SBE SUPPLEMENT: LIGNOCELLULOSIC BIOFUELS



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SBE Update Biofuels

onsidering that the price of oil has plummeted to less than half of what it was a year ago, this SBE supplement on biofuels is quite well-timed. What role can and will biofuels play, both today and in the future?

It is no secret to those of us in the petrochemical industry that oil prices are volatile. Historically, they have risen as demand surged or production declined, and fallen in the reverse situations. During the recession of 2008, the price of oil dropped from \$130/bbl to \$40/bbl in five months. We are in a similar position today: Since June 2014, the price of oil has dropped by more than 50%.

On the supply side, key members of the Organization of the Petroleum Exporting Countries (OPEC) indicate they will not reduce production to maintain higher prices. OPEC controls about 40% of the world market, and Saudi Arabia is OPEC's largest oil producer. The Saudis appear to stand resolute in maintaining current production levels based on their experience in 2008, when their production cuts caused them to lose market share to their OPEC partners as well as competitors such as Russia, Brazil and the U.S. Currently, it is not clear whether any producer (OPEC or non-OPEC) will reduce its oil production and trigger the price of oil to rise.

Also, the emergence of the U.S. as a global energy leader reduces the influences of world energy markets and the impact of OPEC and Russia. Many suggest the U.S. is already the number one producer of energy; the American Petroleum Institute (API) projects that the U.S. will hold that position by the end of this year.

Demand also affects petroleum prices and one of the largest drivers of demand is gross domestic product (GDP). Currently, GDP is strong in the U.S. but weak in Europe and China. If economic stimulation in those regions is successful, then energy consumption will likely grow, causing the demand for oil to expand. The U.S. Energy Information Agency (EIA) predicts that, over the long term, countries outside of the Organization for Economic Cooperation and Development (OECD), such as China, India, and Brazil, will drive the consumption of energy. The EIA's forecast indicates that consumption could increase from 50 MMBtu/yr to 73 MMBtu/yr per capita in non-OECD countries, where population growth is expanding at the highest rates. In the long term, increased demand, coupled with a downturn in production, could create a higher-price environment that would make biofuels attractive.

Biofuels are already attractive in some locations, even at low oil prices. Brazil's sugarcane-based ethanol production is an excellent example of the high energy-to-yield ratio needed for commercial production. Bio-based butanol is another example of a technology that can meet the needs for cleanerburning, octane-boosting fuel that is cost-competitive in certain markets where C4s from petroleum are not readily available. Additionally, biofuels may be especially well-suited for mobile uses where other options would be less viable. Renewables are in the mix for America's energy future. The EIA reports that in 20 years, renewables will grow to 12% of our energy mix, with biofuels accounting for over half.

Of course, there are other issues that could call biofuels into question, and they, too, have received media attention over the past few years. Chemical engineers continue to work alongside other scientists and engineers to balance these critical issues, which include the sustainability of various fuel sources, water use, land use, process efficiencies, carbon management, and the limited nature of oil. For example, researchers are currently focusing on lignocellulosic biomass feedstocks, such as agricultural residues (*e.g.*, sawdust, tree trimmings, cornstalks), as well as municipal wastes.

The articles in this supplement take an in-depth look at lignocellulosics. In the first article, Bruce Dale and Mark Holtzapple discuss the importance of biofuels and the role they will play. Three articles cover the technology platforms — thermochemical, sugar, and carboxylate — for converting cellulosic feedstocks to biofuels. David Edwards then explains how scaling up bioenergy technologies differs from conventional process scale-up and offers suggestions to minimize risk and maximize success. The final article provides a glimpse into this developing industry with a summary of current and planned biofuels production facilities throughout the world.

SBE serves its members through (among other things) events that enable its members to connect. The society is organizing a two-day workshop in September on technology challenges and opportunities in commercializing industrial biotechnology. Chaired by Jeff Lievense of Genomatica and Brian Davison of Oak Ridge National Laboratory, the workshop will cover strain and process development, scale-up and scale-down, and commercialization. Synthetic Biology: Engineering, Evolution and Design (SEED) 2015 will take place June 10–13, 2015, at the Boston Park Plaza. The conference, chaired by Pam Silver of Harvard Univ. and Dan Gibson of Synthetic Genomics and the J. Craig Venter Institute, will highlight the development of new tools and the application of these tools to diverse problems in biotechnology.

If you have an idea as to what SBE should be doing, please contact us and get involved (bio@aiche.org). Once again, on behalf of SBE's Managing and Advisory Boards, I thank you for your support, feedback, and involvement in making SBE a vibrant community.

Darlene Schuster, Executive Director, SBE



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MEET THE AUTHORS

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The Need for Biofuels

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Mark Holtzapple Texas A&M Univ. As fossil energy resources decline, we must develop and deploy renewable energy systems. An attractive alternative is to convert lignocellulosic biomass into transportation fuels.

e take the modern, developed world for granted. This is a mistake. The amenities (*e.g.*, wealth, education, health care, mobility, etc.) enjoyed by developed nations depend on abundant energy, about 85% of which is derived from fossil resources (*i.e.*, oil, coal, and natural gas). Remove abundant energy and the modern world disappears.

Figure 1 shows the strong correlation between wealth production and energy consumption. This relationship is not surprising — the faster we consume energy, the more wealth we produce. Since the Industrial Revolution, the growth of global wealth has depended on using fossil fuels to power machines. In the last few centuries, developed nations have become rich largely by consuming fossil energy.

Do our lives continue to get better as we consume more energy? Beyond a certain point, the answer to this question seems to be no. Figure 2 highlights the link between energy consumption and prosperity — general human well-being that can be estimated by the human development index (HDI), a composite metric of health, education, and living standards. At low rates of energy consumption, HDI rises very rapidly, and then levels off above about 4 kW per capita. Our lives do not continue to improve significantly as we consume more energy beyond approximately 4 kW/person.

These are sobering numbers. By approximately 2025, global population will be about 8 billion. If everyone were to consume primary energy at a rate of 4 kW/person (*e.g.*, the energy consumption rate of Portugal), the global energy consumption rate would be 32 terawatt (TW). Currently, we consume about 16 TW, so if we were to raise the average global living standard to the equivalent of Portugal, we

would need to double primary energy production by 2025. How might that be possible? How will we supply enough energy to maintain current consumption, let alone double it?

Fossil fuels are unsustainable

The vast majority of energy used by human beings comes from fossil fuels — nonrenewable resources that are mined or extracted from the earth. When fossil fuel stores are exhausted, the wealth they produce disappears. In actuality, we will never fully exhaust a given fossil energy resource because the cost of extraction will increase until other energy sources become more economical, assuming that such alternatives exist.



▲ Figure 1. The annual per capita gross domestic product (GDP) increases with per capita primary power consumption. Primary power refers to the rate at which primary energy sources (coal, oil, natural gas, biomass, nuclear, hydro, geothermal, solar, and wind) are consumed; it does not include electricity, which is derived from primary power. Source: (1).



When fossil fuels are extracted and burned, carbon that was previously underground is released as carbon dioxide and accumulates in the atmosphere. Carbon dioxide is a greenhouse gas that absorbs infrared radiation and hence contributes to global warming. The allowable limits for carbon dioxide concentration are the subject of debate; however, a widely accepted limit is 450 ppm (2). At current accumulation rates, we will reach that limit in about 2040.

To address our energy needs, one strategy is to increase energy efficiency, which is critically important. Increased energy efficiency will buy us more time to transition to renewable energy sources, and it will also help us better utilize limited renewable energy resources. However, as a sole strategy, increasing energy efficiency is not sufficient. It simply means that we will reach the bottom of the resource barrel more slowly, or we will more gradually reach the limits of atmospheric accumulation of carbon dioxide.

Thus, large-scale renewable energy systems are not just a good idea — they are essential. Fossil energy resources decline; therefore, fossil energy cannot provide the energy required to enable and underpin long-term prosperity. To ensure sustainable prosperity, we must develop and deploy renewable energy systems at the multi-terawatt scale.

Which renewable energy systems shall we develop? To answer this question, we must first realize that we do not desire energy, per se, but rather energy *services*. Stationary energy services (heating, cooling, illumination, and work) can be provided by renewable electricity derived from many sources (solar, wind, hydro, nuclear, tidal, geothermal, biomass), so there is much flexibility. In contrast, there are fewer choices for renewable mobile energy services.

Mobile energy services are essential

Mobile energy services move goods and people, and provide work on mobile platforms. Although electricity can provide a significant fraction of the energy required for personal vehicles and light-duty transport, it cannot service aviation and ocean shipping. Unless there are significant changes to the existing infrastructure, electricity cannot service most land freight (*i.e.*, heavy truck and rail transport). Also, electricity cannot power most mobile work platforms (*e.g.*, drills, plows, grain combines, construction equipment).

Mobile energy services depend almost completely on high-energy-density liquid fuels, almost all of which are currently derived from petroleum. Unfortunately, the peak of conventional (inexpensive) oil extraction occurred in about 2005. After 2004, oil prices went from elastic to inelastic (3). This means that oil supply cannot meet demand at the prices at which the world economy was formerly accustomed.

Although peak oil is a contentious subject, there is considerable evidence that we are at the peak of inexpensive oil. (A good technical summary of peak oil issues is available at www.peak-oil.org.) Figure 3 shows the total world oil extraction over the last few decades. Since 2005, oil extraction has stayed constant at around 4,000 million m.t./yr. In spite of high demand, it does not appear that the world can extract conventional oil any faster than we currently are extracting it. In the past few years, the primary source of increased oil extraction has been U.S. shale oil and Canadian tar sands, both of which are unconventional, much more expensive, sources of oil.

Figure 4 provides further evidence that we have reached the peak of cheap oil. During the past 10 years or so, the price of liquid fuels (diesel and gasoline) in dollars per gigajoule (GJ) has sharply increased relative to the price of natural gas and coal. Although petroleum prices are volatile, the long-term price trend is clearly upward. After a price dip in 2008 that was even greater from peak to trough than the recent decline, oil prices rebounded to historically high levels.



▲ Figure 2. The human development index (HDI) correlates with per capita power consumption. HDI is a composite of health (life expectancy at birth), education (mean years of schooling and expected years of schooling), and living standards (gross national product per capita). Source: (1).



▲ Figure 3. Global oil extraction rates around the world have changed little since 2005. Source: (1).

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U.S. extraction of petroleum cannot meet consumption (Figure 5). Imports of crude oil or refined liquids are required, which makes the U.S. economy vulnerable to supply disruptions. The recent sharp increase in the oil extraction rate in the U.S. is a result of the shale oil boom, but worldwide, the oil extraction rate has not increased because the extraction rates from old conventional oil wells are declining. The peak of U.S. shale oil extraction is predicted to occur in about 2020 (*5*).

Energy prices

The price of oil is determined by supply and demand, and is impacted by complex interplays among politics, geology, technology, transportation costs, refining capability, and environmental considerations. In the short term, the price of oil can change dramatically. For example, in July 2008, the price of oil reached a high of \$147/bbl; within six months, it had fallen to \$45/bbl. By 2011, the price averaged \$87/bbl. Because short-term prices are very volatile, this article focuses on long-term trends, which is the timescale needed to develop alternative energy systems at the terawatt scale.

To meet growing demand in developing nations (e.g.,



▲ Figure 4. The prices of transportation fuels, such as gasoline and diesel, have risen steadily, significantly more than natural gas and coal prices. Source: (1).



▲ Figure 5. In the U.S., petroleum consumption exceeds extraction. Extraction includes crude oil, lease condensate, and natural gas plant liquids. Source: (4). China, India), the oil industry must exploit unconventional oil resources (*e.g.*, tar sands, shale oil) and employ enhanced oil recovery techniques (*e.g.*, steam flooding, polymer injection, supercritical carbon dioxide flooding), all of which are expensive. In the long term, these factors create an upward push on the price of oil, making alternatives more attractive.

Alternatives to petroleum

The difference between the prices of coal and natural gas and the prices of diesel and gasoline shown in Figure 4 suggests it would be worthwhile to convert low-cost feedstocks into high-value liquids. For example, Sasol converts coal into liquid hydrocarbons in South Africa. Although this approach is technically feasible, the capital cost is very high.

Another alternative is to convert natural gas into liquid hydrocarbons; both Sasol and Shell operate such plants in Qatar. Unfortunately, converting natural gas to liquid hydrocarbons is inherently inefficient. In theory, only 78% of the energy in natural gas can be converted to liquid hydrocarbons; in practice, the efficiency is only 54–63% (6).

Converting inexpensive fossil fuels (coal, natural gas) to liquid transportation fuels is both costly and inefficient. An attractive alternative is to convert lignocellulose into liquid transportation fuels. Lignocellulose is a mixture of cellulose (glucose polymer), hemicellulose (primarily xylose polymer), and lignin (aromatic glue), typically found as the structural component of plants (trunks, branches, stems, leaves, roots). It is much more abundant than seeds or fruits and generally does not compete with food production.

High-yield herbaceous biomass can be produced for \$44 to \$66/dry m.t. at the farm gate (7, 8). Its heat of combustion is about 18 MJ/kg (9), which corresponds to a cost of about \$2.50 to \$3.70/GJ, roughly the price of coal and natural gas. Theoretically, cellulose and hemicellulose can be converted to ethanol with an energy efficiency of 96%, which is much higher than the theoretical efficiency of converting natural gas to liquid fuels.

From 2002 to 2012, U.S. electricity prices increased by 37% (10). During the same time period, the price of liquid transportation fuels increased by 260% (Figure 4). Although it is certainly desirable to develop new, renewable sources of electricity, overwhelmingly the market is signaling the need for liquid transportation fuels from another source, whether renewable or not.

Importantly, biofuels are carbon neutral; the carbon dioxide released from their combustion is recycled via photosynthesis. If political consensus eventually emerges that we must deal more actively with climate change, we will have already started developing the necessary technology and infrastructure. Should that consensus never build, we will still benefit economically by developing a replacement for expensive petroleum.



Biomass resources

Table 1 shows the primary energy sources in the U.S. Biomass provides more than 5% of all primary energy and is the fifth largest source overall. Biomass provides more primary energy than all other solar-based renewables (hydroelectric, wind, solar) combined. The dominant sources of biomass energy are combustion of wood wastes and corn ethanol. Table 2 compares U.S. ethanol consumption to the consumption of petroleum-based liquid transportation fuels.

Figure 6 projects the amount of biomass that could be available by 2030 without compromising land usage for other purposes, such as production of food, feed, and fiber (7, 15). The totals range from 677 million dry ton/yr to 1,633 million dry ton/yr, which represents 13% to 32% of U.S. primary energy production.

Strategies for increasing biomass production include:

• Use existing farmland more intensively. Doublecropping (*i.e.*, planting two crops per year, one after the other, rather than a single crop) enables the sustainable production of biofuels alongside traditional agriculture (*16*, *17*). Increased double-cropping combined with strategic placement of perennial grasses on the landscape could boost biomass production by hundreds of millions of tons annually while also providing large environmental services such as reducing greenhouse gases, increasing soil fertility, and reducing phosphorus, nitrogen, and sediment inputs to groundwater, streams, rivers, and lakes (*16*, *18*, *19*).

• *Make better use of pasture and grazed lands.* Contrary to popular belief, most land is not used to grow human food, but instead provides animal feeds (1). Better management could sustainably increase the amount of biomass produced

Table 1. U.S. primary energy sources in 2013. Source: (11).							
	Annual Production, exajoule/yr	Share of Total Production					
Fossil Fuels							
Coal	21.09	24.39%					
Natural Gas	26.37	30.50%					
Crude Oil	16.67	19.28%					
Natural Gas Liquids	3.80	4.39%					
Nuclear Power							
Reactors	8.72	10.09%					
Renewables	Renewables						
Hydroelectric	2.70	3.13%					
Solar	0.32	0.37%					
Wind	1.68	1.95%					
Biomass	4.87	5.63%					
Geothermal	0.23	0.27%					
Grand total	86.45	100.00%					

for biofuels on current pasture and range lands (over 600 million acres in the U.S.), while still meeting the demand for animal feeds.

• *Increase crop productivity.* Crop productivity depends on fertilizer, pesticides, herbicides, and plant genetics. These are constantly improving, particularly plant genetics. For example, since 1940, corn yields have increased by 500% and continue to improve about 1.2% per year. Currently, U.S. average corn yields are about 3.3 dry ton/acre-yr.

• Substitute high-biomass varieties. Traditional crops can be replaced with high-biomass varieties. For example, conventional sugarcane can be replaced with energy cane, which has twice the total biomass yield (30 vs. 14.6 dry ton/acre-yr) and a higher sugar yield (9 vs. 5.8 dry ton/acre-yr) (20). Meeting global sugar demand (188 million ton/yr) with energy cane will produce an extra 972 million ton/yr of sugar and fiber that could produce about 68 billion gal of gasoline equivalent per year, equal to 50% of U.S. gasoline consumption.

• *Deploy advanced food-processing technology.* Advanced chemical engineering technology can be applied to food processing, and thereby improve biomass availability. For example, conventional sugar mills concentrate sugar solutions using quadruple-effect evaporators powered by inefficient combustion of sugarcane residues. Substitut-

Table 2. U.S. consumption of liquid transportation fuels in 2013. Source: (12–14).						
Fuel	Consumption, billion gal/yr	Power, TW				
Gasoline	135.56	0.5166				
Diesel (distillate)	58.67	0.2540				
Jet Fuel (kerosene)	21.98	0.0941				
Ethanol	13.18	0.0335				
Biodiesel	1.368	0.0054				
Total	230.76	0.9036				



▲ Figure 6. Estimates of biomass availability by the Union of Concerned Scientists (UCS) and Oak Ridge National Laboratory (ORNL). Source: (15).



ing high-efficiency vapor-compression evaporators will free sugarcane residues for use in biofuel production rather than sugar processing.

Using these and other approaches to increase biomass production, biomass for biofuel production in the U.S. could reach 1,000 to 2,000 million dry ton/yr. Assuming that 50% of the embedded energy in biomass becomes liquid fuels, this much biomass could provide about 0.29 to 0.58 TW, or 32% to 64% of liquid fuel consumption (Table 2). These estimates are consistent with various low-carbon energy future scenarios in which approximately 25% of primary energy is provided by biomass (21), or approximately 1 kW for liquid fuels out of the 4 kW per capita required to achieve sufficient levels of human development.

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Closing thoughts

Whether one argues from an economic, energy security, or environmental perspective, the conclusion is clear: Biofuels are not optional. The question then becomes: *How can we develop a large-scale, sustainable lignocellulosic biofuels industry*? That is the subject of this Society for Biological Engineering (SBE) supplement.

To help answer this question, the supplement describes the three main platforms for producing biofuels:

- thermochemical
- sugar
- carboxylate

Another article discusses scaling up bioenergy processes, and demonstrates how the stage-gate process needs to be modified for biofuels processes. The final article details the state of the commercial-scale lignocellulosic biofuels industry and reviews the current and planned biofuels production facilities throughout the world, giving readers a glimpse into this developing industry.

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Producing Biofuels via the Thermochemical Platform

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Sergio C. Capareda Texas A&M Univ. Thermochemical conversion of biomass to liquid fuels employs many of the same processes and equipment as are used with fossil fuel feedstocks.

Biomass resources, such as wood, grasses, agricultural residues, and municipal wastes, can be treated by thermochemical processes to make significant contributions to U.S. fuel and electrical supplies (1). This process uses heat, with or without a catalyst, to convert organic materials into transportation fuels and other co-products. Thermochemical processing capitalizes on existing infrastructure and knowledge by employing unit operations (*e.g.*, gasifiers, reformers, catalytic reactors) that are already used for converting coal and petroleum feedstocks to liquid transportation fuels.

Biomass resources can take one of three thermochemical pathways to be converted to useful energy and fuel: combustion, indirect liquefaction, and direct liquefaction (Figure 1). This article describes these pathways and their associated economic costs.

Combustion

Combustion is the rapid oxidation of solid, liquid, or gaseous fuels to produce high-temperature thermal energy with carbon dioxide, water, and ash as the main byproducts. Steam or gas turbines can convert the thermal energy to electricity.

The thermoelectric power technologies available to convert coal and other fossil fuels to electricity can also be applied to biomass or gasified biomass (called syngas) combustion (2). Although thermoelectric power has been used primarily for stationary applications, it could be used for the growing battery-powered electric vehicle industry. An advantage of this arrangement is that it would be easier to control emissions from a centralized electric power plant than from individual automobiles with internal combustion engines. Biomass combustion produces fewer sulfur and nitrogen emissions than fossil fuel combustion. Modern thermoelectric power plants can have thermodynamic efficiencies in excess of 35%. With the relatively high efficiencies of battery storage and electric motors, combustion of biomass and syngas has the potential to compete with liquid biofuels as a source of low-carbon renewable energy for the transportation sector (3).

However, major barriers must still be overcome before biomass-powered electric vehicles become a reality. Because biomass resources are widely distributed, biomass power plants are considerably smaller than fossil-fuel power plants, and their efficiencies are as low as 25%. The raw materials



Figure 1. Biomass resources can be transformed into liquid fuels or electric power via combustion, indirect liquefaction, or direct liquefaction. also contain alkali metals that promote ash fouling in boilers, which can be difficult to manage. Co-firing biomass with fossil fuels in existing power plants can partially overcome both low efficiency and boiler fouling, but this introduces other issues related to feedstock handling and ash quality (4). Another option is to convert biomass to syngas to resolve the issues associated with direct-fired biomass, but this adds to the capital cost. Additionally, advances will need to be made to the current designs of battery-powered electric vehicles to meet customer expectations for cost and performance.

The future of transportation based on biomass-derived power largely depends on advances in battery technology, rather than on improvements to biomass combustion. Even if battery-powered electric vehicles become widely available, electricity generation from biomass will have to compete with higher-value applications, such as aviation fuels and biobased chemicals. Solar and wind power may be more logical sources of electricity for battery-powered vehicles.

Indirect liquefaction

Indirect liquefaction is the conversion of gaseous, liquid, or solid feedstocks into liquid fuels from an intermediate mixture of carbon monoxide and hydrogen, called syngas (2). Syngas is produced from gaseous or volatile-liquid feedstocks (*e.g.*, methane or other volatile organic compounds [VOCs]) through steam reforming, whereas nonvolatile-liquid and solid feedstocks (*e.g.*, sludge and lignocellulosic biomass) are gasified to syngas. Both processes heat the feedstocks to temperatures as high as 1,200°C, usually in the presence of air, oxygen, or steam. Pressurized operation promotes rapid and complete reaction of the feedstocks and yields syngas at the appropriate pressure for subsequent catalytic synthesis to liquid products. Challenges associated with conveying, reduced reactivity, and potential for contamination complicate the gasification of solid feedstocks.

Several catalytic processes have been developed to



▲ Figure 2. In syngas fermentation, biocatalysts called unicarbonotrophs convert syngas produced from biomass into biofuels. The biocatalysts are less susceptible to inorganic contaminants than the metal catalysts used in other indirect liquefaction methods.

convert syngas into liquid products (2). The most common options are Fischer-Tropsch (FT) synthesis to alkanes, methanol synthesis, and methanol-to-gasoline (MTG) synthesis. A major disadvantage of the FT process is that it produces hydrocarbon products with a wide distribution of molecular weights, including heavy waxes that must be cracked to form molecules appropriately sized for fuel.

These processes employ metal catalysts, predominantly cobalt and iron, which are susceptible to poisoning by sulfur, nitrogen, and other inorganic contaminants present in syngas. As an alternative, biocatalysts can be used to convert syngas into fuels and other products (5). A class of microorganisms known as unicarbonotrophs can grow on one-carbon compounds, using them as their sole source of carbon and energy. Some unicarbonotrophs are used in syngas fermentation to co-metabolize carbon monoxide and hydrogen to produce biofuels (Figure 2). Although they are not as susceptible to inorganic contaminants as metal catalysts, biocatalysts can be inhibited by some byproducts of steam reforming and gasification.

Feedstocks may be cleaned prior to steam reforming or gasification to partially remove inorganic contaminants; syngas must be cleaned as well before it can be used in catalytic synthesis. To achieve the required cleanliness, separate unit operations are required to reduce contaminants to acceptable concentrations (which can be less than 1 ppm).

The chief advantage of indirect liquefaction is that it can convert a wide variety of feedstocks into a uniform substrate for subsequent upgrading to final products. This makes it suitable for any carbonaceous feedstock, including mixed biomass streams, municipal solid wastes, wastewater sludge, and other relatively low-value materials. Almost all of the carbon is converted into a form suitable for synthesis, in contrast with most fermentation processes that can only utilize high-quality carbohydrate feedstock.

Indirect liquefaction is hampered by the need to operate at large scale in order to achieve favorable economics. High capital costs make initial financing of such projects difficult. Factors such as high-pressure operation and the multitude of unit operations required to clean syngas contribute to the high costs.

Advances are needed to reduce the cost of building facilities for indirect liquefaction. Some companies have proposed designs for smaller-scale facilities to reduce capital costs, but this comes with a higher unit cost of production. This may be an acceptable approach for some niche markets, such as international aviation, which is required to reduce its carbon footprint by legislative mandate; however, more general methods for reducing capital costs per unit production must be developed.

Gas-to-liquid processes not premised on pressurized gasification or extensive gas cleaning could advance the



commercial prospects of indirect liquefaction. Syngas fermentation is one such example that can be performed at atmospheric pressure and requires less intensive cleaning.

Direct liquefaction

Direct liquefaction uses heat and sometimes catalysts to convert, in a single step, organic solids into liquids and/or condensable vapors that can be recovered. The liquids formed are either stable emulsions of water-insoluble organic compounds in an aqueous phase that contain watersoluble organic compounds, or separate phases of different kinds of organic compounds. Pyrolysis and solvent liquefaction are two methods of direct liquefaction.

Pyrolysis is the thermal decomposition of organic materials in the absence of oxygen (2). In the case of biomass as a raw material, if heating is very rapid and the products are rapidly quenched, the process is called fast pyrolysis.

The primary product of pyrolysis is bio-oil — an emulsion of lignin-derived phenolic compounds (pyrolytic lignin) in an aqueous phase, composed mostly of carbohydratederived compounds. The phenolic compounds include monomers, dimers, and oligomers of phenol, which include various functional groups, most commonly methyl, methoxy, and vinyl. These reactive components cause the pyrolytic lignin to polymerize during storage or thermal processing, which increases the viscosity and instability of the emulsion. The aqueous phase consists mostly of alcohols, aldehydes, carboxylic acids, esters, furans, pyrans, ketones, monosaccharides, and anhydrosugars derived from the carbohydrates in biomass.

Solvent liquefaction is the thermal decomposition of organic materials in a solvent (6). In many respects, it can be characterized as pyrolysis in a solvent, although there are important differences. Whereas pyrolysis is often an atmospheric process, solvent liquefaction must occur under pressure to prevent the solvent from boiling. In some cases, the solvent not only transports reactants and products, but also affects the course of the reaction by acting as a hydrogen donor. A wide variety of solvents can be employed, such as water, acetic acid, creosol, dioxane, gamma-valerolactone, and various mixtures. When water is used as the solvent, the process is called hydrothermal processing (HTP) or hydrothermal liquefaction (HTL) (Figure 3) (2).

Solvent liquefaction can fractionate rather than liquefy biomass under relatively mild reaction conditions (*i.e.*, low temperatures and pressures). This process is more accurately described as solvolysis or solvent processing. Fractionating lignocellulosic biomass under mild conditions yields pyranose sugars or cellulose fibers, xylose from hemicellulose, and lignin. For lipid-containing biomass, such as microalgae, the fractionated products include sugars from carbohydrates, fatty acids or lipids, and amino acids or proteins. More-severe reaction conditions convert the biomass into two liquid phases that resemble the products of fast pyrolysis, except that they are segregated rather than intermingled as an emulsion. The organic phase contains the majority of lignin- and lipid-derived compounds and a substantial portion of the carbohydrate- and protein-derived compounds. The aqueous phase contains decomposition products from both carbohydrates and proteins in the biomass; the amount depends on the severity of the processing conditions.

The method for upgrading products of direct liquefaction into liquid transportation fuels depends on the nature of the products. Sugars or anhydrosugars recovered as an aqueous solution can either be fermented to ethanol or other products. Sugars and other carbohydrate-derived compounds in an aqueous solution can be catalytically converted in an aqueous-phase process. The organic phase can be hydroprocessed to remove oxygen and produce molecules appropriately sized for fuel.

Direct liquefaction is amenable to distributed processing. The organic fractionate is partly deoxygenated, which reduces the cost of hydroprocessing to fuel molecules. However, feeding solid biomass into a pressurized reactor remains a challenge for commercial-scale reactors and the need for pressure vessels adds substantial costs.

The attraction of fast pyrolysis is that it can convert biomass to liquid fuel at atmospheric pressure and at a relatively small scale. It also utilizes all of the components of biomass, whether lignocellulosic or oleaginous. Commercialization has been hampered by the poor stability of bio-oils and the relatively low yields of hydrocarbons.

Despite potential commercialization setbacks, both methods of direct liquefaction are receiving increased attention because of favorable operating cost projections for the production of hydrocarbon fuels. Additionally, increased understanding of the underlying processes that control thermal deconstruction of biomass has allowed for unprec-



▲ Figure 3. One of the challenges of biofuel production is the need to dry the feedstock to an appreciable extent before processing. Hydrothermal liquefaction avoids this step, as the biomass is fed to the process wet. Source: Adapted from (7).



edented yields of desirable products. Pyrolysis streams are being fractionated into classes of compounds that can be upgraded to fuel, rather than recovered as a single mixture of unrelated compounds (8). In the presence of zeolite catalysts, biomass-derived molecules in pyrolysis processing are deoxygenated to form hydrocarbon products without the need for added hydrogen (9).

Biochar

All thermochemical processes produce a solid residue co-product composed of inorganic compounds (from nutrients and silica) and carbonaceous residue (from dehydrated plant polymers). The combustion process produces ash, which is a solid residue comprised mostly of inorganic material; gasification, pyrolysis, and solvent liquefaction primarily produce a carbonaceous residue called biochar. Biochar is generally characterized as a porous, carbon-containing, solid interspersed with volatile organic compounds and ash, but the specific composition and properties depend on the feedstock and the thermochemical process employed.

It can be burned to provide heat to the thermochemical process or returned to the environment. Because it is relatively recalcitrant to oxidation, it has been proposed as a carbon sequestration agent. When it is incorporated into low-quality soils, it improves soil fertility and serves as a synthetic soil carbon. What was originally considered as low-value boiler fuel has the potential to improve the sustainability of biofuels agriculture (10).

Economics

With over 100 grain-ethanol plants in the U.S., there is plenty of data on the capital cost of a modern ethanol plant (about \$2/gal gasoline equivalent [gge] of annual nameplate capacity). However, because commercial-scale thermochemical biofuels plants are just emerging, there is very little data on the actual capital and operating costs.

To estimate capital and operating costs of future plants, techno-economic analysis uses laboratory data (*e.g.*, temperature, pressure, catalysts, residence time, product yields, and selectivities) and historical costs of similar equipment and operations (6). Capital costs are estimated to be about \$16/gge of annual capacity for indirect liquefaction and between \$4/gge and \$8/gge of annual capacity for direct liquefaction (11). Indirect liquefactor is more expensive because of the high costs of pressurized reactors, gas cleaning, and recycling equipment.

Regardless of the conversion technology employed, operating costs are strongly influenced by the cost of feedstock and fuel yield. Other factors such as capital charges, utilities, and labor contribute to a lesser extent to operating costs. Although thermochemical capital cost estimates are high, lignocellulosic feedstocks are much cheaper than grain; therefore, the difference between the cost of advanced thermochemical fuels and that of grain ethanol is not as large as might be expected (12). The costs for grain ethanol, direct liquefaction (pyrolysis) hydrocarbon fuels, and indirect liquefaction (Fischer-Tropsch) liquids are approximately \$1.60/gge, \$2.60/gge, and \$4.50/gge, respectively.

Closing thoughts

As is the case with other biomass processes, the economic viability depends on the price of crude oil, initial capital cost, and scale of the facilities. Biomass resources that are relatively inexpensive, such as municipal solid wastes, wastewater sludge, and byproducts of other biomass conversion processes, will likely emerge as initial candidates for widespread utilization. Methods to utilize co-products will need to be defined for biofuels to become economical.

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Producing Biofuels via the Sugar Platform

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Whether the feedstock is sugarcane, corn, or lignocellulose, the fermentation and ethanol recovery operations are similar. The differences arise in the way the sugars are released and the co-products produced.

imple sugars (mono and disaccharides) are reactive molecules that can be converted biologically or chemically into fuels, chemicals, food, and animal feed. Sugarcane, sugar beets, sweet sorghum, and a few other types of plants contain significant quantities of simple sugars. In nature, these sugars are often polymerized as storage polysaccharides (e.g., starch) in grains like corn, rice, and wheat. Worldwide, grains are the basis of most human food and are either eaten directly or fed to livestock.

Grain is a small portion of plants. Plants are composed primarily of structural components such as roots, trunks, branches, stems, and leaves. Plant cell walls are composed of lignocellulose - a composite of cellulose (glucose polysaccharide), hemicellulose (often primarily xylose polysaccharide), and lignin (aromatic polymer), along with lesser amounts of other components such as minerals and protein. These complex structural polysaccharides impart strength and rigidity to plants. Several chemical and physical barriers make it difficult to convert hemicellulose and particularly cellulose to simple sugars. This recalcitrance, or resistance to being hydrolyzed into sugars, is the primary economic barrier to low-cost products from lignocellulosic biomass.

Global production of simple sugars (*e.g.*, sucrose) is approximately 200 million m.t./yr at a price of about \$400/m.t. Production of starch in the form of the three major cereal grains (wheat, rice, and corn) is about 2 billion m.t./yr with a value of \$300-\$600/m.t. of starch. This compares with total world oil extraction of about 4 billion m.t./yr at

\$400-800/m.t. (equivalent to roughly \$50-100/bbl).

Other than paper pulp and lumber, large markets do not exist for most forms of lignocellulose; thus, the world utilizes far less lignocellulose than it could. Nonetheless, total lignocellulose production in the biosphere is roughly 100 billion m.t./yr. At the farm gate, some biomass varieties (e.g., high-biomass sorghum) can be produced for about \$60/m.t., which is equivalent to oil at about \$20/bbl on an energy basis. At this volume and cost, lignocellulosic biomass has the potential to replace a substantial amount of petroleum, if it could be economically converted to sugars and then to liquid fuels. Anaerobic fermentation of sugars to fuels is attractive, because well over 90% of the energy in the sugars can be conserved in the fuels.

Figure 1 compares the three branches of the sugar platform (1):

a. Simple sugars from sugarcane. Sugar is extracted from sugarcane and fermented to ethanol, and the resulting ethanol-water mixture is distilled to recover ethanol.

b. Starch from corn via wet or dry milling. The corn is ground and cooked to make the starch available for amylase enzymes to hydrolyze it to sugar; the enzymatically produced sugars are then fermented, and the resulting ethanol is recovered by distillation.

c. Lignocellulose. Biomass is ground and pretreated to disrupt the plant cell walls and make them available for enzymatic conversion to sugars and then to ethanol, which is recovered by distillation.

Article continues on next page





The key to obtaining inexpensive sugars is to achieve high yields and concentrations of readily fermentable sugars from low-cost feedstocks while keeping processing costs low. Sugar and starch feedstock costs are relatively high, but their processing costs are comparatively low. Conversely, lignocellulose feedstock costs are lower, but processing costs are high primarily because of the material's recalcitrance (2).

Ethanol from Brazilian sugarcane and U.S. corn

For many decades, fuel ethanol has been produced commercially by fermenting sugars derived from sugarcane and grains, primarily corn. Ethanol is also the first biologically produced liquid fuel being pursued for large-scale commercial production from lignocellulose. Lessons learned from commercial production of ethanol from sugarcane and corn apply to the emerging lignocellulosic biofuels industry.

Since the auto industry began, ethanol has been used as a fuel in motor vehicles. Henry Ford originally targeted ethanol to power his early vehicles.

Currently, ethanol comprises about 30% of the gasoline mix in Brazil (roughly 6 billion gal/yr of ethanol) and about 10% of the mix in the U.S. (about 14 billion gal/yr). In Brazil, all automobiles are designed to run on different ethanol-gasoline mixtures, and all refueling stations provide a variety of ethanol-containing fuels.

In the U.S., most gasoline now contains about 10% ethanol, and mixtures of 85% ethanol with gasoline (E85) are



available in some states. However, the latter are not widely used due to limited numbers of flexible-fuel vehicles that can run on E85 and the limited number of fueling stations in many parts of the country. In the U.S., ethanol also suffers from an image problem based on widespread anecdotes about problems with fuel systems, lower mileage, and other perceived drawbacks that the Brazilian experience has shown can be overcome successfully. The fact that Indianapolis 500 race cars are fueled with ethanol also speaks to the excellent properties and performance achievable.

For decades, fuel ethanol has been produced in large volumes in both the U.S. and Brazil in response to three national policy goals:

• to improve national energy security and address fuel shortages such as during the mid-1970s oil embargo

• to reduce emissions of carbon monoxide and unburned hydrocarbons, particularly at high elevations during winter

• to stabilize the agricultural sector by providing another market for surplus agricultural products (sugar and corn).

In the last decade, both countries have added a fourth policy goal — to reduce greenhouse gas emissions.

In 1975, the Brazilian National Ethanol Program (PROALCOOL) was formed to directly respond to an oil price spike that caused great economic hardship. As the cumulative volume of sugarcane ethanol produced increased, the cost of production decreased almost threefold (Figure 2). Although these data are somewhat old, the figure demon-

> strates that the cost of production decreases as experience is gained. Because of this learning curve effect associated with extended production experience, the cost of cane sugar now represents approximately 70% of the total cost to produce ethanol — a typical percentage for a commodity product in a mature industry. Similarly, in the U.S., as corn ethanol production volume has increased, production costs have dropped substantially, and ethanol is now the low-cost source of octane for U.S. gasoline. Although additional cost reductions are likely, the corn ethanol industry is likewise mature, with net feedstock costs (feedstock less co-product credits) representing at least 70% of the cost to produce corn ethanol.

> A few visionary companies have recently begun or will soon begin commercial conversion of lignocellulose to ethanol. (See the accompanying article, "Commercial-Scale Production of Lignocellulosic Biofuels," pp. 62–64.) As the lignocellulosic ethanol industry matures through extended operation of

◄ Figure 1. The sugar platform processes for producing ethanol from sugarcane, corn, and lignocellulose have similar fermentation and ethanol recovery operations, but use different approaches to prepare sugars and generate different co-products. Source: Adapted from (1).



these pioneering and subsequent plants, conversion costs will also decrease because of learning curve benefits (3). Technological improvements will also drive conversion and capital costs lower and yields higher. The result will be that feedstock costs will become a much greater portion of the overall cost of making lignocellulosic ethanol. However, just as for sugarcane ethanol, corn ethanol, petroleum, and other energy sources, policy and research support have been — and will be — required to build and stabilize markets for lignocellulose-derived fuels.

The rest of this article discusses lignocellulose conversion technologies based on the sugar platform, and opportunities for improvements that would enhance process economics.

Lignocellulose

Lignocellulose is comprised of about 35-50% cellulose, about 15-25% hemicellulose, and about 10-25% lignin, with the remainder including minerals, oils, free sugars, and proteins (Figure 3) (4).

Cellulose is a polymer of glucose molecules linked by beta bonds that form extended linear chains. These long chains align with each other and are connected by hydrogen bonds to form long fibers that give plants strength and rigidity. Hemicellulose can contain as many as five different sugars: arabinose, galactose, glucose, mannose, and xylose, with the latter often the most prevalent. Lignin is composed of phenyl-propene molecules that are polymerized to form a complex macromolecule.

The cellulose fibers are glued together by a ligninhemicellulose matrix to form nature's composite material. Cellulose is analogous to the glass fiber in fiberglass composites, with the lignin-hemicellulose acting as the epoxy glue.

Although starch is also a sugar polymer, it contains only glucose molecules joined by alpha bonds that are readily hydrolyzed by dilute acids or amylase enzymes, which allows glucose to be recovered at high yields. Sugar and starch are easily metabolized for food.

In contrast, plants employ an elaborate defense mechanism to ward off attack by microorganisms and other predators that would eat the sugars in hemicellulose and cellulose. This recalcitrance has made it possible for lignocellulose such as grasses (*e.g.*, switchgrass), wood (*e.g.*, poplar), and agricultural residues (*e.g.*, wheat straw, corn stover) to grow in a variety of climates and soils around the globe. Thus, converting lignocellulose to fuels and chemicals faces additional challenges because of its recalcitrance, which is not an issue in the production of ethanol from sugarcane or corn (2, 5).

Pretreatment of lignocellulose

Corn requires only mechanical milling and heating to moderate temperatures to make starch sufficiently accessible to amylase enzymes to achieve high glucose yields. In contrast, lignocellulose requires harsher pretreatment conditions to overcome its natural resistance to breakdown. To improve access for enzymes, many physical (*e.g.*, milling, radiation), chemical (*e.g.*, acids, bases, solvents), thermal (*e.g.*, heating to about 200°C), and biological (*e.g.*, fungus) pretreatments have been tested. Most pretreatments require temperatures of 120°C to 210°C to be effective (5).

Adding acids or bases reduces the required pretreatment temperature and enhances overall sugar yields from the combined operations of pretreatment and subsequent enzymatic hydrolysis. However, to be affordable, these chemicals must be either very inexpensive (*e.g.*, dilute sulfuric acid) or readily recycled (*e.g.*, ammonia, sulfur dioxide).

Most pretreatments require short residence times (10–30 min), which allows them to be carried out in small vessels. However, the high pressures needed for some pretreatments and corrosion by pretreatment chemicals may require thick-walled vessels and exotic materials of construction that are more costly.



▲ Figure 2. With operating experience, the price of Brazilian ethanol has declined and is comparable to the cost of gasoline on an energy basis. Source: (22).

Although pretreatment improves enzyme effectiveness,



Figure 3. Lignocellulose consists of cellulose, hemicellulose, and lignin.



Lignocellulose requires harsher pretreatment conditions than corn to overcome its resistance to breakdown.

the enzyme doses required to achieve high yields are still very costly (6). Thus, biological conversion of lignocellulose would benefit greatly from pretreatments that use low-cost and/or recyclable chemicals, require short residence times, allow processing in low-cost vessels, degrade little or no sugar during pretreatment, and produce solids that low enzyme loadings can convert to sugars at high yields (7, 8).

Enzymatic hydrolysis

As illustrated in Figure 1, biological conversion of starch and lignocellulose to sugars requires hydrolysis of the polysaccharides to form simple sugars. Polysaccharide hydrolysis can be performed with mineral acids (*e.g.*, sulfuric); however, acid hydrolysis of cellulose suffers from high acid costs or low yields. As a result, to produce simple sugars, all commercial biological processes that use starch and lignocellulose employ enzymes.

Although the enzymatic hydrolysis of starch and lignocellulose are conceptually similar, cellulose is far more resistant to enzymatic hydrolysis than starch. Starch hydrolysis is readily achieved using amylase enzymes. In contrast, hydrolyzing cellulose and hemicellulose to fermentable sugars requires complex mixtures of cellulases, hemicellulases, and other enzymes (4, 9). Furthermore, because of the recalcitrance of lignocellulose, much more enzyme — 10 to 100 times more — is required to achieve high sugar yields.

In addition, the complex lignocellulose structure (lignin, cellulose, hemicellulose, and other components) creates obstacles that impede enzyme hydrolysis and reduce sugar release rates significantly. The amount of cellulase enzymes needed to achieve high yields costs about \$1.00/gal ethanol (\$1.50/gal equivalent gasoline) (6). Thus, the key opportunities are in:

• improving pretreatments to reduce enzyme requirements

- · recycling enzymes inexpensively
- reducing enzyme production costs
- significantly enhancing enzyme effectiveness.

For over three decades, considerable work has been devoted to the latter two strategies. Thus, at this point, efforts aimed at inexpensive enzyme recycling and improving pretreatments may produce bigger impacts. In addition, major dividends will result from devoting more systematic attention to understanding mechanisms by which pretreatment overcomes biomass recalcitrance, as well as improving pretreatment technologies to make the pretreated solids more amenable to hydrolysis by much lower enzyme doses (7, 8).

To this end, a pretreatment strategy using tetrahydrofuran (THF) as a miscible cosolvent in water containing

very dilute acid has achieved close to theoretical yields. The combined pretreatment and enzymatic hydrolysis of the pretreated solids recovered nearly all of the sugars that could be produced from the cellulose and hemicellulose using less than one-tenth the enzyme doses needed with conventional pretreatments (10). This novel pretreatment, called cosolvent enhanced lignocellulosic fractionation (CELF), recovers virtually all of the sugars from hemicellulose in solution while also removing about 90% of the lignin from biomass to produce solids that are highly enriched in cellulose. Because THF is far more volatile than water, it can be readily recycled to keep operating costs low. The high degree of lignin and hemicellulose removal during CELF appears to be at least partially responsible for such enhanced enzyme effectiveness at low loadings, but further research is in progress to better understand controlling mechanisms.

Fermentation

Figure 1 suggests that fermenting sugars from lignocellulose is similar to fermenting sugars from sugarcane and corn starch. This is an oversimplification. Cane sugar contains predominantly sucrose with small amounts of glucose and fructose, all of which are readily fermented. Similarly, starch contains only glucose. In contrast, lignocellulose contains large amounts of hemicellulose, which is comprised of several different sugars. Conventional yeast or other fermentative organisms cannot fully convert the fivecarbon sugars arabinose and xylose to ethanol. Fortunately, microorganisms have been genetically modified so that this obstacle has been largely overcome (11).

However, another important obstacle remains: ethanol concentration. Cane and corn sugars can be readily mixed at sufficiently high concentrations in fermenters to reach ethanol concentrations of up to about 15%, which is the approximate upper limit of ethanol tolerance by yeast. At this concentration, ethanol recovery by distillation is attractive.

In contrast, loose, uncompacted lignocellulose solids cannot be readily mixed at high concentrations. For example, a mixture of about 10% loose biomass (*e.g.*, straw) and water contains no free water, and cannot be stirred or pumped effectively. Furthermore, the solids contain only about two-thirds carbohydrates, which limits fermentation yields to about 5% ethanol or less at mixable overall solids levels (*12*). Although 5% ethanol concentrations can be recovered at reasonable cost, significant advantages would accrue if ethanol concentrations could be increased to approximately 12%.

Fed-batch and continuous fermentations can approach this target, because enzymatic hydrolysis of solid lignocellulose releases soluble sugars (glucose and others) that keep the suspended solids concentrations within limits amenable to mixing, provided solid feed rates are properly controlled. However, most fermentation research is con-



ducted in a simple batch mode in which all of the ingredients are added at the start. Unfortunately, very little attention has been focused on developing and improving continuous or fed-batch fermentations to reach higher ethanol concentrations, at least partly due to the complexity of running continuous fermentations in conjunction with continuous feeding of solids (13).

In this regard, ammonia fiber expansion (AFEX) pretreatment can achieve high solids loadings that enable high ethanol concentrations. AFEX treats damp lignocellulose with ammonia for a few minutes at elevated temperatures, and then rapidly releases the pressure to recover and recycle the ammonia. After AFEX pretreatment, the biomass is easily pelletized without requiring high temperatures or added binders. The resulting pellets are very durable and can be handled, shipped, and stored like corn. Importantly, AFEX biomass pellets do not absorb nearly as much water as loose biomass. Pellets of AFEX-treated corn stover (straw) have been effectively hydrolyzed at solids loadings of up to 36% (14).

Enzymatic hydrolysis and fermentation may be conducted in series, as separate hydrolysis and fermentation (SHF). However, enzymes are inhibited by sugars released during pretreatment and enzymatic hydrolysis. Thus, to realize acceptable yields, sugar concentrations and therefore ethanol concentrations must be kept low, or even more enzyme must be added.

Decades ago, researchers found that adding yeast along with enzymes would convert glucose and other sugars to ethanol virtually as soon as they were released by enzymatic hydrolysis (15). Because ethanol is far less inhibitory to enzymes than are sugars or sugar oligomers, the result was higher ethanol concentrations, faster rates, and higher yields for a given enzyme loading by this so-called simultaneous saccharification and fermentation (SSF) route. Most SSF experiments are conducted in a batch mode, but fed-batch or continuous operations could make lower enzyme loadings effective, because the lower amount of unreacted lignocellulose in a continuous stirred tank reactor would need less enzyme to achieve high conversions (13).

A new bioconversion process that reduces the amount of unreacted lignocellulose is called rapid bioconversion with integrated recycle technology (RaBIT) *(16)*. RaBIT takes advantage of the fact that enzymatic hydrolysis is rapid during the first 24 hr or so, and then slows dramatically as unreacted cellulose accumulates. To take advantage of the initial high-rate period, the hydrolysis mixture is centrifuged after 24 hr to remove unreacted solids and to recover a clean sugar stream containing no solids. Unreacted solids (about 40–50% of the initial mass) are then mixed with fresh enzyme (about half the initial amount) and additional fresh pretreated biomass to continue the hydrolysis. After another 24 hr of hydrolysis, the centrifugation and addition of fresh

Metabolic engineering aims to change cellular pathways so organisms can both produce appropriate enzymes and ferment the sugars to ethanol at high yields.

biomass and enzyme are repeated for as many cycles as desired. The hydrolyzed sugars are fermented at high cell loadings to achieve rapid fermentation. Because both hydrolysis and fermentation are conducted at high rates, reaction vessels are much smaller.

RaBIT also permits easy recycle of about half of the enzyme, which is adsorbed to the unhydrolyzed solids. Excess cell mass can be easily separated from the clean sugar stream and has potential commercial use as animal feed. In contrast, when cells are mixed with residual biomass solids, using excess cell mass is much more difficult. Despite process improvements such as SSF and RaBIT, enzyme loadings needed to achieve high yields are still quite high and must be further reduced, perhaps by improved pretreatments.

Enzyme production

The most common source of cellulase and hemicellulase enzymes is an aerobic fungus (*Trichoderma ressei*), which the U.S. Army first isolated from rotting cotton shelter halves in the South Pacific after World War II. Production of fungal enzymes is expensive, because the fermentation is slow and requires considerable power to introduce and disperse small air bubbles.

An alternative strategy employs anaerobic fermentative organisms that produce their own enzymes, thereby combining enzyme production, enzymatic hydrolysis, and sugar fermentation to reduce capital costs and power requirements (17, 18). For example, this consolidated bioprocessing (CBP) approach has achieved very high conversion (about 90%) of cellulose in poplar wood pretreated with only hot water in reasonable time periods (about seven days) without adding any external enzymes — much higher yields than are possible with moderate enzyme loadings in a conventional approach.

Conventional fermentative organisms (*e.g.*, yeast) that produce ethanol at high yields and concentrations cannot produce appropriate enzymes that hydrolyze lignocellulose. Conversely, naturally occurring fermentative organisms that do produce cellulase and hemicellulase do not produce ethanol at high yields and concentrations.

To overcome this challenge, metabolic engineering of organisms aims to change cellular pathways so that organisms can both produce appropriate enzymes and ferment the sugars to ethanol at high yields. With some success, enzyme production pathways have been introduced into yeast (19), but making the complex array of enzymes required is very challenging. In an alternative approach, the bacterium



Clostridium thermocellum produces a cellulosome, a tethered array of enzymes that is more effective than mixtures of fungal enzymes.

A promising enzymatic route to overcoming biomass recalcitrance appears to be modifying *C. thermocellum* or other effective CBP organisms that produce their own highly effective enzymes anaerobically and also effectively ferment the sugar product to realize high ethanol yields. Similarly, combining CBP organisms with effective pretreatment, hydrolysis, and fermentation approaches (*e.g.*, RaBIT or THF CELF) is very promising.

Product recovery

The final processing step of all three sugar platform pathways is distillation of the fermentation broth to recover virtually pure ethanol in the overhead, and solids, water, and other low-volatility compounds in the bottoms. However, once again, important distinctions exist. With cane sugar and glucose from wet milling of corn, it is relatively simple to recover ethanol from the fermentation broths, because the liquid contains primarily water, ethanol, yeast, and nutrients. In contrast, the distillation process for lignocellulose-derived ethanol is more complex (Figure 4).

Regardless of the feedstock, ethanol is concentrated to its azeotrope (about 95% ethanol by weight) in the rectification column above the feed tray, and the remaining water is typically removed from the azeotropic solution by molecular sieves to produce fuel-grade ethanol — which must be virtually water-free to prevent phase separation in gasoline. Other materials entering from the fermenters drop down from the feed tray through the beer column to the reboiler.

In the sugarcane pathway, the stream leaving the bottom of the beer column is called vinasse, which can be spread on fields to provide nutrients and water for growing new crops. In the corn wet mill pathway, the yeast and nutrients in the

column bottoms are added to animal feed. In the corn dry mill pathway, all of the ingredients in the corn kernel that are not fermented to ethanol (protein, corn oil, fiber, residual starch) leave the bottom of the beer column and are dried to produce distillers dried grains with solubles (DDGS), an animal feed that contains about 27% to 30% protein.

Current lignocellulose-to-ethanol processes also employ distillation to recover fuel-grade ethanol. However, an important distinction is that the fermentation broth in these processes typically contains unconverted cellulose and hemicellulose, as well

as lignin, fermentation organisms, hydrolysis enzymes, minerals, fermentation nutrients, unrecovered pretreatment chemicals, and other components that depend on feedstock choice and upstream process features. To avoid severe plant maintenance issues, the challenges these components present for distillation must be fully addressed. For example, some pretreatments use sulfuric acid, which is subsequently neutralized with lime to produce gypsum. Gypsum (which has a reverse solubility curve) can foul heat exchanger tubes. The solids can be partially dried and used as boiler fuel to produce heat and electricity for the process (20, 21). It should be noted that the broths produced by the RaBIT and the THF CELF processes consist primarily of water, ethanol, yeast, and nutrients; their similarity to corn and sugarcane ethanol avoids many of the complexities associated with traditional paths to lignocellulosic ethanol.

Providing heat and power

An important distinction among the three sugar-platform pathways that has implications for energy balances and greenhouse gas emissions is how the different processes are powered.

The bagasse residues left after the sugar has been extracted from the sugarcane are burned to provide all the heat and power needed to run the fermentation facility. Because limited fossil fuel inputs are needed to produce sugarcane ethanol, the ratio of ethanol energy output to fossil energy inputs is very high. Furthermore, carbon dioxide released from bagasse combustion is biologically sourced, and therefore is recycled by photosynthesis without net accumulation of carbon dioxide in the atmosphere.

To Atmosphere

Clean

Water

In contrast, the solid residues from corn ethanol production are typically used as animal feed, and the process

.... Vent Scrubber Reer 3 Columr Return to Beer Well 8 Beer Ethanol Product Rectification Column Lignin Separator Water Lignin to Combustor Molecular Sieve Stillage to Water for Adsorption Wastewater Recvcle Treatment

Figure 4. Ethanol is recovered through distillation and molecular sieve adsorption. Source: (21).



is fueled by burning natural gas or coal. Thus, compared to sugarcane, the ratio of ethanol energy output to fossil energy inputs is less favorable.

For lignocellulosic ethanol, burning lignin and undigested cellulosic components can provide all the heat and power needed, with excess electrical power available to export into the grid. Thus, beyond the limited fossil fuels that may be needed to transport feedstock, manufacture fertilizer, and meet other incidental needs, lignocellulosic ethanol has favorable energy ratios and significantly reduces greenhouse gas emissions compared to the use of fossil fuels (20).

Economics of cellulosic ethanol production

To estimate the cost of producing cellulosic ethanol, the National Renewable Energy Laboratory (NREL) has conducted a series of techno-economic studies (21). Some important findings are summarized here.

First, high yields are critical to lower costs and are a necessary, although not sufficient, requirement. For example, for a feedstock that costs about \$80/dry ton at the plant gate, an ethanol yield of 80 gal/dry ton translates into a cost of about \$1.00/gal ethanol (about \$1.50/gal gasoline equivalent).

Because fuel ethanol is a commodity product, feedstock costs are expected to dominate; therefore, to maintain profitability, other costs must be kept low. Thus, it is important to minimize chemical usage for pretreatment, neutralization, pH adjustment, fermentation nutrients, etc. Furthermore, enzyme cost — whether the enzymes are purchased or produced onsite — must be kept low. Current costs are up to about 10/kg of enzyme protein. For typical enzyme loadings and resulting ethanol yields, this enzyme cost translates to about 1.00-1.50/gal ethanol (1.50-2.25/gal gasoline equivalent) (6). This projected enzyme cost is as high as or higher than the anticipated cost of the feedstock (about 1/gal), and is much higher than one would expect to pay for a catalyst used to produce a commodity product. Clearly, enzyme costs remain a challenge.

The cost of lignocellulosic ethanol can also be lowered substantially by developing CBP organisms that can achieve high product yields without added enzymes.

To achieve truly competitive fuel ethanol costs, capital costs must also be kept low. NREL capital investment projections are about \$7/annual ethanol gallon (\$10.40/annual gallon of gasoline equivalent) (21), including onsite enzyme production. Amortizing these costs would contribute approximately \$1.00/gal ethanol (\$1.50/gal gasoline equivalent).

Pretreatment, enzyme production, enzymatic hydrolysis, and fermentation combined are responsible for the largest portion of this overall capital cost (about 36%), with pretreatment and enzymatic hydrolysis (which are needed to overcome lignocellulose recalcitrance) the largest contributors. In addition, making or purchasing enzymes adds significant costs. The cost of overcoming biomass recalcitrance, therefore, dominates overall processing costs.

Equipment to produce electrical power from lignin and unconverted lignocellulose accounts for another 28% of the total capital cost. Wastewater-treatment costs are significant (21%), whereas distillation, product purification, and solids recovery capital costs are low (about 10%). The remaining capital costs are for storage and utilities (5%).

Overall, these estimates highlight the importance of reducing capital costs for deconstructing lignocellulose to sugars. They also show that lignin utilization (by combustion) and wastewater treatment require significant capital investments.

In total, the combined cost of feedstock, enzymes, labor, taxes, etc., and allowing for profit and return on total capital investment, has been estimated to be about \$2.15/gal ethanol (\$3.27/gal gasoline equivalent) (21). However, it is important to keep in mind that cost estimates are very specific to the technology, the site, and the practitioner's risk tolerance, and actual costs can vary considerably from the estimates presented here.

Closing thoughts

Lignocellulosic ethanol offers important advantages for domestic production of liquid transportation fuels and is now reaching commercial production. Because of the limited need for fossil fuels to convert lignocellulose to ethanol, fossil fuel inputs are highly leveraged and therefore reduce net carbon dioxide emissions.

To achieve high product yields, however, biological production of ethanol incurs significant costs for enzymes, as well as large capital and operating costs for pretreatment and enzymatic hydrolysis. Thus, significant advances in pretreatment can dramatically reduce processing costs and thereby accelerate commercialization of lignocellulosic ethanol. In addition, CBP is increasingly recognized as a promising path to achieve this goal by virtually eliminating enzyme production costs, provided product yields and concentrations can be improved.

Regardless of the products targeted (*e.g.*, fuels, chemicals, solvents), the same fundamental recalcitrance barriers must be overcome to achieve low costs for biological conversion of lignocellulose.

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Producing Biofuels via the Carboxylate Platform

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Cesar Granda Earth Energy Renewables The carboxylate platform ferments a wide variety of biomass feedstocks into mixed carboxylic acids and their salts, which in turn can be transformed into hydrocarbon fuels.

ithout added enzymes, the carboxylate platform depolymerizes biomass (*e.g.*, cellulose) into monomers (*e.g.*, glucose), and then ferments these monomers into carboxylate salts (*e.g.*, acetate). Using this platform, nearly all biomass components can be converted into carboxylate salts, which can be chemically transformed into a wide variety of chemicals and hydrocarbon fuels (Figures 1 and 2).

The carboxylate platform capitalizes on fermentations that are thermodynamically driven, and hence does not require sterile operating conditions or genetic engineering. These natural fermentations occur widely, such as in cattle rumen, termite hindguts, swamps, and anaerobic digesters.

Some key intermediate steps require hydrogen, which can be produced from gasified biomass residues. Alternatively, hydrogen can be derived from reformed natural gas, thus creating opportunities for a hybrid system that uses both biomass and abundant natural gas. Some versions of the carboxylate platform derive a large portion of their energy input from hydrogen, which provides an opportunity for



▲ Figure 1. The carboxylate platform converts a wide array of biomass components to carboxylate salts via fermentation.

undigested solid residues or natural gas to contribute significantly to the production of liquid transportation fuels (*e.g.*, gasoline, jet fuel).

Economics

Recent economic evaluations estimate that the minimum selling price of hydrocarbon fuels produced via the carboxylate platform is \$1.00 to \$2.50/gal, depending on the scenario (1, 2). Waste biomass (*e.g.*, municipal solid waste, sewage sludge, manure, agricultural residues) and hydrogen derived from reformed natural gas allow the production of lowerpriced fuels, whereas higher prices are required when the feedstock is an energy crop (*e.g.*, energy cane, high-yield sorghum) and hydrogen is supplied by gasifying undigested residues. At a scale of 2,000 m.t./day, the estimated capital cost is \$3.70/annual-gal of hydrocarbon capacity for a process using biomass gasification, or \$2.60/annual-gal of hydrocarbon capacity for one using reformed natural gas. The latter is comparable to the capital cost of a corn-ethanol plant.







Hydrogen is required to reduce carboxylic acids and increase their energy content (Figure 3). Hydrogen produced from gasifying undigested biomass residues costs about \$3/kg (1); hydrogen derived from natural gas is much less expensive. In the petroleum refining industry, the rule of thumb is that on a Btu basis, hydrogen costs about 30% more than natural gas (including credits for heat recovery, but not capital expenses). When natural gas costs \$5.70/MMBtu (\$5.40/GJ), a refinery with a fully amortized reformer can produce hydrogen for about \$1/kg.

Carboxylate platform

The carboxylate platform ferments glucose to carboxylic acids (*e.g.*, acetic acid). The pH of the fermentation is nearly neutral, so most of the carboxylic acids are present as their carboxylate salts (*e.g.*, acetate), hence the term *carboxylate platform* (3, 4).

In its simplest and most robust form, the carboxylate platform uses a mixed consortium of microorganisms (*e.g., Clostridia, Bacilli*) that transform biomass into carboxylates, namely, short-chain fatty acids (SCFAs, *e.g.*, acetic, propanoic acids) and medium-chain fatty acids (MCFAs, *e.g.*, butanoic, pentanoic, hexanoic, heptanoic, octanoic acids). The mixed-culture fermentation is an example of consolidated bioprocessing, in which the fermenting organisms produce both hydrolytic enzymes (*e.g.*, cellulase) and fermentation products (SCFAs and MCFAs) (5).

Throughout the world, anaerobic digesters are used to break down a wide variety of biomass components (*e.g.*, sewage sludge, manure, food scraps) into biogas, a mixture of methane and carbon dioxide. These digesters are robust, low-tech devices that can be operated by someone with minimal training. Because methane has a low commercial value, it is preferable to inhibit methane production and operate the digester as a stuck fermenter that accumulates the intermediate SCFAs and MCFAs and their salts.

Because of the wide variety of microorganisms present, each with its own specialized niche, a wide variety of biomass components — not just cellulose — can be trans-



Figure 3. Hydrogen is required to reduce carboxylic acids and increase their energy content.

formed into SCFAs and MCFAs (Figure 1). In turn, because so many biomass components (*e.g.*, starch, gums, lipids, proteins) can be digested, this microbial consortium has been described as "the big mouth." The resulting SCFA and MCFA intermediates may be chemically transformed into various chemical and fuel products (Figure 2).

Typically, the sugar platform employs a single microorganism to transform sugar intermediates into final products. Sterile operating conditions are required to ensure that only the desired organism dominates the culture.

In contrast, the carboxylate platform does not require sterility. In fact, soil, rumen fluid, compost, and other natural materials are employed as the inoculum source, and there is no attempt to maintain sterile operating conditions. Nonsterile operating conditions are tolerated, because the carboxylates are nearly at the low energy state; hence, the biological transformations are driven by thermodynamics rather than the challenging task of maintaining monoculture fermentations.

Figure 4 provides more information about the thermodynamics of glucose fermentation. (Cellulose, the main component of lignocellulose, is made of glucose polymer.) The scale quantifies the Gibbs energy efficiency, which is defined as:

$$\eta_G \equiv 1 - (\Delta G^\circ_r / \Delta G^\circ_{combustion})$$

According to this definition, when 1 mole of glucose is converted to 2 moles of lactic acid, the Gibbs energy efficiency is 95.7%. The remaining Gibbs energy (4.3%) is available to be converted to adenosine triphosphate (ATP), an energy molecule that powers cellular metabolism.

Of the various potential products from glucose, lactic acid has the highest Gibbs energy efficiency and, hence, would appear to be the preferred product. However, from the



Figure 4. Gibbs energy efficiency (η_{c}) for biological conversion of glucose to various products.



perspective of the cell, producing lactic acid is not preferred because there is very little energy difference (4.3%) from which to produce ATP. In contrast, cells that produce 3 moles of acetic acid from 1 mole of glucose have a lower Gibbs energy efficiency (91.0%) and a larger energy difference (9.0%) from which to produce ATP. In a mixed culture where there is intense competition for energy resources, cells that can produce acetic acid rather than lactic acid have an advantage because they have more energy available to them.

In an uncontrolled anaerobic digester, products with a lower energy than carboxylic acids can be made. For example, sulfate can be converted to hydrogen sulfide and acetic acid can be converted to methane and carbon dioxide. Both of these reactions are undesirable — hydrogen sulfide is toxic and methane has a low economic value. Fortunately, these undesirable products can be eliminated without much effort. Sulfate-reducing microorganisms can be eliminated by ensuring that sulfate is not added to the fermentation media. Methanogens may be readily eliminated by adding inhibitors or by employing operating conditions that prevent methanogen growth.

In summary, in mixed-culture fermentations of lignocellulosic biomass with modest controls, carboxylic acids and their salts dominate the products.

Biochemistry

Figure 5 summarizes the complex biological pathways that convert cellulose into various products, primarily acids. The biochemistry occurs in three phases:

• enzymatic hydrolysis

• primary fermentation, which converts glucose into various products, such as acids (acetic, propanoic, lactic), solvents (ethanol), and gases (carbon dioxide, hydrogen)

• secondary fermentation, which converts primary products into secondary products, such as MCFAs (butanoic, pentanoic, hexanoic acids) and gases (methane, carbon dioxide).

In the primary fermenters, the first step is glycolysis, a biochemical pathway that converts glucose to pyruvate. Glucose is a more-reduced species than pyruvate; cells capture the difference in reducing potential by converting oxidized nicotinamide adenine dinucleotide (NAD⁺) to its reduced form, NADH. In generic terms, the reduced species, RH_2 , undergoes the following reaction to become the oxidized species R:

 $RH_2 + NAD^+ \rightarrow NADH + H^+ + R$

The enzyme hydrogen dehydrogenase reversibly transforms NADH (and other reduced biological hydrogen carriers) into hydrogen gas:

$$NADH + H^+ \leftrightarrow NAD^+ + H_2$$

In the mixed culture, the hydrogen partial pressure determines whether NAD is in its oxidized form (NAD⁺) or its reduced form (NADH). If the hydrogen partial pressure is low, then the pool of NAD⁺ is abundant, allowing glycolysis to proceed rapidly. If the hydrogen partial pressure is high, the pool of NADH is abundant, thus providing reducing power for many of the subsequent reactions. This interspecies hydrogen transfer, the sharing of reducing power between species, allows the entire consortium of microorganisms to behave as a super-microorganism.

The following classes of microorganisms are typically found in the consortium:

· lactic acid formers convert glucose to lactic acid

• *ethanologens* ferment glucose to ethanol and carbon dioxide (other routes to ethanol include the decarboxylation of lactic acid and the reduction of acetic acid)

• *acidogens* directly ferment glucose to acids such as acetic, propanoic, and butanoic acids (acetic acid can be made from ethanol, which occurs more readily at low hydrogen partial pressure)

acetogens convert carbon dioxide and hydrogen into acetic acid

• *chain elongators* convert carboxylic acids to longerchain carboxylic acids in the presence of reductants (*e.g.*, ethanol, higher alcohols, lactic acid, and hydrogen) or when there is a reducing environment provided by an electrical voltage



▲ Figure 5. The biological pathways in the carboxylate platform include three phases: hydrolysis, primary fermentation, and secondary fermentation.



Table 1. In this mixed-acid fermentation product spectrum, acetic acid is the main component. Chain elongation occurs at low temperatures.							
	Carboxylic Acid Content (by weight)						
Group	Number of Carbons	Systematic Name	Common Name	40°C	55°C		
Short-	2	Ethanoic	Acetic	41%	80%		
Chain Fatty Acid (SCFA)	3	Propanoic	Propionic	15%	4%		
	4	Butanoic	Butyric	21%	15%		
Medium-	5	Pentanoic	Valeric	8%	<1%		
Chain Eatty Acid	6	Hexanoic	Caproic	12%	<1%		
(MCFA)	7	Heptanoic	Enanthic	3%	<1%		
	8	Octanoic	Caprylic	<1%	<1%		
Total 100% 100%							

acetotrophic methanogens convert acetic acid to methane and carbon dioxide

• *hydrogenotrophic methanogens* convert hydrogen and carbon monoxide to methane and water.

The overall reaction sequence is:

$C_6H_{12}O_6 \rightarrow 2 H_3CCO_2H + 2 CO_2 + 2 H_2$	Acidogens
$2 \operatorname{CO}_2 + 2 \operatorname{H}_2 \longrightarrow \operatorname{H}_3 \operatorname{CCO}_2 \operatorname{H}$	Acetogens
$C_6H_{12}O_6 \rightarrow 3H_3CCO_2H$	Net

Theoretically, the carboxylate platform can convert glucose to liquid products with 100% carbon efficiency.

Table 1 summarizes typical product spectrums for mixed-acid fermentations at 40°C and 55°C. In all cases, acetic acid is the dominant component. At elevated temperatures (*e.g.*, 55°C), chain elongation does not occur, whereas it does occur at lower temperatures (*e.g.*, 40°C).

Chemical conversions

The carboxylic acids produced in the fermentation can be converted to chemical and fuel products via three routes:

• *Kolbe electrolysis* (Figure 6). In this route, electrochemistry is used to join two carboxylic acids (or their salts) to form an alkane and two molecules of carbon dioxide. The reaction is slightly exergonic, so, theoretically, the reaction could produce electricity. In practice, however, a small amount of electrical energy input is required to overcome potentials at the electrode surfaces. • Secondary alcohols (Figure 7). Two carboxylic acids are catalytically joined to form a ketone with the loss of one molecule of carbon dioxide. The ketones are hydrogenated to secondary alcohols, which are dehydrated to olefins that are hydrotreated to form saturated hydrocarbons.

• *Primary alcohols* (Figure 8). Carboxylic acids are converted to primary alcohols. Although several routes are possible, here we show a process commercialized by Celanese (6) in which carboxylic acids are catalytically hydrogenated to primary alcohols without the loss of carbon dioxide. The primary alcohols are then dehydrated, oligomerized, and hydrotreated. The reaction conditions during oligomerization (temperature, pressure, residence time, catalyst) determine the mix of products, which include paraffins, olefins, aromatics, and cyclics.

Comparison of options

Table 2 compares options for producing liquid hydrocarbon biofuels. In all cases, cellulose is the biomass source and octane is the hydrocarbon product. Each route requires different amounts of external hydrogen to balance the stoichiometry.

Because the hydrocarbon fuels will be combusted, each approach is compared based on enthalpy efficiency, which is defined as:

$$\eta_H \equiv 1 - \left(\Delta H^{\circ}_r / \Delta H^{\circ}_{combustion}\right)$$

Article continues on next page



▲ Figure 6. Kolbe electrolysis route. Two carboxylic acids are joined to form a hydrocarbon with the loss of two molecules of carbon dioxide.



▲ Figure 7. Secondary alcohols route. Two carboxylic acids are joined to form a ketone with the loss of one molecule of carbon dioxide. The ketones are transformed to saturated hydrocarbons.



Figure 8. Primary alcohols route. Carboxylic acids are converted to primary alcohols, which are transformed to saturated hydrocarbons without the loss of carbon.



Table 2. Comparison of options for producing hydrocarbon fuels from biomass.							
Platform	Yield, kg octane per kg cellulose	ղ _{<i>н</i>}	Input Energy from Hydrogen				
Thermochemical: 2.27 $C_6H_{10}O_5 + 1.14 O_2 \rightarrow C_8H_{18} + 5.64 CO_2 + 2.36 H_2O_2$	0.310	86.0%	0%				
Sugar: 2 $C_6H_{10}O_5 + H_2 \rightarrow C_8H_{18} + 4 CO_2 + 2 H_2O$	0.352	92.9%	4.9%				
Carboxylate (Kolbe Electrolysis): 1.67 $C_6H_{10}O_5 + 5 H_2 \rightarrow C_8H_{18} + 2 CO_2 + 4.33 H_2O_2$	0.422	89.7%	23.4%				
Carboxylate (2° Alcohol): 1.5 $C_6H_{10}O_5$ + 7 $H_2 \rightarrow C_8H_{18}$ + CO_2 + 5.5 H_2O	0.469	88.2%	32.3%				
Carboxylate (1° Alcohol): 1.33 $C_6H_{10}O_5$ + 9 $H_2 \rightarrow C_8H_{18}$ + 6.67 H_2O	0.528	86.8%	40.8%				

Of the five routes, the sugar platform is the most efficient and the thermochemical route is the least efficient; however, the range is narrow (86.0%–92.9%). The reactions are arranged in order from lowest octane yield (31.0%) to the highest (52.8%). The higher yields are achieved by increasing the amount of external hydrogen supplied to the reaction, which reduces the amount of carbon lost as carbon dioxide. The primary alcohol route to hydrocarbon fuels has the highest possible yield, because there is no loss of carbon dioxide.

In principle, all of the routes could achieve this upper limit by collecting the emitted carbon dioxide, reducing it with hydrogen, and converting it to hydrocarbons via Fischer-Tropsch or other appropriate technology. The advantage of the carboxylate platform is that intermediates (*e.g.*, acids, ketones, alcohols) are liquids that can be readily transported.

This approach allows for distributed processing (Figure 9), where biomass is converted to liquid intermediates at a local facility, thus eliminating the need to transport biomass long distances. The liquid intermediates are shipped to a central facility (*e.g.*, oil refinery) equipped with natural gas reformers that produce inexpensive hydrogen. If desired,



▲ Figure 9. Distributed processing using the carboxylate platform. Farms produce high-yield biomass, which is harvested and transported a short distance via truck to satellite fermentors. Fermentation broth is piped to a plant that converts the broth to intermediate liquids (*e.g.*, ketones, acids, alcohols), which are piped to an oil refinery, where they are upgraded to hydrocarbon fuels that are distributed to market via existing pipelines.

the CO_2 produced by the reformer can be sequestered, thus allowing the use of abundant, low-cost natural gas without emitting net carbon dioxide into the atmosphere.

Biological conversions

In addition to the chemical conversion described in the previous section, carboxylates can also be biologically converted to chemicals and fuels. For instance, a well-known process is the biological conversion of SCFAs and MCFAs to polyhydroxyalkanoates (PHAs), which are precursors to bioplastics (7). Some algae, yeast, and bacteria can grow on carboxylates to produce lipids and hydrocarbons that are precursors to chemicals and fuels (8-10).

The biological conversion of carboxylates to other valuable products (*e.g.*, lipids and hydrocarbons) is analogous to the conversion of sugars in the sugar platform. The advantage of the carboxylate platform is that SCFAs and MCFAs are much less expensive to produce than sugars. In addition, because of the "big mouth" characteristic of the carboxylate platform, SCFAs and MCFAs may also be produced from feedstocks that contain little sugar, such as sewage sludge, manure, and cell bodies (*e.g.*, algae) from which high-value product has been extracted.

Closing thoughts

Using a mixed culture of microorganisms, the carboxylate platform ferments a wide variety of biomass feedstocks into mixed carboxylic acids (SCFAs and MCFAs) and their salts. Chemical reactions then transform these biological intermediates into industrial chemicals and hydrocarbon fuels. Depending on the process selected, as much as 41% of the energy content of the fuel can be derived from hydrogen, which can be made inexpensively from abundant natural gas. Also, the carboxylate platform allows for the subsequent biological conversion of carboxylates to valuable products, such as lipids and hydrocarbons. The main advantages of the carboxylate platform include flexible feedstocks, higher yields, scalability, nonsterile operating conditions, and the use of an active and stable natural mixed consortium. Furthermore, the carboxylate platform can be practiced in a distributed manner that integrates well with CEP existing infrastructure.

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Scaling Up Bioenergy Technologies

DAVID EDWARDS, P.ENG. Zeton Inc. The stage-gate technique used for traditional chemical processes must be modified for bioenergy technologies. Follow these recommendations to minimize risk and maximize success.

A stage-gate method can be used to scale up biofuels processes, such as fermentation, thermochemical pyrolysis or gasification, and catalytic and enzymatic processes that convert biomass to ethanol and other fuels and products. However, the approach developed for traditional chemical process industries (CPI) projects must be modified to account for challenges related to processing the fluids and handling the solids in bioenergy processes. Because of these challenges, the scaling factors in going from one scale to the next (*i.e.*, laboratory to pilot to demonstration to commercial) are an order of magnitude lower for bioenergy processes than for similar CPI processes.



▲ Figure 1. A new technology is scaled up through progressively larger-scale stages. The differences between biofuels processes and conventional CPI technologies require modifications to the stage-gate process.

This article discusses the stage-gate approach for scaling up biofuels technologies, emphasizing how this approach differs from the traditional stage-gate process used in the CPI. It identifies the most common challenges encountered when scaling a biofuel process and offers recommendations for addressing these challenges. Finally, the article provides estimates of scaling factors for biofuels processes and compares them to the scaling factors for traditional CPI processes.

Technology stage gates

The stage-gate process (Figure 1) divides the scale-up of a technology into stages, each successively larger in scale than the previous — laboratory, pilot, demonstration, commercial. In this way, the viability of the technology can be assessed without taking on the large financial risks associated with scaling a technology directly from the lab scale to

the commercial scale.

Lab scale. Equipment and systems used in the lab are important earlystage tools for assessing a new biofuels technology. Such systems are highly automated and customized for the application, and are a precursor to larger pilotand demonstration-scale plants. Figure 2 shows a lab-scale ebullated-bed reactor for continuously upgrading bio-oil.

Laboratories typically assess continuous-stirred tank reactor (CSTR) or autoclave processes in batch equipment,





▲ Figure 2. This lab-scale ebullated-bed reactor with internal recirculation is used to upgrade bio-based oil. Photo courtesy of Zeton.

and assess fixed- or fluidized-bed reactors in once-through systems. In batch-autoclave applications, researchers manually load solids into the vessel, close the vessel, and run the system at the desired temperature and pressure for a specific residence time. In once-through fixed- or fluidized-bed reactor applications, the feed is added and the product removed continuously. Researchers can then plot reaction yield and selectivity for a range of operating conditions. Reactor volumes in lab-scale systems are typically less than 1,000 mL.

A frequent challenge for bioenergy projects at the lab scale is reliable solids feeding, especially at the high feed pressures required by some processes. To address this, researchers should test prototype feed systems with a representative

BIOENERGY VS. CHEMICAL PROCESSES

The differences between traditional CPI processes and bioenergy technologies have several important implications:

• Bioenergy demonstration plants are often smaller, with a much lower nameplate capacity, than demonstration plants for traditional CPI processes.

• Bioenergy plants may have limited turndown, because the flow of solids is not as easily controlled as the flow of gases or liquids.

 It might be possible to skip a development step for a traditional CPI process, if there is sufficient confidence in the lab and pilot data. This is rarely the case for bioenergy processes, where the scale-up work is often being carried out for the first time.

 The overall development cycles are longer for bioenergy processes than for traditional CPI processes.

• The commissioning period for bioenergy plants is also longer (up to twice as long) than for traditional CPI plants of similar scale.



▲ Figure 3. Solids handling should be carefully considered as early as possible in the development of biofuels technologies. A lab-scale (100-g/hr) pressurized feed system is shown here. Photo courtesy of Zeton.

biomass sample. The custom-designed lab-scale solids feeder in Figure 3 is capable of feeding biomass (wood) at a nominal rate of 100 g/hr at pressures up to 700 psi.

Pilot scale. Pilot plants provide the first window into continuous processing, and often incorporate unreacted feed or product recycle systems. Figure 4 shows a traditional CPI pilot plant that has been modified to include continuous biomass feeding equipment for a biomass catalytic cracking application.

Catalyst performance tests are carried out to determine, or confirm, yield and selectivity, and the lifetime of the catalyst is measured under varying operating conditions. Reactor size at the pilot-plant scale typically ranges between 1 L and 100 L.

For predominantly batch processes in which solids handling is not a major concern, scale-up from a pilot plant directly to a commercial plant may be possible. Continuous processes, such as those employing fixed- or fluidized-bed reactors, typically require scale-up from pilot to demonstration scale.

Demonstration scale. Demonstration plants differ from pilot plants in that the equipment and process flow much more closely resemble those of commercial-scale operations. Extended operating runs permit catalyst lifetime studies over a longer period of time, and significant quantities of final product can be produced for market testing. The demonstration-plant stage is the final technology hurdle before commercialization.

Demonstration plants can have significantly higher capital and operating costs than pilot plants, and are typically



not employed until the process technology is already well developed. They are often installed at the site of the future commercial plant to take advantage of existing infrastructure, utilities, operating permits, and zoning provisions.

While reactor volumes in traditional catalytic processes are typically 100–1,000 L at the demonstration scale, they are much larger for biological processes (10,000–40,000 L). This is because reaction rates and yields are much lower in biological systems than in catalytic systems. The demonstration plant in Figure 5 features a 40,000-L bioreactor for the production of cellulosic ethanol.

For continuous bioenergy and biofuels processes involving solids handling, the demonstration plant is an essential risk-mitigation step. The inherent risk in scaling continuous biofuels and bioenergy processes directly to the commercial scale based on lab or pilot data is, in most cases, too large to be given serious consideration. Technology developers need to go through the demonstration scale to prove to the market and investors that their technology meets performance expectations and is ready for commercialization.

Challenges in bioenergy process development

While the recommended approach for scaling bioenergy technologies follows steps similar to those for scaling chemical processes, several factors must be carefully considered. Table 1 lists the most common challenges.

Solids handling is much more difficult to scale than liquid and gas handling. Systems for handling solids are commonly constrained by geometry and physical limits. For example, the smallest outlet through which a material can easily flow may be much larger than the process lines in a pilot plant.

Solids-handling applications are also less forgiving than liquid and gas applications. Minor changes, such as changes in moisture content or particle size, can significantly impact solids-handling systems. It is not uncommon for a system to work well for one material and not work at all for another material with similar properties.

Designing a feed system to handle corn stover and pine sawdust illustrates this challenge. Even if their particles are similarly sized, the flowability of these two materials is noticeably different. Pine sawdust has a more uniform particle shape, whereas corn stover consists of long fibers that have a higher propensity for arching. In small-diameter feed screws, the corn stover fibers tend to bind together, which requires a higher mechanical torque. This will likely require the use of multiple screw feeders in custom-machined sizes with variable feed rates tailored for different types of biomass of varying properties.

Solids fluidization is a challenge in pilot-scale reactors. At smaller reactor diameters, wall effects are larger and the propensity for slugging is greater. In some cases, the minimum safe diameter for a reactor dictates the total output of the plant. Thus, it is important to use a system that allows for careful control of the bed particle size, shape, and hardness, and to develop methods to mitigate attrition, such as continuous replacement of bed material.

Leakage may be a concern in high-pressure applications, especially those handling hazardous process gases (*e.g.*, synthesis gas). Continuous processes require feed systems that continuously introduce biomass into the reactor, and all of these components have an inherent leakage rate. The allowance for leakage must be carefully considered at the early stages of the project, as it can significantly affect the capital and operating costs of the commercial plant.

Biomass-handling plants may have limited turndown, because the flow of solids is not as easily controlled as the flow of liquids or gases. For example, a cyclone separator achieves maximum efficiency at a very specific flowrate, and as the volumetric flowrate decreases, the particle-separation efficiency also decreases.



▲ Figure 4. A traditional CPI pilot plant has been modified to include a continuous biomass feed system. Photo courtesy of Zeton.



▲ Figure 5. Coskata's fully integrated demonstration-scale facility was a critical step in the development and demonstration of the company's feedstock-flexible technology. Photo courtesy of Coskata, Inc.



Table 1. Common challenges encounter	ed
in scaling up biofuels technologies.	

Varying physical and chemical properties of solid biomass feeds

Continuous pressurized solids feeding and handling, including collection of solids byproducts and removal of ash and char

Condensing bio-oil vapors and associated formation of aerosol

Hot-gas filtering in thermochemical-conversion processes

Bio-oil upgrading, stability, and varying physical and chemical properties of bio-oil during processing

High-temperature solids circulation and processing

Operating small-diameter fluidized beds with low feed rates at the lab scale

Tar formation and removal in gasification processes

Recommendations

The success of a bioenergy scale-up project will largely depend on how these challenges are addressed. Here are several suggestions for dealing with them:

• Line metal surfaces with a refractory material to handle the high operating temperatures typically seen in thermochemical conversion processes.

• Purge instrument impulse lines to prevent solids plugging, and use gas pulsing to clear filter elements.

• Develop prototype micro- and lab-scale solids-feeding systems using actual biomass feed samples.

• Use multiple screw feeders in custom-machined sizes with variable feedrates that can handle different biomass feeds with varying properties.

• Use specially designed mechanical devices that eliminate tar build-up to prevent plugging.

• Use direct-contact circulating scrubbing systems for bio-oil condensation in thermochemical processes to minimize aerosol formation (rather than using indirect condensation, which is often incapable of condensing bio-oil vapors).

Scaling factors

The scaling factor for any particular process is highly specific to the technology under investigation and management's level of comfort with the scale-up risk. Table 2 compares scaling factors for bioenergy projects with the scaling factors often used for more traditional CPI liquid- and gasbased processes. These factors are based on Zeton's experience in scaling many different bioenergy and traditional CPI technologies.

The typical scaling factors for bioenergy processes are an order of magnitude lower, or more conservative, than those for similar CPI processes. This is a direct result of the inherent challenges with biomass processing, and the fact that there is little published data, and a lack of experience in general, related to the scale-up of advanced bioenergy processes.

lable 2. Scaling factors for biofuels processes are typically lower than those for traditional CPI technologies.						
Scale	Traditional CPI	Biofuels Processes				
Lab/Bench	0.001–0.1 (1–10 mL/min)	0.01–0.1 (1–10 g/hr)				
Pilot	1 (1–5 L/hr)	1 (1–5 kg/hr)				
Demonstration	100–1,000* (5–100 bbl/day)	10–100 [†] (1–5 m.t./hr)				
Commercial	10,000–30,000 (30,000–100,000 bbl/day)	1,000–5,000 (200–1,000+ m.t./hr)				

* For well-understood and established processes for which a commercial plant already exists, data from the pilot plant can be correlated directly to the commercial scale, bypassing the demonstration plant stage.

[†] The demonstration plant is an essential risk-mitigation step for bioenergy and biofuels projects involving solid-biomass handling, as well as for more traditional CPI gas and liquid processes involving novel or unproven technologies.

Closing thoughts

Consider these key tips for scaling up a bioenergy technology:

First, in planning the timeframe to develop the technology through the pilot and demonstration stages, remember that the start-up and commissioning time for such plants will be longer than for traditional CPI plants due to the extra time required to fine-tune the solids-handling system.

Second, the scaling factors used from lab through pilot and demonstration to commercial scale are an order of magnitude lower for bioenergy plants than for traditional CPI processes due to the challenges associated with solids handling.

Third, it is important to answer questions regarding the intellectual property (IP) involved in the bioenergy technology you are scaling up. Partnering with suppliers with a proven track record of success in similar applications will shorten the technology scale-up cycle, while also, with appropriate foresight, protecting and strengthening your company's IP position.

ADDITIONAL RESOURCES

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Commercial-Scale Production of Lignocellulosic Biofuels

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or the biofuels industry, 2014 proved to be a breakthrough year. Three new commercial-scale cellulosic ethanol plants started production in the U.S. Two additional facilities, one each in Brazil and Italy, came online, and many others are being planned for Brazil, China, India, Italy, Macedonia, Malaysia, Slovakia, and the U.S.

These cellulosic biofuels plants are relatively small, even by the standards of the grain-ethanol industry, ranging in size from 3 million gal/yr (MGY) to 50 MGY. As the technology matures, it is expected that plants will approach 100 MGY, a practical limit imposed by the logistics of moving and storing up to 2,000 m.t./day of low-density cellulosic biomass.

A few cellulosic biofuel facilities have begun operation, and others are slated to start up in the coming years.

> This article reports on the status of existing and planned cellulosic biofuels plants throughout the world, offering a glimpse into this developing industry.

Thermochemical platform

Table 1 summarizes the commercial cellulosic-biofuel plants based on the thermochemical platform that are planned or currently in operation. While some of these plants have achieved their operational goals, others have encountered obstacles.

For example, a hybrid gasification plant built by INEOS Bio in 2013 has experienced some operational

Table 1. Commercial-scale cellulosic-biofuel projects using the thermochemical platform currently in operation or expected to open.							
Company	Pathway	Location	Opening Year	Capacity, MGY	Feedstock	Cost, US\$ million	
INEOS Bio	Gasification and fermentation to ethanol	Vero Beach, FL	2013	8	Wood and vegetable waste	\$130	
Enerkem	Gasification and synthesis of methanol and ethanol	Edmonton, AB Canada	2014	10	Municipal waste	\$75	
Lanzatech	Gasification and fermentation to ethanol	Soperton, GA	2015	10	Wood waste, miscanthus	N/A	
CoolPlanet	Catalytic pyrolysis to reformate and fuel oil	Alexandria, LA	2016	10	Yellow pine	\$56	
Fulcrum Sierra Biofuels	Gasification and synthesis to ethanol	McCarren, NV	2016	11	Municipal waste	\$266	



difficulties. The facility biologically ferments syngas produced during gasification to ethanol. However, unexpectedly high concentrations of hydrogen sulfide in the syngas, which poisons the ethanol-producing microorganisms, have prevented the plant from making significant quantities of fuel.

Operational difficulties and low product yields forced another plant to shut down. KiOR completed construction of a pyrolysis plant in Columbus, MS, in 2012 that was to be the first of several such plants. It produced a few hundred thousand gallons of drop-in cellulosic biofuels, but was unable to overcome a variety of problems, including the generation of fines during feeding and processing as well as difficulties achieving target product yields. Eventually, the company ran out of cash and had to shut down the facility pending its sale.

Sundrop Fuels canceled plans for a gasification plant in

Alexandria, LA, in favor of using less-expensive natural gas as feedstock. The plant was to produce 50 MGY of gasoline from woody biomass using ExxonMobil's methanol-togasification technology.

Sugar platform

Table 2 summarizes the commercial cellulosic-biofuel plants based on the sugar platform that are planned or are currently in operation.

Abengoa, POET-DSM, and DuPont Danisco are responsible for the first U.S. cellulosic-biofuel facilities of their size to become operational. Their success is an important factor in the future of the cellulosic-biofuel industry in the U.S. The Abengoa and POET-DSM plants recently began operation in 2014, while the DuPont Danisco plant is expected to be completed early this year.

Beta Renewables — a joint venture between Chemtex,

Table 2. Commercial-scale cellulosic-biofuel projects using the sugar platform currently in operation or expected to open.							
Company	Pathway	Location	Opening Year	Capacity, MGY	Feedstock	Cost, US\$ million	
Abengoa Bioenergy	Enzymatic hydrolysis to ethanol	Hugoton, KS	2014	25	Corn stover, wheat straw, and grasses	\$231	
Beta Renewables	Enzymatic hydrolysis to ethanol	Crescentino, Italy	2014	20	Wheat straw	N/A	
GranBio	Enzymatic hydrolysis to ethanol	Alagoas, Brazil	2014	22	Sugarcane straw	\$195	
POET-DSM	Enzymatic hydrolysis to ethanol	Emmetsburg, IA	2014	20	Corn stover and cobs	\$250	
Quad County Corn Processors	Enzymatic hydrolysis to ethanol	Galva, IA	2014	2	Corn fiber	\$9	
Raizen	Enzymatic hydrolysis to ethanol	Brazil	2014	10	Sugarcane bagasse	\$100	
DuPont Danisco	Enzymatic hydrolysis to ethanol	Nevada, IA	2015	25	Corn stover	\$276	
Beta Renewables	Enzymatic hydrolysis to ethanol	Clinton, NC	2016	20	Energy grass	\$200	
Canergy	Enzymatic hydrolysis to ethanol	U.S.	2017	25	Energy cane	N/A	
Energochemica	Enzymatic hydrolysis to ethanol	Slovakia	2017	16.5	Wheat and rapeseed straw	N/A	
Mascoma	Consolidated bioprocessing	Drayton Valley, AB Canada	Delayed	20	Hardwood and pulpwood	\$200	
DuPont Biofuel Solutions- Ethanol Europe	Enzymatic hydrolysis to ethanol	Macedonia	N/A	N/A	Agricultural residues	N/A	
MG Chemicals and Anhui	Enzymatic hydrolysis to ethanol	China	N/A	20	Agricultural residues	N/A	
Progetti Italia	Enzymatic hydrolysis to ethanol	Italy	N/A	N/A	Agricultural residues and energy crops	N/A	



Table 3. The planned commercial-scale cellulosic-biofuel project using the carboxylate platform.						
Company	Pathway	Location	Opening Year	Capacity, MGY	Feedstock	Cost, US\$ million
ZeaChem	Gasification and synthesis to ethanol	Boardman, OR	Delayed	25	Agricultural residues, hybrid poplar	\$391

TPG, and TPG Biotech — has an operational plant in Italy and is planning construction of a plant in North Carolina. It has also licensed its technology package for the production of cellulosic ethanol in Brazil, Italy, China, India, and Slovakia. Once in production, these plants will have a total capacity of 200 MGY.

GranBio is a Brazilian second-generation fuels and chemicals producer that licensed Beta Renewable's technology package and started a 22-MGY ethanol plant in northeast Brazil. The company plans to increase its total production to 250 MGY with additional plants by 2020, but this depends on market conditions.

Corn-ethanol producers can add value to their current plants with little capital investment by producing cellulosic ethanol in addition to corn ethanol. For example, Quad County Corn Processors in Galva, IA, produces primarily corn-ethanol. However, it licensed Syngenta Cellerate's process technology to convert waste corn kernel fiber into cellulosic ethanol. The company needed to invest only \$9 million to add to its existing corn-ethanol infrastructure to produce 2 MGY of cellulosic ethanol — a small but significant boost to its 35 MGY of grain ethanol.

A joint venture between Mascoma and Valero planned to build a 40-MGY cellulosic ethanol facility utilizing consolidated bioprocessing (CBP) — an advanced biochemical pathway that some considered to be the future of cellulosic ethanol. The CBP process combines enzyme production, enzymatic hydrolysis, and fermentation of the resulting sugars in a single step. Valero pulled out of this \$232 million project in 2013, and Mascoma's CEO has stated that the project is now unlikely to happen. Mascoma is attempting to gain financing for a second \$200 million, 20-MGY project also based on consolidated bioprocessing.

Carboxylate platform

ZeaChem is currently the only company planning a cellulosic-biofuel plant based on the carboxylate platform (Table 3). Its process extracts sugars from woody biomass and subsequently ferments the sugars to acetic acid, while the lignin-rich residue is gasified to produce hydrogen. The acetic acid is catalytically converted to ethyl acetate and then hydrogenated to ethanol. ZeaChem intends to build a 25-MGY facility using this technology, but plans have been put on indefinite hold because of lack of funding.

Closing thoughts

By the end of 2016, commercial-scale cellulosic-biofuel capacity in the U.S. will be 116 MGY. Of that, 106 MGY is expected to be ethanol; about 60% (by volume) will be made by enzymatic hydrolysis processes, while around 40% will be produced by gasification and pyrolysis technologies. The remaining 10 MGY will be drop-in biofuels — *i.e.*, biofuels that are similar to those derived from petroleum, and therefore can be used at much higher blend rates.

This is well below the 266 MGY of capacity that a 2012 survey of the industry expected to be online within four years (1). Furthermore, it is a small fraction of the 16 billion gal of cellulosic biofuels required to meet the U.S. Renewable Fuel Standard (RFS2) biofuels mandate for 2022. However, the future of the RFS2 is uncertain. In 2013, the U.S. Environmental Protection Agency (EPA) proposed reducing its requirements, and Congress is considering bills to reform or even repeal the mandate.

It seems likely that Brazil and China will continue to invest in and drive down the costs of producing cellulosic ethanol. These countries need low-carbon fuel sources that make better use of land and do not use food as a feedstock.

Large multinational companies will continue to develop technology and reduce costs for converting biomass to ethanol. Most of these larger technology developers have a licensing business model. International companies like Clariant (Germany) and Praj (India) are developing and piloting new conversion technology packages that they hope to license to smaller companies with fewer research and development resources.

Throughout the world, biomass conversion costs are being driven downward by advances in technology. Many countries have low feedstock and capital costs along with growing demand. Therefore, cellulosic ethanol production and consumption are expected to continue to grow in the U.S., as well as globally. The industry's string of successes in 2014 will make it possible for cellulosic biofuel to play a crucial role in a world focused on reducing greenhouse gas emissions, while finding an inexpensive and sustainable alternative to finite petroleum reserves.

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