

**A**mericans pump on average 18 million gallons of gasoline per hour into their cars, but less than half of it comes from oil produced in the United States. To make up for the difference, the United States imports oil from politically unstable regions in the Middle East, Africa, and South America. The United States could lessen its reliance on imports by drilling more oil, but that may only be a temporary solution because many scientists expect that the world's oil resources will eventually dry up.

Another solution is to use crops and plants to make gasoline. It might be hard to imagine, but chemists can convert corn stalks, sawdust, and grasses into gasoline. They do it by breaking down the plant molecules and reshuffling their parts into the same molecules found in gasoline.

This new type of gasoline, called green gasoline, would have many advantages. In addition to reducing U.S. dependence on foreign countries, it would also produce less pollution than oil-derived fuels, because the plants used to produce green gasoline would absorb some of the pollutants. Also, we would not have to worry about running out of fuel because green gasoline is renewable: The plants used to make it can be grown over and over again.

There are other plant-derived fuels, or bio-fuels, such as ethanol, which is produced by the fermentation of plant sugars by yeast, and biodiesel, which is made from vegetable oil or animal fats. But the advantage of green gasoline is that it can directly replace oil-derived gasoline.

"We wouldn't have to buy new cars or build new refineries and pipelines just to use green gasoline," says chemical engineer Jennifer Holmgren of UOP, a company in Des Plaines, Ill., that develops oil-refining technologies.

In as little as 5 years, you might drive up to a filling station and, without even realizing

# Green Gasoline Fuel from Plants

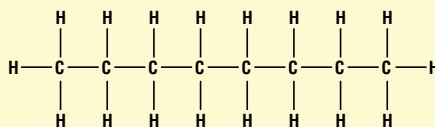
By Michael Schirber



it, fill up your car with gasoline that came directly from plants. At least that is what some researchers foresee. The challenge will be to figure out how to make large quantities of green gasoline because, up until now, only small quantities have been made in the laboratory.

## Non-green gasoline

Gasoline derived from oil has been the main choice for transportation fuel during the past century. It is stable, noncorrosive, and packs a high-energy punch. The energy in gasoline is stored in molecules called hydrocarbons, which are long chains or rings made of carbon and hydrogen atoms. When given a spark, the



Octane

carbon and hydrogen atoms combine with oxygen in the air, resulting in carbon dioxide, water, and a lot of energy.

An example of this is the burning of octane (C<sub>8</sub>H<sub>18</sub>), one of the hydrocarbons found in gasoline:



This reaction is actually an explosion: The amount of energy in a pound of gasoline is more than 10 times that found in a pound of trinitrotoluene, a common explosive. In a car, this energy heats the carbon dioxide, water vapor, and other gases present in the engine, which causes them to expand and to push on the engine's pistons.

Most of the time, gasoline inside a car's engine is not totally broken down to carbon dioxide and water. Some hydrocarbons

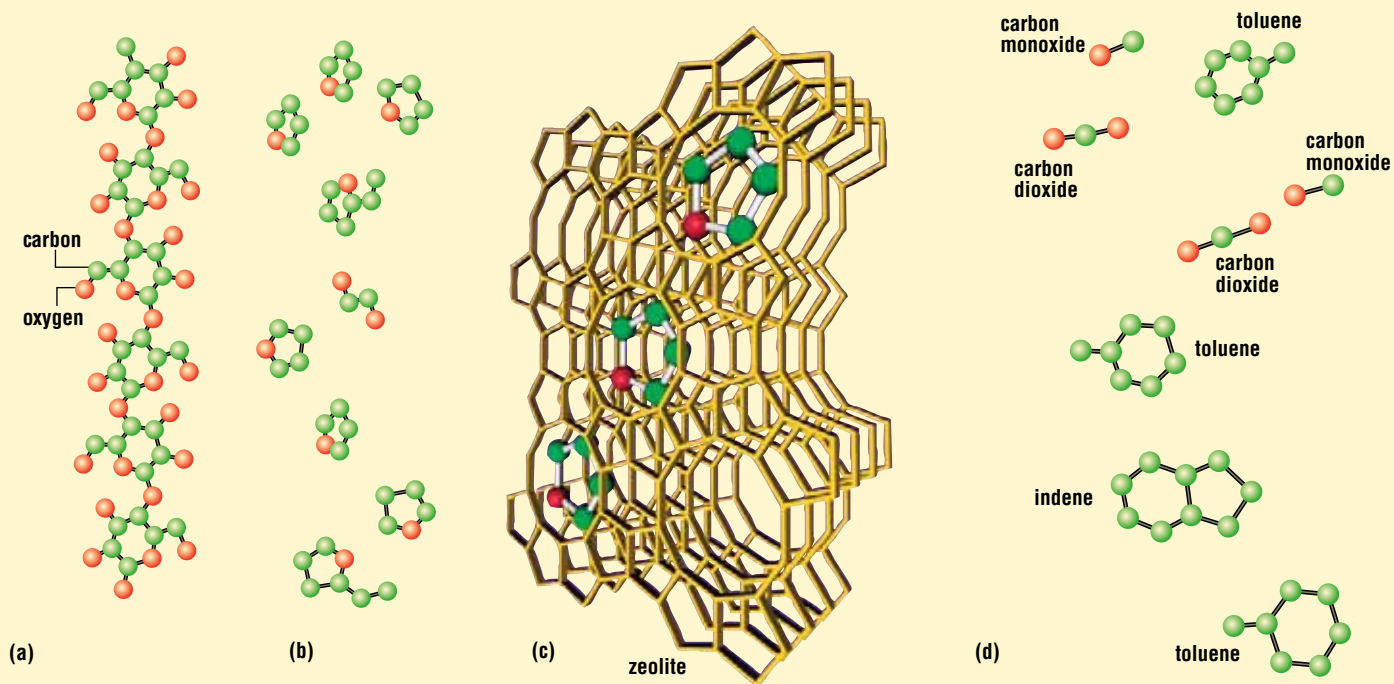
remain, and fragments end up as carbon monoxide (CO), a very toxic gas. The combustion process also can create other pollutants, such as nitrogen oxides (NO and NO<sub>2</sub>), that lead to smog and acid rain.

A good deal of this pollution has been reduced in modern cars. Most of them contain a device called a catalytic converter that filters the pollutants before they are released in a car's exhaust pipe. But this device cannot prevent the emission of carbon dioxide, a gas that mixes in with the atmosphere, traps heat from the sun, and contributes to global climate change.



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ANTHONY FERNANDEZ; ADAPTED FROM "GASOLINE AT THE PUMP," BY GEORGE W. HUBER AND BRUCE E. DALE, SCIENTIFIC AMERICAN, JULY 2009.

Turning cellulose into gasoline: Cellulose (a, hydrogen atoms omitted for clarity) is heated to 500 °C, breaking it apart into smaller molecules (b). These molecules bind to a porous substance called zeolite (c). As they bind to the zeolite, these molecules undergo chemical reactions that remove oxygen atoms from them. These reactions result in aromatic molecules (such as toluene and indene), which are components of gasoline, along with other final products, such as carbon dioxide and water (d).

Green gasoline can help lessen the problem, because plants absorb carbon dioxide and convert it into organic compounds by using energy from sunlight. The carbon dioxide is therefore recycled, going from the air to the plants to green gasoline, and then back to the air, when green gasoline is burned.

Green gasoline is not the only biofuel that recycles carbon dioxide this way, but it has the advantage that it carries the same energy punch as gasoline.

## Packing energy in green gasoline

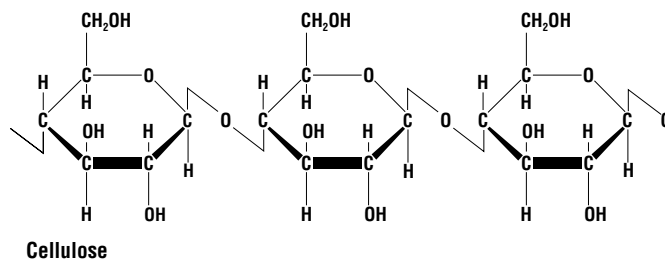
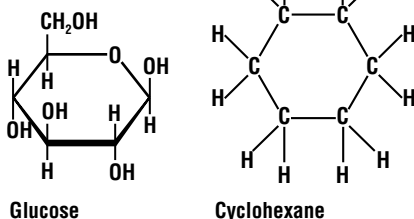
Plants store the energy of the sun in organic molecules called carbohydrates, which include sugars and cellulose—the main constituent of a plant cell wall. This energy can be extracted directly by burning the plants. For example, in the 19th century, some steamships were powered by burning wood. But burning wood or other plant materials to run your car is not practical. They do not flow into the engine like liquid fuels do, and you would need to carry three times as much weight in wood to go the same distance as with gasoline.

"We use gasoline because it packs a lot of energy," says John Regalbuto, director of the

Catalysis and Biocatalysis Program at the National Science Foundation, Arlington, Va. "Gasoline takes less space and is more efficient."

The amount of energy per pound contained in plants can be increased by removing oxygen from the carbohydrate molecules. Octane and other hydrocarbons, as mentioned above, burn by breaking bonds between carbon and hydrogen atoms, which then grab onto oxygen atoms. Carbohydrates burn in the same way, but they already contain some oxygen. In short, if you remove as many oxygen atoms as you can from a molecule, it will pack more energy.

As an example, the sugar glucose ( $C_6H_{12}O_6$ ) is similar in shape to cyclohexane ( $C_6H_{12}$ ), a



hydrocarbon found in gasoline. But glucose contains six additional oxygen atoms, which reduces its energy content. You would need roughly three pounds of glucose to get the same amount of energy as one pound of cyclohexane.



UOP, LLC

Scientists at the University of Wisconsin, Madison, have successfully stripped oxygen atoms from glucose and other sugars to create hydrocarbons similar to cyclohexane. The resulting liquid is essentially gasoline, but it is “green” because it is extracted from plants, not oil.

Virent Energy Systems, a renewable energy company based in Madison, is working on this sugar-to-hydrocarbon process and is planning to produce 100 million barrels of green gasoline in 5–7 years.

## Energy from plant leftovers

Carbohydrates, such as glucose, are typically derived from sugarcane or corn. But using these food crops for the production of green gasoline runs the risk of driving up food



Virent's Liquid Fuel Laboratories

prices. It would be better to make green gasoline with plant materials that are not used. Current research is looking at agricultural and forestry “leftovers,” such as cornstalks and sawdust, and nonfood crops, such as switchgrass and other prairie grasses that can

be grown without much irrigation or fertilizer.

More than 1 billion tons of plant leftovers are available each year in the United States, according to a study by the U.S. Department of Agriculture and the U.S. Department of Energy. This could produce 100 billion gallons

per year of green gasoline—about half the current U.S. annual consumption of gasoline and diesel.

One of the scientists working on the conversion of plant leftovers into gasoline is George Huber, a professor of chemical engineering

at the University of Massachusetts, Amherst. He and his colleagues have developed a technique that can turn almost any plant substance into gasoline.

The plant materials are first placed in a reactor at 500 °C. This breaks down the cellulose and other tough plant parts into smaller molecules, called anhydro sugars. These molecules then go through a porous structure called a zeolite, which is made of aluminum and silica. The pores are designed to be just big enough for the anhydro sugar molecules to enter.

“If the size of the pores is too small, the molecules can’t get in,” Huber says. “If they are too big, too many molecules crowd in, and unwanted reactions occur.” This can result in a carbon-rich material that clogs up the zeolite.

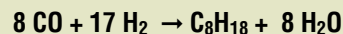
The pores in Huber’s zeolites are about six atoms wide, which is room enough for an anhydro sugar molecule to enter and attach to the surface, where it loses its oxygen and re-forms into a ring-shaped hydrocarbon similar to cyclohexane but with less hydrogen atoms. The full process—from breakdown in the reactor to hydrocarbon formation—takes just a few seconds.

Holmgren and her UOP colleagues are working on a similar project. They start by placing plant materials into a vessel that whips up a tornado of hot sand. This swirling sandstorm rapidly heats the plant matter to 500 °C, thereby cooking it into an oily liquid. This liquid is then processed into gasoline and other fuels.



George Huber poses with a vial of green gasoline compounds.

Other researchers, such as Lanny Schmidt, professor of chemical engineering and materials science, and colleagues at the University of Minnesota, Twin Cities, are heating plant ingredients to higher temperatures (700 °C–1,000 °C) to produce a gas mixture of carbon monoxide (CO) and hydrogen (H<sub>2</sub>). These molecules of gas are then reassembled into hydrocarbons, such as octane, with water as a byproduct:



## The future

All of these processes remain under development. “We are still in the early days of green gasoline,” says Robert Anex, associate professor of agricultural and biosystems engineering at Iowa State University in Ames.

So far, there are logistics problems, such as how to collect cornstalks from widely separated farms and bring them to one central facility. And although the chemistry works well in a laboratory, it is not yet clear whether the same processes will work on a large scale.

But green gasoline holds a lot of promise, and scientists, engineers, and policymakers are now starting to realize it. Says Holmgren, “Energy is the most important challenge facing us today, and chemistry will play a key role in making sure we have an alternative source of energy into the next 100 years.” ▲

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