Bioenergy Research Needs for Heat, Electricity, and Liquid Fuels

Alexander E. Farrell (University of California–Berkeley, USA)
Anand R. Gopal (University of California–Berkeley, USA)

SEE ALSO SIDEBARS:
Cellulosic Ethanol
Engineered and Artificial Photosynthesis

Abstract

Biomass remains a key energy source for several billion people living in developing countries, and the production of liquid biofuels for transportation is growing rapidly. However, both traditional biomass energy and crop-based biofuels technologies have negative environmental and social impacts. The overall research challenge for bioenergy is to develop the technologies to produce useful products at low costs while minimizing the use of scarce resources such as arable land and water. This requires substantial advancements in modern biomass power generation and the success of liquid biofuel technologies that permit the use of lignocellulosic feedstocks or possibly algae. With such technologies, biomass resources could meet a significant fraction (over 10%) of global energy demand. Both improved policies and technologies are needed to ensure that bioenergy contributes significantly to economic, social, and environmental goals.

Introduction

Biomass is the oldest fuel known to humankind and is still widely used in developing countries, where it accounts for about 35% of primary energy consumption, compared to just 3% in Europe and North America.[1] Further, because most of this biomass is used very inefficiently—with adverse impacts on public health—there is a significant, longstanding need for improved bioenergy technologies in the developing world. Recently, there has been renewed interest in the industrialized world in the potential for bioenergy to mitigate global climate change and for liquid biofuels to substitute for expensive imported oil. This unusual synergy of interests has placed biomass electricity and biofuels at the center of both much excitement and much concern about their environmental and socioeconomic implications.[2]

In this article, we provide an overview of the most common technologies currently used to generate heat, electricity, and liquid fuels from biomass. Then, we describe the technical, economic, and environmental opportunities and challenges faced by each of these technologies. Because of the widespread nature and adverse impact of biomass energy use in the developing world, we first address heat and electricity generation from biomass combustion and gasification. We then turn to biofuel production from various feedstocks. We also include a separate section on catalysis, as there is a strong need for research and development in this area (see also Gates et al.'s' article on catalysis in this issue). We conclude with a look at some scenarios on the future of bioenergy.

Combustion

Direct combustion is the oldest known way to use biomass for energy, and this method still accounts for more than 95% of global biomass energy production.[1] There is a wide variation in the technology and applications of biomass combustion.

A key biomass combustion technology is the open, three-stone cooking fire that is used across the developing world. Woody biomass or animal waste is burned underneath a cooking pot supported by the stones. The efficiency of the three-stone fire is very poor at approximately 15%, and its users are directly exposed to emissions of carbon monoxide, particulates, nitrogen oxides, and tars.[3]

The most common modern combustion technology is the biomass-fueled electric power plant, in which the heat from the furnace is exchanged with a working fluid to turn the prime mover, which is attached to an electric generator. In some cases, the plants operate as combined heat and power generators. The system closely resembles coal-fired plants where the working fluid is steam and the prime mover is a steam turbine. Significant differences from coal plants are seen only in the furnace and the gas cleaning system, if one exists. The main pollutants in the flue gas are ash, tars, ammonia, and nitrogen oxides.[4] Flue gas is usually cleaned only if mandated by local air-quality regulations. In some plants, useful heat is recovered from the exhaust gas.

In well-designed systems, combustion of biomass occurs in a furnace. The hot flue gases that exit the furnace carry all of the usable thermal energy from combustion. A good furnace must minimize heat loss and, hence, needs to be well insulated. Various options exist for other design features. It is also possible to add biomass to other fuels, such as coal, in boilers originally designed for only one fuel.[5,6]

In fixed-bed furnaces, biomass fuel is placed on a fixed bed, and air is supplied from two locations to allow for combustion to proceed in steps. Both the biomass feed and the ash removal are typically automated.[7] There are several types of fixed-bed furnaces, and these are still widely used for small-scale power generation (<1 MW).

Fluidized-bed furnaces for biomass combustion were introduced about 25 years ago. In these furnaces, refractory materials such as sand or limestone are suspended by air currents and serve as the medium for heat transfer to the biomass fuel. High air velocities fluidize the heat-transfer medium and the biomass fuel. If the particles remain suspended within the furnace, the furnace is called a bubbling fluidized bed, but if the air velocities are high enough to carry material out of the furnace to be recirculated after it, the furnace is called a circulating fluidized bed. In general, because of the additional energy cost of circulating air at high velocities, fixed beds are a better option for small furnaces.

https://doi.org/10.1557/mrs2008.76 Published online by Cambridge University Press

Combustion: Opportunities and Challenges

An estimated three billion people continue to rely on solid fuels burned in the home to meet their basic energy needs.[8] Approximately two million deaths annually are related to indoor air pollution from the burning of biomass.[9] Apart from the obvious indoor emissions issue, there are other serious impacts of biomass energy use by the poor, including time spent (often by women and children) collecting fuel, deforestation (a limited effect), degradation of soil quality (due to the use of animal wastes as fuel), global warming due to products of incomplete combustion, and costs (mostly to rural families).

In the near term, there is a great need for biomass cookstoves that improve efficiency and dramatically reduce indoor emissions. It is easy to improve the 15% efficiency of the three-stone fire, and any efficiency gains will serve to reduce the associated health and environmental problems. To be most effective, these new technologies must be inexpensive to purchase and maintain, and they must be disseminated widely. In the longer term, optimal solutions should enable the poor to cheaply and easily access cooking fuel that does not damage their local environment or expose them to hazardous emissions. Such technologies could use different fuels but could also continue to be biomass-based. Greenhouse gas (GHG) issues might also be addressed in these new technologies, in ways that basic human energy needs for cooking, heating, and lighting are supported simultaneously with climate change imperatives.

Many biomass combustion power plants are in operation throughout the world. The prime factors determining their location and economics are fuel quality, quantity, seasonality, and ease of access. As a result, biomass power plants exist only in large-scale niche applications such as self-generation for paper, lumber, or sugarcane processing. In order to make these plants more competitive with fossil fuels, several key areas of research need to be pursued.

In the very near term, co-combustion of biomass in coal plants shows great promise as a low-cost solution to cut CO_2, sulfur, and nitrogen oxide emissions.[10] In the short term, improvements in the efficiency and alterations in the scale of combustion technology, including its ability to handle various fuels of inconsistent heating value, can greatly help increase capacity factors. Because the quality of biomass is much more variable than that of most fossil fuels, improved fuel collection, handling, and preprocessing can dramatically improve efficiency. In the long term, efforts are needed to bring about a significant increase in the efficiency of the entire combustion–generation system. Currently, typical efficiencies are in the 20–25% range for electricity generation from biomass.[11] It might well be more effective and economical to focus research efforts on generation from biomass gasification, as this technology holds more promise for improvements in efficiency, and to phase out large-scale generation from combustion. Breakthroughs in the following specific materials research areas can make a substantial contribution to biomass combustion technology:

- improved refractory materials for furnace walls that will result in better thermal insulation and hotter flue gases, leading to increased thermal efficiency, and
- reactor design and fuel processing methods that will result in more complete combustion.

Gasification

Gasification is a process in which solid or liquid carbonaceous material, such as biomass, coal, or oil, reacts with air, oxygen, and/or steam to produce a gas product called syngas or producer gas that contains primarily CO and H_2, along with lesser amounts of CO_2, CH_4, and N_2. This combustible mixture of gases is then burned to produce energy. About 70–85% of the energy in the biomass can be transferred to a gaseous form.[12] Biomass gasification begins at a lower temperature than coal gasification because biomass is more reactive than coal. Biomass also contains potassium, sodium, and other alkali metals that can cause deposition of liquefied ash (slagging) and fouling problems in conventional gasification equipment. Biomass gasification is an old technology, but research and development in it has stagnated because of low fossil fuel prices. Many industrial routes for the utilization of biomass gasification exist, such as production of H_2 by the water–gas shift reaction and production of diesel fuel by the Fischer–Tropsch process.[12]

Gasifiers come in many designs, but all use one of two oxidizing agents: air or oxygen. The main advantage of oxygen gasification is the production of high-heating-value gas that can be suitable for use in conventional natural gas turbines and also for pipeline distribution if necessary. However, a substantial penalty is incurred in terms of the cost and safety issues entailed by an oxygen handling subsystem.[13] Hence, oxygen gasification is rarely used, but its potential advantages should make it an active area for research.

In steam gasification, steam is used as a reducing agent to produce a gas of higher heating value. The steam reacts with both methane and carbon monoxide to produce larger amounts of hydrogen. However, the costs for the subsystems associated with steam gasification are currently very high.[14]

Larger scale (>1 MW) gasifiers are generally used for power production with an engine or, less frequently, with gas turbines. Gas turbines require the fuel to be compressed, and technologies are being developed to gasify biomass under pressure to eliminate the considerable energy cost of compressing the producer gas. Currently, most pressurized gasifiers are of the fluidized-bed type, but the technology is far from commercial.[7]

Fixed-bed updraft gasifiers are the oldest and simplest gasification technology, in which biomass fuel is introduced at the top of the reactor and air is introduced at the bottom. The producer gas exits from the top of the reactor. The main advantages of an updraft gasifier are its ability to handle fuel with a high moisture content, its simplicity and low cost, and its ability to handle fuel with a high ash content. The main disadvantages are the high tar content of the gas and the low efficiency of conversion.

In a fixed-bed downdraft gasifier, the biomass fuel and the air move downward together; thus, the intermediate product gases move through the hottest zones of the reactor. This burns off most of the tars to produce much cleaner gas, which is the main advantage of downdraft gasifiers. The main disadvantages are the need for strict moisture limits in the fuel and the high amounts of nitrogen oxides and particulates in the product. This design is very popular in applications up to 1 MW.

Fluidized-bed gasifiers are very similar to fluidized-bed combustion furnaces. A heat-transfer medium such as sand is fluidized along with the biomass fuel by high air velocities. Like combustors, fluidized-bed gasifiers are also designed to be bubbling or circulating. Because of the high energy cost of air-blowing subsystems, the benefits of fluidized-bed reactors are realized only at larger scales of operation. Some of the major advantages of fluidized-bed gasifiers are similar to those of fluidized-bed combustors, including high reaction rates and conversion efficiencies and the ability to tolerate a wide variation in fuel types and characteristics.

The producer gas from a gasifier is directly used as a working fluid for power generation, which is essential to the efficiency advantage of gasification over direct combustion, but which also means that the gas must be free of contaminants. The

https://doi.org/10.1557/mrs2008.76 Published online by Cambridge University Press

same is true of syngas used to produce biofuels, as discussed further below. Thus, gas cleaning downstream of the gasifier is an integral part of any gasification technology. Biomass-derived producer gas can contain up to several hundred parts per million (ppm) of sulfur, depending on the source. Although this is far below the levels from coal gasification, sulfur must be removed from biomass-derived producer gas to levels approaching 1 ppm for fuel synthesis. In addition, removal of tars, alkali, chlorine, ammonia, and particulates is required for virtually all downstream conversion processes. The main contaminants, the problems they cause, and the cleanup options are summarized in **Table I**.

Table I: Produced Gas Contaminants, Problems, and Cleanup Processes.

Contaminants	Examples	Problems	Cleanup Process
Particulates	Ash, char, bed material	Erosion	Filtration, scrubbing
Alkali metals	Sodium compounds	Corrosion	Condensation, filtration, adsorption
Tars	Long-chain aliphatics	Deposition on turbine blades, clogging of filters	Tar cracking, tar removal
Fuel nitrogen	Ammonia, HCN	NO_x formation	Scrubbing, catalytic reduction
Sulfur, chlorine	H_2S, HCl	Corrosion, air pollution	Lime scrubbing, adsorption

Source: Reference 13.

The removal of particulates and alkali metals is simple but inefficient. Thus, there is much to be gained from the development of materials and technology to remove these contaminants at high temperatures.

Tars in the producer gas can either be removed or be destroyed by cracking. Water scrubbing is the most widely used method for the physical removal of tars. However, the removal efficacy is not nearly as good for scrubbing as for cracking, mainly because tars need to be coalesced and cooling alone is not sufficient to remove them from the gas stream. In addition, this technique is fairly expensive and generates large amounts of polluted water.[7] Thermal cracking avoids these problems, but on the other hand, is less effective and also has an added energy cost. Catalytic cracking can be very effective at temperatures of 800–900°C with up to 99% tar destruction, but is expensive.[13]

Nitrogen compounds in biomass are also volatilized as ammonia and hydrogen cyanide. During combustion, these can form NO_x. Fuel-bound nitrogen can be reduced in the following ways: selecting biomass without much nitrogen, applying water scrubbing, controlling combustion to reduce NO_x formation, and using selective catalytic reduction at the exhaust.[13]

Gasification: Opportunities and Challenges

More than 70% of the energy content of most types of biomass is easily volatilized in a gasifier, and when gasification is combined with partial oxidation, up to 85% of the energy content can be gasified.[15] Such a high energy recovery through gasification is not possible for many other fuels including coal. When this benefit is combined with efficiency gains through combined-cycle gas turbine generation in a process known as biomass integrated gasification combined-cycle (BIGCC) generation, the potential advantage of gasification over combustion is easily apparent.

In theory, gasifiers can accept mixed fuel inputs, making it possible to use heterogeneous, diffuse wastes. However, significant barriers remain before this potential can be realized. Biomass gasification is not significantly commercialized, so its costs are much higher than those of conventional combustion-based electricity generation. In addition, some serious technical issues need to be overcome before biomass gasification can become widespread. Foremost among these are yet-to-be-proven treatment technologies for the producer gas to remove contaminants that can damage internal combustion engines and gas turbines.

In the long term, gasification should be able to offer benefits to the vast unelectrified areas of the developing world that have dispersed and low-quality fuel. Small (<50 kW), low-cost gasifiers that could operate reliably in rural villages, vary output readily, and handle heterogeneous biomass fuel would be in great demand. These units also need to be rugged and prefabricated for easy assembly and low-maintenance operation in the rural areas of the developing world.

Anaerobic Digestion

Anaerobic digestion (AD) is the breakdown of organic material by a microbial population that operates in an oxygen-free environment. AD is of great interest in energy production because the main product of the digestion process is methane, a powerful greenhouse gas. However, AD is primarily used as a waste management technology to eliminate pathogens, reduce odors, prevent nutrient contamination of groundwater, produce useful fertilizers, and eliminate releases of methane.[16] In addition, AD can produce a gas that can be used for heating or electricity generation.

Because AD was commercialized as a waste management technology, it is substantially more mature than many other renewable energy technologies. In the United States and Europe, AD has primarily been employed in animal husbandry and in wastewater treatment as a cheap, effective, and environmentally low-impact means of dealing with waste. The product gas from AD is not necessarily used for electricity and heat generation, but simple retrofits are feasible for most digester systems.

Although little attention has been paid to AD in recent years, this technology can play an important role in reducing GHG emissions in two ways.[17] First, untreated organic waste matter aerobically decomposes to release methane and carbon dioxide. When waste is instead collected and directed to a digester and used for energy production, these methane emissions are avoided. Second, the biogas produced can be used for combined heat and power, frequently offsetting a more GHG-intensive source of power. The avoided methane and CO_2 emissions from waste collection are, in most cases, much larger than the emissions offset by electricity and heat production.[18] Lower chemical fertilizer use in farms where the solid residues of AD are spread on the field is another source of avoided emissions that must be counted.

Opportunities to capitalize on these GHG emissions reductions are important for the adoption of AD technologies. In their absence, many AD installations in the United States and Canada do not produce power because the economics dictates against it.[19] Further, small animal farms across the developing world are responsible for substantial methane emissions. These farmers could afford AD technologies if they were able to access carbon markets that would make such investments worthwhile. Once a

https://doi.org/10.1557/mrs2008.76 Published online by Cambridge University Press

digester is installed, it is extremely simple to use the biogas it produces for heating needs such as cooking. Therefore, widespread installation of digesters on small farms could lead to reduced wood and charcoal use for domestic heat, which would have beneficial implications for indoor air quality, climate change, quality of life, and deforestation.

Although AD is clearly a mature technology, researchers see great potential in novel uses for it. In the near term, digester gas can be upgraded to natural gas quality and injected into regular natural gas pipelines in places where electricity production is not appropriate. In the long term, there is great interest in the engineering of microorganisms that can produce hydrogen directly from anaerobic digestion of biomass.[20,21] This effort is still early in the research phase, but it shows great promise as an inexpensive source of hydrogen if successful. Another novel concept is an integrated biofuel–feedlot facility where animal feed is a coproduct of biofuel production and AD is used to augment power generation. (One such facility is now in commercial operation in Mead, Nebraska; see www.e3biofuels.com.)

Electricity Generation

Electricity generation technologies, and especially their gas quality requirements, create some of the key challenges for bioenergy technology improvements. Such technologies typically include internal combustion (IC) engines and gas or steam turbines. (The latter two can be operated together for more efficient combined-cycle generation.) In addition, there have been several recent installations in which AD gas is used to power medium-scale molten carbonate fuel cells. Microturbines could function as possible generators, but this technology is still battling to overcome durability problems.

The steam turbine is the most common technology currently used for the generation of power from biomass. Because the flue gas is not a working fluid, it does not need to meet any quality requirements when it powers a steam cycle. (Air emission requirements might apply, however.) Steam cycle efficiencies are low, between 15% and 25%.[7] In contrast, biomass-based gas turbines and combined-cycle units require very clean gas and compression, but they can be up to 60% efficient. These higher efficiencies explain the great interest in biomass gasification technologies.

Advantages of IC engines include ready scalability and (up to 100 kW scale) better tolerance of high levels of gas impurities than gas turbines. However, these parameters vary greatly depending on engine size and operating temperature. Overall, engines can be coupled with ambient-pressure gasifiers much more easily than can turbines.

To produce commercially viable large-scale BIGCC plants, the research agenda must target two key issues: the producer gas heating value and gas quality requirements for a gas turbine. The heating value of the producer gas from air-blown gasifiers is insufficient to power most contemporary gas turbines. (The cleaning of producer gas has already been discussed.) Turbine blades are very sensitive to acids, alkalis, tars, and particulates entrained in the fuel gas. Reliable data on these tolerances are difficult to obtain, but it is unlikely that turbines can be built to accept more of these impurities. Hence, the onus is on superior gas cleaning technology to enable gas turbines to run reliably on gasified biomass.

Biofuels

Modern biofuels have been used in some countries since the late 1970s, as one response to the oil price shocks of that time. Over 90% of current biofuel production today is ethanol produced through fermentation, which is described in the sidebar by Wyman on cellulosic ethanol. Current biofuels are essentially traditional agricultural commodities that have been put to a new purpose as fuel, but they are not particularly good fuels.[22] For instance, ethanol has a low energy density, can make fuel blends corrosive, can increase air pollution in some fuel blends, and is relatively expensive to produce. (The costs of production of cellulosic ethanol are unclear because no commercial-scale plants exist, although six pilot plants are now being built with the aid of grants from the U.S. Department of Energy. The experience gained in their construction and operation will probably lower production costs significantly.) These negative attributes suggest why biofuels have needed significant government support in the form of consumption mandates and various subsidies to attain even the relatively minor levels of market penetration that they have today. Support for biofuels is essentially an agricultural policy designed to provide added income to producers and processors.[22] Subsidies for biofuels are estimated to have reached $15 billion in 2007 for the Organization for Economic Cooperation and Development (OECD) as a whole.[23]

However, the recent rise in the price of crude oil has made some biofuels economically attractive, which, when combined with significant production subsidies and consumption mandates, has led to a rapid expansion of world biofuel use. Current consumption of biofuels globally constitutes about 2% of transportation fuels by energy content, and this could expand to about 10% by 2020.

More recently, achieving reductions in GHG emissions has been added to the rationales for biofuel policies.[24,25] However, the GHG emissions of current biofuels range from somewhat lower to greater than those from fossil fuels.[26] Without appropriate incentives and regulations that lead to technological innovation, biofuels are likely to worsen climate change.[2,23]

Figure 1 illustrates the fact that dozens of biofuel pathways are possible and that many of them produce animal feed or electricity as coproducts. Today's dominant biofuel production pathways are highlighted in **Figure 1:** corn ethanol, sugarcane ethanol, soy biodiesel, and palm biodiesel.

The first research challenge for biofuels is to address the problems these compounds entail when used as fuels (as previously described). It is likely that new compounds with superior properties and better production processes will emerge.[12,27] Also, note that multiple pathways to biofuel-based hydrocarbons, electricity, and hydrogen exist. Because hydrocarbons are excellent liquid fuels, they might be promising in the short run, whereas in the long run, electricity and hydrogen pathways might offer a preferred technology.

The second research challenge for biofuels is related to their environmental performance. Current biofuel production can have high GHG emissions, as noted above, and also causes considerable pollution in some cases, consumes significant quantities of water, and may involve large monocrops of genetically modified organisms. All of these issues need to be addressed.

Most importantly, the currently dominant biofuel production pathways all require fertile land because they originate with agricultural crops, which is unsurprising given how biofuel production is supported. Thus, biofuel feedstock production competes with other land uses, such as food production and wilderness protection. The availability of fertile land is likely to be a limiting factor (along with water) for the volume of biofuels that can be produced. (See the sidebar by Gust et al. for a discussion of this issue.) Increasing biofuel production will induce land use change, including conversion of natural ecosystems into agricultural land (e.g., deforestation). This releases tremendous amounts of GHGs and threatens ecosystems. Although the effects of land use change are indirect and often

https://doi.org/10.1557/mrs2008.76 Published online by Cambridge University Press

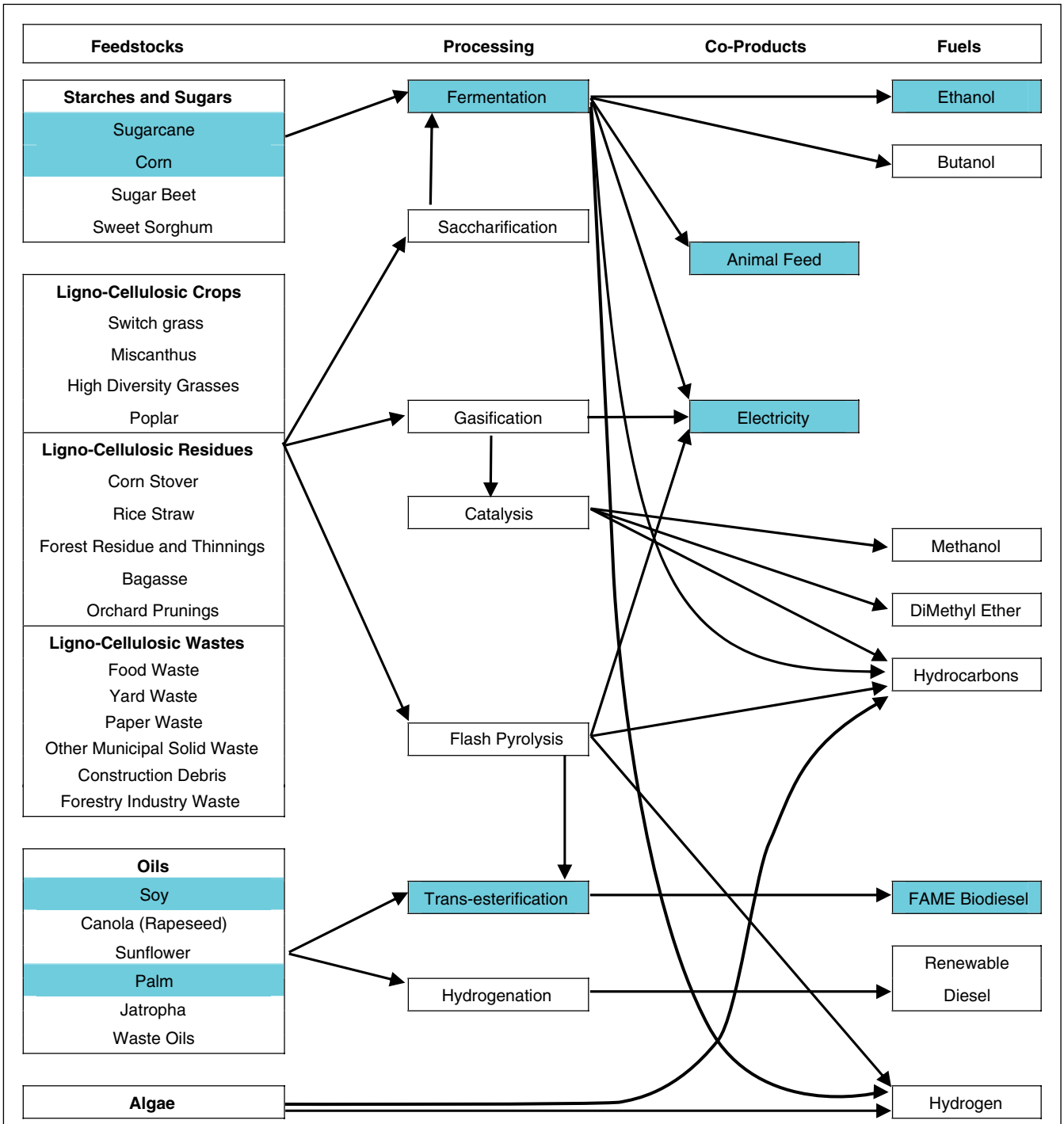

Figure 1. Selected biofuel production pathways with currently dominant pathways highlighted. (Based on a figure drawn by A.D. Jones for Reference 24.)

ignored, it is increasingly being recognized that, because of the effects of changes in land use, agricultural-based biofuels have much higher GHG emissions than is commonly believed.[25,28]

Sustainable biofuels that reduce GHG emissions and protect ecosystems are likely to require nonagricultural feedstocks, such as wastes and residues, as well as plants grown on low-quality land.[29] Another approach might be the increased integration of biomass feedstock production with food production, possibly improving nutrient and water management as well.[30]

The overall research challenge for biofuels, therefore, is to develop the technologies for producing more useful compounds at low cost while minimizing the use of scarce resources such as arable land and water. This means less reliance on the current suite of agricultural crops and greater use of wastes, residues, and feedstocks that can grow on low-quality land. Crucially, these feedstocks include lignocellulosic materials and algae.

Therefore, the development of low-cost methods for producing biofuels from lignocellulosic feedstocks or algae is the

https://doi.org/10.1557/mrs2008.76 Published online by Cambridge University Press

key to solving the challenge of sustainable biofuels. Such advances could permit large-scale production of biofuels without using fertile land, there by releasing it for food production or allowing it to remain as wilderness.

Lignocellulosic production pathways for biofuels include either biological (fermentation) or thermochemical (e.g., gasification) steps. Fermentation by yeasts or other microorganisms requires simple sugars (e.g., glucose), which can be obtained directly from some feedstocks (e.g., sugarcane) or through the depolymerization of starch or cellulose. Because less processing is needed for sugar-bearing plants, biofuels made from these feedstocks are inherently less costly to process (and have lower GHG emissions), followed by starches and then by lignocellulosic material. Thus, cellulosic feedstocks are abundant and cheap, but currently expensive to process. This is why many of the key biofuel research issues are in the area of biotechnology to develop new and improved methods for overcoming the recalcitrance of cellulose and decomposing it into constituent sugars (called depolymerization). The sidebar by Wyman discusses some key issues.

In addition to biofuels, interest in developing new bioproducts has also grown recently.[31,32] Although bioproducts might substitute for products currently based on fossil fuels, there is no room for a discussion of them here.

Pyrolysis

Pyrolysis is the chemical decomposition of organic materials by heating in the absence of oxygen; it is the process used to produce charcoal from wood and an early step in gasification.[33] Biomass pyrolysis products include volatile liquids, combustible gases, and solid char, the proportions of which are controlled through the temperature and the rate of reaction. The combustible gases can be used to generate power or heat, and the liquids can be converted to biofuel. Recent interest has focused on the synthesis of biofuels from pyrolysis. In the 1980s, "fast pyrolysis" was developed as a means of increasing to 80% the liquid fraction, called bio-oil or bio-crude, which can be processed further into biofuels. Bio-oil mixtures can contain more than 400 different compounds, including alcohols, aldehydes, esters, and aromatic compounds. Fast pyrolysis of biomass typically occurs at 400–900°C and takes less than 2 s.[12] During the past two decades, several different reactor designs have been explored that meet the rapid heat-transfer properties required.[33] However, there is a great need for the development of better process controls to consistently achieve target liquid yields with the desired chemical composition.

Several commercial biomass pyrolysis technologies that produce bio-oils currently exist. However, bio-oils have significant drawbacks, including low volatility, high viscosity, coking, and corrosiveness. Bio-oils must be upgraded or blended to be used as a transportation fuel. Techniques for upgrading include hydrogenation, zeolite upgrading, and steam reforming, all of which use catalysts but none of which have been perfected.[12] Few studies have focused on the use of catalysts for biomass cracking (*in situ* upgrading) to generate fuels.[33]

Catalysis

A number of different catalytic processes might be important in future biofuel production pathways, including Fischer–Tropsch synthesis (FTS), hydrodeoxygenation of bio-oils, steam reforming, catalytic gasification, and biocatalysis.

FTS uses Co-, Fe-, or Ru-based catalysts to produce linear hydrocarbons and oxygenates, including unrefined gasoline, diesel, and waxes. This technology was used by Germany during the 1930s and 1940s to produce liquid fuels from coal and is still in use in South Africa.[34] The product distribution obtained from FTS depends on the catalyst and the process parameters such as temperature, pressure, and residence time.[34] When either iron- or cobalt-based catalysts are used in the temperature range of 210–250°C, about 60% of the FTS product is heavier than diesel, but this product can be hydrocracked selectively to yield about 80% aromatic free diesel.[35] The diesel yield can be increased further by additional processing. Because FTS products are predominantly linear hydrocarbons, they have an excellent cetane number (about 75 versus the typically required minimum of 45). High-temperature fluidized-bed FT reactors with iron catalysts are ideal for the production of linear olefins, which are higher-priced petrochemicals.

Biomass gasification yields mainly H_2, CO, CO_2, and CH_4, which is not suitable for direct use in FTS but can be tailored by CH_4 reforming, water–gas shift, and CO_2 removal. Unfortunately, the FTS process appears always to yield products that range all the way from methane (normally unwanted) to high-carbon-number (up to 22) hydrocarbons.[35] In addition to olefins and paraffins, oxygenated products such as alcohols, aldehydes, and carboxylic acids are also produced. As these oxygenated products are predominantly linear, it could be of commercial interest to develop suitable catalysts and operating conditions to maximize their selectivity.

Hydrodeoxygenation of bio-oils involves treating bio-oils at moderate temperatures (300–600°C) with high-pressure H_2 in the presence of heterogeneous catalysts to remove the oxygen and form saturated C–C bonds. The energy content of the fuel is significantly increased, and the stability of the fuel increases during hydrodeoxygenation.[12]

Most hydrodeoxygenation work has focused on sulfided CoMo- and NiMo-based catalysts, which are industrial hydrotreating catalysts for the removal of sulfur, nitrogen, and oxygen from petrochemical feedstocks. However, bio-oils can also be upgraded using zeolite catalysts to reduce the oxygen content and improve the thermal stability. Temperatures of 350–500°C and atmospheric pressure are used for zeolite upgrading. The advantages of using a zeolite catalyst are that no H_2 is required, atmospheric processing reduces operating cost, and the temperatures are similar to those for bio-oil production. However, poor hydrocarbon yields and high yields of coke limit the usefulness of zeolite upgrading.[12]

Steam reforming of fossil fuels is a well-established technology, and steam reforming of bio-oils is an extension of this technology. Steam reforming reactions are performed at high temperature (600–800°C) and short residence time, usually with a Ni-based catalyst. This reaction predominantly produces CO and H_2 syngas. Commercial catalysts consist essentially of Ni supported on alumina. Steam reforming of bio-oils is complicated because some bio-oil components are thermally unstable and decompose upon heating. Deactivation of the catalysts due to coking is one of the major problems, and bio-oils have more deactivation problems than do petroleum-derived oils. To address some of the above issues, a high temperature is needed in the reactor to gasify coke deposits formed by thermal decomposition, and large quantities of steam are necessary to avoid catalyst deactivation by coking.[12]

In addition to traditional noncatalytic gasification processes (described above), catalytic gasification of biomass can be used to lower the operating temperature, making the process more economically feasible. Typically, temperatures above roughly 750°C are required for noncatalytic gasification. Gasification catalysts can lower the operating temperature to around 600°C, resulting in substantial energy savings. A common gasification catalyst is dolomite [$CaMg(CO_3)_2$], an inexpensive carbonate. However, rapid deactivation by tar formation at the lower temperatures of catalytic gasification has led to the search for more

https://doi.org/10.1557/mrs2008.76 Published online by Cambridge University Press

tar-resistant, but still active, gasification catalysts. Ni-based catalysts have been widely studied, but they are usually based on steam reforming formulations and have not been optimized for catalytic gasification reactions and still suffer from deactivation by tars.[36]

Catalysis research can also aid in more efficient gas cleanup from gasification. Currently, catalysts for the decomposition of tars downstream of the gasifier (as opposed to in-bed tar removal) are typically based on Ni catalysts, which operate at 700–900°C. These catalysts are subject to deactivation, but relatively few systematic studies of the deactivation process or how to regenerate the catalyst, particularly *in situ*, have been performed. Improvements in these technologies could be important.[36] One other objective of catalysis research in gas cleanup is to intensify the processes/materials required to remove all of the contaminants, simplifying them into as few continuous operations as possible. Examples include combining alkali and particulate removal and catalytic tar and ammonia decomposition on a particulate-resistant support.[36]

Specific research areas for catalysis include the following:

- FT catalysts and/or process conditions with better selectivity for carbon number. Meeting these objectives would require the successful manipulation of the FT chain-growth mechanism. Unfortunately, to date, none of the hotly contested proposed FT mechanisms have indicated how this goal could be achieved.[35]
- Cost-effective gasification catalysts that are resistant to deactivation and that will help improve the overall economics.[36]
- Novel catalytic reactor designs tailored to the typically smaller scale of biomass conversion processes.[36]
- Mechanically stronger FT catalysts to reduce erosion.
- Catalysts for downstream adjustment of the H_2/CO ratio for specific end products and for the reforming of biomass-derived liquids (e.g., from pyrolysis).
- Production of hydrogen-rich gases for subsequent hydrogen-powered energy devices.

Novel Concepts

Several novel concepts are now emerging in the area of biofuels. One is the potential of using free-floating algae to produce biofuels, perhaps similarly to how they are used today to produce food supplements such as spirulina.[37–40] Most research efforts in this area are biological in nature, but research needs include materials and processes to maintain adequate growing conditions and catalysts or other processes to convert algae-derived materials into suitable fuels.

Microbial fuel cells (MFCs) are a special class of fuel cells in which biocatalysts such as microorganisms or enzymes are employed instead of metallic inorganic catalysts.[41,42] Such devices were discovered over a century ago and largely abandoned, but recent advances in nanoscale science and technology might make it possible to overcome key drawbacks, such as short lifetime and low power density, that have limited enzyme-based biofuel cells from being used for practical applications. Various nanostructures exhibit the potential to stabilize and activate enzymes with much improved performance. The large surface areas that nanostructures provide for the attachment of enzymes can increase the enzyme loading and possibly improve the power density of biofuel cells. In that sense, nanoscale engineering of the biocatalysts appears to be critical in the next stage of advancement of biofuel cells.

One innovative approach would be to join biomass and coal gasification with carbon capture and sequestration (CCS) in a single production pathway.[43] Several studies have shown that the generation of negative atmospheric carbon emissions by integrating CCS and biomass energy technologies is potentially economical. The ability of biomass–CCS to generate negative atmospheric carbon emissions could fundamentally change the role of biomass in achieving deep emissions reductions by providing a mechanism to offset emissions anywhere in the economy.[44,45] Recently, there has been extensive discussion of the possibility of using a biomass integrated gasification Fischer–Tropsch (BIG–FT) process.[46] A BIG–FT plant would cogenerate electricity, heat, and fuel from biomass and potentially lower GHG emissions significantly.

Another novel concept is the use of nuclear process heat in biofuel production, leaving more of the scarce biomass to be turned into fuel.[47] Further, if nuclear-derived hydrogen were available, all of the carbon could be converted to high-quality hydrocarbon liquid fuels, possibly doubling the volume of available biofuels.

Bioenergy Supply Projections

The predicted volume of bioenergy in the global supply over the next half-century is much contested.[2,48] The wide variation in projections is not surprising given the wide range of forces that can drive bioenergy use. Key uncertainties include differing predictions regarding the state of bioenergy and fossil fuel technologies, feedstock costs, the rate of global economic growth, climate policy, and the need for and availability of land for energy crops, among others.

Berndes et al.[48] usefully categorized studies of bioenergy supply as shown in **Table II**. Demand-driven studies assess the demand for bioenergy that is determined by policy, economic, and environmental drivers. Resource-focused studies estimate the bioenergy resource base that can be feasibly extracted. **Table II** shows the upper and lower bounds of both types of studies, which suggest that the share of bioenergy might provide 5–40% of the total primary energy supply in 2050.

Table II: Bioenergy Supply Projections in 2050.

	Demand-Driven Studies	Resource-Focused Studies
Low estimate (EJ/year)	22	47
High estimate (EJ/year)	320	460

Note: Global energy demand is about 470 EJ/year.

However, resource-focused assessments assume that energy crops make up the majority contribution to the bioenergy supply. The potentials for wastes, biomass production on degraded lands, and novel concepts such as algae-derived biofuels have not been considered in these studies, although they could be substantial. For instance, a recent evaluation found that, in the United States, municipal solid waste and forestry residues could contribute the equivalent of 10–30% of annual gasoline demand.[49]

Thus, it appears that bioenergy can eventually supply a substantial fraction of world energy (up to several tens of percent). However, for such levels to be environmentally sustainable and to not adversely affect the food security of the poor, improvements in both technologies and policies are needed.[2]

Conclusions

Biomass remains a key energy supply for several billion people living in developing countries, and with near-record oil prices, the production of liquid biofuels for transportation is growing rapidly. However, both traditional biomass energy and

https://doi.org/10.1557/mrs2008.76 Published online by Cambridge University Press

crop-based biofuels technologies have negative environmental and social impacts that are unlikely to continue to be acceptable. Therefore, technological innovation will be needed in bioenergy, and changes in public policies will be equally critical.

Most immediately, enhancements in cookstoves can have multiple benefits such as improved indoor air quality and improved quality of life for the rural poor in developing countries. Further, resources that are diffuse or are currently wasted, such as grasses and organic waste, could, with improved technology, serve as fuels for distributed electricity generators that supply the rural poor.

In terms of biofuels technologies, the most important areas for research are those that enable the use of lignocellulosic feedstocks and yield high-quality liquid fuels, such as bio-based hydrocarbons. The ability to use lignocellulosic feedstocks, in turn, permits biofuel production without the use of productive land, releasing the land for food production or allowing it to remain as wilderness. Other biofuel technologies that require little or no arable land, such as algae, are similarly important. If carbon capture and sequestration technologies can be successfully applied, bioenergy production could become carbon-negative, creating a potentially lucrative opportunity. Fortunately, many possible production pathways from lignocellulosic feedstocks to high-quality biofuels could become feasible with materials (and other) research.

Technological progress will not be sufficient, however, as agricultural land might be used to grow energy crops instead of food crops because of the higher market value of the former, and the implications such land use can have for food prices appears to be adverse.[50,51] This could force the poorest communities to compete for food with the richest attempting to buy fuel. Moreover, under current policies, the environmental effects from biofuel production might be worse than those from fossil fuels.

With improved policies and technologies, however, bioenergy could contribute significantly to economic, social, and environmental goals. Eliminating the traditional mindset of biofuels as simply a new market for agricultural crops, subject to major support policies such as subsidies, will be essential to the development of cost-competitive biofuels. Policies that limit environmental impacts of biofuels, such as deforestation and greenhouse gas emissions, will help advance improvements in technology. The increased demand for biomass for energy could potentially improve farm incomes, and with well-designed policies, it could benefit the poorest farmers.

References

1. A. Demirbas, *Energy Sources A: Recovery, Utilization, Environ. Effects* **29**, 303 (2007).
2. A.D. Sagar, S. Kartha, *Annu. Rev. Energy Environ.* **32**, 131 (2007).
3. J.P. McCracken, K.R. Smith, *Environ. Int.* **24**, 739 (October 1998).
4. A.V. Bridgewater, *Fuel* **74**, 631 (1995).
5. D.A. Tilman, *Biomass Bioenergy* **19**, 365 (2000).
6. A.L. Robinson, J.S. Rhodes, D.W. Keith, *Environ. Sci. Technol.* **37**, 5081 (November 15, 2003).
7. P. Quaak, H. Knoef, H. Stassen, *Energy from Biomass: A Review of Combustion and Gasification Technologies* (The World Bank, Washington, DC, 1999).
8. *Multiple Links between Household Energy and the Millenium Development Goals* (World Health Organization, Geneva, Switzerland, 2007).
9. M. Ezzati, D.M. Kammen, *Annu. Rev. Energy Environ.* **27**, 233 (2002).
10. L. Baxter, *Fuel* **84**, 1295 (2005).
11. A. Faaij, R. van Ree, L. Waldheim, E. Olsson, A. Oudhuis, A. van Wijk, C. Daey-Ouwens, W. Turkenburg, *Biomass Bioenergy* **12**, 387 (1997).
12. G.W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **106**, 4044 (September 2006).
13. A.V. Bridgewater, *Fuel* **74**, 631 (1995).
14. C. Higman, M. van der Burgt, *Gasification* 391 (Elsevier, San Francisco, CA, 2003).
15. A.C. Caputo, M. Palumbo, P.M. Pelagagge, F. Scacchia, *Biomass Bioenergy* **28**, 35 (2005).
16. D.A. Burke, *Dairy Waste Anaerobic Digestion Handbook* 57 (Environmental Energy Company, Olympia, WA, 2001); www.makingenergy.com.
17. P. Borjesson, M. Berglund, *Biomass Bioenergy* **30**, 469 (2006).
18. P. Borjesson, M. Berglund, *Biomass Bioenergy* **31**, 326 (2007).
19. E. Ghafoori, P.C. Flynn, M.D. Checkel, *Int. J. Green Energy* **4**, 339 (2007).
20. Z. Bagi, N. Ács, B. Bálint, L. Horváth, K. Dobó, K. Perei, G. Rákhely, K. Kovács, *Appl. Microbiol. Biotechnol.* **76**, 473 (2007).
21. M. Cooney, N. Maynard, C. Cannizzaro, J. Benemann, *Bioresour. Technol.* **98**, 2641 (2007).
22. D.M. Kammen, A.E. Farrell, R.J. Plevin, A.D. Jones, M.A. Delucchi, in *OECD Research Round Table: Biofuels: Linking Support to Performance, S.* Perkins, Ed. (Organisation for Economic Cooperation and Development, Paris, 2007), p. 28.
23. Joint Transport Research Center, *Biofuels: Linking Support to Performance* (Organisation for Economic Cooperation and Development, Paris, 2007); www.cemt.org/JTRC/EconomicResearch/RoundTables/RTbiofuelsSummary.pdf.
24. A. Schwarzenegger, Executive Order S-01-07: Low Carbon Fuel Standard (Sacramento, CA, 2007).
25. A.E. Farrell, D. Sperling, A.R. Brandt, B.K. Haya, J. Hughes, B.M. Jenkins, A.D. Jones, D.M. Kammen, C.R. Knittel, M.W. Melaina, J.M. Ogden, M. O'Hare, R.J. Plevin, *A Low-Carbon Fuel Standard for California Part 1: Technical Analysis* (Transportation Sustainability Research Center, University of California, Berkeley, CA, 2007); http://repositories.cdlib.org/its/tsrc/UCB-ITS-TSRC-RR-2007-2.
26. A.E. Farrell, R.J. Plevin, B.T. Turner, A.D. Jones, M. O'Hare, D.M. Kammen, *Science* **311**, 506 (January 27, 2006).
27. C.A.C. Sequeira, P.S.D. Brito, A.F. Mota, J.L. Carvalho, L. Rodrigues, D. M.F. Santos, D.B. Barrio, D.M. Justo, *Energy Convers. Manage.* **48**, 2203 (July 2007).
28. A.E. Farrell, D. Sperling, A.R. Brandt, A. Eggert, B.K. Haya, J. Hughes, B.M. Jenkins, A.D. Jones, D.M. Kammen, C.R. Knittel, M.W. Melaina, M. O'Hare, R.J. Plevin, *A Low-Carbon Fuel Standard for California Part 2: Policy Analysis* (Transportation Sustainability Research Center, University of California, Berkeley, CA, 2007); http://repositories.cdlib.org/its/tsrc/UCB-ITS-TSRC-RR-2007-3/.
29. D.A. Tilman, J. Hill, C. Lehman, *Science* **314**, 1598 (December 8, 2006).
30. R.P. Anex, L.R. Lynd, M.S. Laser, A.H. Heggenstaller, M. Liebman, *Crop Sci.* **47**, 1327 (July–August 2007).
31. R.D. Perlack, L.L. Wright, A. Turhollow, R. Graham, B. Stokes, D. Erbach, *Biomass as a Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply* (Oak Ridge National Laboratory, Oak Ridge, TN, 2005).
32. W.E. Mabee, D.J. Gregg, J.N. Saddler, *Appl. Biochem. Biotechnol.* **121**, 765 (Spring 2005).
33. D. Mohan, C.U. Pittman, P.H. Steele, *Energy Fuels* **20**, 848 (May 2006).
34. A. Demirbas, *Prog. Energy Combust. Sci.* **33**, 1 (February 2007).
35. M.E. Dry, *Appl. Catal. A* **276**, 1 (November 2004).
36. J.J. Spivey, *Catal. Today* **100**, 171 (February 2005).
37. A.P. Carvalho, L.A. Meireles, F.X. Malcata, *Biotechnol. Prog.* **22**, 1490 (December 2006).
38. J.M. Gordon, J.E.W. Polle, *Appl. Microbiol. Biotechnol.* **76**, 969 (October 2007).
39. B. Hankamer, F. Lehr, J. Rupprecht, J.H. Mussgnug, C. Posten, O. Kruse, *Physiol. Plant.* **131**, 10 (September 2007).
40. N. Ladygina, E.G. Dedyukhina, M.B. Vainshtein, *Process Biochem.* **41**, 1001 (May 2006).
41. Z.W. Du, H.R. Li, T.Y. Gu, *Biotechnol. Adv.* **25**, 464 (September–October 2007).
42. J. Kim, H.F. Jia, P. Wang, *Biotechnol. Adv.* **24**, 296 (May–June 2006).
43. R.H. Williams, E.D. Larson, H. Jin, *8th International Conference on Greenhouse Gas Control Technologies,* 6 (Trondheim, Norway, 2006).
44. C. Azar, K. Lindgren, E. Larson, K. Mollersten, *Clim. Change* **74**, 47 (January 2006).
45. J.S. Rhodes, D.W. Keith, *Biomass Bioenergy* **29**, 440 (2005).
46. M.J.A. Tijmensen, A.P.C. Faaij, C.N. Hamelinck, M.R.M. van Hardeveld, *Biomass Bioenergy* **23**, 129 (2002).
47. C.W. Forsberg, *Assessment of Nuclear–Hydrogen Synergies with Renewable Energy Systems and Coal Liquefaction* (Oak Ridge National Laboratory, Oak Ridge, TN, 2006); p. 41.
48. G. Berndes, M. Hoogwijk, R. van den Broek, *Biomass Bioenergy* **25**, 1 (2003).
49. A.D. Jones, M. O'Hare, A.E. Farrell, *Biofuel Boundaries: Estimating the Medium-Term Supply Potential of Domestic Biofuels* (Transportation Sustainability Research Center, University of California, Berkeley, CA, 2007); http://repositories.cdlib.org/its/tsrc/UCB-ITS-TSRC-RR-2007-4.
50. D.J.A. Johansson, C. Azar, *Clim. Change* **82**, 267 (June 2007).
51. U.A. Schneider, B.A. McCarl, *Environ. Res. Econ.* **24**, 291 (April 2003). □

https://doi.org/10.1557/mrs2008.76 Published online by Cambridge University Press