Agricultural Chemistry and Bioenergy

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Renewed interest in converting biomass to biofuels such as ethanol, other forms of bioenergy, and bioenergy byproducts or coproducts of commercial value opens opportunities for chemists, including agricultural chemists and related disciplines. Applications include feedstock characterization and quantification of structural changes resulting from genetic modification and of the intermediates formed during enzymatic and chemical processing; development of improved processes for utilizing chemical coproducts such as lactic acid and glycerol; development of alternative biofuels such as methanol, butanol, and hydrogen; and ways to reduce greenhouse gas emission and/or use carbon dioxide beneficially. Chemists will also be heavily involved in detailing the phytochemical composition of alternative energy crops and genetically improved crops. A resurgence of demand for agricultural chemistry and related disciplines argues for increasing output through targeted programs and on-the-job training.

THE NEW IMPERATIVES FOR BIOENERGY

Renewable energy, particularly to augment or replace gasoline as a transportation fuel, is now capturing a good share of the headlines in the United States and worldwide. Among many factors driving this trend are the cost and uncertain supplies of fossil fuels; the rising levels of carbon dioxide in the atmosphere; the rapid development of sugarcane- and corn-based biorefineries producing bioethanol—the replacement liquid fuel of choice for the present at least; and continuing development of vegetable-based biodiesel fuels that can substitute for petroleum diesel.

The perspectives provided by Professor Bruce Dale based upon his comments upon receiving the USDA Agricultural Research Service Sterling B. Hendricks award in 2007 (*1*) point out several opportunities for research to support a sustainable, biobased economy for the future. This paper will follow this theme, focusing on research needs that chemists in general, and agricultural chemists in particular, are well suited to address. This is an exciting time to be in agricultural research, considering the rapid expansion of biofuels production, the need to reduce greenhouse gas emissions, and society's adoption of the concept of "greening".

For bioethanol production, present technology relies largely on the fermentation of sugars or starch to ethanol using fermentation technology that has been known for many years (*2*). The cost of enzymes for hydrolysis has been reduced considerably, and other processing costs continue to improve as market economics and competition between producers evolves. This represents a maturing of pre-existing technologies rather than fundamental new breakthroughs in the underlying

science, although major improvements in fermentation technology and other related areas are taking place with renewed urgency (*3*). Conversion of cane sugar, corn starch, or other sugar or starch feedstocks can only partially break our "addiction to oil" (*4*). The U.S. currently produces only enough ethanol from corn to meet roughly 3% of its liquid transportation fuel requirements (by volume) and does so using ~25% of domestic corn supply. More specifically, current U.S. ethanol capacity (as of January 2008) is 7.5 billion gallons per year from 136 plants, with another 62 plants under construction with potential additional capacity of 5.8 billion gallons (*5*). In 2005, the United States passed Brazil and became the world's number one ethanol producer. The Energy Independence and Security Act of 2007 expands the Renewable Fuels Standard (RFS) by requiring annual use of 36 billion gallons of renewable fuel by 2022.

Even at the relatively modest 2008 levels, ethanol production has caused a significant effect in the agricultural commodity markets, with corn roughly doubling in price from only a few years ago, and food and feed prices up significantly (i.e., milk prices are up 29% in 2007 alone). Spot market wheat prices, which remained under $4/bushel for years, have risen to beyond $18/bushel. Ramping up to a supply of 6% or more of U.S. transportation fuel using corn grain as the primary feedstock, while technically feasible, could even more dramatically affect the "food/feed versus fuel" dynamic (*6*). Questions are also being raised about the environmental costs of biofuels production and the overall affect on global carbon emissions. As the food supply tightens, in part because of biofuels, more land is required to meet our agricultural needs, increasing pressure to deforest lands such as the Amazon basin.

The term "biorefinery" itself raises some questions. A biorefinery is defined by the National Renewable Energy Laboratory (http://www.nrel.gov/biomass/biorefinery.html) as a facility that integrates biomass conversion processes and equip-

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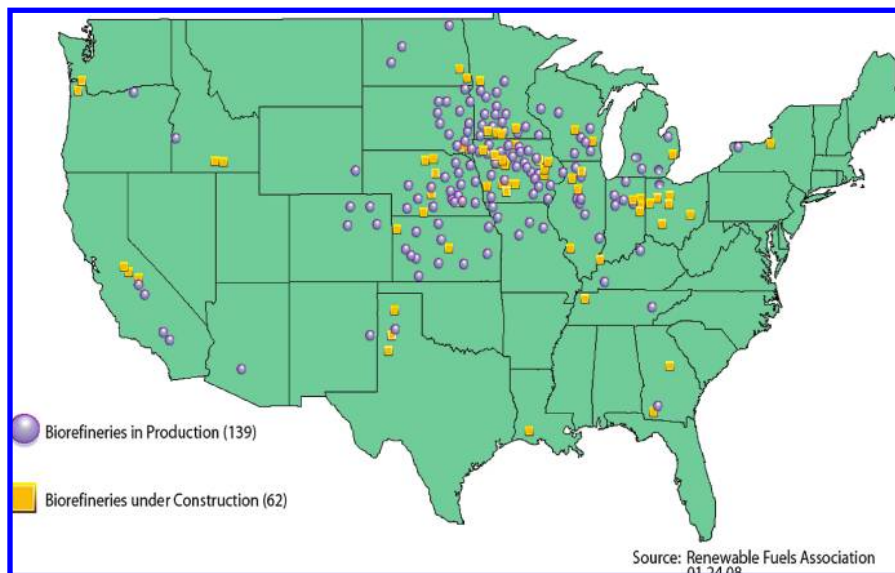*J. Agric. Food Chem.,* Vol. 56, No. 11, 2008   **3893**

Figure 1. Map of ethanol biorefineries in the United States (*5*).

ment to produce fuels, power, and chemicals from biomass, analogous to today's petroleum refineries. By some definitions, a corn wet mill and a sugar mill that produces sugar, molasses, energy, and bagasse are biorefineries. More and more, though, this term is used to describe plants that focus on bioenergy production, such as the more efficient corn dry-grind mills that have better "energy returns" than most wet mills.

CELLULOSIC CONVERSION

It is clear that large-scale use of ethanol will require conversion of cellulose and other underutilized biomass feedstocks (*7*). Cellulosic feedstocks increase available biomass beyond the grain supply, reducing competition with food but not necessarily feed. More importantly, cellulosic conversion provides a better return on input energy (i.e., the fuel required during production) and has the potential to reduce the emission of greenhouse gases per unit of energy produced (*7*).

Another argument for cellulosic ethanol is geographic, that is, the need to supply ethanol beyond the U.S. Corn Belt via diverse feedstocks. A map of ethanol biorefineries in the United States (**Figure 1**) (*5*) shows that the majority of ethanol production is in the U.S. Midwest, not near the majority of the country's largest cities and not near existing oil refineries, which are almost exclusively near the coasts; i.e., Houston, the Gulf Coast, California, and the New York area. Ethanol cannot be transported in existing gas pipelines because of water uptake and corrosion issues and so must be shipped long distances by rail or tank trucks. Conversion of cellulosic feedstocks to biofuels via commercially viable processes would expand the available feedstocks beyond corn, adding much needed geographical flexibility to the U.S. biofuels industry. For example, cellulosics isolated from municipal solid waste (MSW) are available now to provide additional ethanol using a pre-existing transportation infrastructure. MSW to ethanol can potentially bridge the gap until substrates such as straw, bagasse, energy crops, and timber sources reach commercial viability. MSW is already converted to methane and electricity via advanced digesters and incineration systems, respectively, although this practice is only in its starting phase in the United States, with fewer than 107 such garbage-fueled waste-to-energy plants (*8*). Europe and Asia are much further along in this particular arena.

CHEMICAL COMPONENTS OF THE PLANT CELL WALL

Future technological advances in cellulosic conversion will be based on better understanding of plant cell walls (*9*), their polysaccharide and lignin components, the morphological arrangement of these components, and the ways to economically unwind their complex structures. Plants contain three primary types of carbon-based polymers, cellulose, hemicellulose, and lignin (**Figure 2**). Cellulose, a glucose-based polymer consisting of two β-1,4 linked glucose residues (cellobiose) in their repeating units (**Figure 2a**) can be hydrolyzed to monomeric glucose. The microfibril scaffold of the cell wall consists of both crystalline and amorphous domains within a largely cellulosic core—a structure that limits methods for hydrolysis.

Hemicellulose (**Figure 2b**), a branched polymer of predominately xylose and related pentoses, may be the "weak link" in cellulosic conversion technology. It is not readily converted to biofuels by traditional microbes in industrial-scale fermentation. Improved yeasts (*10, 11*) and bacteria (*12, 13*) allow for utilization of hemicellulose-derived sugars, but hemicellulose conversion is not without cost. The longer fermentation times resulting from use of xylose sugars incur significantly greater capital costs (larger fermentors). Hemicelluloses are cross-linked via ester linkages to predominately cinnamic (ferulic) acids (**Figure 2c**), forming covalent linkages with lignin (*14*), making plant cell wall hydrolysis even more difficult.

Lignin, a highly branched aromatic polymer of largely guaiacyl and syringyl monomers with connecting three-carbon aliphatic sidechains (see **Figure 2d**), provides structural rigidity to cell wall architecture and increases its hydrophobicity—factors that, along with cellulose crystallinity, impede the breakdown of cell walls for facile conversion to ethanol (*3*).

Historically seen as a waste product (*15*), lignin will likely become a valuable source of renewable energy to the biorefinery, minimizing the need to purchase external fuel. The future may see development of other significant uses for lignin, especially as chemists make improvements in gasification, syngas reformation (i.e., Fischer−Tropsch catalysis), new plastics and adhesives, and new chemical platforms derived by utilizing lignin's phenolic-rich composition. Assessing economic viability will depend on advanced analysis of thermodynamics, coupled with
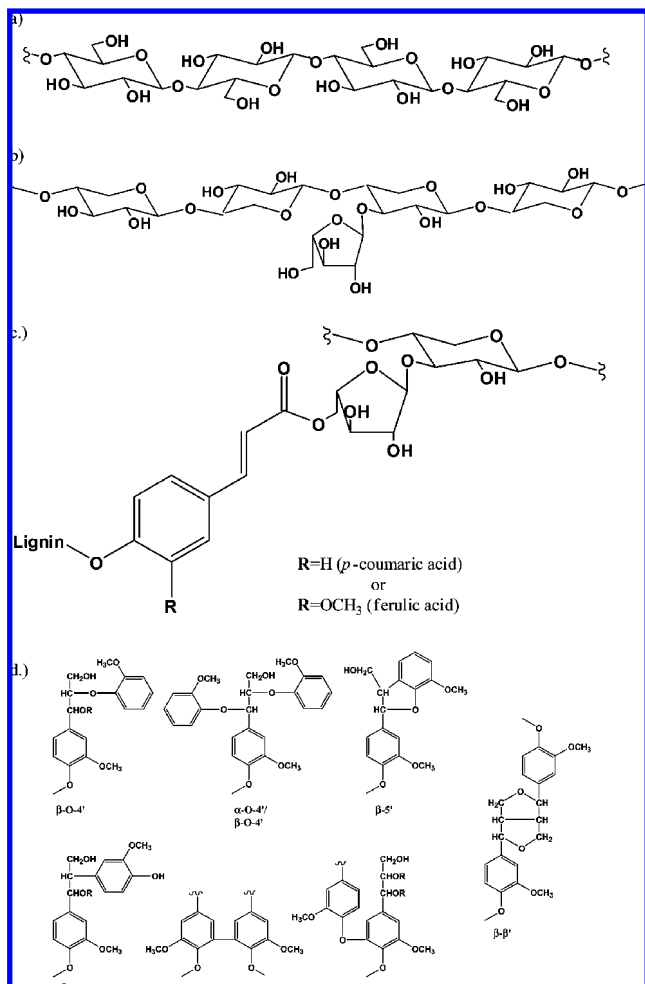
Figure 2. Structures of (**a**) cellulose, (**b**) arabinoxylan (an example of hemicellulose), (**c**) ferulic linkages between xylans and lignin, and (**d**) lignin subunit linkages. Lignin consists of random copolymers of these major subunits.

life cycle analysis, areas that have long been prime areas of interest to agricultural engineers and chemists.

Optimal conversion of cellulosic feedstocks to biofuels represents both a challenge and an opportunity as biofuels and biobased products increasingly become the targets for future development. Specific research needs include

• feedstock characterization, including deciphering unknowns associated with plant cell wall architecture,

• optimizing hydrolysis of cellulose and hemicellulose to "fermentable" sugars,

• characterization/minimization of fermentation inhibitors,

• utilization of the potential energy of lignin through cogeneration and/or syngas conversion to liquid transportation,

• new value-added products from lignin,

• production of other fuels besides ethanol (e.g., methanol, butanol, or hydrogen)

• production of gas or liquid fuels via thermal methods (pyrolysis, gasification),

• optimizing production of methane from biomass and other anaerobic fermentation products, and

• development of nonfuel coproducts (solvents, monomers, etc.) from cellulosic feedstocks.

NEW APPLICATIONS OF ANALYTICAL CHEMISTRY

All of these research opportunities require new applications of chemistry, with a significant requirement for inter- and

multidisciplinary research. Techniques familiar to organic chemists, such as NMR (including solid state NMR) and near-infrared spectroscopy, offer potential for in situ characterization of plant matter on both the macroscale and microscale. Proteomics and companion fields in their relative infancy—glycomics and lipomics—can allow more rapid and complete characterization of proteins, complex carbohydrates, and lipids present in biomass, for characterizing biomass compositional differences between plant sources, from different parts of plants, and for plants subjected to different stresses or environmental growing conditions. Metabolomics methods look at products in their mixed state, avoiding the tedious separation and purification in conventional approaches that precede identification of individual components in complex mixtures. Metabolomics (*16*) could find increasing use for characterizing complex mixtures of metabolites such as often encountered during cell wall polymerization or disassembly.

Lu and Ralph (*17–20*) selectively degraded ether linkages in lignin to produce identifiable fragments by a chemical technique termed Derivatization Followed by Reductive Cleavage (DFRC). Additionally, they dissolved whole, acetylated cell walls and applied solution state NMR (*18*) with advances including cryoprobe 3D NMR (*20*). Such developments in lignin characterization, especially rapid screening techniques, are critically important.

Bootten et al. (*21*) used ^{13}C NMR to delineate xyloglucan—cellulose interactions in plant cell walls in situ. Additionally, FT-IR microspectroscopy, along with pyrolysis beam mass spectrometry (*22*), pyrolysis GC-MS (*23*), and confocal Raman spectroscopy (*24*) are among the techniques employed for in situ cell wall characterization. Direct visualization of microfibrils using atomic force microscopy led to mapping of the ultrastructure of the native primary cell wall in maize (*25*). Not surprisingly, much of the past driving force for biomass characterization came from the need for animal feed/forage analysis; however, the same factors responsible for digestibility of feeds in animals also govern enzymatic conversion efficiency for bioenergy uses (*26*). Transferring this branch of agricultural chemistry to biofuels production can help to optimize conversion of cellulosics to "fermentable" sugars and ultimately bioenergy.

Implied in these discussions is the need to carry out cross-disciplinary research, a capability that is not always easy to achieve in individual university departments. This work has been made easier through "user" facilities, such as the U.S. Department of Energy's Joint Genome Institute under their Genomes: GTL program (formerly Genomics to Life program), as well as the European Union's "framework programmes", which emphasize cross-disciplinary research. Another working example is the DOE-funded Research Centers, such as the Joint BioEnergy Institute (JBEI) Center in Berkeley CA. JBEI combines advanced molecular biology with state-of-the-art structural analysis via their association with (1) the Advanced Light Source (ALS), (2) the Joint Genome Institute, (3) the Molecular Foundry, and (4) multiple University of California—Berkeley and National Laboratory departments. Such associations combine research under one organization in, for example, applied microbiology, protein analysis, proteomics, genome sequencing, X-ray crystallography, 2D topographical analysis, advanced NMR, and structural modeling to describe deconstruction of plant materials during its conversion to energy.

Efficient biomass conversion has been aided significantly by collaborative efforts of leading researchers who joined together in the Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) project (*27*). Researchers from Auburn

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Table 1. Effect of Pretreatment Methods on the Chemical and Physical Structure Changes of Cellulosic Biomass, Based on Mosier et al. (*28*)[a]

treatment	removes hemicellulose	removes lignin	decrystallizes cellulose	alters lignin structure
liquid hot water	↑		ND	→
pH-controlled hot water	↑		ND	ND
water flow-through	↑	→	ND	→
dilute acid	↑			↑
acid flow-through	↑	→		↑
ammonia explosion, AFEX	→	↑		↑
ammonia recycle percolation	→	↑		↑
lime	→	↑	ND	↑
steam explosion	↑			→
organosolv	↑	↑	→	↑

[a] ↑, significant effect; →, moderate effect; ND, not determined. No entry indicates no change observed.

University, Dartmouth College, Michigan State University, the National Renewable Energy Laboratory (NREL), Purdue University, Texas A&M University, and University of California, Riverside, compared results using identical "standardized" biomass samples and standardized analytical methods. Corn stover supplied by NREL was fractionated by (1) ammonia explosion, (2) aqueous ammonia recycle, (3) controlled pH, (4) dilute acid, (5) water/acid flow-through, and (6) lime.

On the basis of conversion of biomass to usable sugar alone, it would be difficult to pick one pretreatment over the others; all treatments released roughly 90% of theoretical "fermentable" sugars. Thus, as important as the CAFI results (*28*) are to the field, they raise as many questions as they answer because of their differences (**Table 1**). Biorefinery design will depend on how chemists and engineers address differences in such pretreatment results, with research opportunities that include

• handling differences in effluent output (optimized wastewater treatment),

• avoiding inhibitors (*29*) that slow conversion to ethanol,

• optimizing lignin use after its isolation,

• dealing with differences in cellulose after treatment (degree of crystallinity), and

• optimizing uses of hemicellulose-derived (C-5) sugars following their separation from cellulose-derived (C-6) sugars.

C-5 AND C-6 PLATFORMS

The optimal use of hemicellulose-derived (C-5) sugars is important to the success of cellulosic biorefinery operations, which will depend on cofermentation of both C-5 and C-6 sugars made possible by novel microbes that metabolize both sources. As described above, though, such microbes can add time to biofuels production. Alternatively, biorefineries can be designed to isolate the slower-fermenting sugars and utilize them in other platforms, providing a broad range of products from the biorefinery (just as in petroleum refining). Any use of xylose to make either biofuels or platform chemicals circumvents the food versus fuel issue and adds significant value to the entire operation. The following list of complementary "platform chemicals" describes those already under significant development.

Lactic Acid. Worldwide demand for lactic acid has surpassed 120,000 tonnes/year (*30*) for use in cosmetics, specialty products, and food preservatives. The production of poly(lactic acid) (PLA) has expanded market demand, providing the first
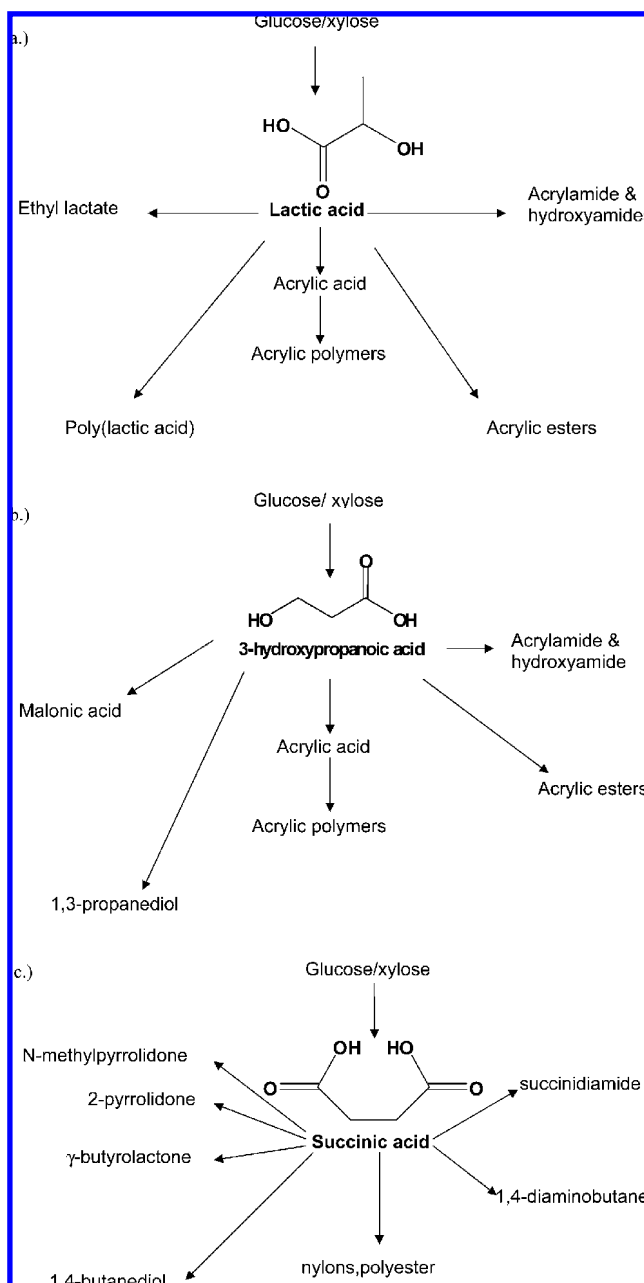
Figure 3. Biorefinery platform chemicals beyond ethanol, showing, for example, new applications for (**a**) lactic acid, (**b**) 3-hydroxypropanoic acid, and (**c**) succinic acid.

commercially viable biodegradable thermoplastic resin. Lactic acid can be derived from glucose and/or xylose (**Figure 3a**) and can be used to make a host of products and even other polymers.

1,3-Propanediol (PDO). DuPont and other companies created a market for PDO, a colorless glycol liquid derived from fermentation of sugars. PDO can replace propylene glycol and butylene glycol in formulations and ingredients in which non-petroleum-based ingredients are desired. More importantly, PDO is a critical copolymer ingredient in a new textile fiber that is being marketed for its "green" nature and also because it provides improved properties relative to other commercial textile fibers.

3-Hydroxypropanoic Acid (3-HP). 3-HP can be used to create specialty chemicals, to form polymers, and even to form PDO (**Figure 3b**). The opportunity to convert C-5 sugars to 3-HP could significantly enhance its market position.

Succinic Acid. Succinic acid is a C-4 dicarboxylic acid that occurs naturally in plant and animal tissues. It has a wide range of mostly nonfood industrial uses (**Figure 3c**), with the worldwide market at 2.7×10^8 kg/year and supply generally met by production in corn wet mill biorefineries. Uses include application as a plasticizer for polymers, solvents and lubricants, epoxy curing agents, corrosion inhibitors, and cosmetic and pharmaceutical applications. Succinic acid can be made efficiently from xylose, opening new avenues for hemicellulose utilization.

Itaconic Acid. Itaconic acid is an interesting fermentation product produced either from glucose (C-6) or from xylose (C-5) by *Aspergillus terreus* and *Aspergillus itaconicus* (*31*). Its reactive dicarboxylic acid functionality can be utilized in polymerization reactions to create nylons and polyesters, plus it has an unsaturated double bond suitable for further polymerization to expand product properties.

Isosorbide. Isosorbide is an anhydrosugar alcohol made from sorbitol (a common coproduct from biorefineries) that is well established in the pharmaceutical and specialty chemical industries. Recent patent activity (*33–36*) shows its potential applications in the polymer field. Of interest is the copolymerization of isosorbide with polyethylene terephthalate to produce poly(ethylene-*co*-isosorbide) terephthalate (PEIT), which increases the strength and rigidity of the polymer, reduces the amount of polymer used, and increases the glass transition temperature such that beverages can be hot-filled and pasteurized.

Polyethylene and Polyamides (Traditional Polymers) from Biorefinery Conversion. Both BrasKem (Brazil) and Dow are exploring commercial production of high-density polyethylene derived from ethanol. Commercialization of this "green polyethylene" is expected at the end of 2009 with potential output as much as 200,000 tons annually.

Polyamides from Biorefinery Conversion. In one interesting example, Frost et al. (*37, 38*) produced feedstocks for nylon polymers using engineered *Escherichia coli* by bioconversion of adipic acid to 3-dehydroshikimic acid and then to *cis,cis*-muconic acid. The final step, hydrogenation to adipic acid, provides a feedstock for nylons, with the world adipic acid market at 2.3 million metric tons/year.

OTHER APPROACHES TO REDUCING GREENHOUSE GAS EMISSIONS

Wood alcohol (methanol) is an alternative liquid transportation fuel and potentially a hydrogen source for fuel cells (*39*). Various aspects of methanol as a feedstock and fuel are discussed in *Beyond Oil and Gas: The Methanol Economy* (*40*). Although methanol from wood is technically feasible, methanol from coal seems to be the favored current source, certainly in coal-rich countries such as China where expanded coal-to-methanol production facilities are under development. Efficient conversion of CO_2 to methanol by hydrogenation or electrochemical conversion represents another research challenge.

Alternative platform chemicals and biofuels from cellulose, such as butanol and methanol, are advantageous in several ways. They provide a "hedging strategy" for ethanol producers, similar to the way in which petroleum refineries can market an array of commodities and products. More importantly, these and other products of biomass conversion capture, contain, and recycle the excess carbon dioxide and methane effluents that contribute to global warming (*7*). Controlling greenhouse gases through economic drivers such as carbon credits represents a way to add value to bioenergy, a concept that will require significant political leadership, strong economic analysis, and marketplace

validation (*41*). But, most of all, it must be based on sound scientific data and analysis—another research opportunity for agricultural and environmental chemists. CO_2 cycling in the environment is complex and poorly understood (*42*). More "systems" research and systems modeling is needed to delineate chemical and physical interactions of CO_2, including in soils (*43*) and in the oceans. How will decisions in agriculture affect the release of CO_2 and methane (which is ~23 times more destructive as a greenhouse gas than CO_2)? Questions remain relating to biofuels in terms of bioconversion processes, CO_2 recapture, and farming practices, especially as expansion into energy crops (switchgrass, sweet sorghum, sugarcane, etc.) is realized. Such debates have begun to permeate the international popular press, such as the international cover story in *Time* magazine, April 7, 2008 (*44*).

NATURAL PRODUCTS CHEMISTRY AND BIOCHEMISTRY

Chemistry also comes into play in selection of the most promising feedstocks, either for bioethanol or for biodiesel production. Analysis is required to classify traditional crop plants via phytochemical analysis for energy conversion or for analysis of the products of genetically modified plants. As "energy crops" become closer to reality, more attention will be devoted to redesigning plants (*45*); for example, to decrease the amount of lignin or change the structure of the lignin in the plant (*46*) or to insert enzymes such as ferulic acid esterase in the plant cell wall to allow plants to decompose more readily after harvest. How will genetic transformations affect the chemical nature of biopolymers (and other phytochemicals) and, more fundamentally, how do they modify biosynthetic pathways leading to the range of products of commercial interest as well as those that might be detrimental? Plant biochemistry and natural product chemistry have important roles in fitting to the new needs posed by bioenergy and biobased products. For example, the phenylpropanoid pathway to lignin is attracting renewed interest, including ways to potentially modify it to improve bioprocessing (*47*).

There may be plants yet to be exploited that are particularly adapted to producing hydrocarbons, not unlike petroleum hydrocarbons. Plant leaf waxes, for example, consist largely of C-16 and higher straight- and branched-chain alkanes. These form the cuticular waxes that play a significant role in water conservation in plants. Deswarte et al. (*48*) isolated wax from wheat straw using supercritical CO_2 extraction. C_{28-31} alkanes and various sterols were predominant isolates, along with fatty acids, alcohols, and lipids. Collectively the longer chain hydrocarbons comprised 1% or more by weight in wheat straw and similar biomasses. Even nonwaxy plants such as rice have measureable quantities of cuticular hydrocarbons (*49*). Not surprisingly, many desert plants are hydrocarbon rich, perhaps affording clues to new types of "energy crops".

Terpenes are another potential source of tomorrow's fuels and chemical feedstocks. Turpentine, largely α-pinene, derived from the oleoresin exudate of tapped pine trees, has found many uses. *Pinus elliottii* averaged over 7 kg of oleoresin per tree per year under one treatment regimen (*50*). Hodges and Johnson (*51*) reported an alternate method of tapping *P. elliottii* using bore hole drilling. The gum rosin and turpentine have a variety of uses, and the semivolatile fraction has potential as a liquid biofuel. Are there other plants or algal sources of hydrocarbons (e.g., high in wax, terpenes, sterols, or other reduced photosynthates) yet to be discovered and exploited? The possibility of obtaining useful hydrocarbons from algae (*52*) is especially intriguing, considering the ability of algae to assimilate CO_2.

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Microbiologists, enzyme biochemists, and agricultural chemists will benefit from more cross-talk and multidisciplinary research in extracting and using byproducts from plant wastes or residues, such as glycerol, lignin, essential oils, proteins (*52*), and other byproducts of biofuel production. Corn biorefining is already benefitting by the large number of other products derived from the biochemical and chemical conversion of starch and ancillary coproducts. For example, the potential of corn fiber derived during milling has yet to be fully realized. Novel work such as studies showing that heat pretreatment of both corn fiber and the corn germ can improve extractable tocopherols and tocotrienols will only improve commercial applications by adding value to these streams (*54*). Olive mill wastes (*55*), almond hulls, and grape pomace (*56*) are being explored as sources of phenolic antioxidants—dietary supplements with health-promoting qualities. Additionally, many of these crop residues could be converted to energy as biorefinery technology develops.

Large-scale production of energy crops will almost certainly be accompanied by issues of pest control, optimal fertilization requirements, balancing water usage and reuse, and disposing of unwanted byproducts—issues that may require new pesticides, biopesticides, genetically engineered crops, etc. Genetically modified crops that can fix their own nitrogen, control root rot, and in some way augment their value by producing useful metabolites may be in the offing. Agricultural chemistry will be a cornerstone of such developments.

FUTURE BIOREFINERIES

Chemistry, biochemistry, and biochemical engineering will contribute to developing all aspects of biorefinery operation, providing, in an analogous way to present day petroleum refineries, fuels, lubricants, chemical solvents, intermediates, and polymer products (*2, 57*). In addition, these plants will produce other bioproducts, such as soil amendments, food and feed components, fibers, biodegradable plastics, building materials, and various nutraceutical products.

An intriguing example of the biomass-to-biofuels biorefinery potential somewhat akin to the more developed sugarcane biorefineries is afforded by guayule, presently under intense study and development as a domestic U.S. source of high-value latex rubber. The guayule shrub, which is grown in marginal desert land in the American southwest, contains approximately 15% dry weight of rubber and 10% resin and produces 48% bagasse (*58*). As the cost of producing the bagasse is borne by the value of the latex, the cost of the bagasse as a feedstock for biofuel is essentially zero. In addition, the bagasse is aggregated at the mill where latex extraction is carried out, so, in fact, there is a cost to not utilizing the bagasse. Feasibility studies indicate that up to 1000 gallons of ethanol per acre could be produced from this bagasse, which represents a significant additional value after profiting from the rubber latex and other potentially profitable coproducts from processing, such as termite inhibitors (*59*).

This perspective has focused primarily on the biomass-to-biofuels biorefinery applications in the Americas. In Europe the picture is significantly different for alternative transportation fuels because of its relative dependence on diesel (and thus biodiesel). A vexing issue with biodiesel production is that transesterification of plant oils, largely esters of glycerol and fatty acids, produces glycerol as a byproduct (roughly 1 kg of impure glycerol is produced for every 10 kg of biodiesel). Although purified glycerol has value in cosmetics and paints, the potential oversupply of glycerol from expanded biodiesel production represents a short-term hurdle but a longer term opportunity for chemists and chemical engineers in developing new glycerol-based products. Glycerol can be converted to methanol, ethylene, and propylene glycol, solvents, and many other products using existing, but not necessarily commercially viable, processes. Glycerol can also be a substrate for enzymatic conversion or fermentation routes to fuels such as methane (*60*) and many of the fermentation products mentioned above. Specifically, if glycerol were to become as inexpensive as glucose as a fermentation feedstock, one could envision metabolic pathways for fermentation conversions that are more efficient than sugar conversion, with fewer moles of CO_2 effluent. At minimum, glycerol derivatives may be applied as plasticizers in many polymer formulations or more directly as fuel additives.

Pyrolysis or gasification of biomass can produce potential liquid fuels by a variety of processes (*61*). The optimal biorefinery may not consist of only one type of conversion, such as fermentation, but may rely on a fully integrated system that employs fermentation, gasification/pyrolysis, and even digestion. An essential argument put forth by Dale (*1, 62*) can be paraphrased simply as "not all BTUs are equal". A higher market value is placed on liquid transportation fuel above other energy forms, whereby liquids are preferred over gases (natural gas) or even more over solids (coal). A well-designed biorefinery considers this energy hierarchy by capturing all of the energy from biomass, thus adding optimal value to more of the carbon.

Pyrolysis (high-temperature heating in the absence of air or oxygen) produces a pyrolysis oil, a complex mixture of components that is generally a low-quality fuel in itself, but one that can be upgraded by hydrocracking or catalytic cracking. Pyrolysis oils from defined biomass sources, including agricultural processing wastes (oat, walnut, almond, or peanut hulls) or residues such as grain or grass straws are convertible to liquid fuels as well as commodity chemicals. Gasification (high-temperature conversion in the presence of limited oxygen) produces a synthesis gas from biomass feedstocks consisting largely of CO and hydrogen. It can be used directly as a fuel for heat recovery or can be further processed by Fischer–Tropsch synthesis to methanol, dimethyl ether, mixed alcohols, and/or a mixture of hydrocarbons. The key is in the choice of catalysts that carry out the re-formation reactions, as well as the choice of feedstocks.

New biorefinery designs are needed now, as well as when energy crops begin to be utilized. At present, sugar mills are still hampered with disposal costs for their vanasse, that is, the remaining soluble matter (roughly 10% of the original biomass) after the fermentation–distillation process of sugarcane molasses as well as the nonvolatile fermentation byproduct. Viable solutions include using vanasse as cattle feed (*63*) and/or cogenerated energy feedstock using sophisticated incinerators (*64*). Additionally, further research is needed to deal with other byproducts, such as aconitic acid, that may inhibit fermentation (*65*).

Biorefinery development for lignocellulosic feedstocks is happening on several fronts. Brazilian companies have long been the leaders of sugarcane conversion—direct from sugar syrup—and are now applying technologies to utilize their lignocellulosic bagasse. Chevron Corp. and forest products company Weyerhaeuser Co. have announced (*66*) the creation of a 50/50 joint venture company, Catchlight Energy LLC, focused on developing renewable transportation fuels from nonfood sources especially poplar and energy crops such as sorghum and switchgrass. Chevron and Texas A&M University are also

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partnering on research efforts to achieve accelerated harvesting of nonfood crops, especially sorghum and sweet sorghum, for conversion into biofuel products. Verenium, a new company formed from the union of Diversa and Celunol, recently announced (*67*) a demonstration-scale cellulosic ethanol facility in Jennings, LA, based on biofuels production via conversion of sugar and sugarcane bagasse. These are multiyear, multimillion dollar commitments toward the development of the next-generation biorefinery.

Boatang et al. (*68*) are exploring wheat and other straw residues for on-farm gasification in more remote, rural environments, with a potential for conversion to liquid fuels for on-farm use as transportation/equipment fuels and to generate electricity. In fact, small-scale, even portable biomass conversion to bioenergy/biofuels by a variety of processes (gasification, enzymatic conversion) offers much opportunity for research and development in the coming years as agricultural and food processors search for alternatives to increasingly expensive petroleum, electricity, and natural gas. Augmenting conventional energy sources utilizing their own waste or byproduct materials is increasingly attractive.

AGRICULTURAL CHEMISTS NEEDED

It is likely that much of the coming revolution in bioenergy will be based on biotechnology, including fermentation and conversion technology using improved microorganisms (*69*) and plants (*9*). Chemistry will be an essential tool in the arsenal for characterizing feedstocks and maintaining composition of feedstock streams, identifying and dealing with inhibitors, separating dilute and impure ethanol from a fermentation broth to a more refined and concentrated form of commercial grade consistency, identifying new coproducts that can add value to biorefineries, extracting the energy from biofuels with increased efficiency, and storing and using the "new" energy captured from plants more efficiently. Developments in such fields as photovoltaics, fuel cells, catalysts, and nanotechnology will need to be incorporated in the developing technologies associated with bioenergy. Also important will be expanded global cooperation—putting into practice lessons learned in nations such as Brazil (*70, 71*)—and new multinational cooperative programs, such as EPOBIO (*72*).

Will a new generation of agricultural chemists be available to address the challenges associated with biomass conversion, biorefining, biobased products and coproducts, and bioenergy? The challenges are multidisciplinary, requiring background in multiple fields, including chemistry, biochemistry, microbiology, molecular biology, and engineering. Improving and expanding present degree programs in agricultural chemistry/engineering and allied scientific and bioengineering disciplines and increasing opportunities for on-the-job training in research organizations and in industry will be important if research and development are to keep pace with society's expectations for bioenergy.

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