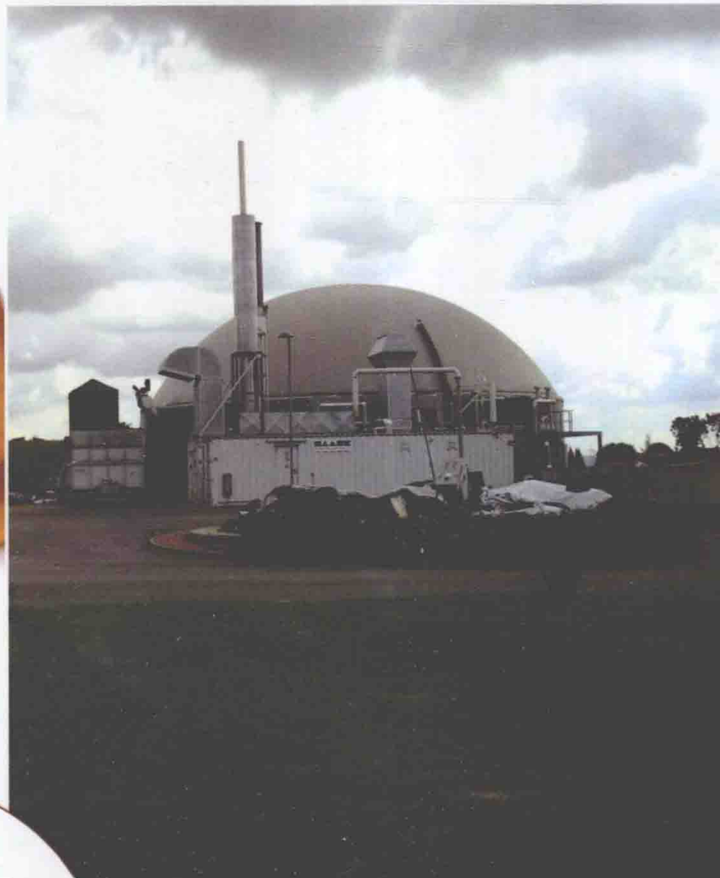
BIOFUELS from AGRICULTURAL WASTES and BYPRODUCTS



Hans P. Blaschek,
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Edited by

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Preface

The demand for energy is rising and given that energy demand is projected to keep rising with constrained oil supplies, oil prices seem unlikely to fall significantly in the near future. Because 60% of U.S. petroleum supplies are imported, there is a need to develop alternative fuel supplies for future energy demands. Bioenergy has become a subject of increasing attention around the world. But the use of crop biomass such as grains, roots, and tubers as a raw material for bioenergy production may compete with food and feed supplies. U.S. fuel ethanol and biodiesel production is at an all-time high, but the industry is also facing a significant problem on how to deal with byproducts and wastes such as corn fiber, dried distillers' grains and solubles (DDGS), glycerin, food, and animal wastes. For instance, production of 10 lb of diesel results in 1 lb of glycerin and for every bushel of corn converted into ethanol (2.7 gallons), 18 lb of DDGS is generated. Waste, despite being one of the leading environmental problems, has the potential to become one of the largest bioenergy resources. Livestock production worldwide has grown rapidly in light of increased demand, and this has environmental implications especially in the area of waste management. In New York State alone, the dairy cow population is about 700,000, generating a significant amount of manure. At 40 lb of waste per cow per day, the energy potential is great. By eliminating the animal waste on a farm, a farmer alleviates or eliminates environmental problems, such as odor and water pollution, and may be able to increase the size of his herd. Animal waste digestion offers many economic benefits (biogas and fertilizer production). Therefore, finding new energy sources from livestock waste streams will be a major strategy to treat the waste and sustain the growth of the livestock industry.

Currently, there is no book on the market that is focused on the production of liquid biofuels and biogas from agricultural byproducts and wastes. This book will provide a comprehensive text on the science of production of liquid biofuels (ethanol and butanol) and biogas (methane) from agricultural byproducts as well as animal and food industry wastes. The book is intended for university researchers (professors, students, libraries), industry scientists (large company QA/QC management, bioenergy companies, start-up companies, microbiologists), as well as engineers and microbiologists from government agencies. This book should serve as an up-to-date reference resource for university and industry scientists in the area of biofuel research, waste treatment, and integrated farm management.

About the Editors

Hans P. Blaschek is a Professor of Microbiology and Director of the Center for Advanced BioEnergy Research (CABER) at the University of Illinois. He also serves as Assistant Dean of Biobased Research Initiatives in the Office of Research in the College of Agricultural, Consumer and Environmental Sciences, and is the theme leader of the Molecular Bioengineering of Biomass Conversion Research Theme of the Institute for Genomic Biology. His research is focused on the acetone-butanol-ethanol fermentation and he is cofounder of a company called TetraVitae Biosciences that is currently commercializing the production of bio-butanol.

Thaddeus C. Ezeji received his PhD in Microbiology in 2001 from the University of Rostock Germany under the supervision of Prof. Dr. Hubert Bahl. He joined Dr. Hans Blaschek's laboratory at the University of Illinois Urbana-Champaign in 2001 as a postdoctoral research associate. Dr. Ezeji has been a faculty member of The Ohio State University since 2007, and his research has focused on fermentation, microbial strain development, metabolomics, and processes regulating the conversion of agricultural byproducts, coproducts, or wastes into biofuel and value-added products.

Jürgen Scheffran is a professor in climate change and security at KlimaCampus and the Institute for Geography of Hamburg University in Germany. Until summer 2009, he held positions at the University of Illinois at Urbana-Champaign (UIUC), in the Program in Arms Control, Disarmament and International Security, the Departments of Political Science and Atmospheric Sciences, and the Center for Advanced BioEnergy Research. After his physics PhD at Marburg University, he worked at Technical University of Darmstadt, the Potsdam Institute for Climate Impact Research. Recent activities include the Renewable Energy Initiative at UIUC and related projects funded by the Environmental Council, the Department of Energy, and the Energy Biosciences Institute.

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Chapter 1
Biofuels from Agricultural Wastes and Byproducts: An Introduction

Hans P. Blaschek, Thaddeus C. Ezeji, and Jürgen Scheffran

Around one-tenth of global primary energy use is based on bioenergy sources, of which about 10% are produced from modern bioenergy in the form of power, heat, and fuel. Biofuels for transportation account for 2.2% of all bioenergy, with a strong increase over the last decade. The total sustainable technical potential of bioenergy is estimated to be around a quarter of current global energy use.

Different from biomass specifically cultivated for energy purposes, residues and wastes are available as a byproduct of other processes. A significant amount of renewable energy is being generated from biogenic wastes and residues that do not require additional land and/or greenhouse gas emissions. Using their energy content would avoid methane emissions from slurry or landfills. Wastes and residues are quite heterogeneous: They arise in different sectors (agriculture and forestry, manufacturing, municipal enterprises, and private households) and at different stages of the value chain (biomass production and harvesting, processing, consumption, and disposal).

The technical potential of biogenic wastes and residues worldwide is estimated to be around 80 exajoules (EJ) per year. Research is needed in order to determine how much of this technical potential can be utilized in a sustainable and cost-effective way. A Department of Energy study has calculated in 2006 that over 1.3 billion dry tons per year of biomass from forestland and agricultural land alone are potentially available in the United States, a large fraction of which is from wastes and residues. This amount is sufficient to meet more than one-third of the current demand for transportation fuels while still meeting food, feed, and export demands. This biomass resource potential can be produced with relatively modest changes in land use, or agricultural and forestry practices.

Global production of biofuels in 2007 amounted to 16.4 billion gallons per year. Ethanol is currently the most important renewable liquid biofuel in the United States, which produces about half of the world's ethanol, compared with 38% in Brazil and 4.3% in the European Union. As the worldwide demand for fuels and chemicals surges and petroleum deposits are depleted, producers of ethanol fuel are increasingly looking beyond corn, potatoes, and other starchy crops as substrates for ethanol fuel production. Especially promising is cellulosic ethanol that can capitalize on microbial engineering and biotechnology to reduce costs.

Derived from low-cost and plentiful feedstocks, it can achieve high yields, has high octane, and other desirable fuel properties. Lignocellulosic feedstocks, such as switchgrass, woody plants, mixture of prairie grass, agricultural residues, and municipal waste, have been proposed to offer environmental and economic benefits. Compared to current biofuel sources, these biomass feedstocks require fewer agricultural inputs than annual crops and can be grown on agriculturally marginal lands.

After crop harvesting, the residues usually represent relatively large amounts of cellulosic material that could be returned to the soil for its future enrichment in carbon and nutrients or could be made available for further conversion to biofuels. Similarly, animal wastes are high in cellulose content and can also be converted to liquid biofuels. Such agricultural byproducts can play an important role in triggering the transition to sustainable biofuels.

Increasing demand for bioenergy has generated a strong interest in the bioconversion of agricultural wastes and coproducts into fuels and chemical feedstocks. To reduce the impact on land resources available for the production of food crops, a further increase in ethanol production will require the use of agricultural materials not directly tied to food, especially lignocellulosic biomass such as corn stover and corn fiber, wheat straw and rice straw, paper and wood processing waste, landscape waste and sugarcane waste. Some of the technologies to be utilized also generate coproducts such as electricity, hydrogen, ammonia, and methanol.

The chapters in this book cover a wide range of topics and demonstrate the potential for production of biofuels and chemicals from agricultural wastes and byproducts.

The chapter by *Nasib Qureshi, Stephen Hughes*, and *Thaddeus Ezeji* describes recent progress in emerging technologies to produce ethanol from lignocellulosic substrates, overcoming inhibitors generated during pretreatment, development of genetically improved cultures, simultaneous product recovery, and process integration. It addresses problems associated with inhibitor generation and detoxification, fermentation of both hexose and pentose sugars to ethanol, and the development of efficient microbial strains. Simultaneous product recovery, process consolidation, and integration will further improve the economics of production of biofuels from biomass. Coproducts serve as additional sources for generating revenue.

Fermentation of lignocellulosic biomass to ethanol requires additional processing steps for hydrolysis of biomass to simple sugars before these sugars can be fermented. These extra processing steps add to the overall cost of the substrate. Generally, the chemicals that are used to pretreat lignocellulosic substrates include dilute acid or alkali, and their use results in higher sugar yields when compared to pretreatments such as hot water or ammonia. These pretreatments generate products that inhibit cell growth and/or the fermentation process or both. Another challenging problem with respect to fermentation of biomass involves the inability of some fermentation microorganisms to use pentose sugars for growth and production of biofuels. Lignocellulosic biomass contains up to 30% pentose sugars, which are not utilized by the traditional ethanol-producing cultures such as *Saccharomyces cerevisiae*. Although recombinant cultures of *S. cerevisiae* have been developed, the overall productivity and ethanol concentration that can be achieved by these strains are not optimal.

Next-generation alternative renewable liquid biofuels are under development. Butanol can be used in internal combustion engines. It has higher energy content, is more miscible with diesel, is less corrosive, and has a lower vapor pressure and flash point than ethanol. Butanol can also be used at higher blend levels with gasoline or even at 100% concentration in car engines with little or no engine modification. Because of the solubility characteristics of butanol, it can be transported in existing fuel pipelines and tanks. Butanol can be produced by the fermentation route using renewable biomass. The low vapor pressure of butanol facilitates its use in existing gasoline supply lines. As opposed to ethanol-producing cultures, butanol-producing cultures (e.g., *Clostridium acetobutylicum* or *Clostridium beijerinckii*) can use both hexose and pentose sugars released during hydrolysis of lignocellulosic biomass. During World War I and World War II, butanol plants existed worldwide, including those in the United States, the former Soviet Union (Russia), Canada, China, Japan, Australia, India, Brazil, Egypt, and Taiwan. As a result of various technological developments, attempts are being made to revive commercial production of butanol from agricultural residues for both chemical and biofuel use.

One of the major problems associated with bioproduction of butanol is the cost of substrate, which has led to recent interest in the production of butanol from alternative, inexpensive materials. However, much of the proposed alternative substrates, such as corn stover and fiber, wheat and rice straw, or dedicated energy crops such as switchgrass and *Miscanthus*, present challenges that need to be overcome before they can be used as commercial substrates for butanol production. The chapter by *Thaddeus Ezeji* and *Hans Blaschek* details the butanol pathway, including pretreatment and hydrolysis; generation of lignocellulosic degradation products; effects of degradation products on growth and butanol production by fermenting microorganisms; and strategies for improved utilization of lignocellulosic hydrolysates.

Most bacteria use glucose as a preferred carbon source for growth, and only when glucose is limiting are the pentose sugars utilized, making fermentation of complex mixture of sugars in lignocellulosic hydrolysates challenging. The solventogenic acetone-butanol-ethanol (ABE)-producing clostridia have an added advantage over many other cultures in that they can utilize both hexose and pentose sugars, which are released from wood and agricultural residues upon hydrolysis in order to produce ABE. Pretreatment can result in the formation of a complex mixture of microbial inhibitors that are detrimental to growth of fermenting microorganisms. Options for the reduction or elimination of lignocellulosic degradation products during pretreatment include the removal of inhibitors prior to fermentation, development of inhibitor-tolerant mutants, or a combination of the above approaches. The development of inhibitor-tolerant mutants via culture adaptation appears to be the most viable approach from an economic standpoint, a research area in which the authors are currently involved.

Largus T. Angenent and *Norman R. Scott* discuss practical aspects and future directions for methane production from agricultural wastes. Anaerobic digestion is a proven technology for bioconversion of agricultural waste that is high in organic material to gaseous biofuel. It provides an efficient energy recovery system because methane and carbon dioxide are automatically and constantly removed from the process by degassing (bubble formation). Intermediate products in the food chain are converted into methane with very low concentrations of carboxylic acids in the digester effluent and hydrogen in the off gas. While methane formation is a remarkable conversion process that circumvents product inhibition, it is susceptible to instabilities. This chapter discusses the anaerobic digestion of mixed cultures in which the waste material can be complex and variable in composition over the operating period. Practical studies assess the performance, stability, and limitations of methane fermentation, and the economic or environmental benefits in the conversion of agricultural residues.

In addition, upgrading the energy carrier methane to more valuable products may be necessary to guarantee economical viability. With the need for co-digestion, an opportunity exists to link agriculture, rural communities, and industry for sustainable rural community development, providing a number of specific case studies. A U.S. example for this system approach is BioTown in Richmond, Indiana, where the goal is to create an energy self-sufficient community using an anaerobic digester as an integrated technology to create biogas from animal manures, food wastes, organic municipal wastes, and crop residues. Communities such as these illustrate that anaerobic digestion is a significant and working technology with relatively high-energy efficiencies and that agricultural wastes play an essential role in such systems. Anaerobic digestion of agricultural wastes is a mature technology with numerous full-scale digesters all over the world. Even though the level of maturity is high, research on reactor stability is necessary. More powerful techniques, such as metagenomics and stable-isotope probing, are starting to shed light on our understanding of anaerobic digestion. For wastes from agriculture with complex nutrient and water cycles, anaerobic digestion should be seen in the larger context of an integrated system in which nutrients and water from digester effluent are continuously recycled.

The chapter by *Edward A. Bayer, Raphael Lamed, Bryan A. White, Shi-You Ding*, and *Michael E. Himmel* addresses the current status of knowledge regarding the function of cellulases and cellulosomes, and how they might be used in biomass conversion to biofuels. This includes a description of various types of cellulosic biomass in agricultural wastes and the pretreatment strategies required to enhance enzymatic hydrolysis and to avoid toxic byproducts that would interfere with enzyme action and fermentation. The search for novel enzymes, and strategies for mutation and modification of cellulases and cellulosomes for future application to bioenergy initiatives are considered as well. Some of the bottlenecks and pitfalls in providing efficient processes for conversion of cellulosic biomass to fermentable sugars for biofuels production are addressed. To develop successful future bioconversion processes, it is promising to mimic the concerted action of the cellulolytic microbes, the bacteria, and fungi that have evolved to produce cellulases and cellulosomes.

Structural biomass is a rich and renewable source of fermentable sugars for industrial production of biofuels. In attempting to utilize polysaccharides in lignocellulosic carbohydrates at the commodity scale, one must consider a key principle set forth in the evolutionary development of the cell wall of terrestrial plants, namely essential recalcitrance to deconstruction. The major bottleneck in this process is the deconstruction of the plant cell wall, liberating both C6 and C5 sugars. Nature has evolved microbes and their enzymes to deal primarily with damaged and decaying vegetation. Progress is being made in this endeavor, although the key cost challenges remain the subject of considerable international research focus today. New and improved enzyme systems closely coupled to related process technologies, such as biomass pretreatment, are required to provide cost-effective and large-scale quantities of liquid fuels from biomass.

Syed Shams Yazdani, Anu Jose Mattam, and *Ramon Gonzalez* describe the production of fuel and chemicals from glycerin (or glycerol) that is generated as an inevitable byproduct during the biodiesel production process, as well as at oleochemical and bioethanol production plants. Due to the tremendous growth in the biofuels industry, glycerin is now regarded as a waste product that needs to be disposed at a cost. Glycerol is not only abundant and inexpensive, but also offers the opportunity to produce fuels and reduced chemicals at yields higher than those obtained with the use of common sugars. Anaerobic fermentation converts abundant and low-priced glycerol streams generated in the production of biodiesel into higher-value products and represents a promising route to achieving economic viability in the biofuel industry. A number of organisms are able to ferment glycerol and synthesize products with a wide range of functionalities. There are many advantages for the use of glycerol over sugars, which together translate into lower capital and operational costs.

As the chapter shows, there are few organisms that are able to utilize glycerol in the absence of external electron acceptors and that produce high-value chemicals such as 1,3-propanediol, succinic acid, propionic acid, and biosurfactant. In their recent studies, the authors have discovered that *Escherichia coli* can fermentatively metabolize glycerol and have established the pathways, mechanisms, and conditions enabling this metabolic process. The knowledge base created by the authors has opened up a new platform to engineer *E. coli* for the production of several fuels and chemicals, including the production of ethanol along with coproducts hydrogen and formate at high yields and productivities.

Commercial scale utilization of lignocellulosic biomass is not a trivial task and is quite different from the use of grain. As *Klein E. Ileleji, Shahab A. Sokhansanj*, and *John S. Cundiff* show, farm-gate to plant-gate delivery of lignocellulosic feedstocks from plant biomass for biofuel production is a key cost factor. The logistics and handling cost of feedstock can be very expensive and is one of the major reasons for the high cost of producing liquid fuels and power from lignocellulosic feedstocks. While diverse types of biomass may be chemically similar, they are quite different with respect to their times of harvest/collection and physical characteristics. This means the unique differences of these feedstocks need to be considered when designing an effective biomass logistics system. Harvest is followed by transportation to on-farm storage, preprocessing, or biorefinery plants. Sustainable supply of feedstock from on-farm storage must be delivered to the biorefinery plant year round. To minimize costs, the design, operation, and coordination of efficient feedstock delivery systems is vital.

The chapter compares three herbaceous biomass logistic systems (cotton, sugarcane, and grain) with a woody biomass system (fuel chips) and explores the linkage between harvesting, in-field hauling, and over-the-road hauling. In all short-haul systems, truck productivity is maximized when the load time and unload time is minimized. Given the variability of field conditions, logistic systems must provide for efficient flow of material into and out of at-plant storage, which is critically important for any plant that has a high cost penalty for shutdown. Typically, the feedstock cost constitutes one-third to one-half of the total production cost of ethanol or power, where the actual percentage depends upon biomass species, yield, location, climate, local economy, and the type of systems used for harvesting, gathering and packaging, processing, storing, and transporting of biomass as a feedstock.

A logistic system for forage chopping has basically the same challenges as the sugarcane system, but as the authors note, it is not practical in the United States to have several hundred farmers chopping biomass and delivering on their own schedule to the bioenergy plant. Baling provides a disconnect between the harvest and in-field operations, which is a significant advantage. One operator can bale an entire field with no requirement to coordinate with any other operation. A systems integration approach is increasingly important to design systems and analyze pathways along the whole supply chain, including harvest, storage, and transport. A systems approach examines the complete system to see what processes can be combined for synergy of resources, reduction in waste, and cost reduction. An integrated approach seeks to combine multiple tasks, for instance, by harvesting grain and fiber together and subsequently separating them. Systems integration also helps to overcome bottlenecks and lack of close collaboration, which allows everyone to see the bigger picture of how everything fits in place and harness the optimal strengths of the complex production chain as a whole.

Numerous opportunities exist to make ethanol plants more productive by reducing waste and expanding the diversity of both inputs and outputs. According to *Timothy C. Lindsey*'s assessment, byproducts and wastes from other industries such as food processing, landscaping, paper, and municipal solid waste facilities could be substituted for crops as feedstocks and processed into ethanol and other high-value products, thereby reducing the strain on food resources. A wide variety of cellulose-based biomass wastes and byproducts is available for conversion to biofuels, including agricultural residues (corn stalks and cobs, straws, cotton gin trash, and palm oil wastes); paper (paper mill sludge, recycled newspaper, and sorted municipal solid waste); wood waste (sawdust, wood chips, and prunings); and landscape waste (leaves, grass clippings, and vegetable and fruit wastes). Most of these materials are available at very low cost and some even command tipping fees associated with their disposal as wastes. This chapter points out that the United States currently converts approximately 15 million tons of agricultural products into ethanol and biodiesel, and discards approximately 270 million tons of agriculturally derived residues in the form of harvestable crop residues, animal manure, forest residues, and the organic fraction of municipal solid wastes.

This contribution describes two incremental opportunities and modifications for implementing existing technology that would enable expansion of existing dry-mill ethanol operations to biorefineries with respect to feedstocks and products. Modification of existing processes to incorporate cellulosic feedstocks into existing operations could greatly improve the diversity and flexibility of feedstock options. Recovery of oil from byproducts such as germ, thin stillage syrup, or dried distillers' grains and solubles (DDGS) could expand greatly the quantities and value of products produced from dry-mill plants and also provide valuable feedstock options for biodiesel producers. The DDGS could be further fractionated to separate and pelletize high-protein/high-value components from lower-value materials.

Furthermore, cogeneration systems could be implemented to burn lignin and other coproducts to simultaneously produce steam and electricity, thereby reducing requirements from external sources and providing electrical power for additional biorefining operations. Ethanol is an important industrial ingredient and has widespread use as a base chemical for other organic compounds (e.g., ethyl halides, ethyl esters, diethyl ether, acetic acid, butadiene, and ethyl amines) that could provide unique opportunities for expanding operations in the future.

Emphasizing that cellulosic biomass is an inexpensive and abundant resource to collect and store large-scale solar energy, *Bin Yang, Yanpin Lu*, and *Charles E. Wyman* demonstrate that agricultural residues are particularly promising for initial commercial applications because of their potential low cost and near-term availability. Because feedstock costs are dominant in processing economics, it is critical to seek those for first applications that are low cost and sufficiently abundant. High product yields and ease of processing are also vital to minimizing costs, while sufficient amounts must be available to achieve reasonable economies of scale. Agricultural residues are expected to serve as a major biofuels feedstock, and their potential low cost and current availability can be particularly important in the near term.

The rapidly evolving tools of biotechnology can significantly lower conversion costs and enhance yields, making biological processing a particularly promising approach to converting these solids into liquid fuels and chemicals and providing environmental, economic, and strategic benefits. The most expensive processing step is the breakdown of cellulosic materials into cellulose and hemicellulose to release fermentable sugars, while pretreatment has pervasive impacts on all other major operations.

This chapter summarizes estimated amounts of major agricultural residues and their potential for making ethanol, including environmental factors that determine their availability, composition, and reported yields. Emphasis is given to approaches, needs, and costs for harvesting, transporting, and storing agricultural residues with only little degradation of the feedstock. The economics of processing residues to ethanol demonstrates the importance of feedstock composition, availability, and cost to good returns on capital. Finally, opportunities and strategies for advanced technologies to lower the cost of biological processing to ethanol and other products are outlined. In estimating the potential for large-scale fuel production,