

Chapter 2

Fuels from Biomass

2.1 Introduction

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 (Demirbas, 2008a). Biomass is the plant and animal material, especially agricultural waste products, used as a source of fuel. It is a rather simple term for all organic materials that comes from plants, trees, crops and algae.

Biomass is commonly recognized as an important renewable energy, where solar energy is stored as chemical energy via photosynthesis during the growth of plants and trees, which can be released via direct or indirect combustion. Figure 2.1 shows the main steps of photosynthetic biomass growth.

A useful way to analyze the biosphere system is to trace the work potential, or exergy, of the various energy flows from the sources, such as the Sun, to its eventual destruction in natural decay or human utilization. Photosynthesis is a natural mechanism for capturing and concentrating carbon dioxide directly from the air. Chemical energy and organic carbon are obtained by organisms either directly or indirectly via the photosynthetic conversion of solar energy. These organisms have evolved metabolic machineries for the photochemical reduction of carbon dioxide to organic matter. The majority of the bioengineering strategies for biochemically derived fuels involve options for the disposition of organic matter produced via

photosynthate. The bulk of the presently exploited photosynthate is directed toward the production of wood, food, and feed. During processing and consumption, waste organic materials are generated, which can be used for energy production via combustion, pyrolysis or biochemical conversions to ethanol, hydrogen, methane, and isopropanol.

All biomass is produced by green plants converting sunlight into plant material through photosynthesis. Photosynthesis is the fundamental process in biomass energy whereby energy in sunlight is captured and stored in the chemical bonds of the tissues of living plants. Photosynthesis is a carbon fixation reaction by the electrochemical reduction of carbon dioxide. The fixation or reduction of carbon dioxide is a light-independent process. Although some of the steps in photosynthesis are still not completely understood, the overall photosynthetic equation has been known since the 1800s. The productivity of biomass depends on the presence of the required amounts of sunlight, water, and various nutrients, as well as proper environmental conditions including temperature and humidity.

The photosynthetic apparatus and the mechanisms by which it operates have been intensively investigated over the past 40 to 50 years. The photosynthesis is that of three series of interconnected oxidation-reduction reactions: The first involves the evolution of oxygen from water. The second is the transfer of H atoms to a primary hydrogen acceptor. The third is the reduction of CO_2 to carbohydrates by the primary hydrogen acceptor. The light energy required for photosynthesis is used to drive the H atoms against the potential gradient.

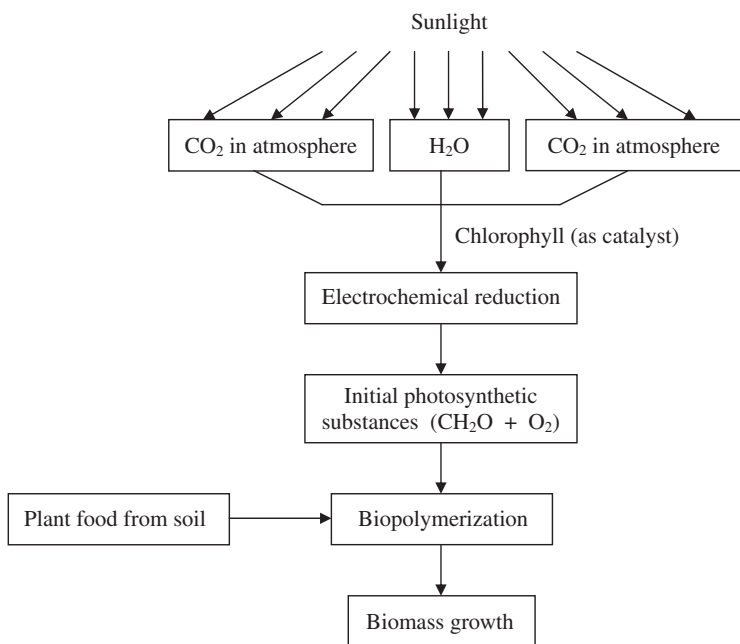


Fig. 2.1 The main steps of photosynthetic biomass growth

The photochemical stage of photosynthesis consists of two separate steps, I and II. The products of light reaction II are an intermediate oxidant and a strong oxidant which is capable of oxidizing water to oxygen. An intermediate oxidant and a strong reductant that can reduce carbon dioxide are produced in light reaction I. The two light reactions involve two pigment systems, photosystems I and II, interconnected by enzymatic reactions coupled with photophosphorylation yielding adenosine triphosphate (ATP).

2.2 Biomass Feedstocks

The biosphere processes large amounts of energy of varying types and quality. 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 pre-treatment by chemical, physical, or biological means to open up the structure of biomass. The major categories of biomass feedstock are given in Table 2.1.

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

Table 2.1 Major categories of biomass feedstocks

Forest products	Wood, logging residues, trees, shrubs and wood residues, sawdust, bark, etc.
Biorenewable wastes	Agricultural wastes, crop residues, mill wood wastes, urban wood wastes, urban organic wastes
Energy crops	Short-rotation woody crops, herbaceous woody crops, grasses, starch crops, sugar crops, forage crops, oilseed crops, switchgrass, miscanthus
Aquatic plants	Algae, water weed, water hyacinth, reed and rushes
Food crops	Grains, oil crops
Sugar crops	Sugar cane, sugar beets, molasses, sorghum
Landfill	Hazardous waste, non-hazardous waste, Inert waste, liquid waste
Organic wastes	Municipal solid waste, industrial organic wastes, municipal sewage and sludges
Algae	Prokaryotic algae, eukaryotic algae, kelps
Mosses	Bryophyta, polytrichales
Lichens	Crustose lichens, foliose lichens, fruticose lichen

reasons. First, it is a renewable resource that could be sustainably developed in the future. Second, it appears to have formidably positive environmental properties by reducing GHG emissions, possibly reducing NO_x and SO_x depending on the fossil fuels displaced. However, there are also negative impacts, such as the release of polycyclic aromatic hydrocarbons, 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 is a sustainable feedstock for chemicals and energy products that could potentially enhance the energy independence of the world. 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 noted that in comparison with solid fossil fuels, biomass contains much less carbon and more oxygen and has a low heating value. With higher oxygen content than fossil fuels, biomass feedstocks have fundamentally lower energy content. The maximum useful energy that can be theoretically extracted from biomass feedstock is its chemical exergy. Table 2.2 shows the elemental analyses and higher heating value (HHV) of biomass samples.

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., isopropanol, isobutanol, isopentanol). 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.

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 is 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 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, non-durable goods, containers and packaging, food scraps, yard trimmings, and miscellaneous inorganic wastes from residential, commercial, and industrial sources (Demirbas, 2004).

Forests are a principal global economic, as well as ecological, resource. Forests have played a big role in the development of human societies. The prime 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 per 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 (Demirbas, 2003). Figure 2.2 shows the use

Table 2.2 Elemental analyses (wt.%) and calorific values (HHV, MJ/kg) of biomass samples

Biomass sample	C	H	O	N	Ash	Higher heating value (MJ/kg)
Olive husk	50.0	6.2	42.2	1.6	3.6	19.0
Hazelnut shell	52.9	5.6	42.7	1.4	1.4	19.3
Hazelnut seedcoat	51.0	5.4	42.3	1.3	1.8	19.3
Softwood	52.1	6.1	41.0	0.2	1.7	20.0
Hardwood	48.6	6.2	41.1	0.4	2.7	18.8
Wheat straw	45.5	5.1	34.1	1.8	13.5	17.0
Wood bark	53.1	6.1	40.6	0.2	1.6	20.5
Waste material	48.3	5.7	45.3	0.7	4.5	17.1
Water hyacinth	39.8	5.0	34.3	1.9	19.0	14.6
Corn cob	49.0	5.4	44.6	0.4	1.0	18.4
Corn stover	45.1	6.0	43.1	0.9	4.9	17.4
Brown kelp	28.4	4.1	24.3	4.8	38.4	10.8
Tea waste	48.6	5.5	39.5	0.5	1.4	17.1
Bagasse	45.3	5.1	40.2	0.1	9.3	16.9
Spruce wood	51.9	6.1	40.9	0.3	1.5	20.1
Beech wood	49.5	6.2	41.2	0.4	1.4	19.2
Poplar wood	49.0	6.1	42.8	0.1	1.0	18.8
Ailanthus wood	49.5	6.2	41.0	0.3	1.7	19.0

of world wood products including lumber, plywood, paper and paperboard between the years 1970 and 2005. The availability of fuelwood from forests is continually declining at an ever-increasing rate due to indiscriminate deforestation and slow regeneration, as well as afforestation (Jain and Singh, 1999). 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).

Wood biomass involves trees with commercial structure and forest residues not being used in the traditional forest products industries. Available forest residues may appear to be an attractive fuel source. Collection and handling and transport costs are critical factors in the use of forest residues. Although the heat produced from wood wastes is less than that from oil or gas, its cost compared to fossil fuels makes it an attractive source of readily available heat or heat and power. The most

effective utilization of wood wastes, particularly in the saw milling and plywood industry, plays an important role in energy efficient production. Table 2.3 shows the sources of available forest and wood manufacturing residues. Wood preparation involves the conversion of roundwood logs into a form suitable for pulping and includes processes for debarking, chipping, screening, handling, and storage.

Forest residues typically refer to those parts of trees such as treetops, branches, small-diameter wood, stumps and dead wood as well as undergrowth and low-value species. The conversion of wood to biofuels and biochemicals has long been a goal of the forest products industry. Forest residues alone count for some 50% of the total forest biomass and are currently left in the forest to rot (Demirbas, 2001).

Agricultural residues, grasses, algae, kelps, lichens and mosses are also important biomass feedstocks in the world. Algae can grow practically in every place where there is enough sunshine. Some algae can 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). Microal-

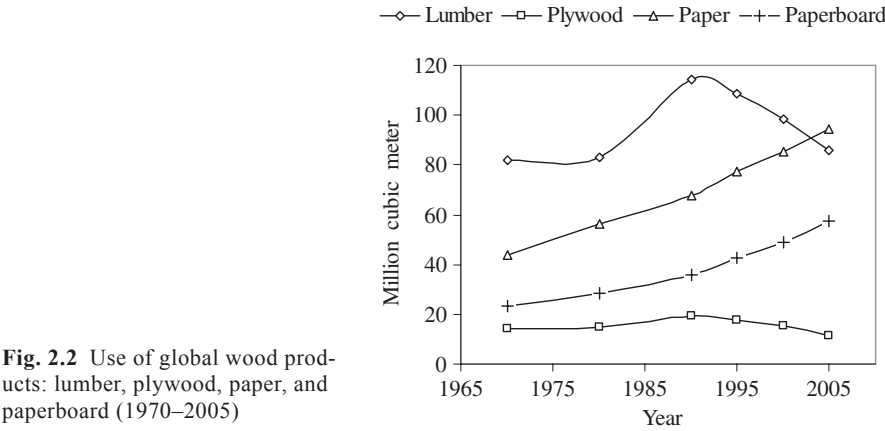


Fig. 2.2 Use of global wood products: lumber, plywood, paper, and paperboard (1970–2005)

Table 2.3 Sources of available forest and wood manufacturing residues

Source of residue	Type of residue
Forest operations	Branches, bark chips, leaves/needles, stumps, roots, and sawdust
Lumber production	Bark, sawdust, clippings, split wood
Saw milling	Bark, trimmings, split wood, sawdust, planer shavings, sander dust
Plywood production	Bark, sawdust, veneer clippings and wastes, panel trim, sander dust
Paper production	Slab chips, pulping reject, sawdust, clippings
Paperboard production	Bark, sawdust, screening fines, panel trim, sander dust

gae are the fastest growing photosynthesizing organisms. They can complete an entire growing cycle every few days. Approximately 46 tons of oil/hectare/year can be produced from diatom algae. Different algae species produce different amounts of oil. Some algae produce up to 50% oil by weight.

2.3 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 macromolecules. Three structural components are cellulose, hemicelluloses and lignin, which have rough formulae as $\text{CH}_{1.67}\text{O}_{0.83}$, $\text{CH}_{1.64}\text{O}_{0.78}$, and $\text{C}_{10}\text{H}_{11}\text{O}_{3.5}$, respectively.

The basic structure of all wood and woody biomass consists of cellulose, hemicelluloses, lignin and extractives. Their relative composition is shown in Table 2.4. 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.

Cellulose is a remarkable pure organic polymer, consisting solely of units of anhydroglucose held together in a giant straight-chain molecule. 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.

By forming intramolecular and intermolecular hydrogen bonds between OH groups within the same cellulose chain and the surrounding cellulose chains, the chains tend to be arranged in parallel and form a crystalline supermolecular structure. Then, bundles of linear cellulose chains (in the longitudinal direction) form a microfibril which is oriented in the cell wall structure. Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis (Demirbas, 2008b).

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

Table 2.4 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

or swellable in water. Hemicelluloses (arabinoglycuroxylan and galactoglucomannans) are related to plant gums in composition, and occur in much shorter molecular 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 (Demirbas, 2008b).

Among the most important sugar of the hemicelluloses component is xylose. In hardwood xylan, the backbone chain consists of xylose units which are linked by β -(1,4)-glycosidic bonds and branched by α -(1,2)-glycosidic bonds with 4-O-methylglucuronic acid groups. In addition, O-acetyl groups sometime replace the OH groups in position C₂ and C₃. For softwood xylan, the acetyl groups are fewer in the backbone chain. However, softwood xylan has additional branches consisting of arabinofuranose units linked by α -(1,3)-glycosidic bonds to the backbone. Hemicelluloses are largely soluble in alkali and, as such, are more easily hydrolyzed (Demirbas, 2008b).

Lignins are polymers of aromatic compounds. Their functions are to provide structural strength, provide sealing of the water-conducting system that links roots with leaves, and protect plants against degradation. Lignin is a macromolecule, which consists of alkylphenols and has a complex three-dimensional structure. Lignin is covalently linked with xylans in the case of hardwoods and with galactoglucomannans in softwoods. The basic chemical phenylpropane units of lignin (primarily syringyl, guaiacyl and p-hydroxy phenol) as shown in Fig. 2.3 are bonded together by a set of linkages to form a very complex matrix. This matrix comprises a variety of functional groups, such as hydroxyl, methoxyl and carbonyl, which impart a high polarity to the lignin macromolecule (Demirbas, 2008b).

Pyrolysis of lignin, e.g., during combustion, yields a wide 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

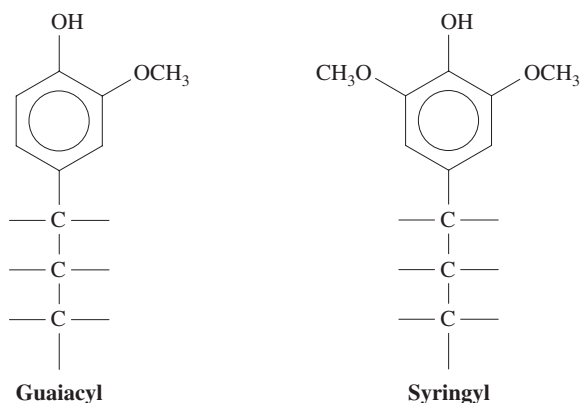


Fig. 2.3 Schematic illustration of building units of lignin

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 glucosides are transported through the cell membrane to the apoplast. The glucose is then removed and the monolignols are polymerized into lignin. Four main monolignols in the lignin structure are given in Fig. 2.4.

Wood and woody biomass also contain lesser amounts of tannins, simple sugars, starches, pectins and organic soluble extractives. Extractives are the organic substances which have low molecular weight and are soluble in neutral solvents. Extractives include terpenes, tall oil and the fatty acids, esters, and triglycerides, which contribute to paper mill pitch problems. Resin (combination of the following components: terpenes, lignans and other aromatics), fats, waxes, fatty acids and alcohols, terpenes, tannins and flavonoids are categorized as extractives.

Biomass has some advantageous chemical properties for use in current energy conversion systems. Compared to other carbon-based fuels, it has low ash content and high reactivity. 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.

The compositions of biomass among fuel types are considerably varied, especially with respect to inorganic constituents important to the critical problems of fouling and slagging. Alkali and alkaline earth metals, in combination with other fuel elements such as silica and sulfur, and facilitated by the presence of chlorine, are responsible for many undesirable reactions in combustion furnaces and power boilers.

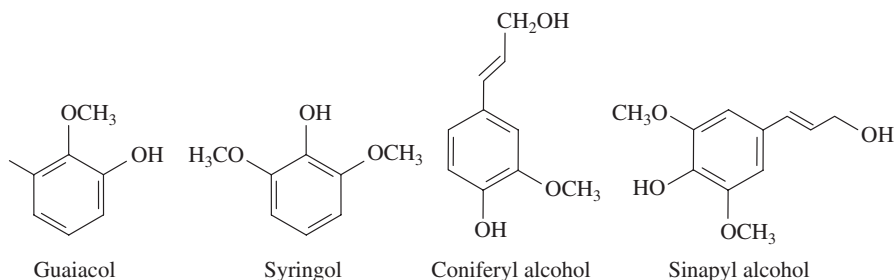


Fig. 2.4 Four main monolignols in the lignin structure

2.4 Production of Fuels from Wood Sources

Biomass includes 60% wood and 40% non-wood materials. The conversion of wood into biofuels and biochemicals is technically feasible. Wood valorization processes include fractionation, liquefaction, pyrolysis, hydrolysis, fermentation and gasification. Fast pyrolysis utilizes wood biomass to produce a product that is used both as an energy source and a feedstock for chemical production. The bio-oils from wood pyrolysis were composed of a range of cyclopentanone, methoxyphenol, acetic acid, methanol, acetone, furfural, phenol, formic acid, levoglucosan, guaiacol and their alkylated phenol derivatives. When wood is rapidly heated in a reduced oxygen environment, the feeding material does not combust but rather becomes a synthetic gas (syngas), a combination of hydrogen (H_2) and carbon monoxide (CO). Wood can be converted by hydrolysis into sugars and subsequently fermentation of sugars.

The wood pyrolysis is attractive because forest and industrial wood residues can be readily converted into liquid products. These liquids, as crude bio-oil or slurry of charcoal of water or oil, have advantages in transport, storage, combustion, retrofitting and flexibility in production and marketing (Demirbas, 2007). In the first step of pyrolysis of carbohydrates dehydration occurs and at low temperatures dehydration predominates. Dehydration is also known as a char-forming reaction. Between 550 and 675 K volatile products, tar, and char are formed. The volatile products are CO_2 , CO, H_2O , acetals, furfural, aldehydes and ketones. Levoglucosan is the principle component in tar.

Gasification is carried out at high temperatures in order to optimize the gas production. Most wood gasification systems utilize air or oxygen in partial oxidation or combustion processes. The resulting gas, known as producer gas, is a mixture of carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen. As mentioned above, when wood is rapidly heated in a reduced oxygen environment, the feeding material becomes a synthetic gas (syngas), a combination of H_2 and CO. Syngas can be combusted directly in a boiler or used in a gas turbine to generate electricity. The hydrogen from syngas can be isolated and used to power fuel cells. Syngas has the potential to produce a wide range of commercial fuels and chemicals, including synthetic diesel, methanol and lower carbon alcohols, acetic acid, dimethyl ether, etc. (Demirbas, 2000).

2.5 Production of Fuels from Crops

Biofuels such as liquid fuels, bio-oil and biochar, and biogas can be produced from crops. Agriculture-based liquid biofuels include bioethanol, biodiesel, biomethanol, methane, and bio-oil components. Various agricultural residues such as grain dust, crop residues, and fruit tree residues are available as the sources of agricultural energy. Bioenergy from biomass, both residues and energy crops, can be con-

verted into modern energy carriers. Bioethanol is derived from renewable source feedstocks; typically plants such as wheat, sugar beet, corn, straw and wood. Biodiesel is a non-fossil fuel alternative to petrodiesel, which can be obtained from vegetable oil and animal fats by transesterification. 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.

2.5.1 Fuels from Cereal Crops

Biofuels such as bioethanol and biodiesel originate from cereal crops such as plant oils, and sugar beets. Today the production cost of bioethanol cereal crops is still too high, which is the major reason why bioethanol has not made its breakthrough as a fuel source yet. When producing bioethanol from maize or sugar cane the raw material constitutes about 40–70% of the production cost.

Feedstock for bioethanol is essentially comprised of sugar cane and sugar beet. The two are produced in geographically distinct regions. Sugar cane is grown in tropical and subtropical countries, while sugar beet is only grown in temperate climate countries.

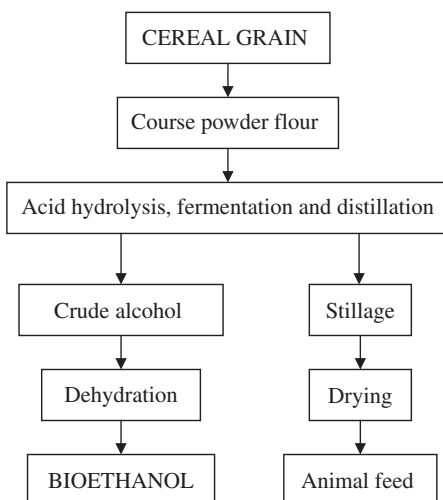
In European countries, beet molasses are the most utilized sucrose-containing feedstock. Sugar beet crops are grown in most of the EU-25 countries, and yield substantially more ethanol per hectare than wheat. The advantages with sugar beet are a lower cycle of crop production, higher yield, and high tolerance of a wide range of climatic variations, low water and fertilizer requirement. Sweet sorghum is one of the most drought resistant agricultural crops as it has the capability to remain dormant during the driest periods.

Another type of feedstock, which can be used for bioethanol production, are starch-based materials. Starch is a biopolymer and is defined as a homopolymer consisting of only one monomer, D-glucose. To produce bioethanol from starch it is necessary to break down the chains of this carbohydrate for obtaining glucose syrup, which can be converted into ethanol by yeasts. The single greatest cost in the production of bioethanol from corn, and the cost with the greatest variability, is the cost of the corn. Figure 2.5 shows the flow chart for the production of bioethanol from cereal grain or straw.

Bioethanol can be produced from a large variety of carbohydrates with a general formula of $(\text{CH}_2\text{O})_n$. Chemical reaction is composed of enzymatic hydrolysis of sucrose followed by fermentation of simple sugars. Fermentation of sucrose is performed using commercial yeast such as *Saccharomyces cerevisiae*. First, invertase enzyme in the yeast catalyzes the hydrolysis of sucrose to convert it into glucose and fructose.



Fig. 2.5 Flow chart for the production bioethanol from cereal grain



Second, zymase, another enzyme also present in the yeast, converts the glucose and the fructose into ethanol.



Glucosylase enzyme converts the starch into D-glucose. The enzymatic hydrolysis is then followed by fermentation, distillation and dehydration to yield anhydrous bioethanol. Corn (60–70% starch) is the dominant feedstock in the starch-to-bioethanol industry worldwide.

Lignocellulosic perennial crops (e.g., short-rotation coppices and grasses) are a promising feedstock because of high yields, low costs, good suitability for low-quality land (which is more easily available for energy crops), and the low environmental impacts.

2.5.2 Fuels from Non-Cereal Crops

Agricultural residues such as straws, nut shells, fruit shells, fruit seeds, plant stalks, green leaves and molasses are potential renewable energy resources.

A methane digester system, commonly referred to as an anaerobic digester is a device that promotes the decomposition of manure or digestion of the organics in manure to simple organics and gaseous biogas products. Several types of biodigesters have been developed including the floating drum, the fixed dome, the bag, the plastic tube (Beteta, 1995), the plug flow and the up-flow anaerobic sludge blanket digesters. Figure 2.6 shows an on-farm biogas system.

The following describes the process of manure and straw mixture digestion. For the first 3 days, the methane yield is almost 0% and carbon dioxide generation is roughly 100%. In this period, digestion occurs as aerobic fermentation to carbon

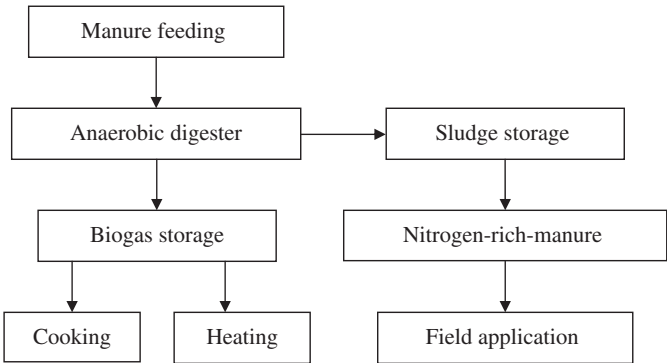


Fig. 2.6 An on-farm biogas system

dioxide. The yields of methane and carbon dioxide gases are then 50-50 on the eleventh day. At the end of the twentieth day, 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 a 30-day digestion period, approximately 80–85% of the biogas is produced in the first 15–18 days. This implies that the digester retention time can be designed to be 15–18 days instead of 30 days.

Anaerobic digestion yields of the slurries are given in Table 2.5. Due to the higher proportion of lipids in manure, the methane production is higher than in wheat straw. The total amounts of lipid and protein, in particular, are lower in straw than in manure and thus the theoretical methane yield is significantly lower in wheat straw than in manure (Table 2.5). The average methane yields of manure and wheat straw were 14.7% and 10.4% of volatile solids, respectively (Demirbas and Ozturk, 2004).

Table 2.5 Anaerobic digestion yields of the slurries

Run	Inoculated solution (ml)	Manure (g)	Straw (g)	Volatile solids (wt.%)	Biogas yield (wt.% of VS)	Methane yield (wt.% of VS)
1	930	280	0	89.2	29.8	14.7
2	960	0	294	81.3	21.6	10.4
3	945	143	144	85.3	26.8	12.9
4	900	90	180	83.4	24.0	11.9
5	927	185	93	85.7	27.6	14.2
6	936	70	210	82.9	23.5	11.5
7	942	214	72	88.3	28.4	14.0

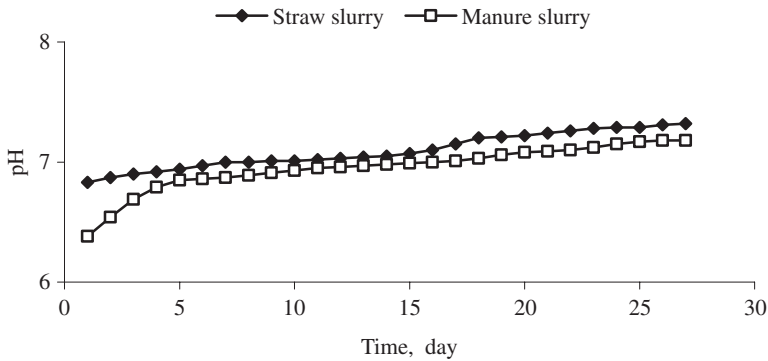


Fig. 2.7 The pH values plotted against time for wheat straw and manure slurries

Figure 2.7 shows pH values plotted against time for wheat straw and manure slurries. The pH value of slurry is a sensitive parameter for the digestion rate. 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 was around 7.0–7.1 at the maximum methane production rate. Digester pH increased to its neutral value (6.9–7.1) due to the process stability and the optimal activity of methanogenic bacteria (Demirbas and Ozturk, 2004).

When the pyrolysis temperature increased the biochar yield decreased. The biochar yield increased with increasing particle size of the sample. The yield of bio-oil from pyrolysis of the samples increased with temperature. Anaerobic biogas production is an effective process for conversion of a broad variety of agricultural biomass to methane to substitute natural gas and medium calorific value gases.

Pyrolysis of agricultural residues can be used for the production of bio-oil if flash pyrolysis processes are used. Production of this type is currently in the pilot stage (EUREC Agency, 1996). Some problems in the conversion process and use of the oil need to be overcome; these include poor thermal stability and corrosivity of the oil. Upgrading by lowering the oxygen content and removing alkalis by means of hydrogenation and catalytic cracking of the oil may be required for certain applications. Table 2.6 shows the yields of pyrolysis liquid products from hazelnut shell, tea waste, and tobacco stalk samples at different temperatures. As seen in Table 2.6, the yields of liquid products for the samples increased with increasing temperature

Table 2.6 Yields of bio-oil by pyrolysis from agricultural residues at different temperatures (K)

Sample	675	725	775	825	875	925	975	1050
Hazelnut shell	38.0	39.5	40.4	41.9	42.2	41.0	39.2	38.5
Tea waste	34.9	35.8	36.0	36.2	38.0	37.0	35.5	33.4
Tobacco stalk	41.0	41.8	43.0	40.2	40.0	40.6	37.3	36.8

from 675 to 875 K and then decreased. The maximum liquid yields from the hazelnut shell, tea waste, tobacco stalk, and yellow pine samples were 42.2%, 38.0%, and 43.0%, respectively (Güllü, 2003).

2.5.3 Fuels from Energy Crops

The term “energy crop” can be used both for biomass crops that simply provide high output of biomass per hectare for low inputs, and for those that provide specific products that can be converted into other biofuels such as sugar or starch for bioethanol by fermentation, or into vegetable oil for biodiesel by transesterification.

Energy crops such as short-rotation woody crops, herbaceous woody crops, grasses, starch crops, sugar crops, forage crops, oilseed crops, switchgrass, and miscanthus can be converted to liquid biofuels by thermochemical and biochemical conversion processes.

Energy crops can be divided into short-rotation energy crops that are harvested on a cycle of anything from 2 to 20 years, depending on the crop and the system, and herbaceous energy crops that are harvested annually. Herbaceous energy crops such as the woody, perennial, rhizomatous grasses like miscanthus offer the advantage of an annual harvest, though typically establishment costs are high. All crops, including some biennial, permanent and multiannual crops, are produced for energy purposes. Energy is generated by burning plants grown for the purpose, often after the dry matter is pelletized. Energy crops are used for firing power plants, either alone or co-fired with other fuels. Alternatively they may be used for heat or combined heat and power (CHP) production.

Biogas plants can be directly supplemented with energy crops. European production of biodiesel from energy crops has grown steadily in the last decade, principally focused on rapeseed used for oil and energy. In the United States, biodiesel is being made from soybean oil because more soybean oil is produced than all other sources of fats and oil combined. There are many candidates for feedstocks, including recycled cooking oils, animal fats, and a variety of other oilseed crops. The European Union accounted for nearly 89% of all biodiesel production worldwide in 2005. By 2010, the United States is expected to become the world’s largest single biodiesel market, accounting for roughly 18% of world biodiesel consumption, followed by Germany.

Switchgrass is a perennial grass native to North America. Switchgrass makes for a great energy crop because it grows fast, capturing lots of solar energy and turning it into chemical energy, which is stored as cellulose. Switchgrass reaches its full yield potential after the third year planted, producing approximately 6 to 8 tons per acre; that is 500 gallons of ethanol per acre.

Miscanthus is a tall perennial grass that has been evaluated in Europe during the past 5 to 10 years as a new bioenergy crop. Like other energy crops, the harvested stems of miscanthus may be used as fuel for production of heat and electric power, or for conversion to other useful products such as ethanol.

Sweet sorghum can be considered as an energy crop, because it can be grown in all continents, in tropical, subtropical, temperate regions as well as in poor quality soils. Sweet sorghum is a warm-season crop that matures earlier under high temperatures and short days. Sweet sorghum is an extraordinarily promising multifunctional crop not only for its high economic value but also for its capacity to provide a very wide range of renewable energy products, industrial commodities, food and animal feed products. Sweet sorghum biomass is rich in readily fermentable sugars and thus it can be considered an excellent raw material for fermentative hydrogen production. Integrated production of several crops (sweet sorghum/sugar cane/sweet sorghum corn/sweet potatoes, etc.) and simultaneous processing of the full crop components (starch, sugar, lignocellulosic) can improve the global economics of bioenergy schemes considerably in view of a viable production of bioethanol.

Summary

Biomass refers to the non-fossilized and biodegradable organic material that originates from plants, animals and microorganisms. Biomass is the world's fourth largest energy source, 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 positive environmental properties, for example, reducing greenhouse gas emissions, possibly reducing NO_x and SO_x depending on the fossil fuels displaced. Third, it appears to have significant economic potential provided that fossil fuel prices increase in the future.

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 macromolecules. Three structural components are cellulose, hemicelluloses and lignin, which have rough formulae as $\text{CH}_{1.67}\text{O}_{0.83}$, $\text{CH}_{1.64}\text{O}_{0.78}$, and $\text{C}_{10}\text{H}_{11}\text{O}_{3.5}$, respectively.

Biomass includes 60% wood and 40% non-wood materials. The conversion of wood into biofuels and biochemicals is technically feasible. Wood valorization processes include fractionation, liquefaction, pyrolysis, hydrolysis, fermentation and gasification.

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