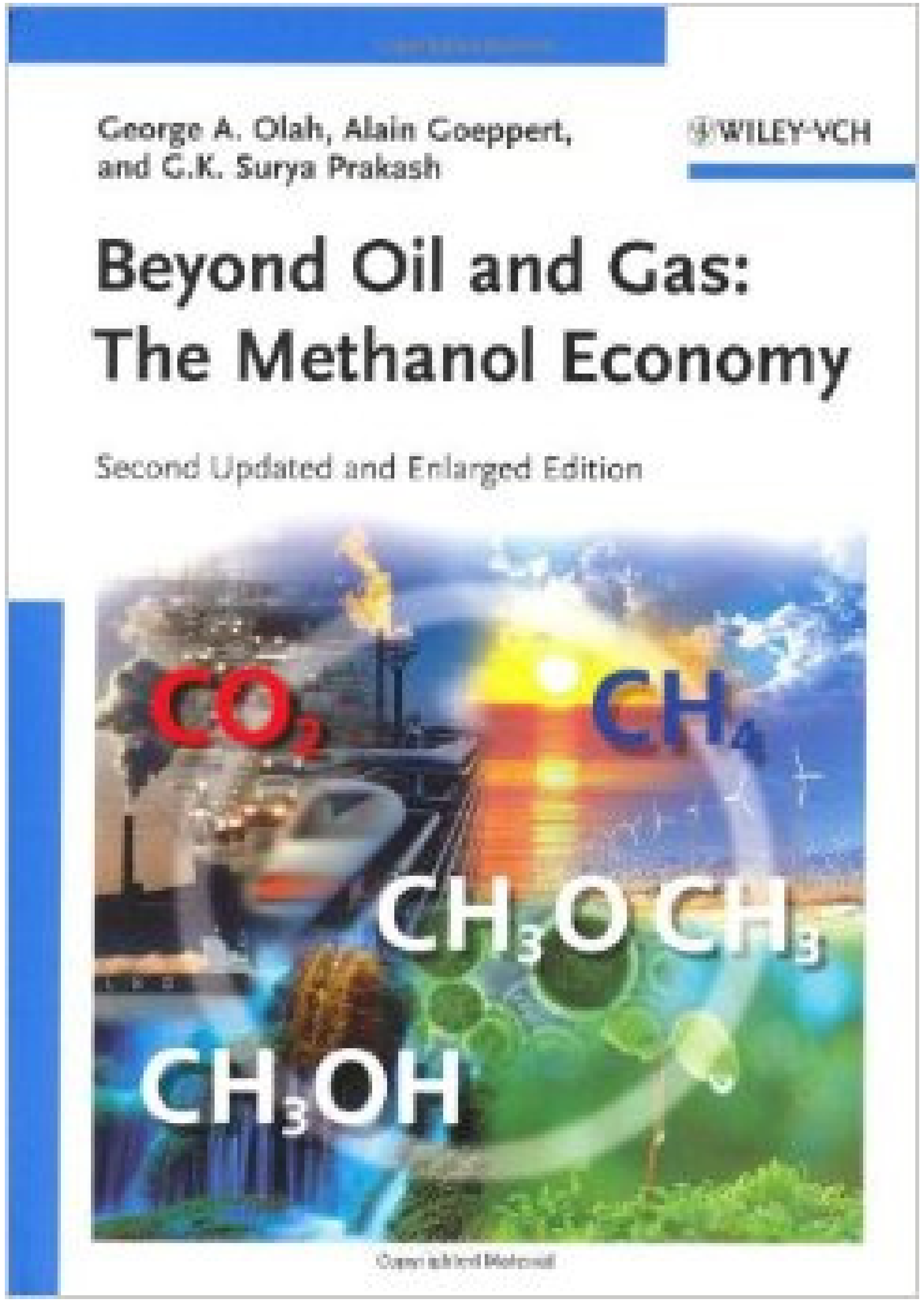
George A. Olah, Alain Goeppert,
and G.K. Surya Prakash
WILEY-VCH
Beyond Oil and Gas:
The Methanol Economy
Second Updated and Enlarged Edition
CO2
CH4
CH3OCH3
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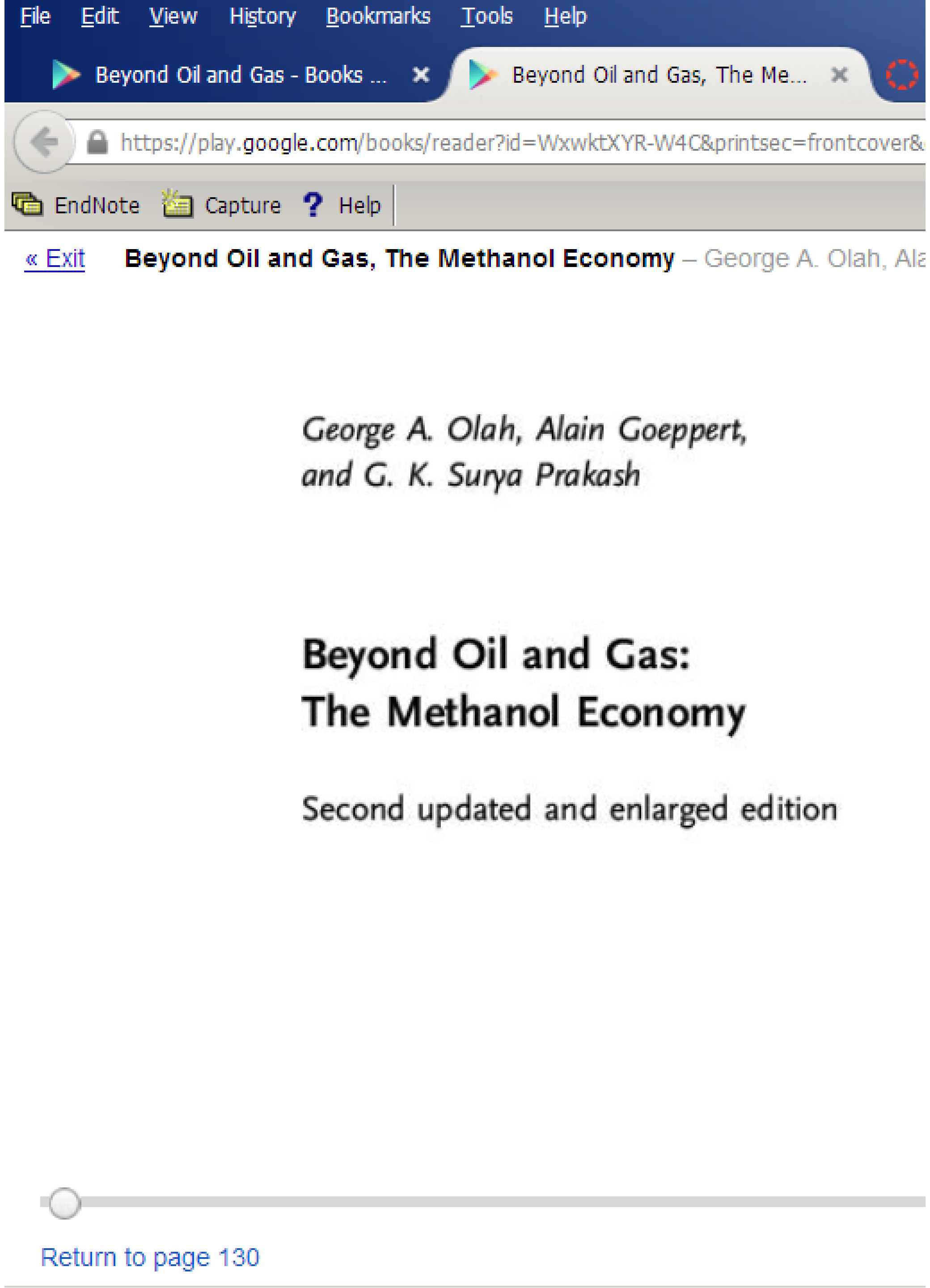
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and variable energy sources, especially wind energy [131–133]. Of course, energy storage will add to the cost of electricity produced from these renewable sources. With continued research and technological improvements, however, solar energy will, in the long run, certainly become an important part of our overall energy-mix. As mentioned, using solar energy to convert CO_2 with hydrogen generated by electrolysis of water is certainly a promising approach.

8.6 Bioenergy

Bioenergy or biomass energy refers to the use of a wide range of organic materials as fuels. These are produced by biological processes, and include forest products, agricultural residues, herbaceous and aquatic plants, and also municipal wastes. In principle, bioenergy is inexhaustible and renewable, provided that new plant life is grown to replace the ones harvested for energy. Biomass can either be burned to produce heat or electricity, or transformed into liquid fuels such as ethanol, methanol or biodiesel. Biomass has been our predominant source of fuel well into the nineteenth century. Whereas dried plants, plant oil, animal fat or dried dung were used for lighting and cooking needs, the most common biomass source was wood. Its dominance was progressively replaced by fossil fuels, first coal and then oil and gas during the nineteenth and twentieth centuries. Today, biomass supplies about 10% of the world's primary energy consumption. Indeed, in many poor countries it continues to be the most important source of energy for heating and cooking purposes, whereas in developed nations only a small fraction of the energy needs are covered by biomass.

8.6.1 Electricity from Biomass

The cheapest, most utilized and simplest way of using biomass to generate energy is to burn it. On a commercial scale, this process is carried out in a similar way to the one used for burning coal to produce electricity or heat. In these applications, wood, wood waste and municipal solid waste are the most utilized fuels. The average plant is generally small (around 20MW) with an efficiency ranging from 15 to 30% for conversion into electricity [100]. With co-generation of electricity and heat, the total efficiency can reach 60%. Methane-rich biogas, if captured and collected from landfills, can also be used to generate sizeable amounts of energy.

New technologies that are commercially available for converting biomass into electricity include co-firing and gasification. Co-firing power plants use biomass as a supplementary energy source with a conventional fuel, typically coal. Gasification converts solid biomass, through partial oxidation at high temperature, into a combustible gas containing mainly carbon monoxide and hydrogen. The gas produced can then be burned in a gas turbine or internal combustion engine to generate electricity. Notably, during the Great Depression and World War II, small gasifiers were used for cars to convert wood and charcoal into gas that was then fed to the engine. These vehicles were not very efficient and needed extensive maintenance, but nevertheless functioned quite well.

The cost of biomass energy varies widely, depending on the fuel, its quality and the technology used. Electricity-generating costs are, however, generally higher than those for fossil-fueled plants because of lower efficiencies, higher capital and fuel costs. Most estimates for the fuel cost are in a range $150–250 per tonne, but this can be much lower in cases where the fuel is a by-product from some other process [100].

Table 8.1 Production of electricity from biomass and waste in 2006.

Data source: EDF and IEA key statistics.

Country	Production (TWh)	Percentage of world electricity production from biomass	Percentage of the country's total electricity production
United States	58.7	29.3	1.5
Germany	19.7	9.9	3.4
Brazil	14.6	7.3	3.9
Finland	11.8	5.9	14.0
Japan	11.6	5.8	1.1
United Kingdom	9.3	4.6	2.5
Canada	9	4.5	1.6
Spain	8.2	4.1	3.1
Rest of the world	57.2	28.6	0.6
World	200.1	100	1.2

Among the OECD countries (Organization for Economic Cooperation and Development, including most developed nations), electricity from bioenergy represented 1.5% of the total electricity generation in 2005 [121]. More than halfwas produced from solid products such as wood and agricultural residues, while waste also accounted for an important part of electricity produced by biomass. In 2006, in forest-rich Finland, electricity from bioenergy represented 14% of the total electricity production, but only 1.5% in the United States (which has the largest overall electricity-generation capacity from biomass, but also the highest electricity consumption) (Table 8.1).

8.6.2 Liquid Biofuels

Biofuels are liquid fuels produced from crops or biomass feedstock through different chemical or biological processes. Today, they are the only available renewable source for producing high-value liquid biofuels such as ethanol or biodiesel. These fuels can offer renewable alternatives to transportation fuels that presently are obtained almost exclusively from oil. Bio-ethanol, the most common biofuel, is produced by fermentation of annually grown crops (sugarcane, corn, grapes, etc.). In this process, starch or carbohydrates (sugars) are decomposed by microorganisms to produce ethanol. Ethanol can be produced from a wide variety of sugar or starch crops, including sugar beet and sugarcane and their by-products, potatoes and corn surplus. In Russia after the Bolshevik revolution, Lenin proposed the use of agricultural alcohol to produce industrial fuels and products. Because this process would have diverted the Russian people's beloved source of vodka to industrial use, the plan was soon abandoned. During World War II in Europe, blends of ethanol with gasoline were used, but only anhydrous ethanol is miscible with gasoline, phase separation otherwise causing stalling of the engines. Ethanol has been promoted and used more recently and extensively in Brazil and the United States as a response to the OPEC oil embargoes and rising gasoline prices (but also to subsidize farmers). Initially, Brazil–one of the largest sugarcane producers in the world–gave farmers financial incentives to switch from sugar to ethanol production. This plan was implemented, and by the mid-1990s about 4.5 million vehicles were running on pure ethanol, and the remainder on a blend of gasoline containing up to 24% ethanol by volume. With falling oil prices and the end of price subsidies for ethanol at the end of the 1990s, however, the sale of pure ethanol cars fell to almost zero (Figure 8.12) [134, 135]. Increasing oil prices, experienced more recently, have revived interest in ethanol. The production of ethanol from sugarcane in Brazil reached some 22 millionm3 per year in 2007 [136]. The extraordinarily high productivity of sugarcane (up to 80t cane per hectare, compared to 10–20t for most plants cultivated under temperate climates), associated with low wages, has contributed to a great extent to the competitiveness of ethanol in Brazil. So-called flexible fuel vehicles (FFV), able to run on any mixture of gasoline and ethanol, have also been introduced recently. In only a few years the market share for FFV has increased to over 70% of the cars sold in Brazil. However, the amount of ethanol produced annually in Brazil represents only the equivalent of some 10–11 million tonnes of petroleum oil, less than the quantity consumed by the world in a single day. Besides alcohol, sugarcane by-products–principally bagasse (sugarcane husk)–are burned to supply Brazil's grid with about 600MW of electricity [137]. This again, is less than the output of a single large-scale fossil-fuel or atomic power plant.

Figure 8.12 Percentage ofethanol-powered automobile produced in Brazil compared to the country's total automobile production. (Source: Associação Nacional dos Fabricantes de Veículos Automotores ANFAVEA, *Brazilian Automotive Industry Yearbook 2007*.)

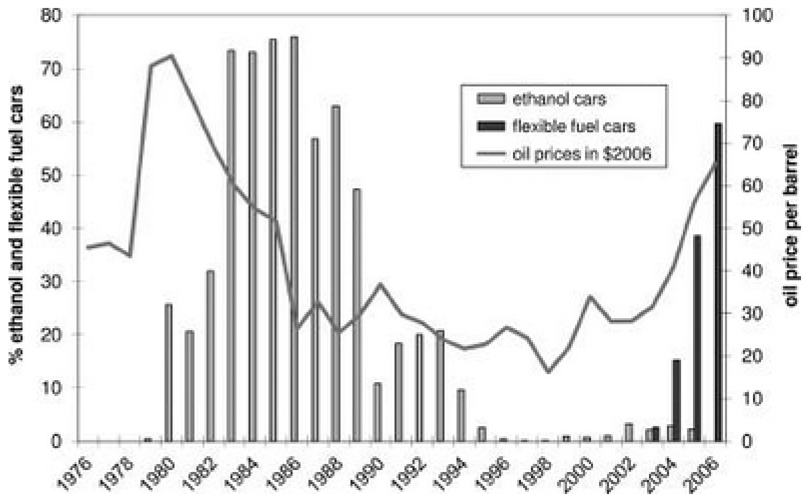
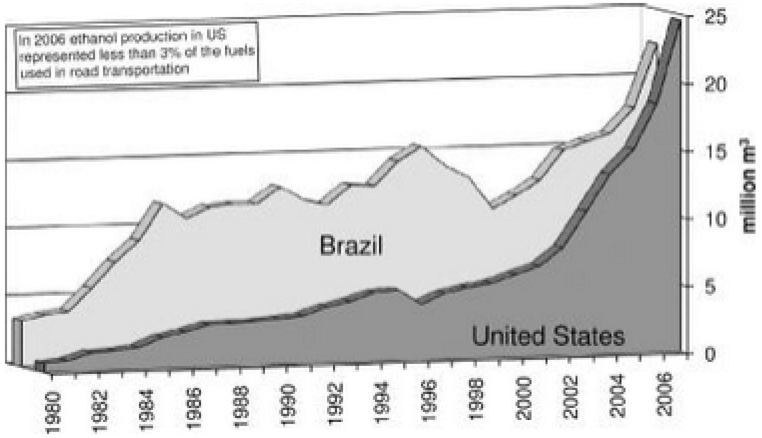
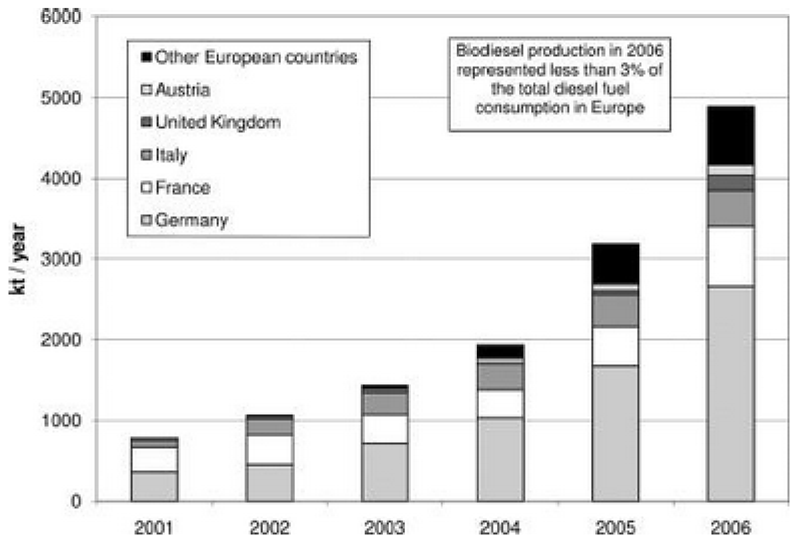


Figure 8.13 Historic production of ethanol in the United States and Brazil. (Based on data from Renewable Fuel Association and Sao Paulo Agroindustry Union (UNICA).)



In the United States, ethanol produced from corn has been used in gasohol, a blend of 10% ethanol and 90% gasoline, as well as an oxygenated additive in gasoline since the early 1980s (Figure 8.13). E85, a blend containing 85% ethanol and 15% gasoline, is also available in a limited number of gas stations. However, ethanol has to be dry to be mixed with gasoline to avoid phase separation. Drying ethanol is an energy-intensive process, since ethanol readily forms azeotropic mixtures with water. Azeotropic mixures cannot be separated by simple distillation. Furthermore, ethanol is only economically competitive because of significant tax subsidies. Besides the current $0.51 per gallon federal subsidy for blending ethanol into gasoline there are also other direct and indirect federal and state subsidies directed to ethanol fuel. Total subsidies for ethanol fuel in the United States have been estimated at between $1.05 and $1.38 per gallon [138]. Growing corn for ethanol production is also very energy intensive because of the need and cost of fertilizing, harvesting and transporting the corn, as well as subsequent fermentation and distillation, which requires large amounts of energy that are generally provided from oil and natural gas. It should be emphasized that ethanol produced from corn produces at most only 25–35% more energy than was consumed in its production [139, 140]. Indeed, some claims state that the process is a net energy user [141–144]. In any case, corn used for ethanol production is far from an ideal feedstock, though dedicated energy crops and new genetically engineered crops could increase the energy efficiency. Utilization of the cellulose content of plants, which is resistant to fermentation, to produce ethanol has in the past only been possible by prior hydrolysis with sulfuric acid. Currently, the development of new strains of microorganisms capable of digesting cellulose directly is being explored, and this may allow for the use of other types of vegetation with lower production costs to be processed to ethanol, making the overall process cheaper and more efficient.

Figure 8.14 Production of biodiesel in Europe. (Source: European Biodiesel Board and Eurobserver.)



Biodiesel, processed from seed crops such as rape, sunflower and soy are currently produced mainly in Europe (Figure 8.14) and the United States on a limited scale. Market penetration is small and the production costs are relatively high, although interest is growing. In 2006, biodiesel represented only 1.8% of the 300 Mt fuel (gasoline and diesel fuel) consumed by road transport in Europe (EU 25) [145, 146]. The direct use of plant oils in diesel engines is not recommended as it will considerably reduce the engine's lifetime. This drawback has been mitigated by reacting these oils with methanol or ethanol in a so-called transesterification process to yield commercial biodiesel. Biodiesel can be blended without major problems with regular diesel oil in any proportion. The production of biodiesel is also less energy intensive than ethanol from corn because no fermentation and distillation is necessary. However, biodiesel from oil-seed crops requires up to five times more land per unit of energy produced than ethanol. A plant that is gaining wide interest as a biodiesel source is the Jatropha tree. The nuts of this tree contain a significant amount of oil but are not suitable for human consumption. As it can be planted even in degraded lands, the Jatropha tree does not compete with crops for arable land [147, 148]. India has identified 40 million hectares were Jatropha can be grown and hopes to use this resource to replace 20% of its diesel consumption in 2011. China, the Philippines, the US and many others are also pushing for the use of Jatropha.

In Brazil, biodiesel is also produced from sugarcane-based ethanol involving ethylene as an intermediate.

8.6.3 Biomethanol

Methanol was once produced from wood, and is therefore sometimes still referred to as wood alcohol. This process (called pyrolysis) was used well into the beginning of the twentieth century and involves the heating of wood in the absence of air to yield a mixture of solid, liquid and gaseous products from which methanol could be extracted in low yields. Today, methanol is predominantly produced by steam reforming of methane (natural gas) and subsequent reaction of the produced syngas to methanol. However, any source of carbonaceous material could be converted into syn-gas and thus methanol. These materials also include biomass, which could therefore become a source of methanol in the future.

8.6.4 Advantages and Limitation of Biofuels

Recently, considerable scrutiny and criticism has been directed to the production of ethanol and biodiesel from food crops. Their production has contributed to a significant extent to the sharp increases in food prices experienced in recent years [10]. Higher prices and subsidies have resulted in the conversion of forests, savannahs, grasslands and so on into cropland, especially in Southeast Asia and the Americas. The Brazilian Amazon is being converted into soybean cultivation and the Brazilian Cerrado Savannah into sugarcane and soybean production. In Malaysia, plantations of oil palms for biodiesel production have been held responsible for 87% of the deforestation. Growing demand for biofuels is only expected to increase the pace of destruction of rain forest in biologically rich ecosystems such as the islands of Sumatra and Borneo. Land clearing also releases large amounts of CO_2 as a result of fires set to clear the land and the decomposition of leaves and other plant material through microbiological processes. The vast amounts of CO_2 released from the land conversion is considered as a "carbon debt." Some studies suggest that the CO_2 emissions avoided by using current biofuels (ethanol from corn, palm oil and soybean biodiesel) compared to fossil fuel based gasoline would take between 35 and 450 years to repay this carbon debt [149, 150]. These results raise questions about the value of presently used biofuels based on agricultural crops to cut greenhouse gas emissions. In Europe these concerns have already prompted changes in future energy policies [151–154]. Besides green house gas emissions, biofuel production also has other environmental effects such as loss of biodiversity when large tracks of rainforest have to be cleared for sugarcane or palm monocultures, and utilization of vast amounts of water for irrigation [155–158].

Biomass as an energy source has, however, many advantages. It is renewable, provides a convenient way of storing energy (e.g., in the form of wood), which is not the case for wind or solar energy, and it can be found in different forms all over the world. It can reduce the energy dependence on foreign countries. Biomass is also versatile as it includes solid fuels such as wood or crop residues, liquid biofuels such as ethanol and biodiesel, and gaseous fuels in the form of biogas or syn-gas. Environmentally, biomass can help mitigate climate change, as the CO_2 released by use of bioenergy is captured from the atmosphere by the growing plants and should therefore result in no net CO_2 emissions (i.e., it is carbon neutral). However, the conversion of solar energy into biomass is only achieved at an efficiency of around 1% or less, which is very low even compared to the inefficient conversion of solar energy into electricity with solar cells (in excess of 10%). To generate bioenergy on a large scale, vast areas of land and water resources are necessary. Also, great care must be taken in choosing crops for energy production, as these should have a high photosynthetic efficiency, grow rapidly, use minimal amounts of fertilizers, herbicides and insecticides, and have limited water needs to minimize energy input for their cultivation. These "energy crops" should also preferably be grown on land not dedicated to food crops to avoid competition with food production. The use of land that has been degraded by human activities over historical times in particular should be promoted to stabilize erosion and related problems such as desertification and deterioration of watersheds. The vast expanses of the seas can also be used to grow algae, which can be utilized to produce bioenergy, and experimental facilities in the United States and Japan have explored this possibility. With the present technology, a large part of the world's agricultural land would have to be devoted to energy crops if they were to supply a substantial amount of our energy needs. Even if the use of bioenergy could be cost effective in certain cases for the production of heat and electricity, it has generally higher costs than conventional energy sources. An economical and sustainable large-scale use of this resource will therefore require technological advances or breakthroughs, especially in the bioengineering field, to design suitable high-yield energy crops. In the transportation sector, the production of cellulose-based ethanol and other liquid fuels, particularly methanol through biomass gasification, will allow a higher yield per unit of land [159]. Algae grown in ponds, tanks or the sea might also eventually extend the scope of bioenergy [160].

8.7 Ocean Energy: Tidal, Wave and Thermal Power

Energy contained in the oceans, which cover more than 70% of the earth's surface, exists in two forms: (i) mechanical energy in the waves, tides and marine currents; (ii) thermal energy absorbed from the sun's heat. Because ocean energy is abundant, all of these sources have been considered for energy production and are at various stages of development.

8.7.1 Tidal Energy

Tidal energy exploits the rise and fall of tides caused by the interaction of the gravitational fields of the moon and sun. Tidal movements are both periodic and predictable, and were already used before 1100 AD in tide mills in the United Kingdom and France to grind grain. Their modern version, the tidal power plant, which takes advantage of the difference in water levels between low and high tide, operates on the same principle as an ordinary hydroelectric plant. Behind a dam constructed across a bay or estuary, water flowing through sluices is stored during high tide and later released at low tide through turbines to generate electricity. To be exploitable for electricity generation, however, differences between high and low tides must be significant. Only a few locations worldwide, generally in river estuaries, are suitable. Today, the only large-scale tidal power station, with 240-MW generating capacity, is situated at the estuary of the Ranee River, near Saint-Malo, France. It was built in the 1960s and has now completed more than 30 years of successful operation. Since then, the only other, much smaller, tidal power plants constructed have been an 18-MW project in Annapolis, Bay of Fundy, Canada, a 3.2-MW facility in China and a very small 0.4-MW unit near Murmansk, Russia [161]. In the European Union, the technically exploitable resource is estimated at about 100TWh per year, with only around 50TWh per year economically viable. Most possible sites (90%) are located in France and the United Kingdom. Beyond the EU, Canada, the states of the Former Soviet Union, Argentina, Western Australia and Korea have potential sites that have been investigated. Taking advantage of this resource, South Korea has recently announced its plans to construct the world's largest tidal plant (260MW capacity). Tidal energy is a mature technology, but it requires high capital expenditure, long construction times and has low load factors, leading to long payback periods and high electricity generating costs. Governments, thus, are likely to remain the only entities to undertake such large-sized projects. One significant factor for the limited use of tidal power raised by