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Bioenergy Solutions

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Energy

Generally, energy is defined as the capacity to do work, and it is basic to understand life. Life is a state of activity controlled genetically and driven by energy to maintain and reproduce its cellular organization (Mendoza and Mendoza 2011). What is surprising is that all known living organisms share the same energy and cell synthesis processes.

The autotrophs produce their own chemical energy sources from solar energy as well as water and CO₂, whereas the heterotrophs consume

organic matter derived from other organisms to obtain energy. Since most autotrophs obtain their energy from the sun, the solar energy is the main source of life.

This chapter deals first with the basic energy processes in living organisms (bioenergetics) and second with the most sustainable technological applications of bioenergy (also called biofuels), especially the production of biogas, which has shown to be one of the most abundant, viable energy sources now that fossil fuels have become scarce, expensive, and environmentally unsustainable.

Entropy and Life

Living beings are open systems that interchange matter and energy with the environment (Mendoza and Mendoza 2011). The flow of energy through an ecosystem is governed by two laws. The first law states that energy may not be created or destroyed, the second that no energy transformation is 100% efficient (Spellman and Drinan 2001). Energy flows from autotrophs to heterotrophs; between each of these trophic levels there is a loss of energy as heat (called entropy). Eventually, all energy flowing through the trophic levels is dissipated as heat losing its capacity to do work (Margalef 1998) be it chemical, osmotic, thermal, or mechanical. This state in which a system is unable to use energy is called thermodynamic equilibrium and is attained after one organism dies. However, living beings are highly organized systems, able to pass their genetic information to their progeny. This is one means whereby life challenges the second law and escapes thermodynamic equilibrium. The other means is through recycling dead organisms, a role assigned to degraders. Degraders transform dead cells into simple molecules, used as energy sources and other nutrients by autotrophs.

Every day we lose energy and our technologies do not replace it. Even recycling uses energy that comes automatically with an increase in entropy. Therefore, it is critical that we find ways to reduce energy loss (Schmitz 2007). One such way is to recycle waste using biological systems. In biogas systems as opposed to fossil fuels, living beings continuously reorganize the matter and energy mineralizing organic compounds making them available in the form of nutrients to new life and as a byproduct they make a fuel available to humans. Also, if solid waste is not transformed into fertilizer and biogas, humans have to resort to fossil fuels to obtain these products and this has to be done at a high energy cost, which includes lengthy prospection, long-haul transport, and, with some frequency, oil spill remediation (Adler et al. 2007). Producing biogas and fertilizer from solid waste leads to less entropy than an equivalent production using fossil fuels. Finally, nonbiological systems use energy and do not reproduce themselves, and so energy is lost replacing them. These systems are not able to recycle themselves as are biological systems.

Bioenergetics

Overall, the main functions in living beings in which energy transformations are carried out are movement, nutrient transport, and synthesis of new molecules. However, it must be emphasized that in every energy conversion one part is converted into heat.

The capture and use of energy in living systems includes two processes: photosynthesis and respiration. Photosynthetic organisms (autotrophs) capture the sunlight, water (H_2O), and carbon dioxide (CO_2) to form glucose and O_2 that is released into the atmosphere. Heterotrophic organisms get the energy from photosynthetic and other organisms (as food) releasing CO_2 to the atmosphere. The oxidation of glucose by organisms is called respiration and it can be aerobic (with oxygen) or anaerobic (without oxygen). Respiration converts the chemical bonds' energy of glucose to the usable energy of adenosine triphosphate (ATP) required for metabolic processes: (1) catabolism (degradation of chemical compounds to withdraw nutrients and release energy) and (2) anabolism (synthesis of new molecules).

Bioenergy

Biomass refers to material of biological origin (excluding material embedded in geological formations) and therefore is renewable. Bioenergy is the use of biomass to produce energy (O'Connell et al. 2009). When the energy stored in biomass is used, greenhouse gases such as CO_2 or methane (CH_4) are emitted, but the amount is the same as that produced by natural decomposition processes if the human rate of their use does not overshoot the natural rate. In contrast to the direct use of solar energy or wind power that is not always available, biomass can be produced and stored at all times, and be converted to electricity, heat, or fuel (German Solar Energy Society [DGS] and Ecofys 2005).

Biofuels today only supply 12.7% of the world's total primary energy consumption; 7% correspond to woodfuels. However, the global bioenergy potential could equal the current world energy consumption by 2050 (Food and Agriculture Organization of the United Nations [FAO] 2002; International Energy Agency [IEA] 2012).

Sustainable bioenergy follows the Earth's biogeochemical cycles to obtain energy and minimize the accumulation of waste in the environment; this is done by recycling domestic and industrial wastes. Bioenergy life-cycle analyses comprise production, harvesting, storage, transportation, distribution, greenhouse gas emissions, social and ecological impacts, pollutant emissions and their remediation, as well as comparative economic costs. Considering these elements, bioethanol from corn and sugarcane, or biodiesel from palm oil or oilseeds have been criticized due to their competition for land and water with food production and their lack of waste recycling. This is why

TABLE 10.1

Currently Available Biofuels

Source	Advantages	Disadvantages
Biomethane	It can be obtained from organic waste under anaerobic conditions. It can be used directly after the anaerobic process, separating it from other gases. CO ₂ emissions are minimal compared with other biological processes.	Exerts 23 times the greenhouse effect of CO ₂ . High emissions when digesters are not sealed. It is abundant in the Earth atmosphere; however, there is no technology to store it yet.
Biodiesel	Algae, bacteria, or cyanobacteria may be used instead of oil grains.	Water demand. Conversion of natural areas to energy crops. Soil acidification, fuel and fertilizer use, biodiversity loss, toxicity from biocides.
Bioethanol	Cellulose from seaweed, switchgrass, jatropha, cyanobacteria, and green algae may be used instead of food crops.	Water use demand. Conversion of natural areas to energy crops. Soil acidification, fuel and fertilizer use, biodiversity loss, toxicity from biocides.
Woodfuels	Direct use of woodfuel for heat. Charcoal, pellets, or briquettes may be produced.	Production of greenhouse gases by combustion (CO ₂ and H ₂ O). Generation of aerosol particulates, black carbon, or soot that increase irradiation sorption. Continuous reforestation is needed to close the cycle.

the generation of biogas from organic waste remains the most sustainable option until now (Table 10.1). Therefore, biogas is described with more detail in the following sections.

Biomethane: As Old as Life on Earth

Methane exists in the solar system and beyond, where it is abiotically produced. It is the simplest hydrocarbon, the main component of biogas and fossil natural gas, and probably the most abundant organic compound on Earth (Petrescu-Mag et al. 2011), where it is biogenically produced by the degradation of organic matter without oxygen. Methane generation on Earth involves different groups of organisms, mainly bacteria and methanogenic archaea. The latter seem to have metabolisms adapted to the early conditions of Earth. Methanogenic organisms are found in places where oxygen (O₂) is absent, and hydrogen (H₂) and carbon dioxide (CO₂) are present. Methanogens use mainly H₂ as an energy source and CO₂ as a carbon source

for growth. Methanogens are found in marine and freshwater sediments, hot springs, swamps, wastewater treatment plants, digestive tracts of termites, ruminants, and humans. This shows that despite their intolerance to oxygen, the methanogens are still widely distributed on Earth.

Biogas Applications

Compared to other hydrocarbon molecules that have more carbon atoms, burning methane produces less CO₂ for each unit of heat released. The ratio of methane's heat of combustion (891 kJ/mol) to its molecular mass (16.0 g/mol, of which 12.0 g/mol is carbon) is 55.7 kJ/g, which is more heat per mass unit than more complex hydrocarbons.

It is estimated that a landfill with 5.6 million tons of solid waste can produce enough biogas to power a 5 MW plant for 10 years. The digesters used in the landfills must be airtight to avoid atmospheric emissions, which can be higher than 65% of the landfill-generated biogas in the United States (Themelis and Ulloa 2007). This means that all organic solid waste should be anaerobically digested rather than disposed of to a landfill, on pollution and energetic grounds.

In many cities, methane is already being piped into homes for domestic heating, cooling, and cooking purposes. There are also countries with sufficient volumes of methane to be used industrially as fuel (DGS and Ecofys 2005).

Land and Maritime Transportation

Methane in the form of compressed natural gas is used as a vehicle fuel and is more environmentally friendly than other fossil fuels such as gasoline/petrol and diesel. Some cities in European countries have started to distribute biomethane in gasoline stations as a solution for green transportation. In Sweden and Denmark, organic waste is imported from other countries to generate biogas, which is used for urban transport (Røstad 2012). In several countries liquid natural gas (LNG) has been introduced in railways, passenger cars, and vans. Since 1985 several ferries around the world have been powered by more than 70% natural gas and diesel. Japanese companies are investing in Mexico to generate biogas from organic waste to produce cars (EcoSecurities International 2009).

Data Centers

Several projects are underway to power data centers with biogas, in an attempt to curb Internet downtime episodes. Microsoft's Wyoming facility will rely on a system of pipes extracting methane from wastewater, cleaning it, and moving it into fuel cells. The fuel cell will chemically turn the biogas into electricity (LaMonica 2012). Apple's North Carolina data center will tap landfills for biogas, which will then be converted into electricity also using fuel cells (Kerr 2012).

Space Travel

NASA is working on the use of methane as fuel for rockets (Morring 2009). The assembly of a liquid oxygen/liquid methane rocket engine has been completed (Figure 10.1a). One advantage of methane is that it is abundant in many parts of the solar system (Figure 10.1b) and this may be collected on the surface of another planetary body providing fuel for a return trip (Lorentz and Mitton 2002).

Methane Production

Methanogenesis

Archaea generate CH_4 to obtain metabolic energy in the form of ATP and molecules for biosynthesis (Thauer and Shima 2006). It is thought that the biological conversion of solid wastes under anaerobic conditions follows four steps (Figure 10.2). The first step involves enzyme-mediated hydrolysis of high molecular mass compounds to make them transferable into cells for use

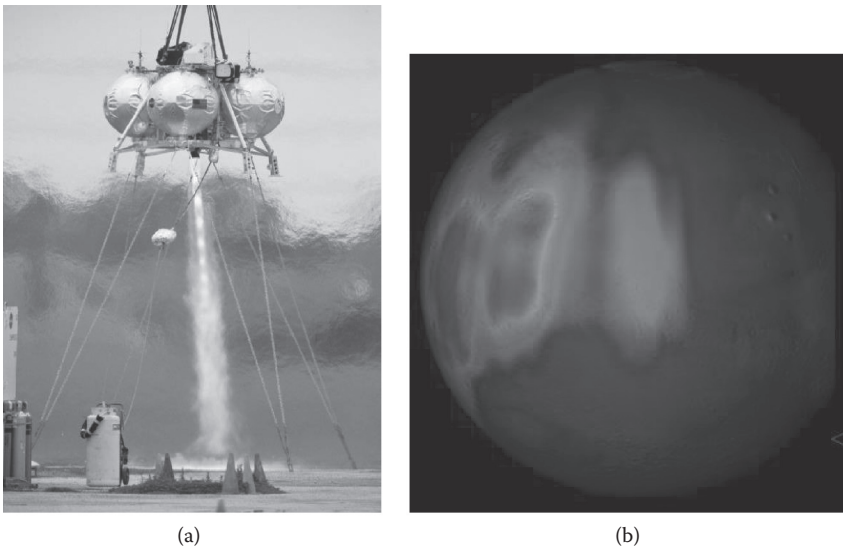


FIGURE 10.1 (See color insert.)

The possibility of methane-propelled spaceships. (a) The Morpheus lander take-off test. (Reproduced from the National Aeronautics and Space Administration [NASA], 2012a, Morpheus testing picks back up at Johnson Space Center. http://www.nasa.gov/centers/johnson/exploration/morpheus/morpheus_tests_pickup.html.) (b) Methane release concentrations in the northern summer on Mars. (Photo by Trent Schindler. Reproduced from NASA 2012b, Mars: NASA explores the red planet. http://www.nasa.gov/mission_pages/mars/news/marsmethane_media.html.) Other planets with abundant methane are Jupiter, Saturn (Atreya 2007), Uranus, and Neptune, plus Titan, the moon of Saturn.

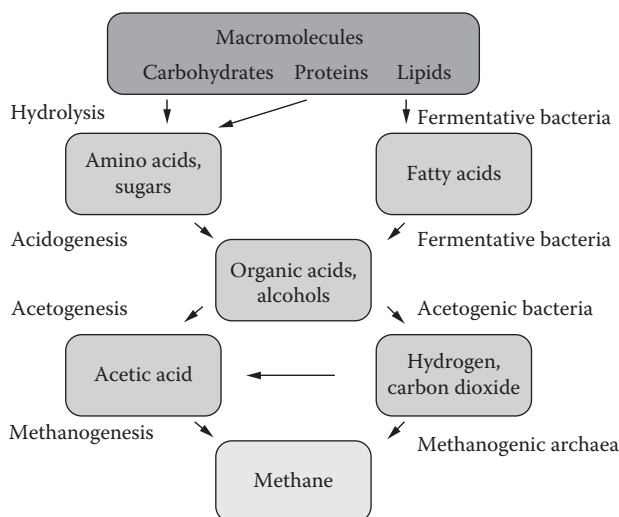


FIGURE 10.2
Methanogenesis and its different stages.

TABLE 10.2

Biogas Composition

Compound	Percentage
CH ₄	50%–80%
CO ₂	20%–50%
H ₂	<1%
NH ₃	<1%
H ₂ S	<1%
N ₂	<1%

Source: German Solar Energy Society (DGS) and Ecofys, 2005, *Planning and installing bioenergy systems: A guide for installers, architects and engineers*, London: James & James.

as an energy source. The second step involves bacterial conversion to lower molecular mass sugars, amino and fatty acids. In the third step, compounds with a methyl group (–CH₃) are produced. Finally, methanogens produce biogas whose main components are CH₄ and CO₂ (Table 10.2). Almost two-thirds of the methane produced in manmade digesters are produced this way.

The benefits of anaerobic digestion include: (1) biogas to generate electricity, heat, or engine fuel; (2) organic fertilizer with a mineral content similar to fresh excreta and equally useful for soils, crops, and plankton; (3) destruction of pathogenic microorganisms, parasite eggs, and weed seeds contained

in fresh excreta; and (4) reduction of pollution and organic waste (up to 50%) during the degradation of the organic material (Tchobanoglous et al. 1994; Masera and Fuentes 2006).

Anaerobic Reactors

The benchmark reactor is the rumen of cattle, which completes digestion in only 24 hours with an efficiency of food conversion of up to 80%. Far away from that benchmark are manmade digesters able to convert lignocellulose, with a comparable conversion rate following 30 to 90 days.

The main operation task is to promote 60°C temperatures favorable to thermophilic organisms. Decreased yields are obtained from mesophilic (36°C optimum) and psychrophilic organisms (20°C) (Ortega 2000). In regions where environmental temperature is too low (<8°C) heating equipment for digesters is compulsory.

The pH is important because of the constant production of acidic intermediates; methanogens do not tolerate pH values below 6.0, which are linked to excess substrate (feed) input. Observed organic dry matter loading rates for different substrates are shown in Table 10.3. Sometimes hydrolysis and acidification are carried out in a first reactor while in a second reactor acetogenic and methanogenic activities prevail. As in the first reactor the pH can decrease below 5, its output needs to be mixed thoroughly with the content of the second digester to neutralize the pH. The operation of this kind of digesters usually is more stable.

When complete mineralization (i.e., digestion) of organic matter occurs, the quantity and composition of the resulting biogas tends to follow the Symons and Buswell relation (1933): 0.79 m³ biogas kg⁻¹ substrate and 50% methane concentration for the conversion of carbohydrates; 1.25 m³ kg⁻¹ and 68% methane concentration for the conversion of lipids; and approximately 0.7 m³ kg⁻¹ and 71% methane concentration for the conversion of proteins. Recalcitrant organic matter lowers the biogas yield compared to the theoretical value from Symons and Buswell. Biogas and CH₄ experimental yields from various substrates are a useful reference to assess the performance of an anaerobic reactor (Table 10.3).

Compared to other biofuels where energy-intensive separation is needed, like extraction to produce biodiesel or distillation to produce anhydrous ethanol, the biogas bubbles from the liquid phase of the anaerobic digestion (also called wet biogas), and are in some cases ready to use. Alternatively, adaptations to equipment for natural gas now allow the use of biogas with methane concentrations around 60%. This makes on-site utilization for cooking, hot water, and electricity production possible. Also, energy-efficient conversion of biogas from wastewater treatment plants using fuel cells has been demonstrated in various plants working successfully over many years (Kishinevsky and Zelingher 2003).

TABLE 10.3

Biogas Conversion Rates from Various Substrates

Substrate	DM (% Wet Matter)	oDM (% Dry Matter)	Biogas (m ³ /kg oDM)	Methane (% m ³ CH ₄ /m ³ Biogas)
Cattle manure on wet basis	7.5–13	6.4–10	0.17–0.63 (0.38)	53–62 (55)
Pig manure on wet basis	2.3–11	1.3–7.1	0.–0.88 (0.42)	47–68 (60)
Broiler manure	25	22	0.15–0.53 (0.50)	42–68 (55)
Wheat straw			0.25–0.4 (0.4)	52
Corn straw			0.5	
Grass silage	27–57	25–46	0.21–0.7 (0.60)	52–56
Corn silage	25–37	24–36	0.3–1.13 (0.65)	47–69
Sudan grass	33–46	14–36	0.33–0.38 (0.33)	54–62 (63)
Grease traps residues	48	85	0.7–1.3	60–77
Digestive tract viscera	11–19	9–16	0.2–0.4	60
Rumen contents			0.45–0.55 (0.48)	44–55 (50)
Glycerin	100		(0.85)	50
Ethanol production wastes (wheat)	4.6–76	4.3–71	0.39–0.72 (0.70)	53–55 (55)
Molasses	5		(0.68)	54
Canteen residues	14–19	12–16	0.15–0.68 (0.68)	43–77 (60)

Source: KTBL, 2012, Biogasrechner. <http://daten.ktbl.de/biogas/navigation.do?selectedAction=Startseite#start>, zuletzt aktualisiert am 03.07.2012.

Notes: DM, dry matter; oDM, organic dry matter. Values in parentheses refer to state-of-the-art digesters and are lower than maximum potential yields.

CO₂ Separation

The first step of biogas purification focuses on removing water and hydrogen sulfide (H₂S). In small-scale units H₂S is captured in activated carbon filters, which have to be replaced periodically. In bigger units biological desulfurization is applied with great success. The secondary products of desulfurization are sulfur and sulfate (depending on oxidation conditions), which can be used as fertilizers in agriculture. This kind of purification benefits the biogas facility with a longer equipment lifetime and a lower failure rate.

Further biogas purification produces the more calorific biomethane, equivalent to fossil natural gas. Biomethane has an increased diversity of applications and allows for reduced greenhouse gas emissions as well as a relative independence from fossil fuels (Weber et al. 2012); it is more efficient than

bioethanol (Insam 2010); and can be introduced into the natural gas grid allowing for cogeneration systems whereby small-scale producers contribute to the grid.

A requirement for introducing biomethane into the natural gas grid consists of removing CO_2 and H_2S . In biogas plants, a biological pretreatment for the removal of H_2S may be favorable. Further process steps focus on CO_2 removal by physicochemical treatments like separation in membranes, cryogenic rectification columns, adsorption of CO_2 and H_2S on activated carbon, physical absorption in water or organic solvents like polyethylene-glycol-dimethyl-ether (which, however, is a suspected compound with central nervous system toxic effects), and chemical absorption with some alcoholamines. The characteristics of the processes are different depending on method selectivity, pressure, purity, temperature, energy consumption, and methane leaks. The strategy for purifying depends also on the end use. For example, when liquefied gas is produced, cooling helps in separation as well. A high pressure level is required for using membranes, activated carbon or water absorption, introducing biomethane into grid, or filling the tanks of cars. Technological knowledge of all these processes exists due to the processing of natural gas for many decades. The challenge is to make it economically feasible at a small scale. The technologies based on chemical absorption with alcoholamines may be favorable for producing biomethane because desorption is carried out by heat, lowering the demand of electric energy. Moreover, this process produces the lowest methane slip with 0.1%, whereas in other processes the emission of methane is near 2% (Table 10.4).

Safety

Biogas is flammable and can be burned in gas torches or internal combustion engines. The range of explosion is narrower than for natural gas, which makes it easier to prevent. Danger is mainly attributed to the H_2S content, since levels above 100 ppm are immediately dangerous to life and health (IDLH). The main focus on cleaning biogas consists of removing H_2S before burning because of the formation of corrosive exhausts.

Methane is a greenhouse gas that remains in the atmosphere for approximately 9 to 15 years and is 23 times more effective in trapping heat than CO_2 over a period of 100 years (Intergovernmental Panel on Climate Change [IPCC] 2007). There is a debate as to whether methane is increasing due to human activities (industrial processes, livestock, paddy rice fields, biomass burning, landfills, extraction of oil and natural gas, agriculture, coal mining, and wastewater treatment plants) (Atmospheric Infrared Sounder [AIRS] 2011). Ironically, while petroleum is being depleted as a source of energy, methane, which is another fuel, is being released to the atmosphere in hazardous concentrations, largely above the last 650 thousand years (Wolff and Spahni 2007).

TABLE 10.4

Comparison of Various Technologies for Producing Biomethane

Criteria	Adsorption on Activated Carbon	Water Absorption	Absorption on Tetraethylene-Glycol-Dimethyl-Ether	Chemical Absorption with Methanol-Amine	Chemical Absorption with Diethanol-Amine
Prepurification	Yes	No	No	Yes	Yes
Pressure (bar)	4–7	4–7	4–7	Atmospheric	Atmospheric
Methane slip	<3%	<1%	2%–4%	<0.1%	<0.1%
Methane concentration product	>96%	>97%	>96%	>99%	>99%
Electric energy demand (kWh/Nm ³)	0.25	<0.25	0.24–0.33	<0.15	<0.15
Thermal energy demand (kWh/Nm ³)	Not required	Not required	0.5 at 55°C–80°C	0.7 at 160°C	0.7 at 160°C
Dynamic operation % of nominal power	10%–15%	50%–100%	50%–100%	50%–100%	50%–100%

Source: Fraunhofer, 2009, Verbundprojekt: Biogaseinspeisung http://www.biogaseinspeisung.de/download/Kurzbrochuere_Biogaseinspeisung.pdf.

Oncoming Technologies

Artificial Photosynthesis

Artificial photosynthesis refers to any scheme that captures and stores solar energy in the chemical bonds of a fuel (Concepcion et al. 2012). Photocatalytic water splitting is a research area that aims to convert water into protons (and eventually hydrogen fuel) and oxygen (Sun et al. 2001). Light-driven carbon dioxide reduction is another process that replicates natural carbon fixation. These fields of research encompass the design and assembly of devices for the direct production of solar fuels, photoelectrochemistry and its application in fuel cells, and the engineering of enzymes and photoautotrophic microorganisms for microbial biofuel and biohydrogen production from sunlight (Royal Society of Chemistry 2012). Another area of research is the selection and manipulation of photosynthetic microorganisms, namely, green microalgae and cyanobacteria, for the production of solar fuels. Many strains are able to naturally produce hydrogen. Biofuels from algae such as butanol and ethanol are produced both at the laboratory and commercial

scales. This approach is also being explored to develop organisms capable of producing biofuels (J. Craig Venter Institute 2012).

Biohydrogen

Hydrogen is attractive due to its potentially higher energy efficiency of conversion to usable power and low generation of pollutants. Hydrogen is conventionally produced from natural gas by steam reforming, coal gasification, and electrolysis of water; however, these methods use nonrenewable energy sources and are not sustainable. Biohydrogen production comprises renewable processes, which are classified into four categories: (1) biophotolysis of water (direct and indirect) using algae and cyanobacteria; (2) photodecomposition of organic compounds by photosynthetic bacteria (photofermentation and dark fermentation); (3) biocatalyzed electrolysis; and (4) fermentative hydrogen from organic wastes or energy crops (Manish and Banerjee 2009). However, still low yields and production rates have been major barriers to the practical application of biohydrogen technologies (Hallenbeck and Ghosh 2009).

Animal Power

Animals have allowed mechanical work since animal domestication started 10,000 years ago. Cattle, horses, mules, llamas, camels, dogs, and donkeys provide transport, pull implements, lift water, and enable other processing activities (Karekezi and Kithyoma 2002). The integration of crop and animal production is an efficient symbiosis where animals increase production, income generation, and the sustainability of cropping systems in small-scale agriculture, with complementarity resources from one sector to the other (Devendra and Thomas 2002). Using renewable resources from the local environment, animals are self-recruiting, produce manure, leather, meat, and hide; and through a well-planned grazing and stocking rate they can contribute to the maintenance of a multifunctional landscape (Rydberg and Jansén 2002). The level of investment on farm implements is lower with minimum tillage. Soil compaction from farm equipment traffic is less with animal traction compared to even small tractors. Recent developments in computer-based simulations help to optimize the implement designs and operational conditions of animal use (Gebregziabher et al. 2006). Moreover, some implements have been developed to use biomass and animal force to produce energy, as for example, an animal traction piston press for producing biomass briquettes as household fuel (Mazzù 2007). Animal power is more versatile than machine power on steep and difficult terrains, typical of poor isolated rural areas.

Microbially Produced Electricity

Recent discoveries of microorganisms capable of converting chemical energy into electric current using fuel cells suggest an important biotechnological

avenue. Some examples of such bacteria belong to the δ -proteobacteria, mainly the Geobacteraceae family (Esteve-Núñez et al. 2008). Microbial fuel cells (MFCs) are microorganisms that biologically oxidize organic matter and transfer electrons to an anode. Enriched anodic biofilms have generated power densities as high as 6.9 W per m² (Logan 2009).

Termite Gut

Current research on the termite gut aims to identify the microorganisms that can be useful to produce biofuels in the future (Brune 2007). Microbes in the termite gut have the ability to convert cellulose into sugars that can be turned into ethanol, hydrogen, or methane. Recently, the microbial community of the termite gut was sequenced and a number of novel cellulases have been identified that break down cellulose into sugar. The next goal is to understand and reconstruct a diverse range of metabolic processes that could be scaled up for industrial fuel production (Singer 2007).

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