Chapter 2
Fuels from Biomass

2.1 Introduction

Due to increasing environmental concerns especially related with the use of fossil fuels, new solutions to limit the greenhouse gas effect are continuously sought. With the growing concerns of greenhouse emissions, biomass is set to become an important contributor to the world energy need. Today biomass is seen as the most promising energy source to mitigate greenhouse gas emissions (Khan et al. 2009).

Biomass is very important for implementing the Kyoto agreement to reduce carbon dioxide emissions by replacing fossil fuels. The rapidly increasing energy requirements run parallel to technological development in the world, and research and development activities are forced to study new and biorenewable energy.

In the most biomass-intensive scenario, modernized biomass energy is projected by 2050 to contribute about one half of the total energy demand in developing countries. Direct combustion of biomass has been carried out worldwide since ancient times for cooking and heating. However, since biomass usually contains a high moisture content, and has low density, there are some difficulties of transportation, storage and usage of biomass without any pretreatment. Direct combustion is the old way of using biomass. Biomass thermochemical conversion technologies such as pyrolysis and gasification are certainly not the most important options at present; combustion is responsible for over 97% of the world's bioenergy production.

The first biomass sources used on Earth were wood and dry grass and for a long time these were used for cooking and warming. Products with fuel characteristics that are obtained biotechnologically from plant sources are defined as biomass energy sources. Generally biomass is an easily obtained energy source and therefore it is especially important for countries with forest and agriculture-based economics and with limited sources of energy (Karaosmanoglu and Aksoy 1988).

In the last decade, there has been rapid progress in the biofuel marketing trend: increasing production capacity, increasing international material flows, increased competition with conventional agriculture, increased competition with forest indus-

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tries, increasing international trade flows, and strong international debate about the sustainability of biofuels production. Biomass is the most important bioenergy option at present and is expected to maintain that position during the first half of this century (Hamelinck and Faaij 2006; IPCC 2007).

There are three ways to use biomass: (1) it can be burned to produce heat and electricity, (2) changed to gas-like fuels such as methane, hydrogen and carbon monoxide, or (3) changed to a liquid fuel. Liquid fuels, also called biofuels, include mainly two forms of alcohol: ethanol and methanol. Because biomass can be changed directly into a liquid fuel, it could someday supply much of our transportation fuel needs for cars, trucks, buses, airplanes, and trains. This is very important because nearly one-third of our nation's energy is now used for transportation.

The term *biomass* (Greek *bio* meaning *life* + *maza* meaning *mass*) refers to non-fossilized and biodegradable organic material originating from plants, animals, and microorganisms. The biomass includes products, byproducts, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and biodegradable organic fractions of industrial and municipal solid wastes. Biomass also includes gases and liquids recovered from the decomposition of non-fossilized and biodegradable organic material.

According to another definition, the term biomass refers to wood, short-rotation woody crops, agricultural wastes, short-rotation herbaceous species, wood wastes, bagasse, industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, waste from food processing, aquatic plants and algae animal wastes, and a host of other materials.

Biomass is organic material that has stored sunlight in the form of chemical energy. Biomass is commonly recognized as an important renewable energy, which is considered to be such a resource that during the growth of plants and trees solar energy is stored as chemical energy via photosynthesis, which can be released via direct or indirect combustion.

Although some of the steps in photosynthesis are still not completely understood, the overall photosynthetic reaction has been known since the 1800s. Jan van Helmont began research into the process in the mid-1600s when he carefully measured the mass of the soil used by a plant and the mass of the plant as it grew. After noticing that the soil mass changed very little, he hypothesized that the mass of the growing plant must come from the water, the only substance he added to the potted plant. Photosynthesis is the most important biochemical process in which plants, algae, and some bacteria harness the energy of sunlight to produce food. Organisms that produce energy through photosynthesis are called photoautotrophs. Photosynthesis is a process in which green plants utilize the energy of sunlight to manufacture carbohydrates from carbon dioxide and water in the presence of chlorophyll (Viswanathan 2006).

The initial process in photosynthesis is the decomposition of water into oxygen and hydrogen and oxygen will be released. The simplified photosynthesis pathways are given in Eqs. 2.1–2.3. The hydrogen and the carbon and oxygen of carbon dioxide are then converted into formaldehyde (Eq. 2.1), and then a series of increasingly complex compounds result finally in a stable organic compound, hexose (typically glucose) (Eq. 2.2). This phase of photosynthesis utilizes stored energy and therefore

Table 2.1 Structural composition of wood (wt.% of dry and ash-free sample)

Wood species	Cellulose	Hemicelluloses	Lignin	Extractives
Hardwood	43–48	27–35	16–24	2–8
Softwood	40–44	24–29	26–33	1–5

can proceed in the dark. Hexose is polymerized into hexosan (typically glucosan) or carbohydrates (Eq. 2.3).

$$CO_2 + H_2O + \text{Solar energy} \xrightarrow{T > 285\,\text{K, Chlorophyll}} CH_2O + O_2 \quad (2.1)$$

Glucose formation:

$$\underset{\text{Formaldehyde}}{6CH_2O} \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} \quad (2.2)$$

Glucosan formation via polymerization:

$$\underset{\text{Glucose}}{nC_6H_{12}O_6} \rightarrow \underset{\text{Glucosan}}{(C_6H_{12}O_6)n} \quad (2.3)$$

The basic structure of all wood and woody biomass consists of cellulose, hemicelluloses, lignin and extractives. Their relative composition is shown in Table 2.1. Softwoods and hardwoods differ greatly in wood structure and composition. Hardwoods contain a greater fraction of vessels and parenchyma cells. Hardwoods have a higher proportion of cellulose, hemicelluloses and extractives than softwoods, but softwoods have a higher proportion of lignin. Hardwoods are denser than softwoods.

2.1.1 Biomass Feedstocks

Biomass feedstocks are marked by their tremendous diversity, which makes them rather difficult to characterize as a whole. Feedstocks that can be utilized with conversion processes are primarily the organic materials now being landfilled. These include forest products wastes, agricultural residues, organic fractions of municipal solid wastes, paper, cardboard, plastic, food waste, green waste, and other waste. Non-biodegradable organic feedstocks, such as most plastics, are not convertible by biochemical processes. Bio-based materials require pretreatment by chemical, physical, or biological means to open up the structure of biomass.

The major categories of biomass feedstock are as follows:

1. Forest products
   - Wood
   - Logging residues

   - Trees, shrubs and wood residues
   - Sawdust, barks, roots, etc.
2. Biorenewable wastes
   - Agricultural wastes
   - Crop residues
   - Mill wood wastes
   - Urban wood wastes
   - Urban organic wastes
   - Municipal solid wastes
   - Domestic solid wastes
3. Energy crops
   - Short-rotation woody crops
   - Herbaceous woody crops
   - Grasses
   - Starch crops
   - Sugar crops
   - Forage crops
   - Oilseed crops
4. Aquatic plants
   - Algae
   - Water weed
   - Water hyacinth
   - Reed and rushes
5. Food crops
   - Grains
   - Oil crops
6. Sugar crops
   - Sugar cane
   - Sugar beets
   - Molasses
   - Sorghum
7. Landfill
8. Industrial organic wastes
9. Algae and mosses
10. Kelps and lichens

Biomass is the world's fourth largest energy source worldwide, following coal, oil and natural gas. Biomass appears to be an attractive feedstock for three main reasons. First, it is a renewable resource that could be sustainably developed in the future. Second, it appears to have formidably positive environmental properties, reduced GHG emissions, possibly reduced NO_x and SO_x depending on the fossil fuels displaced. However, it also has negative impacts, such as polycyclic aromatic hydrocarbons including dioxins, furans, volatile organic compounds, and heavy metals especially when combusted in traditional stoves. Third, it appears to have significant economic potential provided that fossil fuel prices increase in the future.

Biomass for energy, especially biofuels, has positive attributes that contribute to a healthy environment and economy. Biomass utilization can reduce forest management costs, help mitigate climate change, reduce risks to life and property, and help provide a secure, competitive energy source. Biomass is a sustainable feedstock for chemicals and energy products that could potentially enhance the energy independence of the world, which lack energy resources. As an energy source that is highly productive, renewable, carbon neutral, and easy to store and transport, biomass has drawn worldwide attention recently.

Biomass offers important advantages as a combustion feedstock due to the high volatility of the fuel and the high reactivity of both the fuel and the resulting char. However, it should be noticed that in comparison with solid fossil fuels, biomass contains much less carbon and more oxygen and has a low heating value.

The waste products of a home include paper, containers, tin cans, aluminum cans, and food scraps, as well as sewage. The waste products of industry and commerce include paper, wood, and metal scraps, as well as agricultural waste products. Biodegradable wastes, such as paper fines and industrial biosludge, into mixed alcohol fuels (e.g., iso-propanol, iso-butanol, iso-pentanol). The wastes are first treated with lime to enhance reactivity; then they are converted to volatile fatty acids (VFAs) such as acetic acid, propionic acid, and butyric acid, using a mixed culture of microorganisms derived from cattle rumen or anaerobic waste treatment facilities. Pulp and paper wastes may also be treated to produce methane. The contents of domestic solid waste are given in Table 2.2 (Demirbas 2004).

Typical solid wastes include wood material, pulp and paper industry residues, agricultural residues, organic municipal material, sewage, manure, and food processing byproducts. Biomass is considered one of the main renewable energy resources of the future due to its large potential, economic viability and various social and environmental benefits. It was estimated that by 2050 biomass could provide nearly 38% of the world's direct fuel use and 17% of the world's electricity. If biomass is produced more efficiently and used with modern conversion

Table 2.2 Contents of domestic solid waste (wt.% of total)

Component	Lower limit	Upper limit
Paper waste	33.2	50.7
Food waste	18.3	21.2
Plastic matter	7.8	11.2
Metal	7.3	10.5
Glass	8.6	10.2
Textile	2.0	2.8
Wood	1.8	2.9
Leather and rubber	0.6	1.0
Miscellaneous	1.2	1.8

technologies, it can supply a considerable range and diversity of fuels at small and large scales. Municipal solid waste (MSW) is defined as waste durable goods, nondurable goods, containers and packaging, food scraps, yard trimmings, and miscellaneous inorganic wastes from residential, commercial, and industrial sources (Demirbas 2004). Figure 2.1 shows the use of world wood products (lumber, plywood, paperboard) between the years of 1970 and 2005.

Generally speaking, in producing fuels from biomass, one overall objective is to remove oxygen; biomass feedstocks often contain 40–60 wt.% oxygen and conventional fuels and oils typically have only trace amounts, under 1%. Oxygen heteroatom removal occurs most readily by dehydration, which removes oxygen in the form of water, and by decarboxylation, which removes oxygen in the form of carbon dioxide. Thermodynamically, since both water and carbon dioxide are fully oxidized and have no residual heating value, they can make ideal compounds in which to remove oxygen without losing heating value to the oxygen-containing chemicals removed (Peterson et al. 2008). Table 2.3 shows the elemental analyses of typical fuel samples given in the literature (Demirbas 2004).

The importance of biomass in different world regions is given in Table 2.4. As shown in this table, the importance of biomass varies significantly across regions. In Europe, North America and the Middle East, the share of biomass averages to 2–3% of total final energy consumption, whereas in Africa, Asia and Latin America, which together account for three-quarters of the world's population, biomass provides a substantial share of the energy needs: a third on average, but as much as 80–90% in some of the poorest countries of Africa and Asia (e. g., Angola, Ethiopia, Mozambique, Tanzania, Democratic Republic of Congo, Nepal, and Myanmar). Indeed, for large portions of the rural populations of developing countries, and for the poorest sections of urban populations, biomass is often the only available and affordable source of energy for basic needs such as cooking and heating.

Agricultural residues, grasses, algae, kelps, lichens and mosses are also important biomass feedstocks in the world. Algae can grow practically in every place

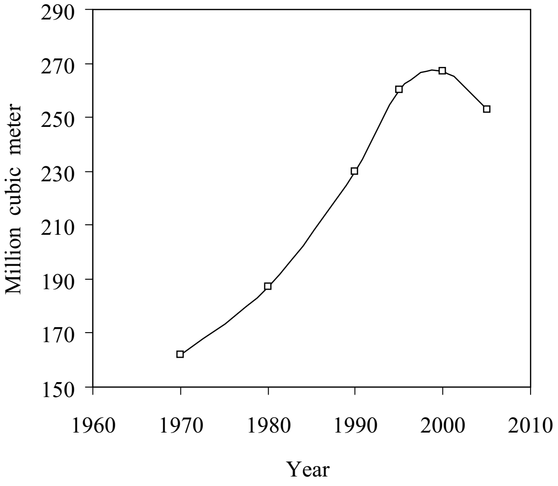


Fig. 2.1 Use of world wood products (1970–2005)

Table 2.3 Elemental analyses of typical fuel samples given in the literature (wt.% of dry fuel with ash)

Fuel sample	C	H	N	S	O (by difference)
Hazelnut shell	52.8	5.6	1.4	0.04	42.6
Sawdust	46.9	5.2	0.1	0.04	37.8
Corn stover	42.5	5.0	0.8	0.20	42.6
Red oak wood	50.0	6.0	0.3	–	42.4
Wheat straw	41.8	5.5	0.7	–	35.5
Olive husk	49.9	6.2	1.6	0.05	42.0
Poplar wood	48.4	5.9	0.4	0.01	39.6
Beech wood	49.5	6.2	0.4	–	41.2
Spruce wood	51.9	6.1	0.3	–	40.9
Corncob	49.0	5.4	0.5	0.20	44.5
Tea waste	48.0	5.5	0.5	0.06	44.0
Walnut shell	53.5	6.6	1.5	0.10	45.4
Almond shell	47.8	6.0	1.1	0.06	41.5
Sunflower shell	47.4	5.8	1.4	0.05	41.3
Rice husk	47.8	5.1	0.1	–	38.9
Cotton gin	42.8	5.4	1.4	0.50	35.0
Sugarcane bagasse	44.8	5.4	0.4	0.01	39.6
Peach pit	53.0	5.9	0.3	0.05	39.1
Alfalfa stalk	45.4	5.8	2.1	0.09	36.5
Switchgrass	46.7	5.9	0.8	0.19	37.4

where there is enough sunshine. Some algae can even grow in saline water. The most significant difference of algal oil is in the yield and hence its biodiesel yield. According to some estimates, the yield (per acre) of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils (Sheehan et al. 1998). Microalgae are the fastest growing photosynthesizing organisms. They can complete an entire growing cycle every few days. Approximately 46 tons of oil per hectare per year can be produced from diatom algae. Different algae species produce different amounts of oil. Some algae produce up to 50% oil by weight.

Wood fuel is classified into three main commodities: fuelwood, charcoal, and black liquor. Black liquor is the spent pulping chemicals and the lignin component of wood after chemical pulping. It is fired in a chemical recovery boiler and process steam and electricity are also produced. Fuelwood and charcoal are the traditional wood forest products, and even today almost half of all of the forest harvest is for energy, with the remainder for industrial use.

Table 2.5 shows wood fuels consumption in 2005, given in petajoules (1 PJ = 10^9 MJ).

Table 2.4 The importance of biomass in different world regions

Region	Share of biomass in final energy consumption (%)
Africa (average)	62.0
Burundi	93.8
Ethiopia	85.6
Kenya	69.6
Somalia	86.5
Sudan	83.7
Uganda	94.6
South Asia (average)	56.3
East Asia (average)	25.1
China	23.5
Latin America (average)	18.2
Europe (average)	3.5
North America (average)	2.7
Middle East (average)	0.3

Table 2.5 Wood fuel consumption in 2005 (1 PJ = 10^9 MJ)

	Fuelwood	Black liquor	Charcoal
Asia	7795	463	135
Africa	5633	33	688
Latin America	2378	288	485
Europe	1173	644	14
North America	852	1284	40
Oceania	90	22	1
Total	17 921	2734	1361

2.1.2 Modern Biomass, Bioenergy, and Green Energy

The term *modern biomass* is generally used to describe the traditional biomass used through efficient and clean combustion technologies and a sustained supply of biomass resources, environmentally sound and competitive fuels, heat and electricity using modern conversion technologies. Modern biomass produced in a sustainable way excludes traditional uses of biomass as fuelwood and includes electricity generation and heat production, as well as transportation fuels, from agricultural and forest residues and solid waste. On the other hand, *traditional biomass* is produced in an unsustainable way and it is used as a non-commercial source – usually with very low efficiencies for cooking in many countries (Goldemberg and Coelho 2004).

Traditional biomass markets have been inefficient but technological developments have reduced energy, emission, and material flows through the system thus improving the efficiency of biomass energy systems. The energy market demands cost effectiveness, high efficiency, and reduced risk to future emission limits. Modernization of biomass conversion implies the choice of technologies: (a) offers the potential for high yields, (b) economic fuel availability, (c) low adverse environmental impacts, and (d) suitability to modern energy systems. A number of systems that meet the mentioned criteria for modernized biomass conversion can be identified (Larson 1993).

Bioenergy is energy derived from organic sources such as all lignocellulosic materials, trees, agricultural crops, municipal solid wastes, food processing and agricultural wastes and manure. Generally, bioenergy is an inclusive term for all forms of biomass and biofuels.

Bioenergy is one of the forms of renewable energy. Biomass has been used for bioenergy for thousands of years, ever since people started burning wood to cook food and today, wood is still our largest biomass resource for bioenergy. The use of bioenergy has the potential to greatly reduce our greenhouse gas emissions. Replacing fossil fuels with energy from biomass has several distinct environmental implications. If biomass is harvested at a rate, which is sustainable, using it for energy purposes does not result in any net increase in atmospheric carbon dioxide, a greenhouse gas.

Green energy is an alternate term for renewable energy and refers to the energy generated from sources that are considered environmentally friendly (e. g., hydro, solar, biomass (landfill) or wind). Green power is sometimes used in reference to electricity generated from "green" sources. Green energy production is the principal contributor to the economic development of a developing country. Its economy development is based on agricultural production and most people live in the rural areas. Implementation of integrated community development programs is therefore very necessary.

Green power refers to electricity supplied from more readily renewable energy sources than traditional electrical power sources. Green power products have become widespread in many electricity markets worldwide, which can be derived from renewable energy sources. The environmental advantages of the production and use of green electricity seem to be clear. Market research indicates that there is a large potential market for green energy in Europe in general. Green power marketing has emerged in more than a dozen countries around the world.

Many green electricity products are based on renewable energy sources like wind, biomass, hydro, biogas, solar, and geothermal (Murphya and Niitsuma 1999). There has been interest in electricity from renewable sources named green electricity or green pool, as a special market (Elliott 1999). The term green energy is also used for green energy produced from co-generation, energy from municipal waste, natural gas, and even conventional energy sources. Using green energy sources like hydro, biomass, geothermal, and wind energy in electricity production reduces CO_2 emissions (Fridleifsson 2003). Emissions such as SO_2, CO_2 and NO_x are reduced considerably and the production and use of green electricity contributes to diminishing the green house effect (Arkesteijn and Oerlemans 2005).

Table 2.6 Electricity production from biomass (TWh)

	1995	2002	2003	2004	2005	2006
Solid biomass	85.3	110.0	118.2	131.4	134.9	140.6
Biogas	6.0	16.9	18.3	20.7	24.8	27.3
Liquid biomass			0.8	0.6	0.9	1.3
Municipal solid waste	13.4	21.3	25.0	24.0	22.8	21.8
Total	104.8	148.2	162.2	176.6	183.4	190.9

In general, a sustainable energy system includes energy efficiency, energy reliability, energy flexibility, energy development and continuity, combined heat and power (CHP) or co-generation, fuel poverty, and environmental impacts. The environmental impacts of energy use are not new. For centuries, wood burning has contributed to the deforestation of many areas. On the other hand, the typical characteristics of a sustainable energy system can be derived from political definitions. A sustainable energy system can be defined also by comparing the performance of different energy systems in terms of sustainability indicators (Alanne and Sari 2006). By definition, sustainable energy systems must support both human and ecosystem health over the long term, therefore goals for tolerable emissions should look well into the future. They should also take into account the public's tendency to demand more (UNDP 2000).

Various scenarios have been put forward on estimates of biofuel from biomass sources in the future energy system. The availability of the resources is an important factor in co-generative use of biofuel in the electricity, heat, or liquid fuel market. The largest secondary transformation of biomass after charcoal production is in the electricity sector. For many years biomass-processing industries such as sugar, wood products, and chemical pulping have installed combined heat and power.

In 2006 estimated total electricity generation was about 190 TWh from an installed capacity in excess of 43 GW. The recent negative trend for MSW is a consequence of increased material recycling, together with reductions in the amount of biomass-derived materials entering the waste stream. Table 2.6 shows the electricity production from biomass. Table 2.7 shows the leading biopower-producing countries in 2005 (WEC 2007). The eight leading countries with biomass-based electricity production are all members of the OECD, except for Brazil.

2.2 The Chemistry of Biomass

The components of biomass include cellulose, hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash, and other compounds. Two larger carbohydrate categories that have significant value are cellulose and hemicelluloses (holocellulose). The lignin fraction consists of non-sugar type

Table 2.7 Leading biopower producing countries in 2005

Country	Production (TWh)	Percentage of global total
United States	56.3	30.7
Germany	13.4	7.3
Brazil	13.4	7.3
Japan	9.4	5.1
Finland	8.9	4.9
UK	8.5	4.7
Canada	8.5	4.6
Spain	7.8	4.3
Rest of World	57.1	31.1

macromolecules. Three structural components are cellulose, hemicelluloses, and lignin, which have rough formulae of $CH_{1.67}O_{0.83}$, $CH_{1.64}O_{0.78}$, and $C_{10}H_{11}O_{3.5}$, respectively.

Cellulose is a linear polymer composed of repeating anhydroglucose units. Cellulose is a remarkable pure organic polymer, consisting solely of units of anhydroglucose held together in a giant straight-chain molecule (Demirbas 2000). These anhydroglucose units are bound together by β-(1,4)-glycosidic linkages. Due to this linkage, cellobiose is established as the repeat unit for cellulose chains. Cellulose must be hydrolyzed to glucose before fermentation to ethanol.

The second major chemical species in wood are the hemicelluloses. They are amorphous polysaccharides, such as xylans, galactoglucomannans, arabinogalactans, glucans and galactans. The hemicelluloses, unlike cellulose, not only contain glucose units, but they are also composed of a number of different pentose and hexose monosaccharides. Hemicelluloses tend to be much shorter in length than cellulose, and the molecular structure is slightly branched.

Unlike cellulose, hemicelluloses consist of different monosaccharide units. In addition, the polymer chains of hemicelluloses have short branches and are amorphous. Because of the amorphous morphology, hemicelluloses are partially soluble or swellable in water. Hemicelluloses (arabinoglycuronoxylan and galactoglucomannans) are related to plant gums in composition, and occur in much shorter molecule chains than cellulose. Hemicelluloses are derived mainly from chains of pentose sugars, and act as the cement material holding together the cellulose micelles and fiber (Theander 1985).

Lignin (sometimes lignen) is a chemical compound that is most commonly derived from wood and is an integral part of the cell walls of plants, especially in tracheids, xylem fibers, and sclereids. It is one of most abundant organic compounds on Earth after cellulose and chitin. The empirical chemical formula of lignin is $C_{20}H_{19}O_{14}N_2$. Lignin is a complex, high molecular weight polymer built of hydroxyphenylpropane units. Lignin is a completely different polymeric material, being highly cross-linked and having phenolic-like structures as the monomeric base. It is the lignin that holds the wood cells together and provides the extraordinary composite strength characteristics of a piece of wood.

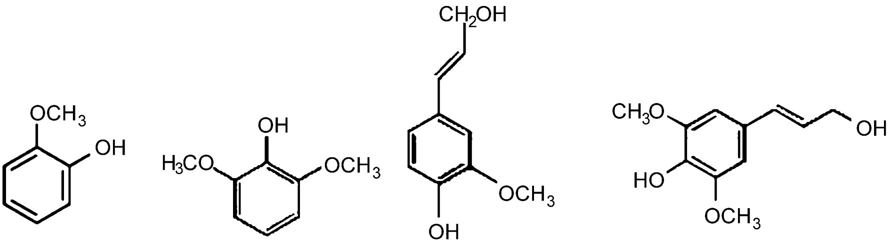
Lignin is a large, cross-linked macromolecule with molecular mass in excess of 10 000 amu. It is relatively hydrophobic and aromatic in nature. The molecular weight in nature is difficult to measure, since it is fragmented during preparation. The molecule consists of various types of substructures, which appear to repeat in a random manner. Lignin plays a crucial part in conducting water in plant stems. The polysaccharide components of plant cell walls are highly hydrophilic and thus permeable to water, whereas lignin is more hydrophobic. The cross-linking of polysaccharides by lignin is an obstacle for water absorption to the cell wall. Thus, lignin makes it possible for plants to form vascular tissue, which conducts water efficiently. Lignin is present in all vascular plants, but not in bryophytes, supporting the idea that the main function of lignin is related to water transport.

Lignins are polymers of aromatic compounds. Their functions are to provide structural strength, provide sealing of water-conducting systems that link roots with leaves, and protect plants against degradation (Glasser and Sarkanen 1989). Lignin is a macromolecule, which consists of alkyl phenols and has a complex three-dimensional structure. Lignin is covalently linked with xylans in the case of hardwoods and with galactoglucomannans in softwoods (Sarkanen and Ludwig 1971).

Pyrolysis of lignin, e. g., during combustion, yields a range of products, of which the most characteristic ones are methoxy phenols. Of those, the most important are guaiacol and syringol and their derivatives; their presence can be used to trace a smoke source to a wood fire. Lignin biosynthesis begins with the synthesis of monolignols. The starting material is the amino acid phenylalanine. The first reactions in the biosynthesis are shared with the phenylpropanoid pathway, and monolignols are considered to be a part of this group of compounds. There are three main types of monolignols: coniferyl alcohol, sinapyl alcohol and paracoumaryl alcohol. Different plants use different monolignols. For example, gymnosperms as Norway spruce have a lignin that consists almost entirely of coniferyl alcohol. Dicotyledonic lignin is a mixture of coniferyl alcohol and sinapyl alcohol (normally more of the latter), and monocotyledonic lignin is a mixture of all three monolignols. Some monocotyledons have mostly coniferyl alcohol (as many grasses), while others have mainly sinapyl alcohols, as some palms. Monolignols are synthesized in the cytosol as glucosides. The glucose is added to the monolignol to make them water-soluble and to reduce their toxicity. The glucose is then removed and the monolignols are polymerized into lignin. Four main monolignols in lignin structure are given in Fig. 2.2.

Wood and woody biomass also contain lesser amounts of tannins, simple sugars, starches, pectins and organic soluble extractives. Extractives include terpenes, tall oil and the fatty acids, esters, and triglycerides, which contribute to paper mill pitch problems (Demirbas 1991).

Characterization of biomass fuels has been reviewed by Bushnell et al. (1989). In general combustion models of biomass can be classified as macroscopic or microscopic. The characterization of the biomass fuels is generally divided into three broad categories: (1) composition and structure, (2) reactivity measures, and (3) ash chemistry.



Guaiacol Syringol Coniferyl alcohol Sinapyl alcohol

Fig. 2.2 Four main monolignols in lignin structure

Properties for microscopic analysis include thermal, chemical kinetic and mineral data (Ragland et al. 1991). Fuel characteristics such as ultimate analysis, heating value, moisture content, particle size, bulk density, and ash fusion temperature of biomass have been reviewed (Bushnell et al. 1989). Fuel properties for the combustion analysis of biomass can be conveniently grouped into physical, chemical, thermal, and mineral properties.

Physical property values vary greatly and properties such as density, porosity, and internal surface area are related to biomass species whereas bulk density, particle size, and shape distribution are related to fuel preparation methods. Important chemical properties for combustion are the ultimate analysis, proximate analysis, analysis of pyrolysis products, higher heating value, heat of pyrolysis, heating value of the volatiles, and heating value of the char.

Thermal property values such as specific heat, thermal conductivity, and emissivity vary with moisture content, temperature, and degree of thermal degradation by one order of magnitude. Thermal degradation products of biomass consist of moisture, volatiles, char and ash. Volatiles are further subdivided into gases such as light hydrocarbons, carbon monoxide, carbon dioxide, hydrogen and moisture, and tars. The yields depend on the temperature and heating rate of pyrolysis. Some properties vary with species, location within the biomass, and growth conditions. Other properties depend on the combustion environment. Where the properties are highly variable, the likely range of the property is given (Ragland et al. 1991).

2.2.1 Biomass Fuel Analyses

Main biomass fuel analyses are: (a) particle size and specific gravity, (b) ash content, (c) moisture content, (d) extractive content, (e) element (C, H, O and N) content, and (f) structural constituent (cellulose, hemicelluloses and lignin) content.

Particle size of biomass should be as much as 0.6 cm, sometimes more, in a profitable combustion process. Biomass is much less dense and has significantly higher aspect ratios than coal. It is also much more difficult to reduce to small sizes.

Ash or inorganic material in plants depends on the type of the plant and the soil contamination in which the plant grows. On average wood contains about 0.5% ash.

Ash contents of hard and softwoods are about 0.5 and 0.4%, respectively. Insoluble compounds act as a heat sink in the same way as moisture, lowering combustion efficiency, but soluble ionic compounds can have a catalytic effect on the pyrolysis and combustion of the fuel. The presence of inorganic compounds favors the formation of char. Ash content is an important parameter directly affecting the heating value. High ash content of a plant part makes it less desirable as fuel (Demirbas 1998).

The composition of mineral matter can vary between and within each biomass sample. Mineral matter in fruit shells consists mostly of salts of calcium, potassium, silica, and magnesium, but salts of many other elements are also present in lesser amounts (Demirbas 2002).

Moisture in biomass generally decreases its heating value. Moisture in biomass is stored in spaces within the dead cells and within the cell walls. When the fuel is dried the stored moisture equilibrates with the ambient relative humidity. Equilibrium is usually about 20% in air-dried fuel. Moisture percentage of the wood species varies from 41.27 to 70.20%. Heating value of a wood fuel decreases with increase in moisture content of the wood. Moisture content varies from one tree part to another. It is often the lowest in the stem and increases toward the roots and the crown. The presence of water in biomass influences its behavior during pyrolysis and affects the physical properties and quality of the pyrolysis liquid. The results obtained show that for higher initial moisture contents the maximum liquid yield on a dry feed basis occurs at lower pyrolysis temperatures between 691 and 702 K (Demirbas 2004).

Again, the heat content, which is a very important factor affecting the utilization of any material as a fuel, is affected by the proportion of combustible organic components (known as extractives) present in it. The higher heating values (HHVs) of the extractive-free plant parts were found to be lower than those of the unextracted parts, which indicate a likely positive contribution of extractives towards the increase of HHV. Extractive content is an important parameter directly affecting the heating value. High extractive content of a plant part makes it desirable as fuel. Extractives raise the HHVs of the wood fuels.

Both the chemical and the physical composition of the fuel are important factors in the characteristics of combustion. Biomass can be analyzed by breaking it down into structural components (called proximate analysis) or into chemical elements (known as ultimate analysis). The heat content is related to the oxidation state of the natural fuels in which carbon atoms generally dominate and overshadow small variations of hydrogen content. On the basis of literature values for different species of wood, Tillman (1978) also found a linear relationship between HHV and carbon content.

Biomass fuels are composed of biopolymers that consist of various types of cells and the cell walls are built of cellulose, hemicelluloses and lignin. HHVs of biomass fuels increase as lignin contents increase.

The higher heating values (HHVs) or gross heat of combustion includes the latent heat of the water vapor products of combustion because the water vapor was allowed to condense to liquid water. The HHV (in units of MJ/kg) of the biomass fuels as a function of fixed carbon (FC, wt.%) was calculated from Eq. 2.1 (Demirbas 1997):

$$\mathrm{HHV} = 0.196\,(\mathrm{FC}) + 14.119 \tag{2.4}$$

In earlier work (Demirbas et al. 1997), formulae were also developed for estimating the HHVs of fuels from different lignocellulosic materials, vegetable oils, and diesel fuels using their chemical analysis data. For biomass fuels such as coal, the HHV is calculated using a modified Dulong's formula as a function of the carbon, hydrogen, oxygen, and nitrogen contents from Eq. 2.2:

$$\mathrm{HHV} = 0.335\,(\mathrm{CC}) + 1.423\,(\mathrm{HC}) - 0.154\,(\mathrm{OC}) - 0.145\,(\mathrm{NC}) \tag{2.5}$$

where CC is carbon content (wt.%), HC hydrogen content (wt.%), OC oxygen content (wt.%), and NC nitrogen content (wt.%).

The HHVs of extractive-free samples reflect the HHV of lignin relative to cellulose and hemicelluloses. Cellulose and hemicelluloses (holocellulose) have a HHV 18.60 MJ/kg, whereas lignin has a HHV from 23.26 to 26.58 MJ/kg. As discussed by Baker (1982), HHVs reported for a given species reflect only the samples tested and not the entire population of the species. The HHV of a lignocellulosic fuel is a function of its lignin content. In general, the HHVs of lignocellulosic fuels increase with increase of their lignin contents and the HHV is highly correlated with lignin content. For the model including the lignin content, the regression equation is:

$$\mathrm{HHV} = 0.0889\,(\mathrm{LC}) + 16.8218 \tag{2.6}$$

where LC was the lignin content (wt.% dry and ash-free and extractive-free basis).

Biomass combustion is a series of chemical reactions by which carbon is oxidized to carbon dioxide, and hydrogen is oxidized to water. Oxygen deficiency leads to incomplete combustion and the formation of many products of incomplete combustion. Excess air cools the system. The air requirements depend on the chemical and physical characteristics of the fuel. The combustion of the biomass relates to the fuel burn rate, the combustion products, the required excess air for complete combustion, and the fire temperatures.

2.3 Biomass Conversion Processes

Biomass can be converted into useful biofuels and biochemicals via biomass upgrading and biorefinery technologies. Biomass conversion processes include fractionation, densification (briquetting, pelleting), liquefaction, supercritical fluid liquefaction, destructive carbonization, pyrolysis, gasification, hydrothermal liquefaction and hydrothermal upgrading, Fischer–Tropsch synthesis, anaerobic digestion, hydrolysis, and fermentation. Figure 2.3 shows the main biomass conversion processes.

Direct combustion is the oldest way of using biomass. Biomass thermochemical conversion technologies such as pyrolysis and gasification are certainly not the

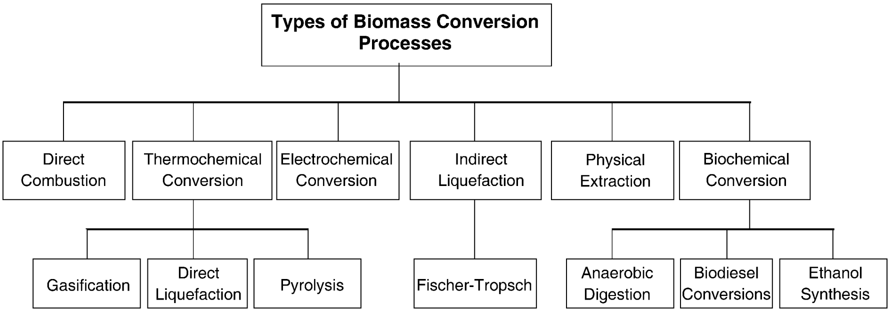


Fig. 2.3 Main biomass conversion processes

most important options at present; combustion is responsible for over 97% of the world's bioenergy production (Demirbas 2004). Direct combustion and co-firing with coal for electricity production from biomass has been found to be a promising method for the near future. The supply is dominated by traditional biomass used for cooking and heating, especially in rural areas of developing countries. The traditional biomass cooking and heating produces high levels of pollutants.

Biomass energy currently represents approximately 14% of total global energy consumption, a higher share than that of coal (12%) and comparable to those of gas (15%) and electricity (14%). Biomass is the main source of energy for many developing countries and most of it is non-commercial. Hence there is enormous difficulty in collecting reliable biomass energy data. Yet good data are essential for analyzing tendencies and consumption patterns, for modeling future trends and for designing coherent strategies.

The three ways to use biomass are: (1) burning it to produce heat and electricity, (2) changing it to gas-like fuels such as methane, hydrogen and carbon monoxide, and (3) changing it to a liquid fuel. Liquid fuels, also called biofuels, include ethanol and methanol. Ethanol, the most commonly used biofuel, is produced from sugarcane, corn, and other grains. A blend of gasoline and ethanol is already used in cities with high levels of air pollution.

There are several ways to make use of the energy contained in the biomass from direct burning to pyrolysis, gasification, and liquefaction. Pyrolysis is the thermochemical process that converts organic materials into usable fuels. Pyrolysis produces energy fuels with high fuel-to-feed ratios, making it the most efficient process for biomass conversion and the method most capable of competing with and eventually replacing non-renewable fossil fuel resources.

Main transportation fuels can be obtained from biomass using different processes, fuels such as sugar ethanol, cellulosic ethanol, grain ethanol, biodiesel, pyrolysis liquids, green diesel, green gasoline, buthanol, methanol, syngas liquids, biohydrogen, algae diesel, algae jet fuel, and hydrocarbons.

In the liquefaction process, biomass is converted to liquefied products through a complex sequence of physical structure and chemical changes. The feedstock of liquefaction is usually a wet matter. In the liquefaction process, biomass is decomposed into small molecules. These small molecules are unstable and reactive, and can repolymerize into oily compounds with a wide range of molecular weight distribution (Demirbas 2000).

Liquefaction can be accomplished directly or indirectly. Direct liquefaction involves rapid pyrolysis to produce liquid tars and oils and/or condensable organic vapors. Indirect liquefaction involves the use of catalysts to convert non-condensable, gaseous products of pyrolysis or gasification into liquid products. Alkali salts, such as sodium carbonate and potassium carbonate, can act as catalysts for the hydrolysis of cellulose and hemicellulose, into smaller fragments. The degradation of biomass into smaller products mainly proceeds by depolymerization and deoxygenation. In the liquefaction process, the amount of solid residue increases in proportion to the lignin content. Lignin is a macromolecule consisting of alkyl phenols, and has a complex three-dimensional structure. It is generally accepted that free phenoxyl radicals are formed by thermal decomposition of lignin above 500 K and that the radicals have a random tendency to form a solid residue through condensation or repolymerization (Demirbas 2000).

The changes during liquefaction process involve all kinds of processes such as solvolysis, depolymerization, decarboxylation, hydrogenolysis, and hydrogenation. Solvolysis results in micellar-like substructures of the biomass. The depolymerization of biomass leads to smaller molecules. It also leads to new molecular rearrangements through dehydration and decarboxylation. When hydrogen is present, hydrogenolysis and hydrogenation of functional groups, such as hydroxyl groups, carboxyl groups, and keto groups also occur.

Pyrolysis is the basic thermochemical process for converting biomass to a more useful fuel. Biomass is heated in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce a hydrocarbon-rich gas mixture, an oil-like liquid and a carbon-rich solid residue. Rapid heating and rapid quenching produce the intermediate pyrolysis liquid products, which condense before further reactions break down higher molecular weight species into gaseous products. High reaction rates minimize char formation. Under some conditions, no char is formed. At higher fast pyrolysis temperatures, the major product is gas.

Pyrolysis is the simplest and almost certainly the oldest method of processing one fuel in order to produce a better one. Pyrolysis can also be carried out in the presence of a small quantity of oxygen (gasification), water (steam gasification) or hydrogen (hydrogenation). One of the most useful products is methane, which is a suitable fuel for electricity generation using high-efficiency gas turbines.

Cellulose and hemicelluloses form mainly volatile products on heating due to the thermal cleavage of the sugar units. The lignin forms mainly char since it is not readily cleaved to lower molecular weight fragments. The progressive increase in the pyrolysis temperature of the wood led to the release of the volatiles thus forming a solid residue that is different chemically from the original starting material (Demirbas 2000). Cellulose and hemicelluloses initially break into compounds of lower molecular weight. This forms an activated cellulose, which decomposes by two competitive reactions: one forming volatiles (anhydrosugars), and the other char and gases. The thermal degradation of the *activated cellulose* and hemicelluloses to form volatiles and char can be divided into categories depending on the reaction temperature. Within a fire all these reactions take place concurrently and consecutively. Gaseous emissions are predominantly a product of pyrolitic cracking of the fuel. If flames are present, fire temperatures are high, and more oxygen is available from thermally induced convection.

The biomass pyrolysis is attractive because solid biomass and wastes can be readily converted into liquid products. These liquids, as crude bio-oil or slurry of charcoal of water or oil, have advantages in many fields such as transport, storage, combustion, retrofitting and flexibility in production and marketing.

Gasification is a form of pyrolysis, carried out in the presence of a small quantity of oxygen at high temperatures in order to optimize the gas production. The resulting gas, known as *producer gas*, is a mixture of carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen. The gas is more versatile than the original solid biomass (usually wood or charcoal): it can be burnt to produce process heat and steam, or used in gas turbines to produce electricity.

Biomass gasification technologies are expected to be an important part of the effort to meet these goals of expanding the use of biomass. Gasification technologies provide the opportunity to convert renewable biomass feedstocks into clean fuel gases or synthesis gases. Biomass gasification is the latest generation of biomass energy conversion processes, and is being used to improve the efficiency, and to reduce the investment costs of biomass electricity generation through the use of gas turbine technology. High efficiencies (up to about 50%) are achievable using combined-cycle gas turbine systems, where waste gases from the gas turbine are recovered to produce steam for use in a steam turbine.

Various gasification technologies include gasifiers where the biomass is introduced at the top of the reactor and the gasifying medium is either directed co-currently (downdraft) or counter-currently up through the packed bed (updraft). Other gasifier designs incorporate circulating or bubbling fluidized beds. Tar yields can range from 0.1% (downdraft) to 20% (updraft) or greater in the product gases.

The process of synthetic fuels (synfuels) from biomass will lower the energy cost, improve the waste management, and reduce harmful emissions. This triple assault on plant operating challenges is a proprietary technology that gasifies biomass by reacting it with steam at high temperatures to form a clean burning synthetic gas (syngas: $CO + H_2$). The molecules in the biomass (primarily carbon, hydrogen and oxygen) and the molecules in the steam (hydrogen and oxygen) reorganize to form this syngas.

2.4 Chemicals from Biomass

Such features of larch wood, as an increased content of extractive compounds and its high density, create some technological problems for the pulping process. It seems that production of high-value-added chemicals is the most profitable from an economical point of view of larch wood valorization. High-value organic compounds such as arabinogalactan, quercitin dihydrate vanillin, microcrystalline cellulose and levulinic acid are obtained from larch wood. Both arabinogalactan and quercitin dihydrate can be extracted from larch wood with boiling water (Kuznetsov et al. 2005).

Chemicals can be obtained from thermal depolymerization and decomposition of biomass structural components; cellulose, hemicelluloses, and lignin form liquids and gas products as well as a solid residue of charcoal. The bio-oils from pyrolysis of biomass are composed of a range of cyclopentanone, methoxyphenol, acetic acid, methanol, acetone, furfural, phenol, formic acid, levoglucosan, guaiacol and their alkylated phenol derivatives. The structural components of the biomass samples mainly have an affect on the pyrolytic degradation products. A reaction mechanism is proposed which describes a possible reaction route for the formation of the characteristic compounds found in the oils. The temperature and heating rate are the most important parameters, which affect the composition of chemicals. The supercritical water conditioning and liquefaction partial reactions also occur during the pyrolysis. Acetic acid is formed in the thermal decomposition of all three main components of biomass. In the pyrolysis reactions of biomass water is formed by dehydration, acetic acid comes from the elimination of acetyl groups originally linked to the xylose unit, furfural is formed by dehydration of the xylose unit, formic acid proceeds from carboxylic groups of uronic acid, and methanol arises from methoxyl groups of uronic acid.

The pyrolysis process can produce mainly charcoal, condensable organic liquids, non-condensable gases, acetic acid, acetone, and methanol. Among the liquid products, methanol is one of the most valuable products. The liquid fraction of the pyrolysis products consists of two phases: an aqueous phase containing a wide variety of organo-oxygen compounds of low molecular weight and a non-aqueous phase containing insoluble organics of high molecular weight. This phase is called tar and is the product of greatest interest. The ratios of acetic acid, methanol, and acetone of the aqueous phase are higher than those of the non-aqueous phase.

Chemicals potentially derived from lignin conversions are syngas, methanol, dimethyl ether, ethanol, mixed alcohols, byproduct C_1 to C_4 gases, hydrocarbons, oxygenates, Fischer–Tropsch liquids, cyclohexane, styrenes, biphenyls, phenol, substituted phenols, catechols, cresols, resorcinols, eugenol, syringols, guaiacols, vanillin, vanilic acid, aromatic acids, aliphatic acids, syringaldehyde and aldehydes, quinones, cyclohexanol/al, cyclohexanal, beta keto adipate, benzene, toluene, xylene (BTX) and their derivates, higher alkylates, substituted lignins, drugs, mixed aromatic polyols, carbon fiber, fillers, etc.

As the temperature is increased there is an increase in the yield of gas. The influence of residence time on the yield of products is small, with a slight decrease in oil yield and increase in char yield. The main gases produced are carbon dioxide, carbon monoxide, methane and hydrogen and there is significant production of oil and char. Pyrolysis of biomass produces high conversion rates to a gas composed mainly of hydrogen and carbon dioxide within addition carbon monoxide and C_1–C_4 hydrocarbons. Similar to conventional gasification processes, oil and char reaction products are produced. The oils are composed of a range of oxygenated compounds, including, cyclopentanone, methoxybenzene, acetic acid, furfural, acetophenone, phenol, benzoic acid and their alkylated derivatives.

Biological processes are essentially microbic digestion and fermentation. High-moisture herbaceous plants (vegetables, sugar cane, sugar beet, corn, sorghum, and cotton), marine crops, and manure are most suitable for biological digestion. Intermediate heat gas is methane mixed with carbon monoxide and carbon dioxide. Methane (high heat gas) can be efficiently converted into methanol.

Cellulose is a remarkably pure organic polymer, consisting solely of units of anhydroglucose held together in a giant straight-chain molecule. Cellulose must be hydrolyzed to glucose before fermentation to ethanol. Conversion efficiencies of cellulose to glucose may be dependent on the extent of chemical and mechanical pretreatments to structurally and chemically alter the pulp and paper mill wastes. The method of pulping, the type of wood, and the use of recycled pulp and paper products also could influence the accessibility of cellulose to cellulase enzymes. Hemicelluloses (arabinoglycuronoxylan and galactoglucomannans) are related to plant gums in composition, and occur in much shorter molecule chains than cellulose. The hemicelluloses, which are present in deciduous woods chiefly as pentosans and in coniferous woods almost entirely as hexosanes, undergo thermal decomposition very readily. Hemicelluloses are derived mainly from chains of pentose sugars, and act as the cement material holding together the cellulose micelles and fiber. Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis. Hemicelluloses are largely soluble in alkali and, as such, are more easily hydrolyzed.

Hydrolysis (saccharification) breaks down the hydrogen bonds in the hemicellulose and cellulose fractions into their sugar components: pentoses and hexoses. These sugars can then be fermented into bioethanol.

Cellulose (hexosan $(C_6H_{10}O_5)_n$) hydrolysis produces glucose (a hexose, $C_6H_{12}O_6$). The hydrolysis of cellulose is catalyzed by mineral acids and enzymes. Hemicelluloses hydrolysis produces both hexose and pentose sugars: mannose, galactose, xylose and arabinose that are not all fermented with existing strains.

2.4.1 Char from Biomass

Agricultural and forestry byproducts may also offer an inexpensive and renewable additional source of activated carbons. These waste materials have little or no economic value and often present a disposal problem. Therefore, there is a need to valorize these low-cost byproducts. Therefore, their conversion into activated carbons would add economic value, help reduce the cost of waste disposal, and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbons. Activated carbon is prepared from dried municipal sewage sludge and batch mode adsorption experiments (Reddy et al. 2006).

Active carbons are carbonaceous materials with highly developed internal surface area and porosity. It is widely used as an effective adsorbent in many applications such as air separation and purification, vehicle exhaust emission control, solvent recovery, and catalyst support because of its high specific pore surface area, adequate pore size distribution, and relatively high mechanical strength. The large surface area results in high capacity for adsorbing chemicals from gases and liquids (Zanzi 2001).

The starting materials used in commercial production of activated carbons are those with high carbon contents such as wood, lignite, peat, and coal of different ranks, or low-cost and abundantly available agricultural byproducts. Active carbons can be manufactured from virtually any carbonaceous precursor, but the most commonly used materials are wood, coal, and coconut shell. The development of activated carbons from agricultural carbonaceous wastes will be advantageous for environmental problems. In water contamination, wastewater contains many traces of organic compounds, which are a serious environmental problem. In the development of activated carbons, agricultural carbonaceous wastes will be used, as this will eliminate the problem of waste disposal while at the same time societies will derive great economic benefits from such commercialized products.

Activated carbons are used in the following applications:

1. They can be used as adsorbents for the removal or reduction of gaseous pollutants from the exhaust gases of industrial sources.
2. They can be used as adsorbents for the removal of volatile organic compounds, ozone from air, mercury and dioxin emissions from incinerator flue gas, and hydrogen sulfide emissions from sewage treatment facilities.
3. They can be used to remove chlorine and organic chemicals (such as phenols, polychlorinated biphenyls, trihalomethanes, pesticides and halogenated hydrocarbons), heavy metals and organic contaminants from water.
4. They can be used to extract some harmful elements of cigarette smoke by incorporation in filter tips of the cigarettes.

Lignin gives higher yields of charcoal and tar from wood, although lignin has a threefold higher methoxyl content than wood (Demirbas 2000). Phenolics are derived from lignin by cracking the phenyl-propane units of the macromolecule lattice. The formation of char from lignin under mild reaction conditions is a result of the breaking of the relatively weak bonds, like the alkyl-aryl ether bonds, and the consequent formation of more resistant condensed structures, as has already been noted (Domburg et al. 1974). One additional parameter that may also have an effect on the char formation is the moisture content of the kraft lignin used. It has been found that the presence of moisture increased the yield of char from the pyrolysis of wood waste at temperatures between 660 and 730 K (Demirbas 2006).

The destructive reaction of cellulose is started at temperatures lower than 425 K and is characterized by a decreasing polymerization degree. Thermal degradation of cellulose proceeds through two types of reaction: (1) a gradual degradation, decomposition and charring on heating at lower temperatures, and (2) a rapid volatilization accompanied by the formation of levoglucosan on pyrolysis at higher temperatures. The degradation of cellulose to a more stable anhydrocellulose, which gives higher biochar yield, is the dominant reaction at temperatures less than 575 K (Shafizadeh 1985). At temperatures greater than 575 K, cellulose depolymerizes, producing volatiles. If the heating rate is very high, the residence time of the biomass at temperatures less than 575 K is insignificant. Thus a high heating rate provides a shorter time for the dehydration reactions and the formation of less reactive anhydrocellulose, which gives a higher yield of char (Zanzi 2001). The result is that the rapid heating of the biomass favors the polymerization of cellulose and the formation of volatiles and suppresses the dehydration to anhydrocellulose and char formation. Hence the effect of heating rate is stronger in the pyrolysis of biomass than in coal.

The initial degradation reactions include depolymerization, hydrolysis, oxidation, dehydration, and decarboxylation (Shafizadeh 1982). The isothermal pyrolysis of cellulose in air and milder conditions, in the temperature range 623–643 K, was investigated (Fengel and Wegener 1983). Under these conditions, the pyrolysis reactions produced 62–72% aqueous distillate and left 10–18% charred residue. After the pyrolysis, the residue was found to consist of some water-soluble materials, in addition to char and undecomposed cellulose.

The hemicelluloses undergo thermal decomposition very readily. The hemicelluloses reacted more readily than cellulose during heating. The thermal degradation of hemicelluloses begins above 373 K during heating for 48 h; hemicelluloses and lignin are depolymerized by steaming at high temperature for a short time. The methoxyl content of wet meals decreased at 493 K. The stronger effect of the heating rate on the formation of biochar from biomass than from coal may be attributed to the cellulose content of the biomass (Demirbas 2006). It is well known that the heating rate has a significant effect on the pyrolysis of cellulose. The quick devolatilization of the biomass in rapid pyrolysis favors the formation of char with high porosity and high reactivity. The decreased formation of char at the higher heating rate was accompanied by an increased formation of tar. The net effect is a decrease in the volatile fuel production and an increased yield of biochar cellulose converted to levoglucosan at temperatures above 535 K (Freudenberg and Neish 1968).

2.4.2 Adhesives from Biomass

Wood adhesives play an essential role in the industry. Main wood valorization technologies include pulp and paper making, bio-oil by pyrolysis, synthesis gas by gasification, sugar by hydrolysis, ethanol by sugar fermentation, and finally adhesives by alkali liquefaction and polymerization. Lignin is a complex, high molecular weight polymer built of hydroxyphenylpropane units. There are two types of phenolic resins: resol and novalac. A phenolic resin for partially replacing phenol was used with modified organosolv lignin in phenol-formaldehyde (PF) resin production. Organosolv lignin-phenol-formaldehyde (LPF) resins were produced in a two-step preparation with different additions of lignin.

Adhesion is the state in which two surfaces are held together by interfacial forces, which may be valence forces, interlocking action, or both. The adhesives used in commercial wood composite products are usually synthetic polymer resins, based on the condensation reaction of formaldehyde with phenol, urea, resorcinol or melamine (Cetin and Ozmen 2003). Some structural, semi-structural and nonstructural wood adhesives are listed in Table 2.8. Approximately 1 million metric

Table 2.8 Structural, semi-structural, and non-structural wood adhesives

Structural	Phenol-formaldehyde
	Resorcinol-formaldehyde
	Phenol-resorcinol-formaldehyde
	Emulsion polymer/iso-cyanate
	Melamine-formaldehyde
	Melamine-urea-formaldehyde
	Epoxy
	Iso-cyanate
	Urea-formaldehyde
	Casein
Semi-structural	Cross-linked polyvinyl acetate
	Polyurethane
Non-structural	Polyvinyl acetate
	Animal
	Soybean
	Elastomeric construction
	Elastomeric contact
	Starch

tons of urea-formaldehyde resins are produced annually. More than 70% of this urea-formaldehyde resin is used by the forest products industry for a variety of purposes.

Fermentation residues were obtained by growing the anaerobic cellulolytic bacteria *Ruminococcus albus 7* or *Clostridium thermocellum* ATCC 27405 on a fibrous fraction derived from lucerne (*Medicago sativa L.*). These were converted to an effective co-adhesive for phenol-formaldehyde (PF) bonding of aspen veneer sheets to one another. Testing of the resulting plywood panels revealed that the adhesive was formulated to contain 30% of its total dry weight as fermentation residue (Weimer et al. 2005).

The wood adhesive market is very large, and there are significant problems due to volatile organic compounds and toxic chemicals in many adhesives. In addition, most of the adhesives are derived from depleting petrochemical resources. An environmentally friendly wood adhesive based on renewable resources and produced by microbial fermentation has been explored (Haag et al. 2006).

A method is described for making adhesives from biomass. The liquefaction oil is prepared from lignin-bearing plant material and a phenolic fraction is extracted. The phenolic fraction is reacted with formaldehyde to yield a phenol-formaldehyde resin. At present, the production of wood composites mainly relies on the petrochemical-based and formaldehyde-based adhesives such as PF resins and urea-formaldehyde (UF) resins (Liu and Li 2007). Phenol-formaldehyde adhesives are used to manufacture plywood, flakeboard, and fiberglass insulation. Phenolic resins occur only in dark, opaque colors and can therefore be used only to manufacture dark-colored products.

Phenolic resins are some of the principal thermofixed synthetic polymers, the third most important polymeric matrix for composites (Lubin 1969), and are also known for their high temperature resistance (Kopf and Little 1991). Pure phenolic resin can be obtained through the condensation reaction between phenol (C_6H_5OH) and formaldehyde (CH_2O), producing methylene bridges between the phenol molecules (Leite et al. 2004). Thermosetting polymers make excellent structural adhesives because they undergo irreversible chemical change, and on reheating, they do not soften and flow again. They form cross-linked polymers that have high strength, have resistance to moisture and other chemicals, and are rigid enough to support high, long-term static loads without deforming. Phenolic, resorcinolic, melamine, iso-cyanate, urea, and epoxy are examples of types of wood adhesives that are based on thermosetting polymers.

Resistance to chemical attack is generally improved by resin impregnation, which protects the underlying wood and reduces movement of liquid into the wood. Resistance to acids can be obtained by impregnating with phenolic resin, and to alkalis, by impregnating with furfural resin. The adhesion properties of different natural fillers without the addition of coupling agents by considering the different filler morphology were investigated. The adhesion behavior has been determined in a qualitative way from microscopic observation and has been quantified; its influence on mechanical properties decreases, since in this type of material, tensile strength usually decreases (Crespo et al. 2007).

The reaction of formaldehyde with lignin model compounds in acidic medium is shown to give fast cross-linking of alkali-substituted phenolic and etherified phenolic lignin model compounds at *meta*-positions to the aromatic hydroxyl groups. This reaction differs from the reaction of formaldehyde with phenolic lignin model compounds in alkaline conditions, where the reaction with formaldehyde always occurs at position *ortho-/para-* to the aromatic hydroxyl group (Demirbas and Ucan 1991).

The lignin degradation products and their sodium salts can be converted into very weak organic acids by treating mineral acids. Most phenols have equilibrium constants (K_a) in the neighborhood of 10^{-10}, and are thus considerably weaker than the carboxylic acids (K_a about 10^{-5}). Most phenols are weaker than carbonic acid ($CO_2 + H_2O$), and hence, unlike carboxylic acids, do not dissolve in aqueous bicarbonate solutions. Indeed, phenols are conveniently liberated from their salts by action of carbonic acid (K_a about 10^{-7}) (Morrison and Boyd 1983).

Organosolv lignin-phenol-formaldehyde (LPF) resins were produced in a two-step preparation with different additions of lignin. The method selected for the manufacture of lignin resins dealt with modification of the lignin by the methylolation route. Organosolv lignin-based resins showed comparatively good strength and stiffness. The tensile strength properties of test samples made from organosolv lignin resins were equal to or better than those of test samples made from PF resin only (Cetin and Ozmen 2003).

2.4.3 Valorization of Wood

Forests are principal global economic resources, as well as ecological resources. Forests have played a big role in the development of human societies. The prime direct or marketable product of most forests is wood for use as timber, fuelwood, pulp and paper, providing some 3.4 billion cubic meters of timber-equivalent a year globally. Asia and Africa use 75% of global wood fuels.

The lumber, plywood, pulp, and paper industries burn their own wood residues in large furnaces and boilers to supply 60% of the energy needed to run factories. The availability of fuelwood from the forest is continually declining at an ever-increasing rate due to indiscriminate deforestation and slow regeneration, as well as afforestation. The fuelwoods generally used by local people were identified and analyzed quantitatively to select a few species with the best fuelwood characteristics so that plantation on non-agricultural lands could be undertaken (Jain 1992).

The reduction of particle size and moisture content, together with the most appropriate storage and handling systems are necessary for an efficiently operated wood waste combustion system. Size reduction may be carried out in several stages in a hog or attrition mill, with screening before and in between. The moisture in residues may be reduced either by mechanical pressing, air drying, or the use of hot air dryers, or a combination of all three. Generally slabs, edgings, peeler cores, veneer waste and trimmings would be transported by mechanical conveyors.

Forest energy involves the use of forest biomass, which is currently not being used in the traditional forest products industries. Essentially, this means the forest residues are left after forest harvesting, including residual trees and scrub or under-managed woodland. Forest residues alone count for some 50% of the total forest biomass and are currently left in the forest to rot.

The principal sources of waste wood are two waste streams: municipal solid waste (MSW) and construction and demolition waste (C&DW). Municipal solid waste (MSW) is waste from residential, commercial, institutional, and industrial sources. Each generates distinctly different types of wood waste, with differing degrees and levels of recyclability. The primary components of wood waste are used lumber, shipping pallets, trees, branches, and other wood debris from construction and demolition clearing and grubbing activities. Construction and demolition waste is defined as solid, largely inert waste resulting from the construction, repair, demolition, or razing of buildings, roads and other structures. The term also includes debris from the clearing of land for construction. Other sources of waste wood include chemically treated wood from railroad ties, telephone and utility poles, miner poles, crosstie, constructors, pier and dock timbers, untreated wood from logging and silvicultural operations, and industrial waste wood outside the MSW and C&DW streams. Chemical treatments and costs of collection make much of this material difficult to recover.

The wood waste preparation process generally involves hogging, dewatering, screening, size reduction, bulk storage, blending and drying prior to combustion so as to ensure a reliable and consistent supply of quality fuel to the burners. The handling, treatment and storage of wood waste fuel are considerably more costly and troublesome than that required for traditional fossil fuels.

The most limiting factors for using wood waste as fuel for power generation are transportation costs and its energy content. The economics of wood waste energy generation become more attractive as traditional fuel prices increase.

2.5 Biofuels from Biomass

2.5.1 Introduction

The term biofuel is referred to as solid, liquid, or gaseous fuels that are predominantly produced from biorenewable or combustible renewable feedstocks. Liquid biofuels are important in the future because they replace petroleum fuels. The biggest difference between biofuels and petroleum feedstocks is oxygen content. Biofuels are non-polluting, locally available, accessible, sustainable and reliable fuel obtained from renewable sources. Electricity generation from these fuels is a promising method to use in the near future. The future of biomass electricity generation lies in biomass-integrated gasification/gas turbine technology, which offers high-energy conversion efficiencies.

Biofuels can be classified based on their production technologies: first-generation biofuels (FGBs), second-generation biofuels (SGBs), third-generation biofuels (TGBs), and fourth-generation biofuels.

The FGBs refer to biofuels made from sugar, starch, vegetable oils, or animal fats using conventional technology. The basic feedstocks for the production of first-generation biofuels are often seeds or grains such as wheat, which yields starch that is fermented into bioethanol, or sunflower seeds, which are pressed to yield vegetable oil that can be used in biodiesel. Table 2.9 shows the classification of renewable biofuels based on their production technologies.

Second and third-generation biofuels are also called advanced biofuels, and are made from non-food crops, wheat straw, corn, wood, energy crops using advanced technology. Algae fuel, also called *oilgae* or third-generation biofuel, is a biofuel from algae. Algae are low-input/high-yield (30 times more energy per acre than land) feedstocks to produce biofuels using more advanced technology. On the other hand, an appearing fourth-generation is based on the conversion of vegoil and biodiesel into biogasoline using the most advanced technology.

Table 2.9 Classification of renewable biofuels based on their production technologies

Generation	Feedstock	Example
First-generation biofuels	Sugar, starch, vegetable oils, or animal fats	Bioalcohols, vegetable oil, biodiesel, biosyngas, biogas
Second-generation biofuels	Non-food crops, wheat straw, corn, wood, solid waste, energy crop	Bioalcohols, bio-oil, bio-DMF, biohydrogen, bio-Fischer–Tropsch diesel, wood diesel
Third-generation biofuels	Algae	Vegetable oil, biodiesel
Fourth-generation biofuels	Vegetable oil, biodiesel	Biogasoline

There are two global biorenewable liquid transportation fuels that might replace gasoline and diesel fuel. These are bioethanol and biodiesel. Bioethanol is a good alternate fuel that is produced almost entirely from food crops. Biodiesel has become more attractive recently because of its environmental benefits.

Transport is one of the main energy-consuming sectors. It is assumed that biodiesel can be used as a fossil diesel replacement and that bioethanol can be used as a gasoline replacement. Biomass-based energy sources for heat, electricity, and transportation fuels are potentially carbon dioxide neutral and recycle the same carbon atoms. Due to the widespread availability of biorenewables, this fuel technology may potentially employ more people than fossil fuel-based technology.

Renewable liquid biofuels for transportation have recently attracted much attention in different countries all over the world because of their renewability, sustainability, common availability, regional development, rural manufacturing jobs, reduction of greenhouse gas emissions, and its biodegradability.

2.5.2 *Bioethanol*

Bioethanol can be used directly in cars designed to run on pure ethanol or blended with gasoline to make "gasohol." Anhydrous ethanol is required for blending with gasoline. No engine modification is typically needed to use the blend. Ethanol can be used as an octane-boosting, pollution-reducing additive in unleaded gasoline.

Figure 2.4 shows the world production of ethanol and biodiesel between 1980 and 2007 (Demirbas 2008). Between 1991 and 2001, world ethanol production rose

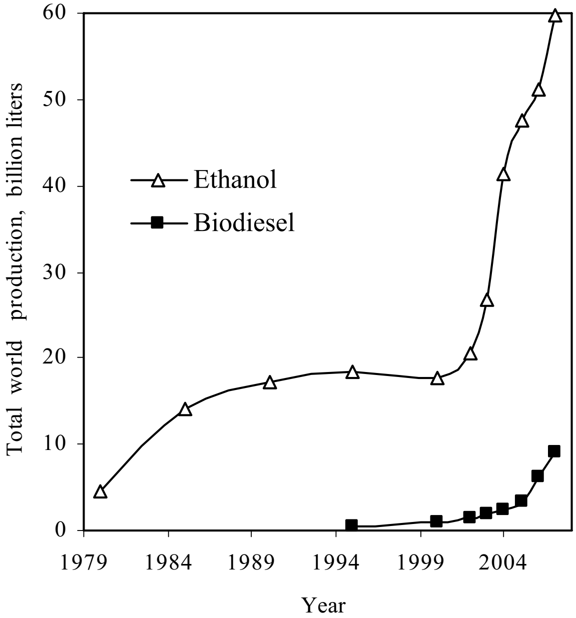
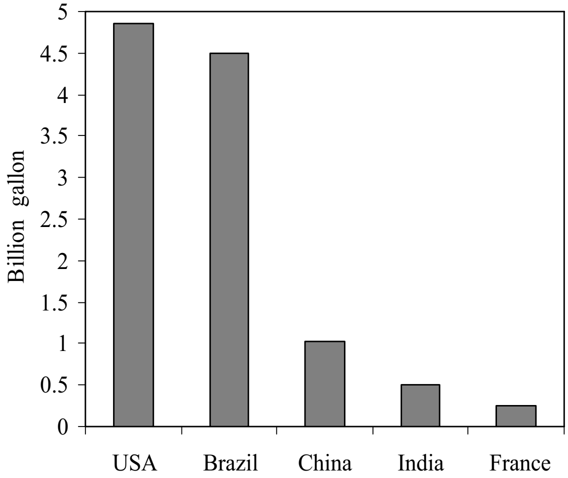


Fig. 2.4 World production of ethanol and biodiesel (1980–2007)

Fig. 2.5 The top five bioethanol producers (billion gallons) in 2006



from around 16 billion liters a year to 18.5 billion liters. From 2001 to 2007, production is expected to have tripled, to almost 60 billion liters a year. Brazil was the world's leading ethanol producer until 2005 when US production roughly equaled Brazil's. The US became the world's leading ethanol producer in 2006. China holds a distant but important third place in world rankings, followed by India, France, Germany and Spain. Figure 2.5 shows the top five bioethanol producers in 2006 (RFA 2007).

The continued increases in the price of crude oil in 2005 and 2006 resulted in a reversal of the traditional relationship between the price of biomass energy and that of crude oil, something not seen since the 1930s. As a consequence of the high prices of traded crude oil, many countries advanced their biofuel goals and, in the case of Brazil and the US, large production gains occurred. Table 2.10 shows the world production of ethanol during 2004 and 2007.

Table 2.10 World production of ethanol during 2004 and 2007 (billion gallons)

Country	2004	2005	2006	2007	Growth rate 2006–2007	Share of total 2007
United States	3.40	3.90	4.86	6.49	33.5%	38.3%
Brazil	3.87	4.25	4.71	5.96	26.5%	35.2%
China	0.93	0.93	0.94	0.99	5.3%	5.9%
India	0.33	0.29	0.44	0.65	47.7%	3.8%
France	0.22	0.24	0.24	0.30	25.0%	1.8%
Others	2.00	2.10	2.40	2.55	6.3%	15.0%
Total	10.75	11.71	13.59	16.94	24.6%	100.0%

2.5.3 Biodiesel

The other significant biofuel is biodiesel, which is currently produced from vegetable oils, animal fats and grease by transesterification. The vegetable oils with carbon chain lengths of between 16 and 22 carbon atoms are generally in the form of triacylglycerides (TAG), which on transesterification with methanol produce fatty acid methyl ester (FAME) as the precursor to biodiesel and glycerol as a byproduct. Vegetable oil (m)ethyl esters, commonly referred to as biodiesel, are prominent candidates as alternative diesel fuels. The name biodiesel has been given to transesterified vegetable oil to describe its use as a diesel fuel. After FAME purification and testing for compliance with either EN 14214 or ASTM D6751 standards the product can be sold as biodiesel and used as blends – typically B5 (5% biodiesel) to B20, depending on the engine warranties.

There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature as compared to conventional diesel, which is a fossil fuel leading to a potential exhaustion. Biodiesel is technically competitive with or offers technical advantages compared to conventional petroleum diesel fuel. The vegetable oils can be converted to their (m)ethyl esters via the transesterification process in the presence of a catalyst. Methyl, ethyl, 2-propyl and butyl esters can be prepared from vegetable oils through transesterification using potassium and/or sodium alkoxides as catalysts. The purpose of the transesterification process is to lower the viscosity of the oil. Ideally, transesterification is potentially a less expensive way of transforming the large, branched molecular structure of the bio-oils into smaller, straight-chain molecules of the type required in regular diesel combustion engines.

The biodiesel esters were characterized for their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion and volatility. The biodiesel fuels produced slightly lower power and torque, and higher fuel consumption than No. 2 diesel fuel. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability.

The cost of biodiesels varies depending on the base stock, geographic area, variability in crop production from season to season, the price of the crude petroleum and other factors. Biodiesel has over double the price of petroleum diesel. The high price of biodiesel is in large part due to the high price of the feedstock. However, biodiesel can be made from other feedstocks, including beef tallow, pork lard, and yellow grease.

The commercial resource base for vegetable oils comprises about 20 different species with soybean oil, rapeseed (Colza), palm/palm kernel oil, sunflower, and coconut oils being the largest sources. Most of the biodiesel that is currently made uses soybean oil, methanol, and an alkaline catalyst. The high value of soybean oil as a food product makes production of a cost-effective fuel very challenging. However, there are large amounts of low-cost oils and fats such as restaurant waste and animal fats that could be converted to biodiesel. The problem with processing these

Table 2.11 Biodiesel production (thousand tons)

	2004	2005	2006
Germany	1035	1669	2681
France	348	492	775
Italy	320	396	857
Malaysia		260	600
United States	83	250	826
Czech Republic	60	133	203
Poland		100	150
Austria	57	85	134
Slovakia	15	78	89
Spain	13	73	224
Denmark	70	71	81
UK	9	51	445
Other EU	6	36	430
Total	2016	3694	7495

low-cost oils and fats is that they often contain large amounts of free fatty acids (FFA) that cannot be converted to biodiesel using an alkaline catalyst.

Biodiesel is an environmentally friendly alternative liquid fuel that can be used in any diesel engine without modification. If the biodiesel valorized efficiently, it would be beneficial in terms of the environment and the local population, job creation, provision of modern energy carriers to rural communities, avoiding urban migration, and reduction of CO_2 and sulfur levels in the atmosphere. Table 2.11 shows the biodiesel production between 2004 and 2006.

The second generation biofuels include renewable and green diesels. The former is a technology that incorporates vegetable oils into the crude oil-derived diesel production process to produce a renewable carbon-based diesel with no oxygen content and a very high cetane number, while the latter is the production of middle distillates by means of Fischer–Tropsch catalysts, using synthesis gas produced by the gasification of biomass. Fischer–Tropsch-like catalysts (synthol process) can also produce ethanol and mixed alcohols.

2.5.4 Bio-Oil

The term bio-oil is used mainly to refer to liquid fuels. There are several reasons for bio-oils to be considered as relevant technologies by both developing and industrialized countries. They include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector.

Bio-oils are liquid or gaseous fuels made from biomass materials, such as agricultural crops, municipal wastes and agricultural and forestry byproducts via biochemical or thermochemical processes. They can serve as substitutes for conventional fuels in vehicle engines, either totally or partially in a blend.

Biomass is dried and then converted to oily product known as bio-oil, by very quick exposure to heated particles in a fluidized bed. The char and gases produced are combusted to supply heat to the reactor, while the product oils are cooled and condensed. The bio-oil is then shipped by truck from these locations to the hydrogen production facility. It is more economical to produce bio-oil at remote locations and then ship the oil, since the energy density of bio-oil is higher than biomass. For this analysis, it was assumed that the bio-oil would be produced at several smaller plants, which are closer to the sources of biomass, such that lower-cost feedstocks can be obtained.

The purpose of this analysis was to assess the economic feasibility of producing hydrogen from biomass via two thermochemical processes: (1) gasification followed by reforming of the syngas (H_2+CO), and (2) fast pyrolysis followed by reforming of the carbohydrate fraction of the bio-oil. In each process, the water–gas shift is used to convert the reformed gas into hydrogen, and pressure swing adsorption is used to purify the product.

Pyrolysis (cracking) is defined as the cleavage to smaller molecules by thermal energy. Hydrogen can be produced economically from woody biomass. Biomass can be thermally processed through gasification or pyrolysis to produce hydrogen. The main gaseous products from biomass are the following:

$$\text{Pyrolysis of biomass} \rightarrow H_2 + CO_2 + CO + \text{Gaseous and liquid hydrocarbons} \quad (2.7)$$

$$\text{Catalytic steam reforming of biomass} \rightarrow H_2 + CO_2 + CO \quad (2.8)$$

$$\text{Fischer–Tropsch synthesis of } (H_2 + CO) \rightarrow \text{Gaseous and liquid hydrocarbons} \quad (2.9)$$

The conventional pyrolysis of biomass is associated with the product of interest that is the high charcoal continent, but the fast pyrolysis is associated with tar, at low temperatures (675–775 K), and/or gas, at high temperatures.

2.5.5 Biogas

The organic fraction of almost any form of biomass, including sewage sludge, animal wastes and industrial effluents, can be broken down through anaerobic digestion into a methane and carbon dioxide mixture known as *biogas*. Biogas is an environment friendly, clean, cheap and versatile fuel.

Anaerobic digestion of biowastes occurs in the absence of air, the resulting gas, biogas, is a mixture consisting mainly of methane and carbon dioxide. Biogas is a valuable fuel, which is produced in digesters filled with the feedstock like dung or sewage. The digestion is allowed to continue for a period from 10 days to a few weeks.

Biogas can be obtained from several sources. It is obtained from decomposing organic material. Biogas is composed of methane (CH_4), carbon dioxide (CO_2), air, ammonia, carbon monoxide, hydrogen, sulfur gases, nitrogen and oxygen. Among its components, methane is the most important one, particularly for the combustion process in vehicle engines. CH_4 and CO_2 make up around 90% of the gas volume produced. The main constituents of landfill gas are methane and carbon dioxide, both of which are major contributors to global warming. Because of the widely varying nature of the contents of landfill sites the constituents of landfill gases vary widely.

Total solids (TS) content in the slurry is determined by drying it in an oven at 378 K until a constant weight is obtained. The dried solid samples from the TS determination are ignited at 1225 K in a furnace for 7 min. The loss in weight is taken as the volatile solids of the substrate slurry.

After the first 6 days of digestion, methane production from manure increases exponentially, after 16 days it reaches a plateau value, and at the end of the 20th day, the digestion reaches the stationary phase. For the wheat straw and the mixtures of manure/straw the rates of digestion are lower than that of manure.

The maximum daily biogas productions are between 4 and 6 days. During a 30-day digestion period, around 80–85% of the biogas is produced in the first 15–18 days. This implies that the digester retention time can be designed to 15–18 days instead of 30 days.

For first 3 days, the methane yield is almost 0% and carbon dioxide generation is almost 100%. In this period, digestion occurs as fermentation to carbon dioxide. The yields of methane and carbon dioxide gases are fifty-fifty on day 11. At the end of day 20, the digestion reaches the stationary phase. The methane content of the biogas is in the range of 73–79% for the runs, the remainder being principally carbon dioxide. During digestion, the volatile fatty acid concentration is lower and the pH higher. The pH of the slurry with manure increased from 6.4 initially, to 6.9–7.0 at the maximum methane production rate. The pH of the slurry with wheat straw is around 7.0–7.1 at the maximum methane production rate.

2.5.6 Fischer–Tropsch Liquids

Syngas (a mixture of carbon monoxide and hydrogen) produced by gasification of fossil fuels or biomass can be converted into a large number of organic compounds that are useful as chemical feedstocks, fuels, and solvents. Many of the conversion technologies were developed for coal gasification but process economics have resulted in a shift to natural gas-derived syngas. These conversion technologies successively apply similarly to biomass-derived biosyngas. Franz Fischer and Hans Tropsch first studied conversion of syngas into larger, useful organic compounds in 1923 (Spath and Mann 2000).

Biofuels, including Fischer–Tropsch liquids, are important as they affect a wide array of topics, including energy security, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. Catalytic conversion will be a primary tool for industry to produce valuable fuels, chemicals, and materials from biomass platform chemicals. The catalytic conversion of biomass is best developed for synthesis gas or syngas. Economic considerations dictate that the current production of liquid fuels from syngas must make use of natural gas as the hydrocarbon source. Biomass is the only renewable that can meet our demand for carbon-based liquid fuels and chemicals. Biofuels as well as green motor fuels produced from biomass by Fischer–Tropsch synthesis (FTS) are the most modern biomass-based transportation fuels. Green motor fuels are the renewable replacement to petroleum-based diesel. Biomass energy conversion facilities are important for obtaining bio-oil by pyrolysis. The aim of FTS is the synthesis of long-chain hydrocarbons from a CO and H_2 gas mixture. The products from FTS are mainly aliphatic straight-chain hydrocarbons (C_xH_y). In addition to the C_xH_y, branched hydrocarbons, unsaturated hydrocarbons, and primary alcohols are formed in minor quantities. The FTS process is a process capable of producing liquid hydrocarbon fuels from biosyngas. The large hydrocarbons can be hydrocracked to form mainly diesel of excellent quality. The process for producing liquid fuels from biomass, which integrates biomass gasification with FTS, converts a renewable feedstock into a clean fuel.

Fischer–Tropsch synthesis (FTS) produces mainly straight-chain hydrocarbons from a syngas rich in CO and H_2, and catalysts are usually employed. Typical operating conditions for FTS are temperatures of 475–625 K and very high pressure, depending on the desired products. The product range includes light hydrocarbons such as methane (CH_4) and ethane (C_2H_6), propane (C_3H_8) butane (C_4H_{10}), gasoline (C_5–C_{12}), diesel (C_{13}–C_{22}), and light and heavy waxes (C_{23}–C_{33}). The distribution of the products depends on the catalyst and the process conditions (temperature, pressure, and residence time). The synthesis gas must have very low tar and particulate matter content.

The FTS is described by the following set of equations (Schulz 1999):

$$nCO + (n + m/2)\,H_2 \rightarrow C_nH_m + nH_2O \tag{2.10}$$

where n is the average length of the hydrocarbon chain and m is the number of hydrogen atoms per carbon. All reactions are exothermic and the product is a mixture of different hydrocarbons, where paraffin and olefins are the main parts.

The first FTS plants began operation in Germany in 1938 but closed down after World War II. Then in 1955, Sasol, a world-leader in the commercial production of liquid fuels and chemicals from coal and crude oil, started Sasol I in Sasolburg, South Africa. Following the success of Sasol I, Sasol II and III, located in Secunda, South Africa, came on line in 1980 and 1982, respectively. The FTS is an essential step to convert carbon-containing feedstocks to liquid fuels such as diesel. Major advantages of the FTS are: (1) flexibility in feedstocks (natural gas, coal, biomass), (2) large and even sustainable resources, (3) ultraclean (low sulfur content) products, (4) suitability for converting difficult to process resources. A major drawback of the Fischer–Tropsch process however is the polymerization-like nature of the process, which yields a wide spectrum of products, ranging from compounds with low molecular mass like methane, to products with very high molecular mass like heavy waxes.

2.5.7 Biohydrogen

Hydrogen is not a primary fuel. It must be manufactured from water with either fossil or non-fossil energy sources. Widespread use of hydrogen as an energy source could improve global climate change, energy efficiency, and air quality. The thermochemical conversion processes, such as pyrolysis, gasification and steam gasification are available for converting the biomass to a more useful energy. The yield from steam gasification increases with increasing water-to-sample ratio. The yields of hydrogen from the pyrolysis and the steam gasification increase with increasing temperature. The list of some biomass material used for hydrogen production is given in Table 2.12. Hydrogen-powered fuel cells are an important enabling technology for the hydrogen future and more-efficient alternatives to the combustion of gasoline and other fossil fuels. Hydrogen has the potential to solve two major energy problems: reducing dependence on petroleum and reducing pollution and greenhouse gas emissions.

A fuel cell is a device or an electrochemical engine that converts the energy of a fuel directly to electricity and heat without combustion. Fuel cells consist of two electrodes sandwiched around an electrolyte. When oxygen passes over one electrode and hydrogen over the other, electricity is generated. Fuel cells running on hydrogen derived from a renewable source would emit nothing but water vapor. Fuel cells are clean, quiet, and efficient.

Hydrogen is currently more expensive than conventional energy sources. There are different technologies presently being practiced to produce hydrogen economically from biomass. Hydrogen can be produced by pyrolysis from biomass. It can be burned to produce heat or passed through a fuel cell to produce electricity. Biomass represents a large potential feedstock resource for environmentally clean hydrogen production. It lends itself to both biological and thermal conversion processes. In the thermal path hydrogen can be produced in two ways: direct gasification and pyrolysis to produce liquid bio-oil, followed by steam reforming. Hydrogen can

Table 2.12 List of some biomass material used for hydrogen production

Biomass species	Main conversion process
Bionut shell	Steam gasification
Olive husk	Pyrolysis
Tea waste	Pyrolysis
Crop straw	Pyrolysis
Black liquor	Steam gasification
Municipal solid waste	Supercritical water extraction
Crop grain residue	Supercritical fluid extraction
Pulp and paper waste	Microbial fermentation
Petroleum basis plastic waste	Supercritical fluid extraction
Manure slurry	Microbial fermentation

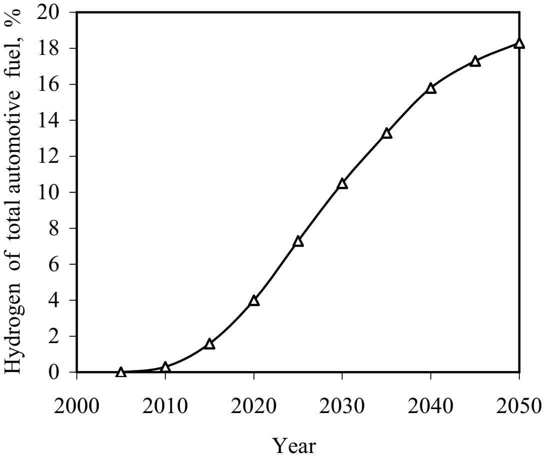


Fig. 2.6 Share of hydrogen in total automotive fuel in the future

alternately be produced by supercritical water gasification of biomass (Byrd et al. 2007).

Biohydrogen technology will play a major role in the future because it can utilize renewable sources of energy. Figure 2.6 shows the share of hydrogen in total automotive fuel consumption in the world as a futuristic view (Demirbas 2008).

Biological generation of hydrogen (biohydrogen) technologies provide a wide range of approaches to generate hydrogen, including direct biophotolysis, indirect biophotolysis, photofermentations, and dark fermentation. Biological hydrogen production processes are found to be more environmentally friendly and less energy intensive as compared to thermochemical and electrochemical processes. Researchers have investigated hydrogen production with anaerobic bacteria since the 1980s.

There are three types of microorganisms of hydrogen generation: cyanobacteria, anaerobic bacteria, and fermentative bacteria. The cyanobacteria directly decompose water into hydrogen and oxygen in the presence of light by photosynthesis. Photosynthetic bacteria use organic substrates like organic acids. Anaerobic bacteria use organic substances as the sole source of electrons and energy, converting them into hydrogen. Biohydrogen can be generated using bacteria such as *Clostridia* by temperature, pH control, reactor hydraulic retention time (HRT) and other factors of the treatment system.

Biological hydrogen can be generated from plants by biophotolysis of water using microalgae (green algae and cyanobacteria), fermentation of organic compounds, and photodecomposition of organic compounds by photosynthetic bacteria. To produce hydrogen by fermentation of biomass, a continuous process using a non-sterile substrate with a readily available mixed microflora is needed (Hussy et al. 2005). A successful biological conversion of biomass to hydrogen depends strongly on the processing of raw materials to produce feedstock, which can be fermented by the microorganisms.

Hydrogen production from the bacterial fermentation of sugars has been examined in a variety of reactor systems. Hexose concentration has a greater effect on

H_2 yields than the hydraulic retention time (HRT). Flocculation is also an important factor in the performance of the reactor.

Hydrogen gas is a product of the mixed acid fermentation of *Escherichia coli*, the butylene glycol fermentation of *Aerobacter*, and the butyric acid fermentations of *Clostridium* spp. Anaerobic fermentation was conducted to improve hydrogen fermentation of food waste in a leaching-bed reactor by heat-shocked anaerobic sludge, and also to investigate the effect of dilution rate on the production of hydrogen and metabolites in hydrogen fermentation.

2.5.8 Sugar from Biomass

Cellulose is a remarkable pure organic polymer, consisting solely of units of anhydroglucose held together in a giant straight-chain molecule. Cellulose must be hydrolyzed to glucose before fermentation to ethanol. Conversion efficiencies of cellulose to glucose may be dependent on the extent of chemical and mechanical pretreatments to structurally and chemically alter the pulp and paper mill wastes. The method of pulping, the type of wood, and the use of recycled pulp and paper products also could influence the accessibility of cellulose to cellulase enzymes. Hemicelluloses (arabinoglycuronoxylan and galactoglucomannans) are related to plant gums in composition, and occur in much shorter molecule chains than cellulose. The hemicelluloses, which are present in deciduous woods chiefly as pentosans and in coniferous woods almost entirely as hexosanes, undergo thermal decomposition very readily. Hemicelluloses are derived mainly from chains of pentose sugars, and act as the cement material holding together the cellulose micelles and fiber. Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis. Hemicelluloses are largely soluble in alkalis and, as such, are more easily hydrolyzed.

Hydrolysis (saccharification) breaks down the hydrogen bonds in the hemicellulose and cellulose fractions into their sugar components: pentoses and hexoses. These sugars can then be fermented into bioethanol.

Cellulose (hexosan, $(C_6H_{10}O_5)_n$) hydrolysis produces glucose (a hexose, $C_6H_{12}O_6$). The hydrolysis of cellulose is catalyzed by mineral acids and enzymes.

Hexosan to hexose:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \tag{2.11}$$

Hemicelluloses hydrolysis produces both hexose and pentose sugars: mannose, galactose, xylose and arabinose that are not all fermented with existing strains.

Pentosan to pentose:

$$(C_5H_8O_4)_m + mH_2O \rightarrow mC_5H_{10}O_5 \tag{2.12}$$

The most commonly applied methods can be classified into two groups: chemical hydrolysis (dilute and concentrated acid hydrolysis) and enzymatic hydrolysis. In addition, there are some other hydrolysis methods in which no chemicals or enzymes are applied. For instance, lignocellulose may be hydrolyzed by gamma ray or electron beam irradiation, or microwave irradiation. However, those processes are commercially unimportant.

Both enzymatic and chemical hydrolyses require a pretreatment to increase the susceptibility of cellulosic materials. In the chemical hydrolysis, the pretreatment and the hydrolysis may be carried out in a single step. There are two basic types of acid hydrolysis processes commonly used: dilute acid and concentrated acid, each with variations.

The dilute acid process is conducted under high temperature and pressure, and has a reaction time in the range of seconds or minutes, which facilitates continuous processing. As an example, using a dilute acid process with 1% sulfuric acid in a continuous flow reactor at a residence time of 0.22 min and a temperature of 510 K with pure cellulose, provides a yield over 50% sugars. In this case, 1000 kg of dry wood would yield about 164 kg of pure ethanol. The combination of acid and high temperature and pressure dictate special reactor materials, which can make the reactor expensive. The first reaction converts the cellulosic materials to sugar and the second reaction converts the sugars to other chemicals. Unfortunately, the conditions that cause the first reaction to occur are also the right conditions for the second to occur.

The biggest advantage of dilute acid processes is their fast rate of reaction, which facilitates continuous processing. Since five-carbon sugars degrade more rapidly than six-carbon sugars, one way to decrease sugar degradation is to have a two-stage process. The first stage is conducted under mild process conditions to recover the five-carbon sugars, while the second stage is conducted under harsher conditions to recover the six-carbon sugars.

Hydrolysis of cellulosic materials by concentrated sulfuric or hydrochloric acids is a relatively old process. The concentrated acid process uses relatively mild temperatures, and the only pressures involved are those created by pumping materials from vessel to vessel. Reaction times are typically much longer than for dilute acid. This method generally uses concentrated sulfuric acid followed by a dilution with water to dissolve and hydrolyze or convert the substrate into sugar. This process provides a complete and rapid conversion of cellulose to glucose and hemicelluloses to five-carbon sugars with little degradation. The critical factors needed to make this process economically viable are to optimize sugar recovery and cost effectively recovers the acid for recycling. The solid residue from the first stage is dewatered and soaked in a 30 to 40% concentration of sulfuric acid for 1 to 4 h as a precellulose hydrolysis step. The solution is again dewatered and dried, increasing the acid concentration to about 70%. After reacting in another vessel for 1 to 4 h at low temperatures, the contents are separated to recover the sugar and acid. The sugar/acid solution from the second stage is recycled to the first stage to provide the acid for the first stage hydrolysis.

The primary advantage of the concentrated acid process is the potential for high sugar recovery efficiency. The acid and sugar are separated via ion exchange and then the acid is reconcentrated via multiple effect evaporators. The low temperatures and pressures employed allow the use of relatively low-cost materials such as fiberglass tanks and piping. The low temperatures and pressures also minimize the degradation of sugars. Unfortunately, it is a relatively slow process and cost effective acid recovery systems have been difficult to develop. Without acid recovery, large quantities of lime must be used to neutralize the acid in the sugar solution. This neutralization forms large quantities of calcium sulfate, which requires disposal and creates additional expense.

Another basic method of hydrolysis is enzymatic hydrolysis. Enzymes are naturally occurring plant proteins that cause certain chemical reactions to occur. There are two technological developments: enzymatic and direct microbial conversion methods.

The chemical pretreatment of the cellulosic biomass is necessary before enzymatic hydrolysis. The first application of enzymatic hydrolysis was used in separate hydrolysis and fermentation steps. Enzymatic hydrolysis is accomplished by cellulolytic enzymes. Different kinds of "cellulases" may be used to cleave the cellulose and hemicelluloses. A mixture of endoglucanases, exoglucanases, β-glucosidases and cellobiohydrolases is commonly used. The endoglucanases randomly attack cellulose chains to produce polysaccharides of shorter length, whereas exoglucanases attach to the non-reducing ends of these shorter chains and remove cellobiose moieties. β-glucosidases hydrolyze cellobiose and other oligosaccharides to glucose (Demirbas 2001).

For enzymes to work efficiently, they must obtain access to the molecules to be hydrolyzed. This requires some kind of pretreatment process to remove hemicelluloses and break down the crystalline structure of the cellulose or removal of the lignin to expose hemicelluloses and cellulose molecules.

2.6 Barriers to the Development of Biofuels

First-generation biofuels (FGBs) refer to biofuels made from sugar, starch, vegetable oils, or animal fats using conventional technology. FGBs produced from food crops such as grains, sugar beet and oilseeds are limited in their ability to achieve targets for oil-product substitution, climate change mitigation, and economic growth. A possible exception that appears to meet many of the acceptable criteria is bioethanol produced from sugar cane. The basic feedstocks for the production of first-generation biofuels are often seeds or grains such as wheat, which yields starch that is fermented into bioethanol, or sunflower seeds, which are pressed to yield vegetable oil that can be used in biodiesel.

The production of FGBs such as sugar cane ethanol in Brazil, corn ethanol in US, oilseed rape biodiesel in Germany, and palm oil biodiesel in Malaysia are characterized by mature commercial markets and well-understood technologies. Future targets and investment plans suggest strong growth will continue in the near future.

Second-generation biofuels (SGBs) produced from (larger) feedstocks from lignocellulosic materials include cereal straw, forest residues, bagasse, and purpose-grown energy crops such as vegetative grasses and short-rotation forests. The SGBs could avoid many of the concerns facing FGBs and potentially offer greater cost reduction potential in the longer term. Many of problems associated with FGBs can be addressed by the production of biofuels manufactured from agricultural and forest residues and from non-food crop feedstocks. Low-cost crop and forest, wood process wastes, and the organic fraction of municipal solid wastes can all be used as lignocellulosic feedstocks.

The key messages related to FGBs and SGBs are as follows:

1. Technical barriers remain for second biofuel production.
2. Production costs are uncertain and vary with the feedstock available.
3. There is no clear candidate for “best technology pathway” between the competing biochemical and thermochemical routes.
4. Even at high oil prices, SGBs will probably not become fully commercial nor enter the market for several years to come without significant additional government support.
5. Considerably more investment in research, development, demonstration and deployment is needed to ensure that future production of the various biomass feedstocks can be undertaken sustainably and that the preferred conversion technologies, including those more advanced but only at the research and development stage, are identified and proven to be viable.
6. Once proven, there will be a steady transition from FGBs (with the exception of sugarcane ethanol that will continue to be produced sustainably in several countries).

There are some barriers to the development of biofuel production. They are technological, economical, supply, storage, safety, and policy barriers. Reducing these barriers is one of the driving factors in the government’s involvement in biofuel and biofuel research and development. The production of biofuels from lignocellulosic feedstocks can be achieved through two very different processing routes: biochemical and thermochemical. Technical barriers for enzymatic hydrolysis include: low specific activity of current commercial enzymes, high cost of enzyme production, and lack of understanding of enzyme biochemistry and mechanistic fundamentals.

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