ENGINEERING

Cellulosic Biofuels—Got Gasoline?

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Several routes are being developed to convert biomass into hydrocarbon fuels instead of ethanol.

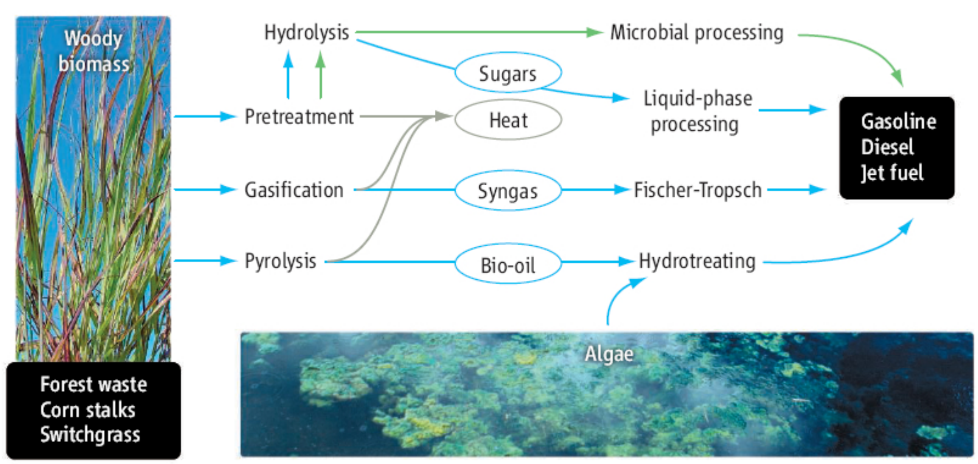
Most people think of ethanol as the only liquid biofuel, and that the major advances in biofuels will revolve around enzymatic conversion of cellulosic or woody biomass (including nonfood stems and stalks of corn stover or switchgrass and wood chips) into simple fermentable sugars (*1*). However, in just a few years the commercial scale production of liquid hydrocarbons from biomass will be possible. Hydrocarbons can be made (see the figure) from the sugars of woody biomass through microbial fermentation or liquid-phase catalysis, or directly from woody biomass through pyrolysis or gasification (*2*). Finally, lipids from nonfood crops as well as algae (*3*) can be converted to hydrocarbons. The resulting hydrocarbon biofuels will be drop-in replacements for gasoline, diesel, and jet fuel; will give much higher gas mileage than ethanol; and will work in existing engines and distribution networks.

Ethanol produced from biomass is already used in automotive fuels in the United States as a high-octane, oxygenated additive to improve combustion, which allows clean air standards to be met. The drawback to using ethanol as a complete replacement for gasoline, however, is not only the high cost of its production from cellulose but also its lower energy density. Ethanol has only two-thirds the energy density of gasoline, and cars running on E85 (85% ethanol and 15% gasoline) get about 30% lower gas mileage (*4*). In the United States, the Energy Independence and Security Act (EISA) of 2007 mandates the production of 16 billion gallons per year of cellulosic (plant-derived) biofuels by 2022. Along with 15 billion gallons/year of corn ethanol and 5 billion gallons / year of other renewable biofuels such as biodiesel, the goal is to replace 20% of current crude oil use in the United States in 15 years. EISA 2007 is not a mandate for cellulosic ethanol but can be met with green gasoline, diesel, and jet fuel as well.

Converting woody biomass to ethanol requires breaking down plant tissues into cellulose, hemicellulose, and lignin. The cellulose and hemicellulose break down further into fermentable sugars. Lignin, which is not readily converted to sugars, constitutes up to 40% of its stored energy, although some of this energy can be recovered to heat the biomass-to-alcohol conversion process. Despite recent developments—including more effi - cient enzymes, more readily deconstructed plants, and consolidation of processing steps (*1*), production costs remain twice that of fermenting corn starch (*5*).

An alternative is provided by processing sugars with genetically altered microorganisms instead of yeast. Some of these microorganisms can ferment sugars into hydrocarbons instead of alcohols (*6*). The altered microbes produce hydrocarbon products at about the same rate as they would produce ethanol, and because the hydrocarbons spontaneously form a separate organic phase, the microbes are not poisoned by the accumulating fermentation product as occurs with alcohol. Companies such as Amyris and LS9 are near the point of commercializing such routes. Amyris plans to produce a drop-in replacement diesel fuel and specialty chemicals from sugar cane. It is currently scaling up the process to large production volumes in the United States and Brazil and expects to commercialize its first product in 2011 (*7*).

Dissolved sugars can also be converted into hydrocarbons through routes that resemble petroleum processing more than fermentation. Dumesic and co-workers have developed several routes in which dissolved sugars react in the presence of solid-phase catalysts under carefully controlled conditions that avoid unwanted by products. They



can convert carbohydrates into targeted ranges of hydrocarbons (*8*, *9*) for use as fuels or chemical feedstocks. Virent Energy Systems has developed a process known as Bioforming that converts water-soluble sugars into green gasoline, diesel, and jet fuel (*10*). In partnership with Royal Dutch Shell, Virent claims to be 5 to 7 years away from commercial production of hydrocarbon fuels at a capacity of 100 million gallons/year, at a price competitive with petroleum at $60/barrel (*11*).

The routes outlined so far process sugars from biomass. In contrast, pyrolytic methods convert woody biomass, including the lignin fraction, in a spontaneous high-temperature reaction into an intermediate called biooil. Traditional versions of pyrolysis simply heated the biomass in the absence of air; the immediate product is very acidic, unstable, and too low in energy content to be a viable fuel. The bio-oil therefore has to be stabilized and upgraded in a subsequent catalytic step. An updated pyrolysis approach developed by Huber and co-workers uses catalysts to convert biomass into high-octane gasoline range aromatics in a single, simple, inexpensive step (*12*, *13*). These chemical methods produce heat and water, which preserves resources and helps lower cost.

One pyrolysis effort is being spearheaded by two companies: UOP, which has a long history in petroleum refining, and Ensyn, which has expertise in producing bio-oil for use as heating oil. The joint venture, Envergent, has stated its intention to "commercialize viable solutions for converting biomass to drop-in transportation fuels" by 2011 (*14*), also at a capacity of about 100 million gallons/ year (*15*).

Another company, KiOR (*16*), is currently developing the "biomass catalytic cracking" process (BCC), which is analogous to fluidized catalytic cracking used in petroleum refineries to convert large hydrocarbons into smaller ones. KiOR intends to commercialize BCC for the production of diesel and gasoline components from forestry or agricultural waste by 2011. The scale of operation is roughly the same as that of the UOP and Virent processes (*17*). Like pyrolysis, gasification also uses whole biomass but converts it spontaneously at very high temperatures into a mixture of carbon monoxide and hydrogen, or syngas, so named as it is a starting material for processes such as Fischer-Tropsch synthesis (FTS). Schmidt and co-workers (*18*) combined the three reactions of older thermal gasification processes into a single, small reactor in which gasification takes place over a catalyst.

The high transportation costs of biomass feedstocks demands economical operation in smaller-scale processing units. Choren Industries in Germany is in the process of commercializing a biomass-to-liquids operation (*19*) based on gasification and FTS. Diesel will be produced from multiple lignocellulosic feedstocks gathered locally (from a distance of about 50 km).

Cellulosic feedstocks could replace about 30% of petroleum used in the United States (*20*). The need to develop other biomass feedstocks has helped rekindle interest in algae after a decade of dormancy (*3*). Algae can be grown with relatively little land and in brackish water. Algae, as well as unsaturated plant oils, can be converted into fuels by hydrotreating; the main issue is the economical production of the algae feedstock. One company, Sapphire Energy, has developed advanced algae farming technology operating on nonarable land with nonpotable water and plan a production capacity of 100 million gallons of gasoline/year by 2016 (*21*). ExxonMobil has announced a partnership with Synthetic Genomics, Inc., with the goal of producing hydrocarbon biofuels from algae in 5 to 10 years (*22*).

Hydrocarbons derived from biomass are attractive because of their high energy density and compatibility with existing energy infrastructure. If recent technological innovations result in competitive production costs, hydrocarbons rather than ethanol will likely be the dominant biofuel.

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