

Opportunities in the Industrial Biobased Products Industry

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Abstract

Approximately 89 million metric t of organic chemicals and lubricants, the majority of which are fossil based, are produced annually in the United States. The development of new industrial bioproducts, for production in stand-alone facilities or biorefineries, has the potential to reduce our dependence on imported oil and improve energy security. Advances in biotechnology are enabling the optimization of feedstock composition and agronomic characteristics and the development of new and improved fermentation organisms for conversion of biomass to new end products or intermediates. This article reviews recent biotechnology efforts to develop new industrial bioproducts and improve renewable feedstocks and key market opportunities.

Index Entries: Bioproducts; thermoplastics; fermentation; solvents; platform chemicals.

Introduction

Industrial biobased products have enormous potential in the chemical and material industries. The diversity of biomass feedstocks (sugars, oils, protein, lignocellulosics), combined with the numerous biochemical and thermochemical conversion technologies, can provide a wealth of products that can be used in many applications. Targeted markets include the polymer, lubricant, solvent, adhesive, herbicide, and pharmaceutical markets. Industrial bioproducts have already penetrated some of these markets, but improved technologies promise new products that can compete with fossil-based products in both cost and performance.

Organic chemicals and lubricants represent the largest and most easily accessible target for bioproducts (Table 1). Within the organic chemicals

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Table 1
Annual Domestic Organic Chemical Production (1–9)

Market (year of production data)	Annual production (million metric t)
Lubricants and greases (2001)	8.9
All organic chemicals ^a	79.6
Polymers (2001) ^b	45.9
Polyolefins (2001) ^b	22.4
Polyethylene terephthalate (2001) ^b	3.1
Polyvinyl chloride (2001) ^b	6.5
Styrenics (2001) ^b	4.1
Nylon (2001) ^b	0.5
Thermosets (2001) ^b	3.6
Other polymers (2001) ^b	5.7
Forest chemicals (1999 and 2000) ^c	1.3
Solvents (2001)	4.8
Glycols (2000)	1.4
Other organic chemicals (1997)	27.6

^a The estimate represents the net volume of organic chemicals produced in the United States and does not double count volumes of intermediates and their derivatives.

^b Data from ref. 2.

^c Tall oil, gum rosin, and crude sulfate turpentine.

market, the polymer industry presents a tremendous opportunity, with an annual production of approx 46 million metric t (2). Other market segments include organic acids, alcohols, solvents, and adhesives.

By using biotechnology and novel chemistries, biomass carbon can be rearranged to yield products that are equivalent or superior to the fossil-based products used today. New genetic mapping techniques allow researchers to sequence genes more quickly and to determine the relationship between structure and function (10). These genetic tools are being used to create new and improved microorganisms to convert biomass components into end products or intermediates that can then be thermochemically upgraded (11). The tools are also being used to improve biomass feedstocks by (1) increasing the content of desired components, (2) decreasing the content of components such as lignin, and/or (3) adding the capability to produce a new component (e.g., a new fatty acid in oil-seeds) (10). This article examines recent biotechnology efforts to develop new industrial bioproducts and improve renewable feedstocks and key market opportunities.

Polymers

Since 1976, plastics have been the most used material in the world (12). According to the American Plastics Council, nearly 46 million metric t of polymers was produced in the United States in 2001 (2). Plastics are often

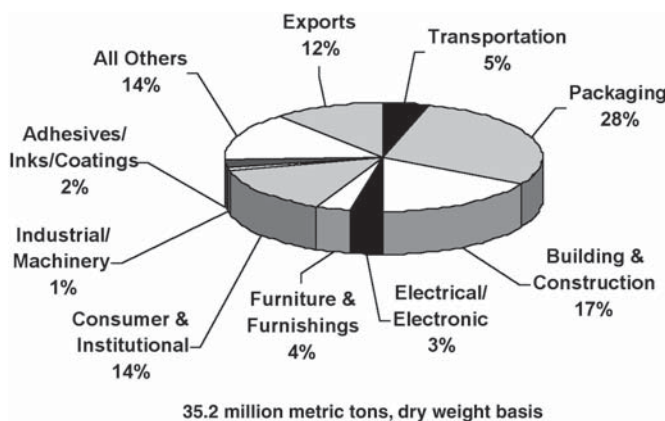


Fig. 1. US total sales and captive use of selected thermoplastic resins by major market for 2001. Major market volumes are derived from plastic resins sales and captive use data as compiled by VERIS Consulting, LLC and reported by the American Plastics Council's Plastic Industry Producers' Statistics Group. Selected thermoplastics are low-density polyethylene, linear low-density polyethylene, high-density polyethylene, polypropylene, nylon, polyvinyl chloride, thermoplastic polyester, engineering resins, acrylonitrile-butadiene-styrene, styrene-acrylonitrile, other styrenics, polystyrene, and styrene butadiene latexes. (Data from ref. 15.)

selected over more traditional materials because of their superior properties (lightweight, corrosion and shatter resistant, long-lasting) and lower cost. Their versatility enables their use in applications ranging from clothing and packaging to high-tech composites, and they are found in nearly all end-use markets (Fig. 1). Biobased polymer manufacturers and researchers are currently targeting packaging and fiber/fiberfill applications, which represent two of the largest uses of polymers (13,14).

Plastic packaging represents the largest single market for polymer resins and is a key focus for new biobased products. Since 1913 when cellophane (a bioproduct), the first fully flexible, waterproof wrap, was developed, the use of plastic packaging has grown owing to its ability to provide the same strength, barrier, and shatterproof properties with a reduction in the packaging weight and at a lower cost (12). In 2000, nearly 10 million metric t of thermoplastics was consumed in packaging applications in the United States (Table 2) (16).

Second behind packaging in the United States is the use of polymers in fiber and fiberfill applications that encompass the apparel, sports equipment, building and construction, electronic, furniture and furnishings, and industrial/machinery markets. In 1998, 4.8 million metric t of manufactured fiber was produced for use in traditional consumer products such as apparel, carpets, upholstered furniture, and bedding as well as in high-tech applications such as composite materials, medical devices, and electronic circuit boards (17). Key fiber types include polyester, nylon, olefin,

Table 2
Thermoplastics Used in Packaging in 2000 in the United States (16)

Thermoplastic	Quantity (million metric t)	Percent
Low-density polyethylene	1.20	12.4
Linear low-density polyethylene	2.05	21.1
High-density polyethylene	3.38	34.9
Polypropylene	1.59	16.4
Polystyrene	0.59	6.1
Nylon	0.05	0.5
Polyvinyl chloride	0.44	4.6
Other	0.38	4.0
Total	9.68	100.0

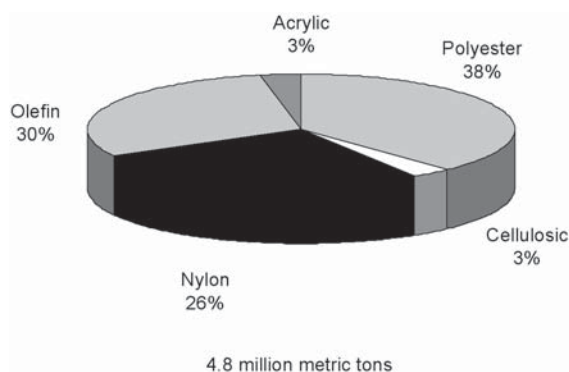


Fig. 2. US fiber production for 1998 (17).

cellulosic, and acrylic (Fig. 2). Some of these are already biobased (cellulosic fibers, rayon, acetate), and there are opportunities for new industrial bioproducts to make inroads in the fiber industry.

Poly(lactide)

Much has been written about Cargill Dow LLC's polylactide (PLA) polymer, also known as NatureWorks™ PLA. PLA is a thermoplastic produced from biomass sugars by fermentation. The fermentation product, lactic acid, is converted into a lactide that is purified and polymerized using a special ring-opening process (18).

In April 2002, Cargill Dow started up its first large-scale PLA plant in Blair, NE. The plant has a capacity of 140,000 metric t, and demand for NatureWorks PLA has been so strong that construction of a second plant is likely to begin within a few years (19). Cargill Dow projects a possible market of 3.6 million metric t by 2020 (20).

PLA is cost-competitive with conventional polymers and offers performance properties equal to or greater than those offered by conventional

polymers such as polyethylene terephthalate (PET) and nylon. Cargill Dow is targeting the food-packaging and fiber/fiberfill applications markets. The high stiffness, superior clarity and gloss, dead-fold, grease resistance, and unique flavor and aroma barrier properties (21) of PLA combined with its environmentally friendly profile are opening inroads in the packaging industry. Cargill Dow has teamed with a number of domestic and international consumer product packaging companies including The Coca-Cola Company (soft drink cups) and Sony Pacific (blister packaging and film wrap for radios and minidisks) (22).

PLA fiber combines the most desired properties of natural fibers, such as wool, and synthetics, such as polyester. This combination of properties opens up a wealth of textile applications including clothing, carpet tiles, diapers/acquisition distribution layers, upholstery, furnishings, and filtration. PLA has a high dyeability, and in comparison with polyester in activewear, it displays superior wicking properties.

Cargill Dow currently relies on corn grain as a source of glucose for PLA production but is working to develop fermentation organisms that convert pentose sugars as well as glucose into polylactide (11). This would enable the use of lignocellulosic material such as corn stover and rice straw, decreasing production costs and providing a higher value outlet for low-value agricultural residues.

Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are a family of natural polymers produced by many bacterial species for carbon and energy storage that exhibit a broad spectrum of performance properties, enabling them to compete with a large share of the plastics market. PHAs can be produced through fermentation, and, more recently, researchers have been working to genetically modify a plant for direct production (23). Since the 1970s, ICI, Zeneca, and, to some degree, Monsanto and others have pursued cost-effective fermentation production routes. In the 1990s, bacterial fermentation of PHAs, specifically poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), was performed commercially by Zeneca and then Monsanto under the trade name Biopol™; however, production costs of PHBV were high (more than \$6.60/kg), and it could not compete with conventional petroleum-based plastics using the fermentation and separation technology available at the time (24).

Metabolix has since developed lower-cost fermentation technology for PHAs, which the company claims would permit commercial-scale production for under \$2.20/kg (25). Production at this cost could open up a significant market for fermentation-based PHAs.

Researchers at the Hawaii Natural Energy Institute, University of Hawaii, have also developed a novel, two-step process that converts organic waste materials such as food scraps into poly(3-hydroxybutyrate) or PHBV (26). Approximately 60% of the organic material is converted into PHAs, and the remaining 40% can be converted into fertilizers (27). The first step

is an anaerobic digestion process that converts food scraps into four major organic acids: acetic, propionic, butyric, and lactic. The acids pass through a dialysis membrane, concentrating them, and then enter the second bioreactor to be consumed by an enriched *Ralstonia eutropha* culture to produce the PHAs. A polymer content of 72.6% of dry cell mass was obtained, comparable to PHA content through pure glucose fermentation (26).

The estimated PHA production cost for the two-step process is between \$2.20 and \$4.40/kg (27). The potential of this process has caught the attention of I-PHA BioPolymers, a Hong Kong-based company involved in environmental biotechnology development, which recently licensed the technology from the University of Hawaii. I-PHA BioPolymers plans to develop and build a pilot plant for the production of PHAs and fertilizers (28).

A still lower-cost route to PHAs is genetic modification of plants to directly produce the final polymer. Monsanto (and others) pursued this approach and is currently being cofunded by the US Department of Energy (DOE) in a collaborative research project led by Metabolix. Switchgrass will be modified to produce PHAs, which can then be extracted from the plant material and processed to obtain a consistent composition and the desired material properties. The plant material remaining after PHA extraction can be used to produce fuels, power, or other products, creating the opportunity for a "plants as factories" biorefinery. Applications for polymers with properties similar to those of PHAs consume on the order of 13.6 million metric t annually, and it is possible that in the future PHAs will figure prominently in the plastics market.

1,3-Propanediol

Together with purified terephthalic acid, 1,3-propanediol is used to produce polytrimethylene terephthalate (PTT), a polymer with remarkable "stretch-recovery" properties. The desirable attributes of PTT have been known since the 1940s, but high production costs prevented its entrance into the polymer market (29). In the 1990s, a new fossil-based route to 1,3-propanediol was developed enabling the production of PTT for higher-value applications, and PTT polymers were introduced into the market by DuPont and Shell Chemicals (29,30).

For DuPont, the commercialization of 1,3-propanediol and PTT has opened up markets for industrial products from renewable resources. Through a partnership with Genencor International, DuPont has recently developed a lower-cost fermentation route that converts biomass sugars into 1,3-propanediol. DuPont plans to transition to the biobased process for 1,3-propanediol production in 2004 (31).

PTT is used in apparel, upholstery, specialty resins, and other applications in which properties such as softness, comfort stretch and recovery, dyeability, and easy care are desired. The properties of PTT surpass nylon and PET in fiber applications, and polybutylene terephthalate and PET in resin applications such as sealable closures, connectors, extrusion coatings, and blister packs (14).

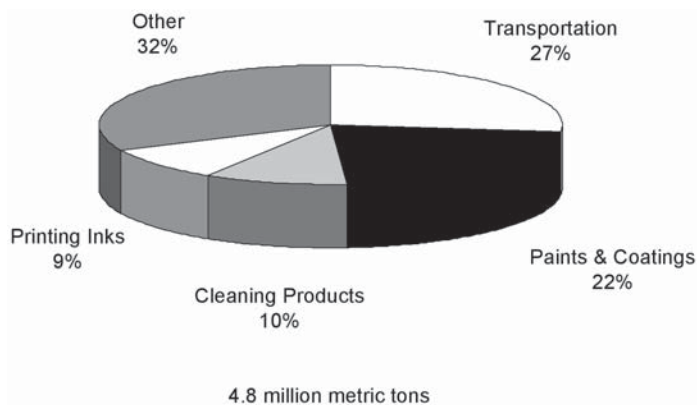


Fig. 3. US solvent demand for 2000 (3).

DuPont expects PTT to stay at the same pricing level as nylon 6, though the company believes that the polymer's properties, and not price, will drive demand (32). Based on its use in PTT, 1,3-propanediol has a potential 2020 market of 230,000 metric t.

In addition to its use in PTT, 1,3-propanediol can replace traditional glycols in urethane-based polymer systems, improving thermal and hydrolytic stability. As a partial substitute for traditional glycols in polyester systems, 1,3-propanediol can improve coating flexibility without affecting other key properties. Other applications include engine coolants and water-based inks (33).

Solvents

Solvents are integral to our lifestyle today, contributing to the manufacture of numerous products such as pharmaceuticals, paints, inks, and microchips. They make it possible to process, apply, clean, or separate materials and are used across many industries (Fig. 3). Different applications require specific solvating or other properties, and solvents can be blended to achieve the properties necessary for a given application.

Growing concern over volatile organic compound and other emissions is motivating manufacturers to modify processes to capture and recycle solvents, reduce solvent use, or switch to solvents with better environmental profiles. A biobased solvent that is benefiting from this shift is ethyl lactate.

Ethyl Lactate

Ethyl lactate is another lactic acid derivative that has recently been commercialized. An environmentally benign solvent with properties superior to many conventional petroleum-based solvents, it can be blended with methyl soyate derived from soybean oil to create custom-tailored solvents for various applications.

Table 3
Selling Price of Common Solvents (37)

Product	Price (\$/kg)
Methyl soyate	0.66–1.00
Aqueous cleaners	~2.65
Semiaqueous cleaners	~8.90
N-Methyl pyrrolidone	3.30–4.00
d-Limonene	Up to 0.88
Methylene chloride	0.66
Trichloroethylene	1.43
Methyl ethyl ketone	1.00
Perchloroethylene	0.77

Until recently, the use of ethyl lactate has been limited owing to high production costs; selling prices for ethyl lactate have ranged between \$3.30 and \$4.40/kg, compared with \$2.00 and \$3.75/kg for conventional solvents (34). With advances in lactic acid fermentation, and separations and conversion technologies, retail costs have been driven down as low as \$1.87/kg (35). DOE has cofunded lactic acid separations technology involving the use of electrodialysis, advanced membranes, and reactive separations capable of converting the lactic acid salts made during fermentation directly into ethyl lactate.

More than 4.5 million metric t of solvents is used in the United States annually, and it has been suggested by industry experts that ethyl lactate could replace conventional solvents in more than 80% of these applications (34). Vertec Biosolvents Inc. is currently using ethyl lactate in soy oil–solvent blends. Applications targeted by Vertec Biosolvents include conventional solvents that are under environmental scrutiny such as methylene chloride, methyl ethyl ketone, and *N*-methyl pyrrolidone (36). Table 3 lists the selling prices of some common solvents.

Platform Chemicals

Platform chemicals are compounds that serve as building blocks for numerous chemical intermediates and end products. An example is ethylene, which serves as the feedstock for derivatives such as acetaldehyde, ethylene dichloride, ethylene oxide, polyethylene, vinyl acetate, and ethyl acetate. Biobased chemicals such as succinic acid, 3-hydroxypropionic acid (3-HP), and butanol also have the potential to be converted into multiple derivatives, some of which are commodity chemicals and others that are higher-value chemicals.

Succinic Acid

Succinic acid and its salts, produced through the fermentation of glucose, form a platform from which many chemicals can be produced. Since most fermentation organisms are not tolerant of acidic conditions, the fer-

mentation is typically neutralized, producing a salt of succinic acid. Conventional separation and recovery involves filtration to separate the solid cell mass, and reacidification of the succinate salt to form free succinic acid while precipitating out a salt.

There has been considerable research over the past 5–10 yr dedicated to improving microorganisms and separations technologies in order to reduce the overall cost of biobased succinic acid, much of which has been cofunded by DOE. This research has resulted in the development of the fermentation microorganism *Escherichia coli* strain AFP111, which exhibits greatly improved productivity. Fermentation with AFP111 to produce succinic acid has recently been successfully tested at commercial scale.

Separations research has resulted in the development of a two-stage desalting and water-splitting electrodialysis system that concentrates, purifies, and acidifies the succinic acid. The base is recycled back to the fermentation, where it is used for neutralization, eliminating the generation of gypsum salt, an unwanted neutralization byproduct that must be disposed of or sold (38).

Succinic acid for industrial use is predominately produced from butane via maleic anhydride, whereas food-grade succinic acid is produced through older fermentation and separation technology. Both routes are costly and this has limited use to specialized areas. Consequently, the world market is relatively small at 15,000 metric t/yr (39).

In 1992, the production costs of succinic acid fermentation ranged from \$3.30 to \$4.40/kg. Advances in fermentation, and especially separation technology for the biobased route, have reduced the potential production costs to about \$1.10/kg. Ongoing advances could significantly reduce the cost of biobased succinic acid even more, and commercialization of these low-cost routes could have a significant impact on the demand for succinic acid, expanding current markets while opening up new markets for the acid and its derivatives.

As shown in Table 4, the real promise of succinic acid lies in its derivatives. A DOE-funded collaboration among Oak Ridge National Laboratory; Argonne National Laboratory; Pacific Northwest National Laboratory; National Renewable Energy Laboratory; and Applied CarboChemicals, Inc. investigated succinic acid derivatives such as tetrahydrofuran, 1,4-butanediol, γ -butyrolactone, and *N*-methyl pyrrolidone. More recently, Applied Carbochemicals has pursued succinate salts that can serve as de-icers and herbicide additives (40,41).

Other companies showing strong interest in the production of biobased succinic acid and its derivatives are Mitsubishi Chemical and Ajinomoto Company, Inc., which have agreed to collaboratively develop a biobased process to convert sugars into succinic acid. These companies plan to construct a succinic acid plant in Japan with an initial capacity of 30,000 metric t/yr (MT) by 2006 (42). Table 4 shows the current market estimates for the fossil-based chemicals, as well as 2020 market estimates for the biobased products potentially based on biobased succinic acid.

Table 4
Potential Near-Term Succinic Acid Derivatives (39,40,43–46)

Chemical	Current US market (metric t) ^a	Market Price (\$/kg) ^b	Potential 2020 market size (metric t) ^c
Tetrahydrofuran	179,100	3.40	>22,700
1,4-Butanediol	373,200	1.40–2.00	>13,60?
γ-Butyrolactone	78,400	?	?
N-Methyl pyrrolidone	50,900	?	Could be displaced by ethyl lactate
2-Pyrrolidone	<29,500	Unknown	?
Succinate salts	Road de-icer: 9,090,900	0.05	Depends on demand for less-corrosive road de-icers
Succinate salts	Aviation de-icer: 91,000	1.00–1.95	Could replace 100% of airport de-icers
Succinate salts	Herbicide: small	?	Small

^aThis is the volume of market opportunities represented by the current and potential applications.

^bThis is the price of the current applications targeted by the biobased product and not the price of the biobased product.

^cThese are authors' estimates of the biobased market in 2020 based on the state of the technology development and current US market size.

Succinate salts (calcium, magnesium, diammonium, ammonium) show near-term market potential. They are produced through the neutralization of succinic acid, an intermediate step in the production of succinic acid by fermentation. Two key applications identified are herbicide additives and de-icing compounds for roads, aircraft, and airport runways. Although herbicide use is high, the active ingredients (herbicide and succinate salt enhancer) may comprise only a small amount of the product, between 0.5 and 3.0 wt% (41). Conversely, in 1990, approx 9,090,900 metric t of salt was used on roads and highways and about 91,000 metric t of aviation de-icers is currently used each year (40,45), and both types of de-icers are under pressure from environmental groups. Federal and state aviation and highway agencies are seeking de-icers with improved performance and reduced corrosiveness, and succinate salts are ideal for this purpose because they offer improved ice penetration characteristics and are less damaging to concrete, asphalt, metals, and the environment.

3-Hydroxypropionic Acid

The fermentation of glucose to 3-HP is just now being actively investigated. Many high-volume products can be made from 3-HP, giving it the

potential to be a platform intermediate similar to lactic acid and succinic acid. The synthesis of acrylic acid, and the salts and esters of acrylic acid derived from 3-HP, has been demonstrated in the laboratory. Other derivatives under consideration include acrylamide, 1,3-propanediol, malonic acid esters, and acrylonitrile (47). As with PLA, there is no commercially viable production route of 3-HP from fossil fuel feedstocks.

The conversion of 3-HP into acrylic acid is expected to be “easier” and may require less energy than the oxidation of propylene to acrylic acid (47). As conversion technologies are developed, the primary challenge will be to make them cost-competitive with the current fossil-based routes.

Butanol

Butanol is a platform chemical with several large-volume derivatives and is used as a solvent and in plasticizers, amino resins, and butylamines (48). Butanol can also be used as a biobased transportation fuel and is more fuel efficient than ethanol on a volume basis.

In 1999, the domestic demand for butanol was 841,000 metric t and it is projected to increase 3% per year (49). During the early twentieth century, the primary method of butanol production was anaerobic fermentation with *Clostridium acetobutylicum* to produce a mixture of acetone, butanol, and ethanol. The butanol yields were low, and as oil prices declined after World War II, petrochemical routes to butanol displaced the fermentation route (50). The primary petrochemical route used today involves the hydrogenation of *n*-butyraldehyde (49), and production costs hover around \$0.66/kg (24).

The US DOE's Small Business Technology Transfer Program is funding research to improve the biobased route to butanol and make it cost-competitive with the petroleum-based route. Researchers are attempting to increase butanol yield by using improved bacteria strains, employing advanced reactor technology, and separating the organic acid production and organic acid-to-alcohol phases into different vessels. A preliminary material and energy balance indicates that a yield of 9.5 L of butanol/bu of corn could be achieved (51).

Feedstock Modification

Advanced genetic engineering techniques are being used to improve existing renewable feedstocks for the production of industrial bioproducts. In some cases, the feedstock composition is modified to increase the content of a desired component and/or decrease the content of an undesired component, whereas in others, a new metabolic pathway is inserted into the plant genes so that the modified plant produces an entirely new component. These research efforts are recent, and very little, if any, published information is currently available. However, we provide brief descriptions of the research activities to give perspective on the opportunities for new industrial bioproducts that may emerge from feedstock modification.

Adhesives and Resins from Soy Oil and Protein (10)

Researchers at the University of Delaware and Kansas State University are working together to optimize the soy oil and protein composition for use in resin and adhesive applications. Work is being performed to understand the relationship between the chemical structures of the oil and protein components, and their performance properties in resin and adhesive formulations. The results of this work will be used to modify the soybean varieties, using conventional breeding and genetic engineering to increase the percentage of specific fats and proteins.

Biobased Products from Optimized Sorghum Grain (10)

Sorghum grain is a very versatile feedstock and is used in a variety of consumer and industrial markets, including ethanol production. However, little has been done to optimize the grain composition or conversion into sugars and industrial products. As such, Orion Genomics, LLC is leading an effort to optimize grain composition for increased starch content and ease of processing to industrial bioproducts. The agronomic characteristics, such as yield per unit resource, will also be improved for more economical sorghum production.

Increased Natural Rubber Content in Guayule

Guayule, another emerging bioproduct-producing plant, is being developed by the US Department of Agriculture (USDA); Yulex Corporation; and Mendel Biotechnology, Inc. It is a desert shrub indigenous to the southwestern United States and northern Mexico and produces a natural rubber latex primarily in the cells of the bark (52). Natural rubber, commonly used in medical device components, currently comes from the Brazilian rubber tree (*Hevea brasiliensis*) and is imported from Southeast Asian countries such as Thailand, Indonesia, and Malaysia. However, several factors, including increased global demand, diminished acreage, and pathogen attack, are endangering the dependability of the world's natural rubber supply.

Rubber production in guayule offers the potential to develop a domestic supply of natural rubber. In addition, guayule rubber does not contain the proteins present in *Hevea* rubber that can cause an allergic reaction. Natural rubber latex allergy has become an issue in the United States: approx 20 million Americans are allergic to the proteins found in *Hevea* rubber (53). Initial target applications for guayule rubber include gloves and other products for which the strength and resiliency of natural rubber is desired without the potential allergic reaction.

Approximately 22.5–56.2 metric t of rubber can be produced per hectare of guayule (20,000–50,000 lb/acre) (54), and researchers at Mendel Biotechnology are working to increase the rubber content of guayule without compromising rubber quality. They are identifying the *Arabidopsis thaliana* transcription factors that can activate promoters of genes in the rubber

synthesis pathway. These transcription factors will then be used to transform guayule for increased rubber yield (55).

Plastics, Coatings, Adhesives, and Lubricants from Castor and Soy Oil (10)

The Dow Chemical Company, Castor Oil, Inc., and the USDA Western Regional Research Center are collaborating to develop the castor plant as a suitable oilseed for specialty oils that can be converted into lubricants, coatings, foams, adhesives, and engineering thermoplastics. Castor oil already contains ricinoleic acid, a fatty acid used in many industrial applications, but project partners hope to produce other industrially desirable fatty acids within the castor bean.

Conclusion

The chemical and lubricant markets represent an enormous opportunity for biobased products, but many obstacles must be overcome on the way to commercialization. To gain acceptance and supplant products made from petroleum, industrial bioproducts will need to be able to compete in terms of both cost and performance; advances in biotechnology will play a key role in surmounting these economic and technical barriers. Given the size of the potential markets and the considerable research under way, the future looks bright for a biobased economy.

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