiesel has helped soften the blow, but that credit is set to expire at the end of the year. Some manufacturers worry that if the credit disappears, so will their business. Tyson had earlier partnered with ConocoPhillips to produce biodiesel at an existing ConocoPhillips refinery in Borger, Tex. But insecurity about the status of the tax break has put the project on hold. *—The Editors*

➥ MORE TO EXPLORE

Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels. A research road map from the Biomass to Biofuels Workshop: **www.ecs.umass.edu/biofuels**

Development of Cellulosic Biofuels. Video lecture given by Chris Somerville, director of the Energy Biosciences Institute at the University of California, Berkeley: **http://tinyurl.com/grassoline**

U.S. Department of Energy Biomass Program Web site: **http://eere.energy.gov/biomass**