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The Path Forward for Biofuels and Biomaterials

Arthur J. Ragauskas,^{1*} Charlotte K. Williams,⁴ Brian H. Davison,⁶ George Britovsek,⁴ John Cairney,² Charles A. Eckert,³ William J. Frederick Jr.,³ Jason P. Hallett,³ David J. Leak,⁵ Charles L. Liotta,¹ Jonathan R. Mielenz,⁶ Richard Murphy,⁵ Richard Templar,⁴ Timothy Tschaplinski⁷

Biomass represents an abundant carbon-neutral renewable resource for the production of bioenergy and biomaterials, and its enhanced use would address several societal needs. Advances in genetics, biotechnology, process chemistry, and engineering are leading to a new manufacturing concept for converting renewable biomass to valuable fuels and products, generally referred to as the biorefinery. The integration of agroenergy crops and biorefinery manufacturing technologies offers the potential for the development of sustainable biopower and biomaterials that will lead to a new manufacturing paradigm.

We are apt to forget the gasoline shortages of the 1970s or the fuel price panic after Hurricane Katrina, but these are but harbingers of the inevitable excess of growing demand over dwindling supplies of geological reserves. Before we freeze in the dark, we must prepare to make the transition from nonrenewable carbon resources to renewable bioresources. This paper is a road map for such an endeavor.

Among the earliest drivers of chemical and biochemical research were the benefits to be gained from converting biomass into fuels and chemical products. At the beginning of the 20th century, many industrial materials such as dyes, solvents, and synthetic fibers were made from trees and agricultural crops. By the late 1960s, many of these bio-based chemical products had been displaced by petroleum derivatives (1). The energy crisis of the 1970s sparked renewed interest in the synthesis of fuels and materials from bioresources. This interest waned in the decades that followed as the oil price abated. However, this meant that global consumption of liquid petroleum tripled in the ensuing years (2). Indeed, energy demand is projected to grow by more than 50% by 2025, with much of this increase in demand emerging from several rapidly developing nations. Clearly, increasing demand for finite petroleum resources cannot be a satisfactory policy for the long term.

Hoffert *et al.* (3) and others (4) have provided a global perspective on these energy challenges and their relationship to global climate stability. As these authors point out,

future reductions in the ecological footprint of energy generation will reside in a multifaceted approach that includes nuclear, solar, hydrogen, wind, and fossil fuels (from which carbon is sequestered) and biofuels. These concerns have also been advanced by the recent Joint Science Academies' statement to the Gleneagles G8 Summit in July 2005, *Global Response to Climate Change*, which asserts that the warming of the planet can be attributed to human activities and identifies the need for action now to pinpoint cost-effective steps to contribute to substantial and long-term reductions in net greenhouse gas emissions (5).

Shifting society's dependence away from petroleum to renewable biomass resources is generally viewed as an important contributor to the development of a sustainable industrial society and effective management of greenhouse gas emissions. In the United States, bioethanol derived primarily from corn contributes ~2% to the total transportation fuels mix; another ~0.01% is based on biodiesel. The U.S. Department of Energy has set goals to replace 30% of the liquid petroleum transportation fuel with biofuels and to replace 25% of industrial organic chemicals with biomass-derived chemicals by 2025 (2, 6). The European Union Directive 2003/30/EC ("the Biofuels Directive") adopted in 2003 targeted 2% of all petrol and diesel transport fuels to be biomass-derived by December 2005 and 5.75% by December 2010. This directive was motivated by concerns to ensure the security of the European energy supply, environmental sustainability, and achievement of Kyoto Protocol targets (2). These biomaterials and biofuels production targets are certainly achievable; Parikka (7) has reported the current sustainable global biomass energy potential at ~10²⁰ joules per year, of which ~40% is currently used.

Given these accomplishments, a key question is "When will biorefineries be ready to

make a major contribution?" One answer, coming from a forum at the 27th Symposium on Biotechnology for Fuels and Chemicals, was that some applications are ready now, but their impact will be limited with current technologies and feedstocks (8). We need commercialization and policy support for current and near-term opportunities to grow the industry from its present base. Equally important, we need research and development to increase the impact, efficiency, and sustainability of biorefinery facilities. The current production and use of bioethanol and biodiesel processes are a starting point. It is our belief that the next generational change in the use of bioresources will come from a total integration of innovative plant resources, synthesis of biomaterials, and generation of biofuels and biopower (Fig. 1).

Innovative Plant Design via Accelerated Domestication

"More, Bigger, and Better," the mantra of modern consumerism, also summarizes—ironically—the goals of research aimed at modifying plant species for use in sustainable biomass production. Interrelated plant traits such as higher yield, altered stature, resilience to biotic and abiotic challenge, and biomass composition will increase industrial crop value in terms of biofuels and biomaterials. The challenge is to weave these different strands of research into an integrated production strategy.

Currently, the global yield for all biomass crops, including woody and herbaceous crops growing in temperate and subtropical regions, varies from ~8 dry Mg ha⁻¹ year⁻¹ (for willow in Sweden) to 10 to 22 dry Mg ha⁻¹ year⁻¹ (for short-rotation woody crops in the United States). Some commercial plantations in Brazil have reported up to 20 dry Mg ha⁻¹ year⁻¹. A conservative global biomass average would be ~10 dry Mg ha⁻¹ year⁻¹, although some small-scale field trials have reported four times this level of biomass production (9, 10). The grand challenge for biomass production is to develop crops with a suite of desirable physical and chemical traits while increasing biomass yields by a factor of 2 or more. Although many annual crops benefit from centuries of domestication efforts, perennial species that could play a central role in providing a renewable source of feedstock for conversion to fuels and materials have not had such attention to date. Doubling the global productivity of energy crops will depend on identifying the fundamental constraints on productivity and addressing those constraints with modern genomic tools (Fig. 2).

An obvious target is manipulation of photosynthesis to increase the initial capture of light energy, which at present is less than 2%. Recently, this approach has had some success using engineered genes from plants and photosynthetic bacteria. For example, ribulose-1,5-

¹School of Chemistry and Biochemistry, ²School of Biology, ³School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA. ⁴Department of Chemistry, ⁵Division of Biology, Imperial College London, London SW7 2AZ, UK. ⁶Life Sciences Division, ⁷Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

*To whom correspondence should be addressed. E-mail: arthur.ragauskas@chemistry.gatech.edu

bisphosphate carboxylase-oxygenase (RuBisCO), the plant enzyme that converts CO₂ to organic carbon by carboxylation during photosynthesis, also conducts a competing, less efficient oxygenation reaction. When an inorganic carbon transporter gene from cyanobacteria was expressed in plants, the more efficient carbon-fixing photosynthetic reaction of RuBisCO was favored. In another approach, the cyanobacterial versions of two rate-limiting enzymes in the chloroplast's carbon-fixing "dark reaction" were overexpressed in tobacco, resulting in an

elevated rate of photosynthesis and increased plant dry weight (11).

In addition to manipulating photosynthesis to increase the initial capture of light energy, the manipulation of genes involved in nitrogen metabolism has also been a successful approach to increasing biomass. For example, in a 3-year field trial of transgenic poplar (*P. tremula* × *P. alba*) overexpressing a glutamine synthase gene (*GSI*), tree height increased to 141% that of control plants by the third year of the study (12). The potential of *GSI* for engineering bio-

mass increase is further emphasized by results showing that quantitative trait loci for yield in maize and maritime pine map to the location of *GSI*. Similar possibilities are evident in the overexpression of a bacterial glutamate dehydrogenase, which increased the biomass of tobacco plants under both laboratory and field conditions (13).

Much research has been devoted to protecting food and fiber supplies from biological and environmental stress by transferring genetically engineered versions of plant defense genes to crop plants. By this method, different plant lines have been generated that, relative to controls, grow at elevated rates under drought and high- and low-temperature stress; they also survive pathogen attack (14). Furthermore, plants typically invest considerable energy in making reproductive structures, and if flowering can be delayed or prevented, this energy may be transferred into increasing the overall biomass of the plant. In addition, by delaying or shortening the winter dormancy of plants, the growth phase of plants can be extended; regulators for this process are being investigated.

Additional research has revealed the coregulation of lignin and cellulose biosynthesis in several studies (15). Repressing a single lignin biosynthetic gene, *4-CL*, resulted in a reduction in lignin content with a concomitant increase in cellulose, an effect that can be amplified by cotransformation of multiple

genes (16). Conversely, an *Arabidopsis* CESA3 mutant, impaired in cellulose biosynthesis, had altered lignin synthesis. In several cases, manipulation of the expression of lignin biosynthesis genes resulted in alteration in lignin structure rather than alteration in quantity. Because the efficiency of biomass conversion depends on hydrolyzing agents gaining access to plant polysaccharides, alteration of plant cell wall structure could yield important advantages. For example, when the lignin biosynthesis gene *CCR* is down-regulated in poplar, the cellulose component of the plant cell wall is more easily digested by the bacterium *Clostridium*

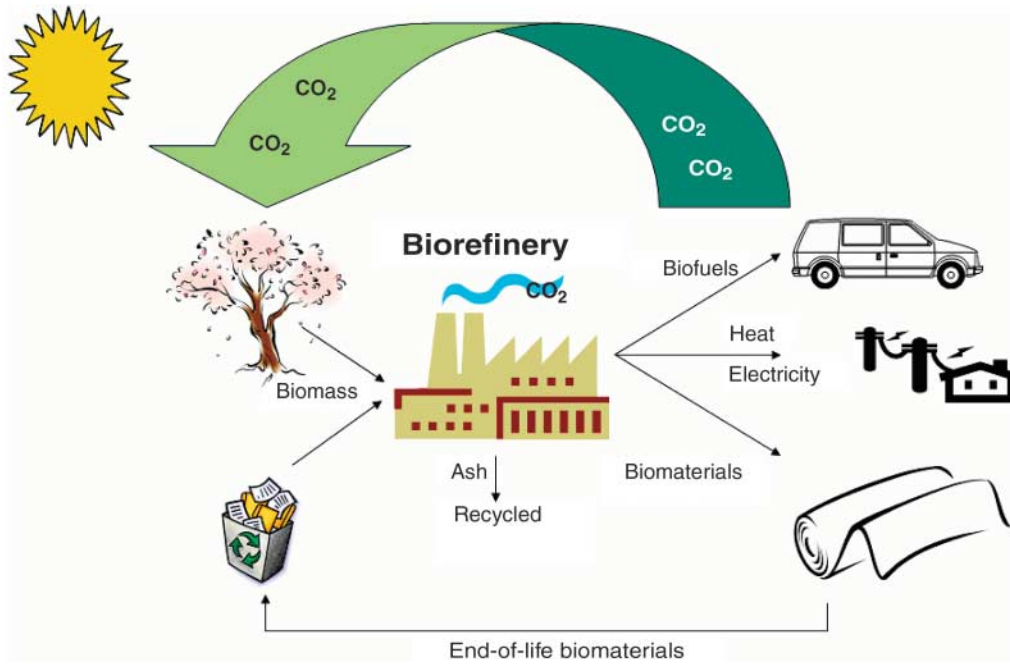


Fig. 1. The fully integrated agro-biofuel-biomaterial-biower cycle for sustainable technologies.

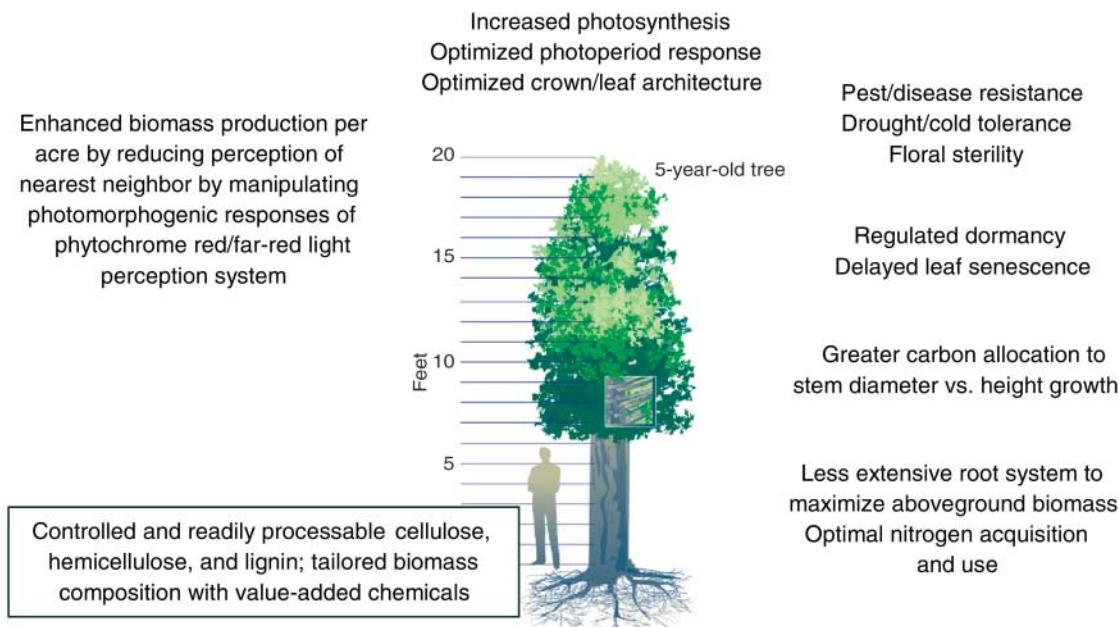


Fig. 2. Overview of plant traits that can be targeted by accelerated domestication for enhanced plant biomass production and processing.

cellulolyticum, and twice as much sugar is released (15). The intensive genetic engineering used to alter lignin structure and content with the goal of improving wood and papermaking quality shows the potential of these approaches (15). In summary, advances in plant sciences and genetics are providing researchers with the tools to develop the next generation of agro-energy/material crops having increased yield and utility tailored for modern biorefinery operations.

Biomaterials from Biorefineries

These advances in plant sciences will need to be captured in subsequent biorefinery operations. In essence, the modern biorefinery parallels the petroleum refinery: An abundant raw material consisting primarily of renewable polysaccharides and lignin (Fig. 3) enters the biorefinery and, through an array of processes, is fractionated and converted into a mixture of products including transportation fuels, co-products, and direct energy.

The power of the biorefinery concept is supported by economies of scale and by efficient use of all incoming bioresources. A key aspect of the biorefinery concept is the imbalance between commodity chemical needs and transportation fuels. Using the petroleum industry as an illustrative example, ~5% of the total petroleum output from a conventional refinery goes to chemical products; the rest is used for transportation fuels and energy. Most visions for integrated biorefineries do not expect this ratio to change (17).

The paradigm shift from petroleum hydrocarbons to highly oxygen-functionalized, bio-based feedstocks will create remarkable opportunities for the chemical processing industry. For example, the use of carbohydrates as chemical raw materials will eliminate the need for several capital-intensive, oxidative processes used in the petroleum industry. Biomass carbohydrates will provide a viable route to products such as alcohols, carboxylic acids, and esters. These natural products are also stereo- and regiochemically pure, thereby reducing dependence on expensive chiral catalysts and complex syntheses that are currently required to selectively install chemical functionality in petrochemicals.

Bio-based feedstocks are already having an impact on some practical applications, including solvents, plastics, lubricants, and fragrances. Bio-derived plastics such as polylactic acid are attracting attention, in part because of their biological compatibility and hydrolytic degra-

dation, which enables them to successfully replace petrochemicals as well as open up new applications. Polylactic acid is currently manufactured on a million-kilogram scale in the United States and on a smaller scale in Europe and Japan (18). This process ferments corn dextrose to produce lactic acid that is subsequently dimerized, polymerized, and used in several applications, including food packaging and the apparel industry. The production of lactic acid by fermentation is economically competitive with its chemical synthesis from acetaldehyde and hydrogen cyanide. Further reductions in cost are expected with improvements in the fermentation process and the use of waste agricultural materials as feedstocks. Another example is the production of 1,3-propanediol by the fermentation of carbohydrates. This process is being exploited to supplement the use of petrochemically derived

volatile nature of most biomass components and the fact that other separation techniques, such as chromatography or membranes, do not yet have the same economies of scale.

Future biorefinery operations will first extract high-value chemicals already present in the biomass, such as fragrances, flavoring agents, food-related products, and high-value nutraceuticals that provide health and medical benefits (19). Once these relatively valuable chemicals are extracted, the biorefinery will focus on processing plant polysaccharides and lignin into feedstocks for bio-derived materials and fuels. This requires the development of innovative separation and depolymerization process chemistries. Supercritical CO₂, near-critical water, and gas-expanded liquids are well suited to these challenges (20, 21). These tunable solvents offer distinct green chemistry processing advantages (22) that could be exploited in the processing of renewable bioresources.

Supercritical fluids exhibit outstanding transport properties coupled with highly tunable solvent properties (such as solvent power and polarity) and ease of solvent removal. Near-supercritical fluids are also highly tunable and generally offer better transport than liquids and better solvent power than supercritical fluids. Gas-expanded liquids are mixtures of a gas with an organic liquid such as methanol or acetone; in our context the gas is CO₂, which is completely miscible with most organics. These solvents exhibit highly tunable solvent power, as small pressure changes yield large changes in composition, and they give much greater solubili-

ties and operate at much lower pressures than supercritical fluids. All of these solvents result in advantages for downstream processing in terms of product purification and/or catalyst recycling.

Water is arguably the most environmentally benign and food-safe solvent that can be used in chemical synthesis. However, the range of water-soluble substrates is quite limited, making ambient water an unsuitable medium for many chemical syntheses. Near-critical water (200° to 300°C) exhibits a reduction in dielectric constant (20 to 30) and density (0.7 to 0.8 g/cm³) relative to ambient water; its ability to dissolve both nonpolar organic molecules and inorganic salts is comparable to that of the popular organic solvent acetone. In addition, under these conditions, the dissociation constant of water into hydroxide and hydrogen ions rises

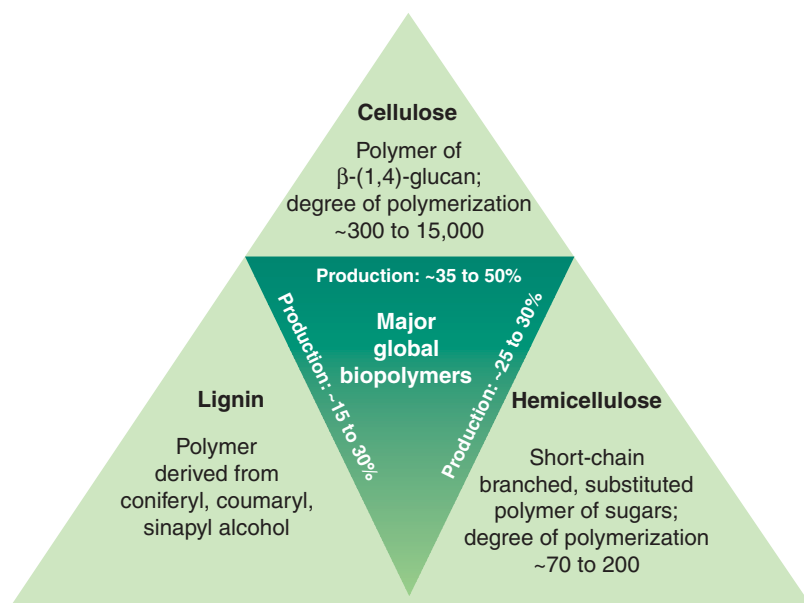


Fig. 3. Key global biomass resources from agricultural residues, wood, and herbaceous energy crops.

1,3-propanediol to make poly(trimethylene terephthalate), a polymer fiber with properties related to nylon and polyethylene terephthalate. These commercially viable processes do, however, require purified feedstocks. The major impediment to biomass use is the development of methods to separate, refine, and transform it into chemicals and fuels.

One of these steps, separation, currently accounts for 60 to 80% of the process cost of most mature chemical processes. As we progress from the oil refinery to the biorefinery, the challenges associated with separation will change, but not diminish, in importance. In the petroleum industry, distillation is the unit operation that dominates the refinery separation scheme. For chemicals derived from biomass, this dominance will be transferred to solvent-based extraction. This is a result of the non-

by more than three orders of magnitude, so that near-critical water also acts as a self-neutralizing acid or base catalyst, eliminating salt waste generation (23). Further, the use of near-critical water in place of organic solvents greatly simplifies product isolation, as non-polar products are insoluble after cooling. The utility of this medium has been demonstrated for a diverse group of organic syntheses (24). High-temperature water has already been proposed for the depolymerization of cellulosic waste materials in the Biometrics process for producing levulinic acid (25).

The sugars in the biorefinery process can be transformed into building-block chemicals by fermentation as well as by enzymatic and chemical transformations. The key building block chemicals will include ethanol, C3 to C6 carboxylic acids (e.g., hydroxypropanoic acid, glucaric acid), and alcohols such as glycerol and sorbitol. It is noteworthy that the current cost of many carbohydrates and their derivatives is already competitive with petrochemicals and solvents such as toluene, aniline, and acetaldehyde (26). The U.S. Department of Energy recently published a comparative study on the top 12 chemicals from carbohydrate biomass, identifying several particularly promising compounds including sorbitol, levulinic acid, and glycerol (27). The effective production and use of these chemicals rely on the development of innovative enzymatic and catalytic green chemistries that will yield a viable range of new bio-derived products.

Biofuels: Biopower from Biorefineries

After extracting value-added chemicals from biomass in the early stages of a biorefinery, the separations and chemical operations will need to be shifted to the production of biofuels. Today's bioethanol plant process relies largely on the fermentation of starch from corn in the United States or from sugar cane in Brazil (2, 7). Enhancing the cost structure of bioethanol generation has moved research attention away from plant grains and more toward corn stovers, trees, and other low-cost agricultural and municipal waste materials (28, 29). These biomaterials typically have higher amounts of cellulose and hemicellulose, and their efficient, cost-effective depolymerization remains a key challenge in their use.

One important tool in reducing the cost of this depolymerization is pretreatment of lignocellulosics to make the biomass matrix more accessible to enzymes. The tailoring of chemical and physical pretreatments for specific biomass resources is a field of growing interest and practicality (30). These pretreatment benefits are leveraged with recent research efforts that have reduced the cost of cellulase by a factor of 5 to 10 (31). Future cost reductions in bioprocessing will be accomplished by combining cellulase/hemicellulase treatments with other process steps. For example, researchers

have proposed combining cellulase production with the fermentation steps via modified micro-organisms capable of both cellulase production and ethanol fermentation, which could provide just-in-time delivery of the optimal mixture of the hydrolytic enzymes (32).

The endogenous production of such polysaccharide hydrolyase enzymes could also be coupled with enhanced plant biomass production made possible by recent advances in molecular farming (33). Exogenous depolymerization enzymes used in the bioethanol process could be replaced with plants that are capable of synthesizing these enzymes *in situ*. Carbohydrate depolymerase enzymes, such as cellulase, could be triggered for plant biosynthesis when an inducer is applied to the plant. A signal sequence from a cell wall protein could be spliced onto the cellulase gene to ensure that the cellulase synthesized by the plant is localized to the plant cell wall. The cellulase signal sequence-coding region would be attached to a chemically induced promoter that would switch on the cellulase gene. Once the modified cellulase transgene is introduced into a host plant, seeds could be produced, planted, and cultivated normally. Just before harvest, the crop would be sprayed with the chemical inducer. The cellulase would then be produced and transported to the cell wall, where it would start to break down the cellulose. After harvesting, the residual plant material would be collected and transported to a biorefinery, during which the *in situ*-generated cellulase would continue to depolymerize cellulose to glucose. An added feature of this approach is that additional depolymerization enzymes could be brought to bear for further, no-cost conversion of plant polysaccharides to mono- or oligosaccharides, facilitating subsequent separation or fermentation operations.

Currently, the fermentation of a mixture of hexoses and pentoses is inefficient because no wild organisms have been found that can convert all sugars at high yield into ethanol. Recently, several groups have made great advances in this field by genetically modifying microorganisms. One promising strategy has been to take a natural hexose ethanologen and add the pathways to convert other sugars. This strategy has been effective in adding pentose conversion to *Saccharomyces cerevisiae* and to *Zymomonas mobilis* (34, 35). The other primary strategy has been to modify a host capable of converting multiple sugars to produce only ethanol from glycolysis. Other remaining microbiological challenges include the need to understand and manipulate ethanol and sugar tolerance and resistance to potential inhibitors generated in presaccharification treatments. Solutions to these issues also will need to accommodate the variability in biomass resources.

Biological processing is not the only refining approach, however. Although biological

protocols of converting polysaccharides to bioethanol are among the most developed process technologies available for biofuels, other burgeoning chemical technologies are being pursued and present promising alternatives. These biofuels technologies are centered on the removal of oxygen from carbohydrates to obtain oxygenated hydrocarbons. As summarized in Fig. 4, controlled elimination of water from sugars has been extensively studied and can provide 5-hydroxymethyl-2-furfural (HMF), levulinic acid, and other organic acids.

Although these materials are too polar for direct liquid fuel applications, they could be used as a resource for subsequent conversion to alternative fuels. For example, controlled decarboxylation and dehydration of hexoses could yield structures such as valerolactone or 2-methylfuran. These relatively nonpolar compounds could be considered as components for novel gasoline blends, which are typically dependent on ~C5 to C10 hydrocarbons. The controlled decarboxylation and dehydration of sugars is an essential objective of this process, as overdehydration will lead to polymeric materials that have little value as biofuels. These proposed products will not provide a viable diesel supplement because diesel fuel typically relies on C12 to C20 hydrocarbons. Given the higher vapor pressure requirements of diesel fuel, these issues could be addressed by subsequent dimerization of HMF, valerolactone, or related compounds, which will increase the chain length of these biodiesel precursors.

Dumesic and co-workers recently demonstrated the potential of this pathway (36). Using a catalytic system containing both acidic and noble metal catalysts, they were able to dehydrate and hydrogenate an aqueous stream of sorbitol to hexane. They also showed that an aldol-crossed condensation between HMF and acetone leads to C9 to C15 alkanes when performed under a hydrogen atmosphere in the presence of a Pt/SiO₂-Al₂O₃ catalyst. This field of study is ripe for further rapid advances as the revolution in catalysis, computational modeling, and combinatorial chemistry will lead to a suite of catalytic systems that will facilitate the conversion of biomass polysaccharides to liquid alkanes and oxyalkanes for fuel applications.

For the biorefinery approach to be widely applicable, the lignin component of lignocellulosics must also be addressed (37). Residual lignin from paper pulping is now burned for heat and power, but lignin thermal-cracking studies using temperatures of ~250° to 600°C have demonstrated the potential of generating low molecular weight feedstocks for further processing (28). These high temperatures suggest that the use of cracking catalysts could lower conversion temperatures and provide improved control over product distributions. Shabtai *et al.* (29) have highlighted this potential in a process whereby a two-stage catalytic reaction with lignin produces a reformulated, partially

oxygenated gasoline-like product. Lignin is first depolymerized by a base-catalyzed treatment into a series of low molecular weight phenolic compounds. This mixture is then subjected to hydro-processing, which primarily yields a mixture of alkylbenzenes useful as a potential liquid biofuel.

This pyrolysis approach to biofuels from lignin is also being pursued with biomass in general, with and without a catalyst; it provides about 58 to 77% conversion of biomass to a condensable gas, 13 to 28% noncondensable gases, and 6 to 13% char formation. The condensable gases can be refined to fuels and chemicals, and the noncondensables can be steam-reformed to synthesis gas (syngas), a mixture of CO and H₂, which can also be used to produce fuels and chemicals (38).

Regardless of which process technologies are incorporated into a biorefinery, almost all will generate some waste products that will be intractable and difficult to convert to value-added biomaterials or biofuels. These spent-biomass residues will contain fragments from lignin, residual carbohydrates, and other organic matter. This residue will need to be treated in an environmentally compatible manner, with the smallest ecological footprint. Such wastes and residues offer important energy sources within the biorefinery, given their chemical energy content, and are an ideal candidate for thermochemical conversion to syngas (39). Syngas is an intermediate in the production of ammonia, methanol, and Fischer-Tropsch hydrocarbons. Production of syngas from coal, natural gas, and other carbonaceous sources is well established. Coal is normally gasified in entrained-flow reactors at temperatures exceeding 1400°C at 20 to 70 bar. Biomass is more reactive than coal and is usually gasified at temperatures between 800° and 1000°C at 20 to 30 bar.

The greatest challenge in producing syngas from biomass is the need to avoid poisoning the noble metal catalysts used in the subsequent downstream conversion to fuels and chemicals. Potential problem products are the alkali metals, halides, sulfur gases, and especially the tars. A high quantity of tar is produced as the organic components of biomass decompose.

Evolution of tar from primary to tertiary species is rapid, but tertiary tar species are degraded slowly to CO and H₂ by water vapor or CO₂ at temperatures below 1100°C. Catalytic conversion of tar in raw syngas to CO and H₂ is practiced, but the quantities of tar that must be converted are large, and robust catalysts that are insensitive to alkali metals, halides, sulfur, and nitrogen need to be developed.

Chloride, the predominant halide in biomass, is converted to HCl or submicrometer aerosols of potassium and sodium during gasification, which poses a corrosion issue. Most of the alkali metal chlorides are removed by filtering the cooled syngas. Sulfur gases can be removed by absorption. Remaining alkali metal

challenges are addressed, the final component of the integrated biorefinery will become available, and the resulting residue products from the biorefinery will become a valuable resource for bio-power, biofuels, and biomaterial generation.

Concluding Remarks

In view of changing world energy needs, a research road map for the biorefinery of the 21st century is vital. This biorefinery vision will contribute to sustainability not only by its inherent dependence on sustainable bio-resources, but also by recycling waste, with the entire process becoming carbon neutral. It leverages our knowledge in plant genetics, biochemistry, biotechnology, biomass chemis-

try, separation, and process engineering to have a positive impact on the economic, technical, and environmental well-being of society.

An integrated biorefinery is an approach that optimizes the use of biomass for the production of biofuels, bioenergy, and biomaterials for both short- and long-term sustainability. The demands of future biorefineries will stimulate further advances in agriculture in which tailored perennial plants and trees will provide increasing amounts of bio-resources, as highlighted in the "Billion-Ton" report (10). The advances in plant science will certainly be influenced by societal policies, land use practices, accelerated plant domestication programs, and research funding to develop this vision. Nonetheless, given humanity's depen-

dence on diminishing nonrenewable energy resources, this is a challenge that must be addressed—and we need to get on with it!

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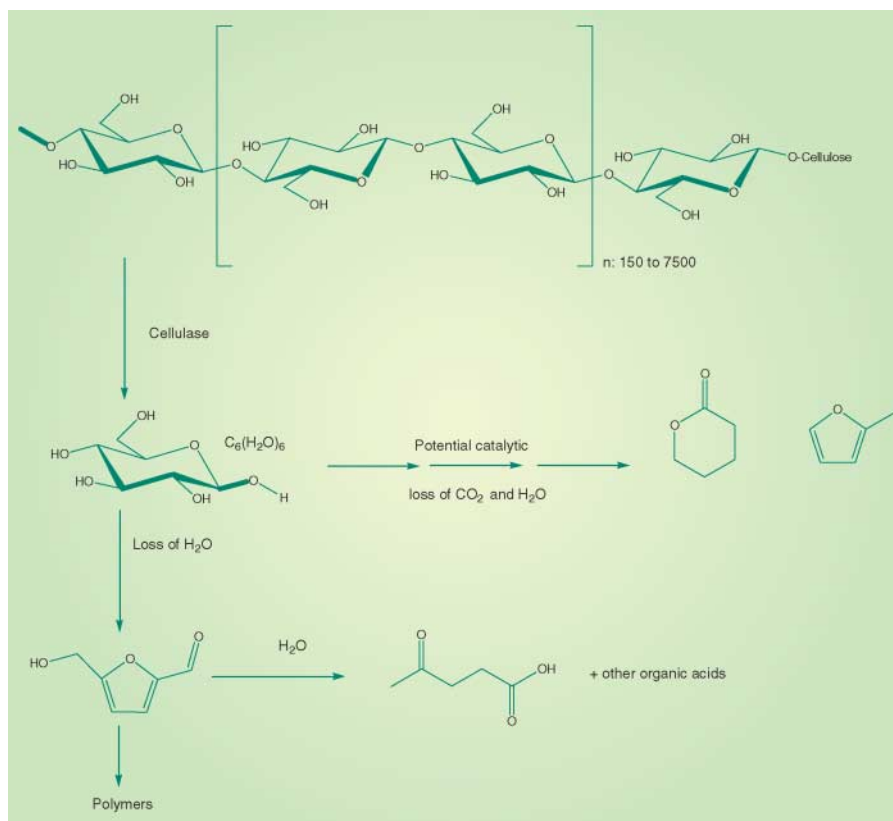


Fig. 4. Dehydration-decarboxylation chemistry of hexoses.

chlorides and sulfur gases are removed by reaction with ZnO in a packed-bed filter. Although these advances in syngas purification technologies are necessary for the catalytic conversion of syngas to other fuels or chemicals, they add further complications and increase the overall cost.

Anaerobic fermentation of syngas into biofuels is a promising competing technology that is far more tolerant of tar and trace contaminants than noble metal catalysts (40). Development of enhanced bioprocesses, reactor designs with improved mass transfer of the syngas into the liquid phase, and enhanced gas and liquid separation methods are needed if the biochemical route is to become economically viable. As these

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