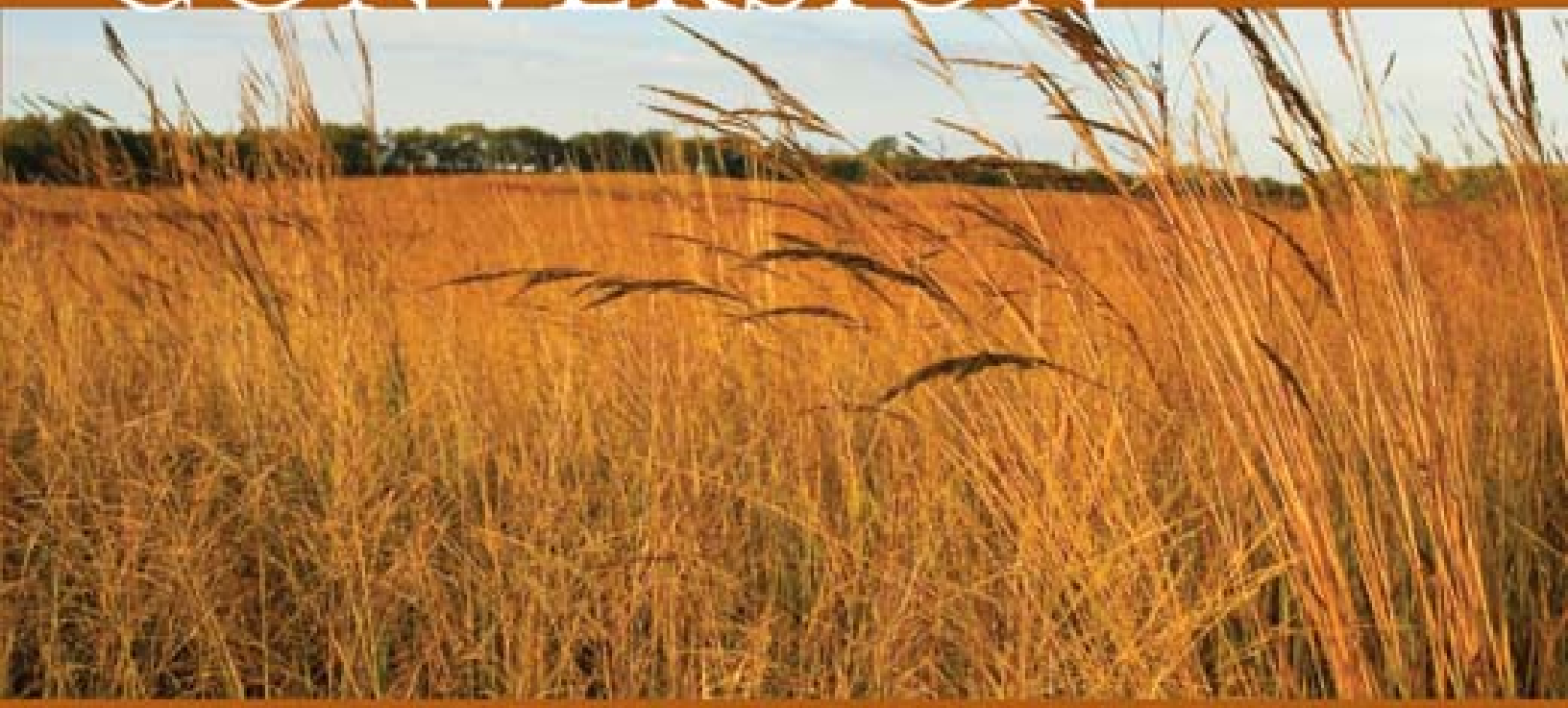
BIOMASS AND BIOFUELS SERIES

# PLANT BIOMASS CONVERSION



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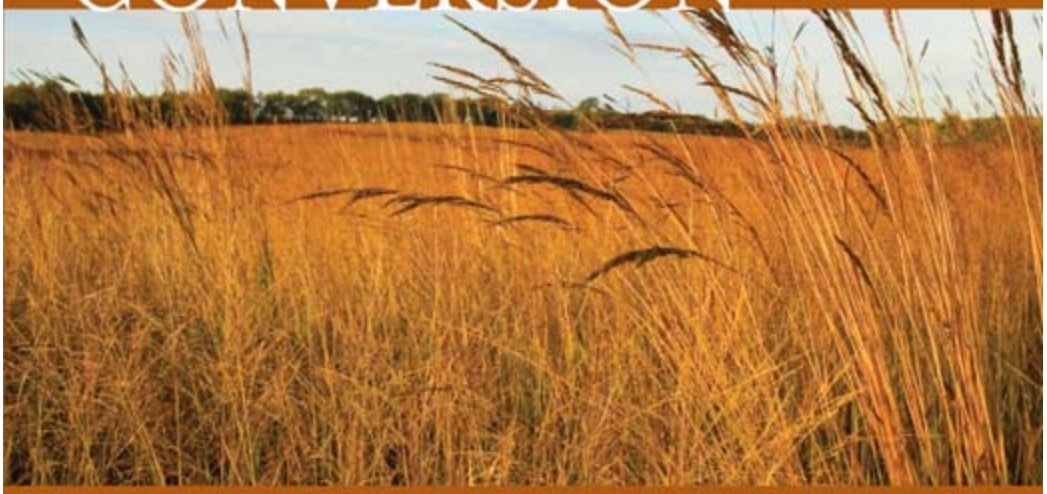

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# Contents

# Plant Biomass Conversion


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# *Preface*

A host of motivations is driving the development of the “renewables” industry—a desire for energy independence in the United States, biodegradable products, global warming, and hopefully, making money. All energy utilized on the earth is ultimately derived from the sun through photosynthesis—the only truly renewable commodity. Capitalizing on this productive process in a balanced way is crucial to our survival as a species.

Crude oil represents an ancient capture of carbon and sunlight by plants. However, the rate at which we are utilizing oil releases ancient fixed carbon into the atmosphere and upsets the balance of nature in a way that is unprecedented in global history. Nature's checks and balances are not able to accommodate this huge increase in carbon from man's activities. Thus, development of a new source of energy and products is imperative.

Many models that describe processes for generating energy from biomass exist. No one book can describe them all. This work focuses on the biochemical (enzymatic) digestion of plant biomass to produce the raw materials that make up plant cell wall polymers. These raw materials can then be used as feedstocks for ethanol and other bio-based products. This volume also is focused on solving the issues for biomass conversion into ethanol and bio-based products now—not the longer-term solutions with modified microbes and modified feedstocks.

The chapters review existing technologies and future expectations for those technologies. They describe multiple feedstocks, multiple pretreatment technologies, enzyme production models, fermentation models, and manufacturing of products in biorefineries. While this is a

snapshot in time of the state of the industry, this volume should serve as a guide and model for describing what is possible and where the issues are, which must be solved.

We hope you enjoy our book.

Elizabeth E. Hood, PhD
Arkansas State University

# *Chapter 1*

# *The Bioeconomy: A New Era of Products Derived from Renewable Plant-Based Feedstocks*

**Peter Nelson, Elizabeth Hood, and Randall Powell**

## 1.1 Introduction

The first two decades of the 21st century will be marked as the turning point when large investments, technology breakthroughs, and new strategic alliances set the stage for the eventual widespread replacement of fossil feedstocks with renewable, plant-based alternatives for the production of fuels, chemicals, and energy. This is not a new idea, as humankind in the pre-industrial era utilized plant-derived chemicals such as proteins, sugars, and cellulose as the primary feedstocks to make a range of necessary materials and industrial products. However, as non-renewable fossil resources now become increasingly scarce, expensive, and produce negative environmental impacts, the need has never been so great to develop and expand agriculture and forestry as the source of sustainable feedstocks to serve a growing global population. Ultimately, renewable resources must feed, clothe, shelter, fuel, and provide for material goods for the planet’s inhabitants, while also addressing

vexing environmental problems including climate change, pollution, access to clean water, and long-term soil health.

In the 20th century, incredible technological improvements in agriculture and forestry were made. These advances included dramatic yield increases, drought tolerance, insect resistance in agricultural crops, and new production methodologies such as conservation tillage, which builds soil health and requires less energy. These productivity and environmental improvements offer much promise for a future bioeconomy in which agriculture and forestry will provide the predominant feedstocks for much more than food, feed, and fiber. Agricultural successes such as the Green Revolution have dramatically increased global crop yields, reduced hunger in the developing world, and expanded access to nutritious foods, but are still heavily dependent upon fossil-derived energy and chemicals. Fortunately, agricultural and forestry-based companies and institutions are now collaborating in new ways with industries traditionally dependent on fossil fuels to expand the use of renewable raw materials in a range of manufactured goods. Over the coming decades, this will lead to a more sustainable, closed-loop-systems-based approach to the production of food, energy, and materials. This biobased transition requires development and integration of a range of technologies encompassing energy, process efficiency, environmental compatibility, and even more advanced agricultural production systems. The increasing application of biotechnology tools—previously focused on human health—to improve agricultural crops and practices, enable clean manufacturing processes, and provide sustainable products is the essential catalyst for this transition.

A renewable “bioeconomy” is now starting to become a reality, but the concept is not new. In the early days of the 20th century, industrial and agricultural leaders such as

Henry Ford and George Washington Carver were proponents and practitioners of the use of plant-derived materials in a range of nonfood products. These innovators demonstrated the commercial utility of renewable biobased feedstocks in hundreds of products, such as automotive composites, glues and adhesives, dyes and inks, plastics, and, of course, biofuels. Unfortunately, the rapid emergence of petroleum as an available and inexpensive feedstock, albeit with unrecognized long-term environmental consequences, drove manufacturers to develop fossil-based rather than renewable products as the initial outputs of the Industrial Revolution. A century later, as the true costs of fossil fuels are realized, renewable feedstocks are re-emerging at commercial scale, largely through innovative partnerships across the value-chain linking agriculture, biotechnology, and the chemical process industries in new ways.

Evidence of this transition has become increasingly apparent over the last 30 years as some organizations began decoupling themselves from traditional businesses to focus on agricultural biotechnology. A leading example is Monsanto Company, which has aggressively divested its mainstay fossil-based chemical manufacturing business to focus on the commercial opportunity to develop new agricultural biotechnology traits in commodity crops such as corn, cotton, and soybeans. Major agricultural commodity companies such as Archer Daniels Midland (ADM) and Cargill have also expanded chemical and fuel product offerings based upon their plant-based raw material resources. More recently, a number of multinational chemical companies—notably Dow and DuPont—are pursuing biobased product platforms, with initial commercial products now entering the marketplace. Increasingly, many traditional agricultural commodity companies, fossil-based chemical companies, and newer industrial biotechnology firms are partnering to integrate knowledge of biobased feedstocks, new

conversion processes, and operational expertise in order to solve future challenges related to energy and useful materials.

The transition to a photosynthesis-based bioeconomy offers commercial opportunity, resource and environmental sustainability, and more equitable global economic development than has been the recent case with fossil resources. However, more intensive agricultural and forestry utilization, and the accompanying deployment of technology must be the products of clear strategic planning and sustainable development practices.

If managed correctly, the transition to a renewable-based economy can create new rural and urban opportunities, offer unique environmental solutions, and create wealth. The new economy based on renewable agricultural and forestry raw materials and clean processes will also serve as a major catalyst for realignment of some of the world's largest companies and institutions, creating many new partnerships across the value-chain. This is an exciting time in which entrepreneurial companies as well as established industries can innovate new farm-to-factory supply chains and establish an early position in the emerging bioeconomy.

Although there are multiple technology platforms and an expanding portfolio of biobased raw materials, which will comprise a future biobased economy, this book will focus on biochemical processing technologies, applied primarily to sugar, starch, and lignocellulosic biomass feedstocks. This platform will be a significant game changer, lend itself to a wide range of potential chemical products, and provide opportunities for new players in the supply chain.

In particular, sugars derived from lignocellulosic biomass represent an abundant feedstock resource that does not compete with food and feed supplies. Commercially viable processes for converting lignocellulosic biomass to biobased products must address two overriding issues: efficient

nonseasonal feedstock supply and logistics, and cost-effective deconstruction of cellulose and hemicellulose polymers to fermentable simple sugars. Feedstock supply and cost issues are being addressed by new crops, new harvesting/storage practices, and decentralized processing models. Technology issues to access sugars (and lignin) within lignocellulosic feedstocks are being addressed through new pretreatment options, genetically modified fermentation organisms, biotechnology-enhanced plants, and plant-based enzyme production systems. The development and commercialization of these new technologies and the requisite biobased supply chain will be profiled in this publication. Despite the early stage and dynamic nature of the industrial bioprocessing industry, the authors hope that the current status and perspectives presented will prove beneficial to the diverse industry stakeholders.

# 1.2 Market Opportunity for Biofuels and Biobased Products

Liquid biofuels including corn-based ethanol, as well as advanced biofuels such as biobutanol or cellulosic ethanol, are assured of a growing market over the next 50 years. As petroleum costs escalate with diminishing supplies, liquid transportation fuels will still be preferred due to energy density, safety, and distribution infrastructure, with increasing growth of biofuels between now and 2035 (IEA, 2008). The biofuels market represents the largest and most consistent demand from which to build a strong sugar and biomass supply chain from field to factory.

The global biofuels market is already estimated to be $150 billion per year (UN, 2009). According to one report focused on the United States market:

> Rapid growth in the consumption of renewable fuels results mainly from the implementation of the US Renewable Fuel Standard (RFS) for transportation fuels and State renewable portfolio standard (RPS) programs. Biofuels production will grow over the next two decades, though is likely to fall short of the 36 billion gallons of RFS target in 2022. However, it may exceed expectations for 2035 including fuels from cellulosic ethanol, renewable diesel, and first generation biofuels. (Newell, 2009)

Beyond biofuels, companies are increasingly targeting higher value biobased chemical products and biomaterials.

Liquid fuels are the ultimate commodity chemicals, representing the highest volume, but lowest value products whether produced from fossil or renewable feedstocks. In the United States, the petroleum-based liquid fuels industry and related energy services account for approximately 67% of petroleum consumed, with an overall industry value of $350 billion dollars. In contrast to commodity fuels, the goods and services resulting from the higher-value plastics, coatings, resins, and related consumer products utilize only 7% of petroleum consumed while resulting in an approximate $255 billion impact (Frost, 2005). Cargill and McKinsey & Company estimate that there is a potential to produce up to two-thirds of chemicals from biobased materials representing over 50,000 products, a $1 trillion annual global market (Jarrel, 2009).

Commercial examples of higher value biobased products are emerging with increased frequency, as profiled in Chapter 12 of this review. By 2007, internal corporate investment in research and development related to biobased chemicals and biomaterials was as much as $3.4 billion, which far outpaced biofuels. This was due primarily to internal research and development investments from a few large pharmaceutical companies, which was in contrast to the United States Government’s continued focus during

the same time period on liquid transportation biofuels (Lundy et al., 2008). While some biobased products are direct replacements for fossil-derived materials, others possess novel properties unique to their biogenic origin. An interesting example is Canadian-based EcoSynthetix (www.ecosynthetix.com) that is producing a starch-based coating product for the paper industry that outperforms its competitive products by requiring less water and heat in production, while exhibiting superior ink adhesive properties. This product is competitive with its petroleum-based counterpart when the price of oil is as low as $30 per barrel. Recent grants from United States Department of Energy (DOE) to support biomass work have not just focused on biofuels. For example a sizable $600 million round of funding awarded in late 2009, included support for Myriant Technologies' succinic acid project and Amyris Biotechnology's process to produce a range of biobased products to complement their biofuel program. It is expected that this trend will continue with both public and private investment focused on a range of high-value biomaterials and chemicals, as opposed to exclusively on biofuels.

# 1.3 Feedstocks

## 1.3.1 Biobased Feedstock Availability and Issues

Globally, ample supplies of renewable feedstocks are available for developing a robust and profitable biobased products industry, including agricultural crops, residues, and forestry materials, as well as future sources such as algae. Lignocellulosic biomass is globally dispersed and can be found in many forms, including agricultural crop and

processing residues, forestry resources, dedicated energy crops such as miscanthus and switchgrass, and municipal solid waste. In the United States alone, resources associated with agriculture and forestry were calculated at 1.3 billion dry tons per year of biomass potential (Perlack et al., 2005). There are additional chapters in this volume that provide detailed information from a variety of perspectives on the availability of lignocellulosic biomass.

It is important to note that the theoretical availability of biomass does not necessarily mean that it is economically feasible or environmentally viable to collect. For example, many primary row crop regions in the United States would produce excellent yields of perennial bioenergy crops, but the economics do not currently support substitution. The availability of agricultural crop residues must also be carefully considered. Crop residues include sustainably removable materials left after harvesting primary crops such as corn and wheat. Such residue availability has often been calculated based on 1:1 corn stover-to-grain ratios provided in the “Billon-Ton Report” published by the United States Department of Agriculture (USDA) and DOE (Perlack et al., 2005). Corn stover is widely considered a prime candidate for bioprocessing, although the actual availability within a working farm system, as well as collection incentives to farmers, may not be understood adequately. Additionally, regional (and global) variables affecting crop residue supply are acknowledged in the Billion Ton Report. For example, in northern climates, corn stover, the stalks and residues left after harvesting the grain, does not degrade quickly due to the cold winter temperatures. This sometimes creates a problem in that there is too much stover for field preparation activities for the next spring. As corn yields increase due to biotechnology, this problem may increase and it will be necessary to remove stover. This is not the case in southern climates, as stover degrades quickly in the

wet, relatively warm winters and is counted on by the farmer as a valuable source of organic matter in the soil.

Rice straw is another potential crop residue source that is widely available. In this case it would be an environmental benefit to remove the straw because currently it must be burned or otherwise disposed of every year to avoid diseases in the following year's rice crop. It would be a great benefit for air quality and the farmer to develop a market for this straw in a biomass application. In California, there has been much work, with limited success, in trying to develop markets for rice straw as a reaction to the Rice Straw Burning Reduction Act of 1991 (AB1378). Projects included the development of construction products and packaging materials from rice straw. Unfortunately, the straw is high in silica, which damages existing harvesting and handling equipment, making it impractical to develop a widespread harvesting system. However, if alternative technologies could extract higher value silica products, economics might support the development of more robust harvesting systems.

The use of wheat straw in biomass processing and biomaterials has potential, as the straw is already harvested in the United States and globally for use in animal bedding and for other applications. Over the last two decades, wheat straw has been used for composite construction materials, filler materials in plastics, and in the development of cellulosic ethanol. Iogen (www.iogen.ca) has based its cellulosic ethanol demonstration plant on wheat straw as a major raw material. The company is planning its first commercial facility in Saskatchewan that will utilize cereal straw feedstocks.

In the near term, especially in the United States, corn cobs may represent the most accessible crop residue for early commercial lignocellosic processing. Harvesting of corn cobs in a one-pass system is feasible and is being developed as a

component of the United States' corn ethanol industry. There is already an existing market in some regions for corn cobs at approximately $80.00 per ton, to be used in the production of chemicals such as furfural. Companies such as POET Biomass, a division of POET (www.poetenergy.com), and DuPont Danisco Cellulosic Ethanol, LLC (www.ddce.com) are developing conversion technologies specifically targeting corn cobs as feedstocks for biochemical conversion using enzymes. There is also significant work by major equipment companies, including CNH America LLC. (www.cnh.com) and Deere & Co. (www.deere.com), on one-pass harvesting systems for corn cobs.

Another potential source for lignocellulosic biomass is dedicated energy crops, both perennials and annuals. Perennials include crops such as miscanthus and switchgrass which have recently been the focus of attention by crop biotechnology and cellulosic ethanol companies. Perennials offer options to farmers and land owners for use of marginal land that is currently in pasture or other use. These crops sequester carbon in their root systems, as well as utilize relatively small amounts of inputs such as fertilizers and pesticides. The economics of producing these crops does not lend itself to replacing prime row crops, but their production may be part of farm-based crop diversification strategies in the future or as part of a program to utilize marginal and unproductive farm land.

Annual crops include sweet sorghum and forage sorghums, both of which require minimal inputs and produce significant biomass. In the case of sweet sorghum, a large sugar content in the crop can be easily converted to ethanol or other biobased products with current technology, while the bagasse could serve as feedstock for lignocellulosic conversion technologies.

Markets for these crops are being developed for biopower applications, even as other higher value uses are being

commercialized. There is a growing market in Europe and in certain regions in the United States for densified wood and energy crop pellets and briquets for home heating, industrial use, and co-firing with coal. The latter use is increasingly being driven by regulatory requirements directed toward renewable power generation and greenhouse gas reduction. Forestry and wood-processing residues and byproducts, as well as short-rotation woody crops, also represent important biomass feedstocks. Collectively referred to as “woody biomass,” these resources are often advantaged by an existing year-round harvesting and collection infrastructure. A detailed analysis of all of the crops, trees, and residues is provided in this volume.

## 1.3.2 Characterization of Lignocellulosic Feedstocks

Woody and herbaceous biomass, or lignocellulosic biomass, primarily comprises three major components—lignin, cellulose, and hemicellulose—along with lesser amounts of minor and trace constituents. Cellulose and hemicellulose are polysaccharides or sugar polymers composed of repeating monomer sugar units bonded together into long chains, much like rail cars are coupled together to form a train. Combined with lignin, these biopolymers comprise the structural components of plant matter and are produced by the photosynthetic process, whereby atmospheric carbon dioxide ($CO_2$) is absorbed by the plant, chemically transformed, and “fixed” into these other useful chemical materials.

Lignin is a natural polymer found in all plant materials, which combines with cellulose and hemicellulose to provide structural strength to the plant. It is not a sugar polymer, but rather an aromatic polymer, meaning its component phenylpropyl molecular units contain the highly stable

benzene-ring chemical structure, which is also the basis for many commercially useful materials produced from petroleum. The aromatic chemical structure also imparts a high caloric value to the lignin molecule, which is valuable for combustion (heat) and also chemical transformations. The lignin polymer can have significant variability in its chemical structure, often differing based upon the biomass source.

Cellulose and hemicellulose are referred to as carbohydrates because they are aliphatic polymers composed only of carbon, hydrogen, and oxygen. Cellulose is the most abundant biopolymer on earth and is made of six carbon or C-6 glucose (sugar) monomers. Cellulose obtained from wood pulp, cotton, and other plants has been used for centuries to produce paper and cardboard, as well as derivative products. Often referred to as dietary fiber, it is not digestible by humans, but with recent technology developments, it can now be commercially hydrolyzed by chemical, enzymatic, or biological processes to its monomer sugars, which can then be readily utilized as feedstocks for bioprocessing. Yeast fermentation of glucose to ethanol (mostly for beverages) has been practiced for centuries, and other natural and genetically modified organisms can convert glucose to various useful chemical molecules.

Hemicellulose is a polymer primarily composed of various five carbon or C-5 sugar monomers with some C-6 sugars as well. Unlike cellulose, it is an amorphous polymer with little structural strength and is easily hydrolyzed to its monomeric sugars with acid/base or enzymes. Unfortunately, C-5 or xylose sugars cannot be fermented using natural yeasts. However, aggressive research and development programs are developing new organisms and genetically modified yeasts to utilize these readily available C-5 sugars as bioprocessing feedstocks, as described in Chapter 8 of this volume.

Fractionation, or separation, of petroleum into its component constituents has been the key methodology to develop high value petrochemical end products. A similar biobased example is corn wet milling, in which the corn kernel is separated into its different components, from which value-added products are produced. As noted above, lignocellulosic biomass feedstocks possess comparable compositional diversity, and several leading technology developers are pursuing fractionation, or separation, of these components in order to facilitate more efficient and targeted downstream conversion of each component to value-added products. Historically, lignocellulose fractionation originated in the pulp and paper industry, where processes were designed to remove hemicellulose and “de-lignify” wood pulp in order to obtain a purified cellulose fraction for paper manufacturing (Agenda 2020 Technology Alliance, 2006). More recent approaches have used a combination of physical and thermal pre-processing followed by aqueous and/or solvent extractions, to afford substantially purified fractions of hemicellulose, lignin, and cellulose for further processing that is specific to each component. As a supporting technology, lignocellulose fractionation may prove to be extremely valuable as an integrated component of biochemical processing, providing sugars for fermentation and also a purified lignin stream as an aromatic chemical platform feedstock. Developmental and commercial lignocellulosic fractionation technologies are fully described in Chapter 12 of this volume.

## 1.3.3 The Role of Agricultural Biotechnology

In order to provide sustainable food, fuel, and material needs of humans, it will be necessary to dramatically increase the yields of agricultural crops and forest resources, as well as develop crops with specific attributes

for biomass feedstocks. Currently, biotechnology traits used to reduce farmers' costs and increase profitability are widely deployed in canola, corn, cotton, soybeans, and sugarbeets, predominantly in the United States. However, more than 13 million farmers in 25 countries currently grow agricultural biotechnology crops. In 2008, the global biotechnology crop area grew by 9.4%, or 26.4 million acres, to reach a total of 309 million global acres. Between 2007 and 2008, the United States alone increased its biotechnology crop acreage from 143 million acres to 154 million, phenomenal growth considering that the first biotechnology crops were not introduced until the mid-1990 s (ISAAA, 2008).

To date, the vast majority of commercialized agricultural biotechnology-derived crops have focused on genetic "input traits," which add value to the farmer and/or environment by reducing the production costs of the farm operation. Examples include Roundup™ Ready soybeans that are resistant to the herbicide glyphosate, allowing soybean farmers to more widely adapt conservation tillage practices. There are other examples related to insect and herbicide resistance. In addition to input traits in commodity crops, plant biotechnology has developed new crops for bioenergy and pharmaceutical applications with enhanced "output traits," which allow the crop to produce certain characteristics desired by food, health, or industrial customers. While the value proposition for input traits is directed to the farmer, output traits are directed to those making products from the crops and ultimately to the consumer. Output traits allow crops to have higher protein and other nutritional properties, stronger fibers, specific oil profiles, novel health benefits, and to produce new products within green plants. In short, output traits enhance the value of the plant as a feedstock for the production of plant-based products. Not all of these technology improvements are created through gene transfer. Some use mutation,

breeding, and other novel techniques to create new crop performance.

**Table 1.1** Selected plant biotechnology companies and products.