

## Chapter 2

# Biomass Feedstocks

### 2.1 Introduction to Biomass Feedstocks

In the most biomass-intensive scenario, modernized biomass energy will by 2050 contribute about one half of total energy demand in developing countries (IPCC, 1997). The biomass intensive future energy supply scenario includes 385 million hectares of biomass energy plantations globally in 2050 with three quarters of this area established in developing countries (Karthi and Larson, 2000). Various scenarios have put forward estimates of biofuel from biomass sources in the future energy system. The availability of the resources is an important factor in the co-generative use of biofuel in the electricity, heat or liquid fuel market.

Biomass is a generic term for all vegetable material. It is generally a term for material derived from growing plants or from animal manure. Biomass has a unique characteristic compared with other forms of renewable energy: it can take various forms such as liquids, gases, and solids, and so can be used for electricity or mechanical power generation and heat. If biomass could be converted into useful energy, the consumption of fossil fuel and greenhouse gas emissions would be decreased. Furthermore, the use of biomass could lead to the creation of a new biomass industry, which would help revitalize agriculture and forestry, leading to social stability as well as economic stimulus (Saga *et al.*, 2008).

The first biomass sources used on Earth were wood and dry grass, and for a long time these were used for cooking and heating. 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 those having limited sources of energy (Karaosmanoglu and Aksoy, 1988).

In the last decade, there has been rapid progress in the biofuel marketing trend. This has increased production capacity, international material flows, competition with conventional agriculture, competition with forest industries, and international

trade flows. In turn, this has led to a 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. It can be burned to produce heat and electricity, changed to gas-like fuels such as methane, hydrogen and carbon monoxide or 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 may 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 (Tewfik, 2004).

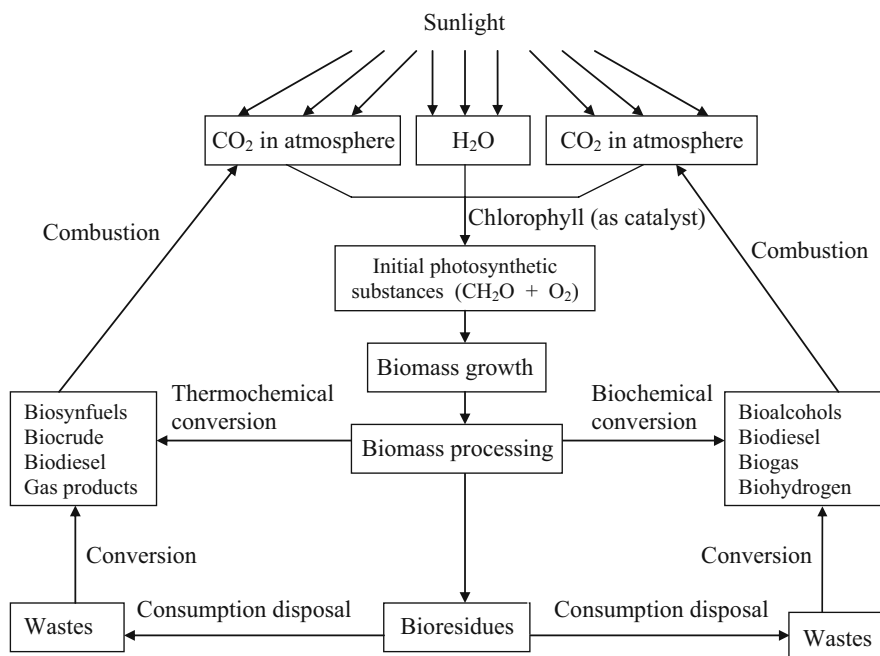
### 2.1.1 Definitions

The term biomass (Greek, bio, life + maza or mass) refers to non-fossilized and biodegradable organic material originating from plants, animals, and microorganisms derived from biological sources. 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. Biomass residues mean biomass byproducts, residues and waste streams from agriculture, forestry, and related industries.

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. Biomass as the solar energy stored in chemical form in plant and animal materials is among the most precious and versatile resources on Earth. It is a rather simple term for all organic materials that stem from plants, trees, crops and algae.

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. Figure 2.1 shows the carbon cycle, photosynthesis, and main steps of biomass technologies.

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



**Fig. 2.1** Carbon cycle, photosynthesis, and main steps of biomass technologies

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 a carbon fixation reaction by 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 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<sub>2</sub> to carbohydrates by the primary hydrogen acceptor. The light energy required for photosynthesis is used to drive the H atoms against the potential gradient.

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 that 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).

### 2.1.1.1 Biomass Components

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 the rough formulae  $\text{CH}_{1.67}\text{O}_{0.83}$ ,  $\text{CH}_{1.64}\text{O}_{0.78}$ , and  $\text{C}_{10}\text{H}_{11}\text{O}_{3.5}$ , respectively.

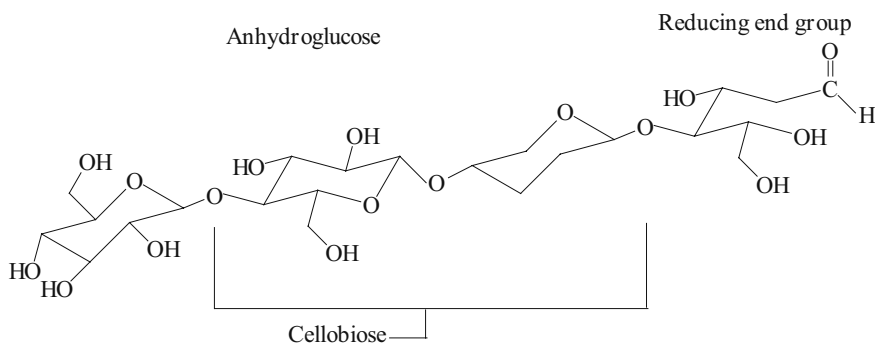
The basic structure of all wood and woody biomass consists of cellulose, hemicelluloses, lignin, and extractives. Their relative composition is shown in Table 2.1. Softwoods and hardwoods differ greatly in wood structure and composition. Hardwoods contain a greater fraction of vessels and parenchyma 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.

Cellulose is a linear polymer composed of repeating anhydroglucose units. Cellulose is a remarkably 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  $\beta$ -(1,4)-glycosidic linkages. Due to this linkage, cellobiose is established as the repeat unit for cellulose chains (Fig. 2.2). 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 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 (Hashem *et al.*, 2007). Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis.

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

**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



**Fig. 2.2** The structure of cellulose. Anhydroglucose is the monomer of cellulose, cellobiose is the dimer

Source: Demirbas, 2008b

hexose monosaccharides. Hemicelluloses tend to be much shorter in length than cellulose, and the molecular structure is slightly branched.

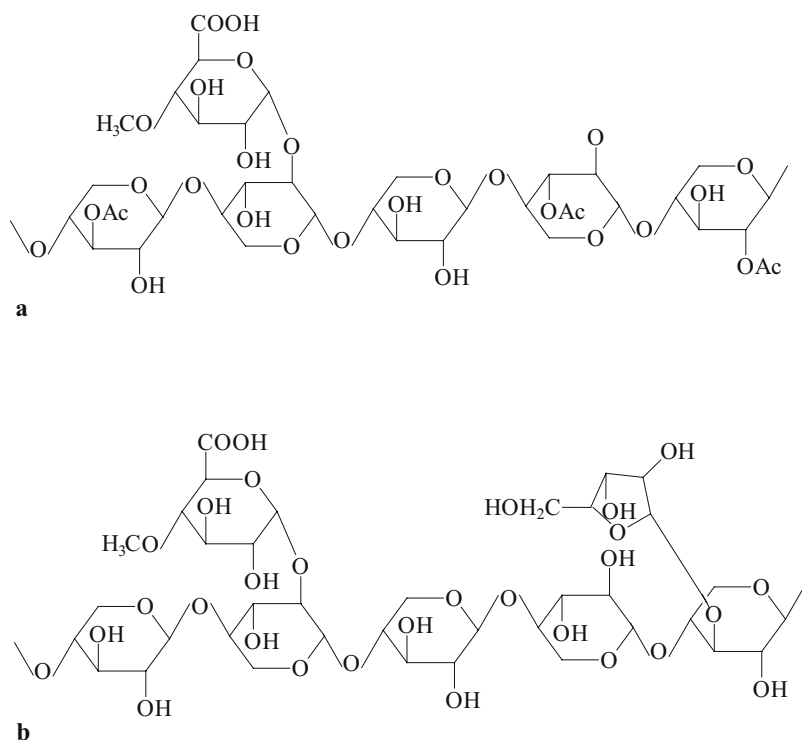
Unlike cellulose, hemicelluloses consist of different monosaccharide units. In addition, the polymer chains of hemicelluloses have short branches and are amorphous. Because of the amorphous morphology, hemicelluloses are partially soluble or swellable in water. Hemicelluloses (arabinoglycuronoxylan and galactoglucanans) 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).

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  $\beta$ -(1,4)-glycosidic bonds and branched by  $\alpha$ -(1,2)-glycosidic bonds with 4-O-methylglucuronic acid groups (Hashem *et al.*, 2007). In addition, O-acetyl groups sometime replace the OH groups in position  $C_2$  and  $C_3$  (Fig. 2.3a). For softwood xylan, the acetyl groups are fewer in the backbone chain. However, softwood xylan has additional branches consisting of arabinofuranose units linked by  $\alpha$ -(1,3)-glycosidic bonds to the backbone (Fig. 2.3b). Hemicelluloses are largely soluble in alkali and, as such, are more easily hydrolyzed (Timell, 1967; Wenzl *et al.*, 1970; Goldstein, 1981).

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 empiric chemical formula of lignin is  $\text{C}_{20}\text{H}_{19}\text{O}_{14}\text{N}_2$ . 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 that appear to repeat in 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 crosslinking of polysaccharides by lignin is an obstacle for water absorption to the cell wall. Thus, lignin makes it possible for plants to form vascular systems that conduct water efficiently. Lignin is present in all vascular plants, but not in bryophytes, which supports 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 a water conducting system that links roots with leaves, and protect plants against degradation (Glasser and Sarkanen, 1989). 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 the case of softwoods (Sarkanen and



**Fig. 2.3** Schematic illustration of xylans: **a** Partial xylan structure from hardwood and **b** Partial xylan structure from softwood

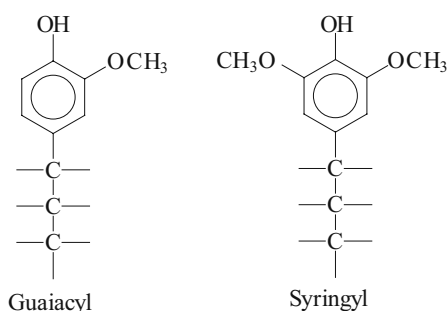
Source: Demirbas, 2008b

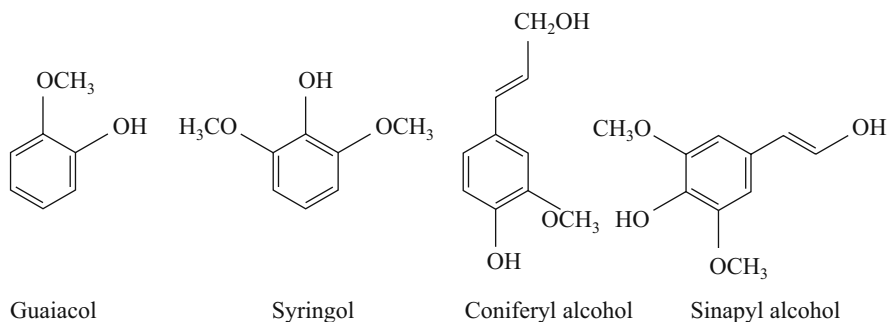
Ludwig, 1971). The basic chemical phenylpropane units of lignin (primarily syringyl, guaiacyl and p-hydroxy phenol) as shown in Fig. 2.4 are bonded together by a set of linkages to form a very complex matrix. This matrix comprises a variety of functional groups, such as hydroxyl, methoxyl and carbonyl, which impart a high polarity to the lignin macromolecule (Demirbas and Kucuk, 1993; Hashem *et al.*, 2007). Cellulose and lignin structures have been investigated extensively in earlier studies (Young, 1986; Hergert and Pye, 1992; Mantanis *et al.*, 1995; Bridgwater, 2003; Garcia-Valls and Hatton, 2003; Mohan *et al.*, 2006).

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 consist almost entirely 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 other 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. 2.5.

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).

**Fig. 2.4** Schematic illustration of building units of lignin  
Source: Demirbas, 2008b





**Fig. 2.5** The four main monolignols in the lignin structure

### 2.1.1.2 Modern Biomass, Bioenergy, and Green Energy

The term “modern biomass” is generally used to describe traditional biomass use through efficient and clean combustion technologies and sustained supply of biomass resources, environmentally sound and competitive fuels, and heat and electricity using modern conversion technologies. Modern biomass produced in a sustainable way excludes traditional uses of biomass as fuel-wood 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). Modern biomass excludes traditional uses of biomass as fuelwood and includes electricity generation and heat production from agricultural and forest residues and solid waste.

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) offer 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. Bioenergy is an inclusive term for all forms of biomass and biofuels. Biomass is renewable organic matter like crops, plant wastes, forest wood byproducts, aquatic plants, manure, and organic municipal wastes.

Bioenergy is one of the forms of renewable energy. It has been used bioenergy, the energy from biomass, 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 that is 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 in 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 and can be derived from renewable energy sources. The environmental advantages of the production and use of green electricity by using green electrons 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 power (Murphy and Niituma, 1999). Green power products have become widespread in many electricity markets worldwide which can be derived from renewable energy sources. There has been interest in electricity from renewable sources named green electricity or green pools as a special market (Elliott, 1999). The term green energy is also used for green energy produced from cogeneration, energy from municipal waste, natural gas, and even conventional energy sources. Green power refers to electricity supplied from more readily renewable energy sources than traditional electrical power sources. The environmental advantages of the production and use of green electricity seem to be clear. The use of green energy sources like hydro, biomass, geothermal, and wind energy in electricity production reduces CO<sub>2</sub> emissions (Fridleifsson, 2003). Emissions such as SO<sub>2</sub>, CO<sub>2</sub> and NO<sub>x</sub> are reduced considerably, and the production and use of green electricity contributes to diminishing the green house effect (Arkesteijn and Oerlemans, 2005).

In general, a sustainable energy system includes energy efficiency, energy reliability, energy flexibility, energy development and continuity, combined heat and power (CHP) or cogeneration, 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). Because, by definition, sustainable energy systems must support both hu-

man and ecosystem health over the long term, goals on tolerable emissions should look well into the future. They should also take into account the public's tendency to demand more (UNDP, 2000).

### **2.1.2 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. Biobased 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, bark, *etc.*
2. Biorenewable wastes:
  - Agricultural wastes
  - Crop residues
  - Mill wood wastes
  - Urban wood wastes
  - Urban organic 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, kelps, lichens and mosses.

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 may be sustainably developed in the future. Second, it appears to have formidably positive environmental properties, reduced GHG emissions, possibly reduced NO<sub>x</sub> and SO<sub>x</sub> depending on the fossil-fuels displaced. However, also negative impacts, such as polycyclic aromatic hydrocarbons including 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 will increase in the future.

Biomass is a sustainable feedstock for chemicals and energy products. Biomass feedstocks are more evenly distributed in 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 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.*, 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. Pulp and paper wastes may also be treated to produce methane. The contents of domestic solid waste are given in Table 2.2.

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

**Table 2.2** Contents of domestic solid waste (percentage 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

*Source:* Demirbas, 2004

of the future due to its large potential, economic viability and various social and environmental benefits. It was estimated that by 2050 biomass may 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 principal global economic as well as ecological resource. 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 (Demirbas, 2003). Figure 2.6 shows the use of world wood products; lumber, plywood, paper paperboard between 1970 and 2005. 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 (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 sawmilling and plywood industry, plays an important role in energy efficient production.

**Fig. 2.6** Use of world wood products: lumber, plywood, paper, and paperboard (1970–2005)

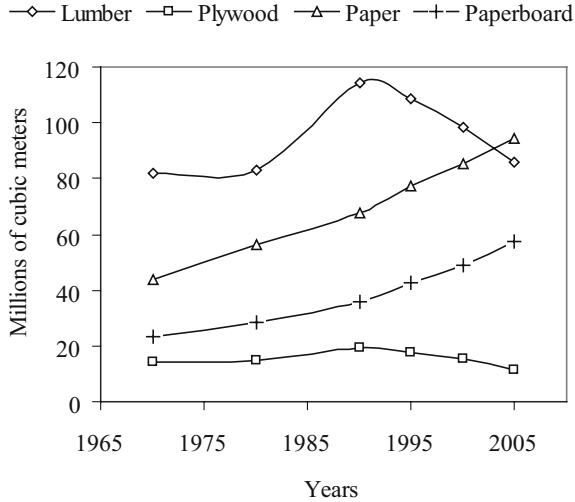


Table 2.3 shows the sources of available forest and wood manufacturing residues. Wood preparation involves the conversion of roundwood logs into a form suitable for pulping and includes processes for debarking, chipping, screening, handling, and storage.

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).

The importance of biomass in different world regions is given in Table 2.4. 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. As shown in Table 2.4, the importance of biomass varies significantly across regions. In Europe, North America, and the Middle East, the share of biomass averages 2–3% of total final energy consumption, whereas in Africa, Asia and Latin Amer-

**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

**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

ica, which together account for three-quarters of the world's population, biomass provides a substantial share of the energy needs: one-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 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). Microalgae 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.

## 2.2 Biomass Characterization

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.

The macroscopic properties of biomass are given for macroscopic analysis, such as ultimate analysis, heating value, moisture content, particle size, bulk density, and ash fusion temperature. 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 Characterization of Biomass Feedstock and Products**

Heterogeneity is an inherent characteristic of biomass materials. Since variability of any biomass cannot be controlled, processes that use biomass feedstocks must be able to monitor the chemical composition of the feedstock and compensate for variability during processing. Chemical changes during the processing of biomass must also be monitored to ensure that the process maintains a steady state in spite of the feedstock variability. Finally, process residues and products must be evaluated to assess overall process economics.

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.

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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 (Demirbas, 2004).

Current methods for chemical characterization of biomass feedstocks, process intermediates, and residues are not applicable in a commercial setting because they are very expensive and cannot provide analysis information in a time frame useful for process control.

### ***2.2.2 Biomass Process Design and Development***

Biomass process design and development requires acquiring the information needed to understand and characterize the fundamental chemical and physical processes that govern biomass conversion at high temperatures and pressures. The models can be used to determine operating conditions that optimize thermal efficiency and to examine design strategies for integrating combined cycles for the production of synthesis gas and electric power with minimum impact on the environment. Biomass gasification and pyrolysis both require precise characterization of the breakdown products being generated, so that processes can be fine-tuned to produce optimal end products.

Near-infrared spectrometry correlated by multi-variate analysis characterizes in minutes what would otherwise require three or four days and cost far more. Opportunities for use in the lumber and paper industries, let alone biorefineries, are almost limitless. Modern biotechnology can not only transform materials extracted from plants, but can transform the plants to produce more valuable materials. Plants can be developed to produce high-value chemicals in greater quantity than they do naturally, or even to produce compounds they do not naturally produce.

The syngas obtained from the processes can be used to produce hydrogen which, in turn, can be used as a fuel or to make plastics, fertilizers, and a wide variety of other products. The syngas can also be converted to sulfur-free liquid transportation fuels using a catalytic process (known as the Fischer–Tropsch Synthesis), or provide base chemicals for producing biobased products.

If biomass is heated to high temperatures in the total absence of oxygen, it pyrolyzes to a liquid that is oxygenated, but otherwise has similar characteristics to petroleum. This pyrolysis oil or bio-oil can be burned to generate electricity or it can be used to provide base chemicals for biobased products. As an example, phenolic compounds can be extracted from bio-oil to make adhesives and plastic resins.

Plant and animal fats and oils are long hydrocarbon chains, as are their fossil-fuel counterparts. Fatty acid methyl esters from transesterification of the fats and oils directly convert to substitutes for petroleum diesel. Known as biodiesel, it



differs primarily in containing oxygen, so it burns more cleanly, either by itself or as an additive. Biodiesel use is small but growing rapidly in the United States. It is made mostly from soybean oil and used cooking oil. Soybean meal, the coproduct of oil extraction is now used primarily as animal feed, but could also be a base for making biobased products. Glycerin is already used to make a variety of products.

Another way to convert waste biomass into useful fuels and products is to have natural consortiums of anaerobic microorganisms decompose the material in closed systems. Anaerobic microorganisms digest organic material in the absence of oxygen and produce biogas as a waste product.

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.

In previous studies, the mechanisms of degradation by direct pyrolysis and cracking as well as catalytic, and liquefaction of biomass were not extensively identified (Demirbas, 2002). The reactions in biomass degradation process are much more complex. Many researchers have tried to investigate and propose reaction mechanisms but no definitive study has been conducted. These proposed reactions are general and the type of biomass will dictate the type of processes or reactions required to breakdown and rearrange molecules. The more complex the raw biomass is chemically, the more complex the reaction mechanisms required, and thus the increased difficulty in determining them (Balat, 2008a–c).

It is difficult to determine exactly what types of reactions occur during thermochemical conversion processes. The processes of carbonaceous materials take place through a sequence of structural and chemical changes that involve at least the following steps.

New techniques are needed to provide analytical support for large-scale processes that convert biomass to fuels and chemicals. One solution is to use established methods to calibrate rapid, inexpensive spectroscopic techniques, which can then be used for feedstock and process analysis. A complete chemical characterization is available in a time frame relevant for process control, meaning that the information can be used to make the process adjustments necessary for steady-state production. Process monitoring is one possible application of these rapid analytical techniques. The new techniques for biomass analysis can support and improve research by providing levels of information that would have been too costly to pursue using traditional wet chemical methods.

## 2.3 Biomass Fuel Analyses

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

### **2.3.1 Particle Size and Specific Gravity**

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.

### **2.3.2 Ash Content**

Ash or inorganic materials in plants depend 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 soft woods 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).

### **2.3.3 Moisture Content**

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%. The heating value of a wood fuel decreases with an increase in the moisture content of the wood. The 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 K and 702 K (Demirbas, 2004).

### **2.3.4 Extractive Content**

Again the heat content, which is a very important factor affecting utilization of any material as a fuel, is affected by the proportion of combustible organic com-

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

### ***2.3.5 Element Content***

Both the chemical and the physical composition of the fuel are important determining factors in the characteristics of combustion. Biomass can be analyzed by breaking it down into structural components (called proximate analysis) or into chemical elements (called 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.

### ***2.3.6 Structural Constituent 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 with increasing their lignin contents. In general, the FC content of wood fuels increases with increase in their FC contents.

### ***2.3.7 The Energy Value of Biomass***

Again the heat content, which is a very important factor affecting utilization of any material as a fuel, is affected by the proportion of combustible organic components (called extractives) present in it. The 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 important parameter directly affecting the heating value. High extractive content of a plant part makes it desirable as fuel. Again the heat content, which is a very important factor affecting utilization of any material as a fuel, is affected by the proportion of extractives present in it.

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breaking it down into structural components (called proximate analysis) or into chemical elements (called 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.

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 MJ/kg) of the biomass fuels as a function of fixed carbon (FC, wt%) was calculated from Eq. 2.1 (Demirbas, 1997):

$$\text{HHV} = 0.196 (\text{FC}) + 14.119 \quad (2.1)$$

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, HHV was calculated using the modified Dulong's formula, as a function of the carbon, hydrogen, oxygen, and nitrogen contents from Eq. 2.2:

$$\text{HHV} = 0.335 (\text{CC}) + 1.423 (\text{HC}) - 0.154 (\text{OC}) - 0.145 (\text{NC}) \quad (2.2)$$

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

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.

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 was

$$\text{HHV} = 0.0889 (\text{LC}) + 16.8218 \quad (2.3)$$

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

Table 2.5 shows moisture, ash, and higher heating value (HHV) analysis of biomass fuels.

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.

**Table 2.5** Moisture, ash, and higher heating value (HHV) analysis of biomass fuels

Fuel common/scientific name	Moisture (wt% of fuel)	Ash (wt% of dry fuel)	HHV (MJ/kg, daf)
Almond shells/ <i>Pranus dulcis</i>	7.5	2.9	19.8
Almond hulls/ <i>Pranus dulcis</i>	8.0	5.8	20.0
Beech wood/ <i>Fagus orientalis</i>	6.5	0.6	19.6
Hazelnut shells/ <i>Corylus avellena</i>	7.2	1.4	19.5
Oak wood/ <i>Quersus predunculata</i>	6.0	1.7	19.8
Oak bark/ <i>Quersus predunculata</i>	5.6	9.1	22.0
Olive pits/ <i>Olea europaea</i>	7.0	1.8	22.0
Olive husk/ <i>Olea europaea</i>	6.8	2.1	21.8
Pistachio shells/ <i>Pistocia vera</i>	8.1	1.3	19.9
Rice straw/ <i>Oryza sativa</i>	11.2	19.2	18.7
Spruce wood/ <i>Picea orientalis</i>	6.7	0.5	20.5
Switchgrass/ <i>Panicum virgatum</i>	13.1	5.9	19.9
Wheat straw/ <i>Triticum aestivum</i>	6.4	8.1	19.3

Source: Demirbas, 2004

## 2.4 Biomass Optimization and Valorization

Biomass is very important for implementing the Kyoto agreement to reduce carbon dioxide emissions by replacing fossil fuels. Developing biorenewable sources of energy has become necessary due to limited supply of fossil fuels. Global environmental concerns and decreasing resources of crude oil have prompted demand for alternative fuels. The global climate change is also the major environmental issue of current times. Global warming, the Kyoto Protocol, the emission of greenhouse gases, and the depletion of fossil fuels are the topics of environmental pleadings worldwide. Rapidly increasing energy requirements parallel technological development in the world, and research and development activities are forced to study new and biorenewable energy investigations. The purpose of the work is to optimize the system's operation. The main reason to build described system is to supply stand alone system using renewable energy sources. So the power plant has to produce energy independent of any weather fluctuations. An energy system is made up of an energy supply sector and energy end-use technologies. The object of the energy system is to deliver to consumers the benefits that energy offers. The energy system commonly consists of energy resources and production, security, conversion, use, distribution, and consumption.

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 adhesives by alkali liquefaction and polymerization.

The main research areas of biomass optimization and valorization are:

- Biogas and organic fertilizer production through anaerobic digestion
- Energy crops production
- Fractionation of biomass

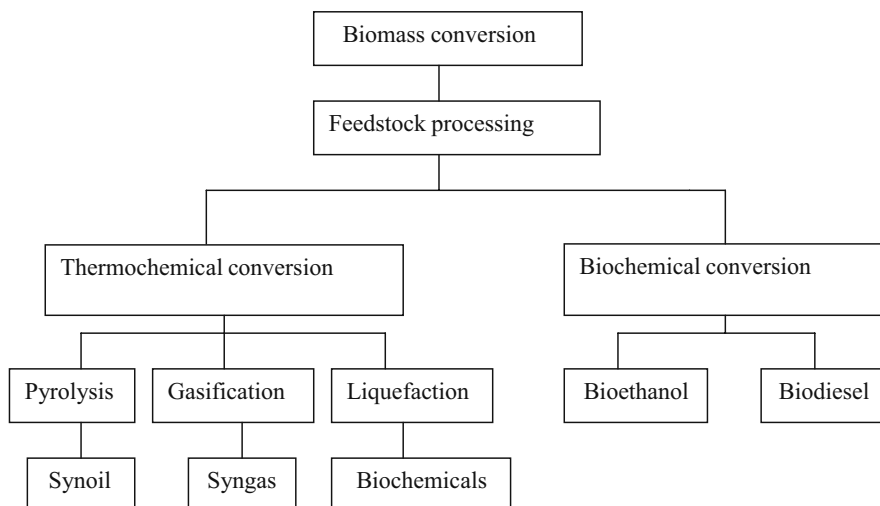
- Biomass modernization
- Biomass cogeneration
- Biomass cofiring
- Biomass economy
- Biomass policy
- Sustainability of biorenewables
- Conversion of biomass into useful fuels and chemicals.

The basic structure of all woody biomass consists of three organic polymers: cellulose, hemicelluloses, and lignin in trunk, foliage, and bark. Added to these materials are extractives and minerals or ash. The proportion of these wood constituents varies between species, and there are distinct differences between hardwoods and softwoods. Hardwoods have a higher proportion of cellulose, hemicelluloses, and extractives than softwoods, but softwoods have a higher proportion of lignin. In general, hardwoods contain about 43% cellulose, 22% lignin, and 35% hemicelluloses, while softwoods contain about 43% cellulose, 29% lignin, and 28% hemicelluloses (Rydholm, 1965).

Biomass has been recognized as a major world renewable energy source to supplement declining fossil fuel resources. Biomass power plants have advantages over fossil-fuel plants, because their pollution emissions are less. Energy from biomass fuels is used in the electric utility, lumber and wood products, and pulp and paper industries. Wood fuel is a renewable energy source and its importance will increase in future. Biomass can be used directly or indirectly by converting it into a liquid or gaseous fuel. A large number of research projects in the field of thermochemical conversion of biomass, mainly on liquefaction pyrolysis, and gasification, have been undertaken.

When biomass is used directly in an energy application without chemical processing then it is combusted. Conversion may be effected by thermochemical, biological, or chemical processes. These may be categorized as follows: direct combustion, pyrolysis, gasification, liquefaction, supercritical fluid extraction, anaerobic digestion, fermentation, acid hydrolysis, enzyme hydrolysis, and esterification. Figure 2.7 shows main biomass conversion processes. Biomass can be converted to biofuels such as bioethanol and biodiesel, and thermochemical conversion products such as syn-oil, biosyngas, and biochemicals. Bioethanol is a fuel derived from renewable sources of feedstock; typically plants such as wheat, sugar beet, corn, straw, and wood. Bioethanol is a petrol additive/substitute. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability.

The energy dimension of biomass use is importantly related to the possible increased use of this source as a critical option to address the global warming issue. Biomass is generally considered as an energy source completely CO<sub>2</sub>-neutral. The underlying assumption is that the CO<sub>2</sub> released in the atmosphere is matched by the amount used in its production. This is true only if biomass energy is sustainably consumed, *i.e.*, the stock of biomass does not diminish in time. This may not be the case in many developing countries.



**Fig. 2.7** Main biomass conversion processes

Biomass is burned by direct combustion to produce steam, the steam turns a turbine, and the turbine drives a generator, producing electricity. Gasifiers are used to convert biomass into a combustible gas (biogas). The biogas is then used to drive a high efficiency, combined cycle gas turbine. Biomass consumption for electricity generation has been growing sharply in Europe since 1996, with 1.7% of power generation in 1996.

### 2.4.1 *Fuels from Biomass*

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 (Demirbas, 2004). Direct combustion and co-firing with coal for electricity production from biomass has been found to be a promising method in the nearest 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 world final 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.

There are three ways to use biomass. It can be burned to produce heat and electricity, changed to gas-like fuels such as methane, hydrogen and carbon monoxide or changed to a liquid fuel. Liquid fuels, also called biofuels, include mainly two forms of alcohol: ethanol and methanol. The most commonly used biofuel is ethanol, which is produced from sugarcane, corn, and other grains. A blend of gasoline and ethanol is already used in cities with high air pollution.

There are several ways to make use of the energy contained in the biomass from old 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.

The main transportation fuels that can be obtained from biomass using different processes are sugar ethanol, cellulosic ethanol, grain ethanol, biodiesel, pyrolysis liquids, green diesel, green gasoline, butanol, 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 wet matter. In the liquefaction, biomass is decomposed into small molecules. These small molecules are unstable and reactive, and can re-polymerize 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 break down 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 increased in proportion to the lignin content. Lignin is a macromolecule, which consists of alkylphenols and has a complex three-dimensional structure. It is generally accepted that free phenoxyl radicals are formed by thermal decomposition of lignin above 230°C 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 produced 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 mainly forms 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. In a fire all these reactions take place concurrently and consecutively. Gaseous emissions are predominantly a product of pyrolytic 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, such 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.

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 the 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 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:  $\text{CO} + \text{H}_2$ ). The molecules in the biomass (primarily carbon, hydrogen, and oxygen) and the molecules in the steam (hydrogen and oxygen) reorganize to form this syngas.

### 2.4.2 Chemicals from Biomass

Such features of larch wood, as an increased content of extractive compounds and its high density create some technological problems for pulping process. It seems that a production of high-value added chemicals is the most profitable way 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 have been obtained from larch wood. Both arabinogalactan and quercitin dihydrate have been extracted from larch wood with boiling water (Kuznetsov *et al.*, 2005).

Chemicals can be obtained from thermal depolymerization and decomposition of biomass structural components, well-known cellulose, hemicelluloses, lignin form liquids, and gas products, as well as a solid residue of charcoal. The bio-oils pyrolysis of biomass are composed of a range of cyclopentanone, methoxyphenol, acetic acid, methanol, acetone, furfural, phenol, formic acid, levoglucosan, guaicol and their alkylated phenol derivatives. The structural components of the biomass samples mainly affect 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 most important parameters affecting 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 mainly produce 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<sub>1</sub> to C<sub>4</sub> 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 derivatives, higher alkylates, substituted lignins, drugs, mixed aromatic polyols, carbon fiber, fillers, *etc.*

As the temperature increases 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 with in addition carbon monoxide and C<sub>1</sub>–C<sub>4</sub> hydrocarbons. Similar to conventional gasification processes, an 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 the 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 remarkable pure organic polymer, consisting solely of units of anhydro glucose 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. The hemicelluloses fraction typically produces a mixture of sugars including xylose, arabinose, galactose, and mannose. These are both pentosans: xylose and arabinose, and hexosans: galactose and mannose. The hydrolysis of hemicelluloses is catalyzed by mineral acids and enzymes.

### 2.4.3 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. 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 has been prepared from dried municipal sewage sludge and batch mode adsorption experiments (Reddy *et al.*, 2006).

Active carbons are carbonaceous materials with a highly developed internal surface area and porosity. Activated carbon 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 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 increases the yield of char from the pyrolysis of wood waste at temperatures between 660 K 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: a gradual degradation, decomposition and charring on heating at lower temperatures, and 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 temperature <575 K (Shafizadeh, 1985). At temperatures >575 K, cellulose depolymerizes, producing volatiles. If the heating rate is very high, the residence time of the biomass at temperatures <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 that 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, has been 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 bi-char from biomass than from coal may be attributed to the cellulose content of the biomass (Demirbas, 2006). It is well known

that heating rate has a significant effect on the pyrolysis of cellulose. The heating rate has a much greater effect on the pyrolysis of biomass than on that of coal. The quick devolatilization of the biomass in rapid pyrolysis favors the formation of char with high porosity and high reactivity (Zanzi *et al.*, 1996). The decreased formation of char at the higher heating rate is 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).

#### 2.4.4 Adhesives from Biomass

Wood adhesives play an essential role in 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 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, semistructural and non-structural wood adhesives are listed in Table 2.6. Approximately 1 million metric tons of urea-formaldehyde resin 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.) were converted to effective co-adhesive for phenol-formaldehyde (PF) bonding of aspen veneer sheets to one another (Weimer *et al.*, 2005).

The wood adhesive market is very large and problems due to volatile organic compounds and toxic chemicals in many adhesives and their production are significant. 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.*, 2004).

A method is described for making adhesive from biomass. The liquefaction oil is prepared from lignin-bearing plant material, and a phenolic fraction is extracted there from. 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 (Knop and Pilato, 1985; 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, isocyanate, urea, and epoxy are examples of types of wood adhesives that are based on thermosetting polymers.

Marine mussel adhesive protein is an excellent example of a formaldehyde-free adhesive from renewable resources. To cope with turbulent tides and waves, mussels stick to rocks or other substances in seawater by secreting an adhesive protein, commonly called marine adhesive protein. (Li *et al.*, 2004).

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

**Table 2.6** Structural, semistructural, and non-structural wood adhesives

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

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. Moreover, it has been quantified that its influence on mechanical properties decreases, since in this type of materials, usually, tensile strength falls (Crespo *et al.*, 2007).

The wood-species dependent performance of polymeric isocyanate resin (PMDI) has been investigated by fracture analysis and solid-state NMR (Das *et al.*, 2007). The surface modification of cellulosic fibers was carried out using organofunctional silane coupling agents in an ethanol/water medium (Abdelmouleh *et al.*, 2004). A new extra-cellular polysaccharide-based adhesive with performance was carried out that may be useful in some wood product applications (Haag *et al.*, 2006). Polysaccharides are generally non-toxic, biodegradable, and produced from renewable resources. In a previous study (Yesil *et al.*, 2007) the bond strengths of three different composite resins bonding to different base substrates were tested.

Hydrogen bonding forces are important in the interfacial attraction of polar adhesive polymers for the hemicellulosics and cellulotics, which are rich with polar hydroxyl groups. These forces of attraction, sometimes referred to as specific adhesion, are particularly important in wetting of water carriers and adsorption of adhesive polymers onto the molecular structures of wood. Water is used as the carrier for most wood adhesives, primarily because water readily absorbs into wood. The relationships between the activation energy and moisture content were investigated. Both the reaction enthalpy and reaction rate increased with the increase in moisture content and remained almost unchanged or increased slightly after the moisture content reached 12% (He and Yan, 2005). The results of a dynamic mechanical analysis technique (DMA), previously developed for estimating the extent of residual cure of phenol-formaldehyde resol resins, depend on the moisture content of the resin (Lorenz and Christiansen, 1995).

There are two types of phenolic resins: resol and novalac. The first one is synthesis under basic conditions with pH conditions with excess of formaldehyde, and the latter is carried out at acidic pH with excess of phenol (Pérez, *et al.*, 2007). They are widely used in industry because of their chemical resistance, electrical insulation, and dimensional stability (Gardziella *et al.*, 2000). There are some published studies involving lignin-resol resins (Danielson *et al.*, 1998; Alonso *et al.*, 2001.) fewer employing lignin-novalac resins for different applications (El-Saied *et al.* 1984; Ysbrandy *et al.* 1992).

It has been demonstrated in the literature by its application in products ranging from wood adhesives to plastics (Hoyt and Goheen, 1971). In these applications the lignin degradation products/fragments are cross-linked to increase their molecular mass (plastic) or to form a rigid three-dimensionally cross-linked structure (adhesive). Formaldehyde reacts with phenol at positions ortho- or para- to the aromatic hydroxyl group (Knop and Scheib, 1979). The alkali lignin produced by the alkaline pulping of softwood consequently contains a low content of positions reactive towards electrophiles such as formaldehyde. In natural lignin the positions

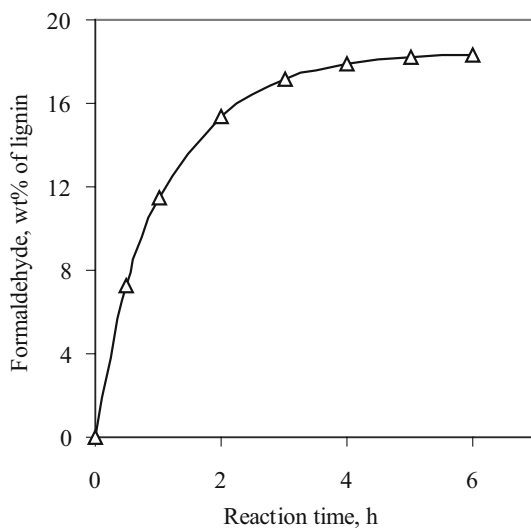


on the aryl rings para- and ortho- to the hydroxyl groups are usually occupied by alkoxy or alkyl substituents (Sarkanen and Ludwig, 1971).

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 positions meta- 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  $K_a$  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 ( $\text{CO}_2 + \text{H}_2\text{O}$ ), 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 ( $K_a$ 's 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 methylation 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). The formaldehyde reactivity of the organosolv lignin is determined in accordance with the method described by Wooten *et al.* (1988). Methylolated lignin-phenol-formaldehyde resins are prepared using the procedure of Sellers (1993). Figure 2.8 shows the curve for lignin-formaldehyde methylation *versus* reaction time.



**Fig. 2.8** Curve for lignin-formaldehyde methylation *versus* reaction time

**Table 2.7** Typical lignin-phenol methylol co-polymerization using organosolv lignin

Constituent	% by weight
Formaldehyde	42.8
Water	22.3
Lignin	19.1
Sodium hydroxide	15.8

**Table 2.8** Typical lignin-formaldehyde-urea methylol co-condensation using organosolv lignin

Constituent	% by weight
Formaldehyde	43.3
Lignin phenolics	40.5
Sodium hydroxide	9.9
Urea	6.3

Typical lignin-phenol methylol co-polymerization using organosolv lignin is given in Table 2.7. Typical lignin-formaldehyde-urea methylol co-condensation using organosolv lignin is shown in Table 2.8.

### 2.4.5 *Valorization of Wood*

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 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 have been 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 are transported by mechanical conveyors.

### 2.4.5.1 Reuse of Wood Wastes

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 left after forest harvesting of residual trees and scrub or undermanaged woodland. Forest residues alone count for some 50% of the total forest biomass and are currently left in the forest to rot.

Wood biomass involves trees with commercial structure and forest residues not being used in the traditional forest products industries. Available forest residues 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 sawmilling and plywood industry, plays an important role in energy efficient production. 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 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 (C&D) 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, crossties, 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 what is required for traditional fossil fuels.

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

### 2.4.5.2 Fractionation of Wood Residues and Wood Wastes

Wood related industries and households consume the most biomass energy. The lumber, pulp, and paper industries burn their own wood wastes in large furnaces and boilers to supply 60% of the energy needed to run the factories. Biomass includes 60% wood and 40% non-wood materials (Demirbas, 2000).

Wood biomass involves trees with commercial structure and forest residues not being used in the traditional forest products industries. 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

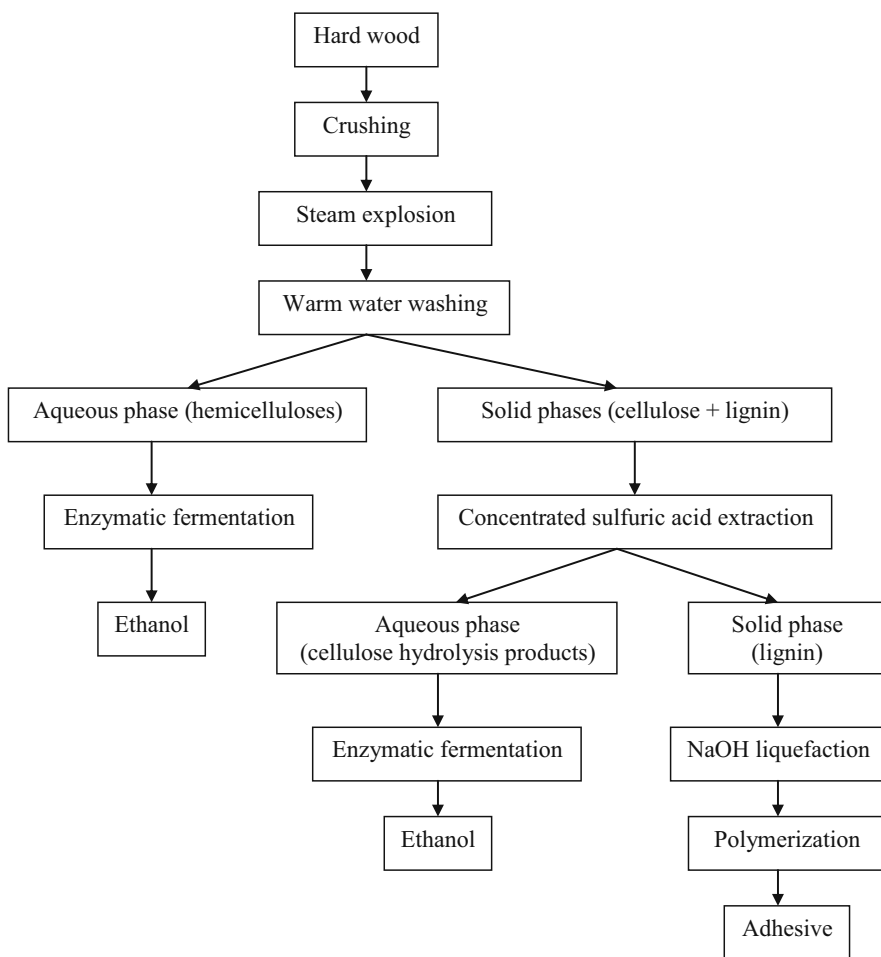


Fig. 2.9 Fractionation of wood and chemicals from wood

products industry. Forest residues alone count for some 50% of the total forest biomass and are currently left the forest to rot.

The opportunity to combine fuelwood production with effluent disposal has many potential environmental benefits. The economic feasibility of woody biomass plantations is difficult to justify at present but if full costing of externalities such as CO<sub>2</sub> emissions are to be applied in the future, then acceptable payback periods for boiler conversions and handling and storage facilities may be achieved (Demirbas, 2000).

Fractionation refers to the conversion of wood into its constituent components (cellulose, hemicelluloses, and lignin). Processes include steam explosion, aqueous separation and hot water systems. Commercial products of biomass fractionation include levulinic acid, xylitol and alcohols. Figure 2.9 shows the fractionation of wood and chemicals from wood.

Main fractionation chemicals from wood ingredients are:

1. Dissociation of cell components → lignin fragment + oligosaccharides + cellulose
2. Hydrolysis of cellulose (saccharification) → glucose
3. Conversion of glucose (fermentation) → ethanol + lactic acid
4. Chemical degradation of cellulose → levulinic acid + xylitol
5. Chemical degradation of lignin → phenolic products.

Wood fuel is a renewable energy source and its importance will increase in future. Three main determinants of the costs of operating and constructing a wood-fired power plant of a given size exist. They are: the availability of the required fuel, the delivered fuel prices, and the financing and construction of the desired power plant. Most previous research has focused on the feasibility of single-source fuel plants. One popular approach has been to examine the feasibility of short-rotation intensive-cultivation plantations.

## References

- Abdelmouleh, M., Boufi, S., Belgacem, M.N., Duarte, A.P., Salah, A., Gandini, A. 2004. Modification of cellulosic fibres with functionalised silanes: development of surface properties. *Int J Adhesion Adhesives* 24:43–54.
- Alanne, K., Sari, A. 2006. Distributed energy generation and sustainable development. *Renew Sust Energy Rev* 10:539–558.
- Alonso, M.V., Rodriguez, J.J., Oliet, M., Rodriguez, F., Garcia, J., Gilarranz, M.A. 2001. Characterization and structural modification of ammoniac lignosulfonate by methylation. *J Appl Polym Sci* 82:2661–2668.
- Arkesteijn, K., Oerlemans, L. 2005. The early adoption of green power by Dutch households. An empirical exploration of factors influencing the early adoption of green electricity for domestic purposes. *Energy Policy* 33:183–196.
- Balat, M. 2008a. Mechanisms of thermochemical biomass conversion processes. Part 1: Reactions of pyrolysis. *Energy Sources Part A* 30:620–635.

- Balat, M. 2008b. Mechanisms of thermochemical biomass conversion processes. Part 2: Reactions of gasification. *Energy Sources Part A* 30:636–648.
- Balat, M. 2008c. Mechanisms of thermochemical biomass conversion processes. Part 3: Reactions of liquefaction. *Energy Sources Part A* 30:649–659.
- Baker, A.J. 1982. Wood fuel properties and fuel products from Woods, in Proc. Fuelwood, Management and Utilisation Seminar, Nov. 9–11, Michigan State Univ., East Lansing, MI.
- Bridgwater, A.V. 2003. Renewable fuels and chemicals by thermal processing of biomass. *Chem Ind J* 91:87–102.
- Bushnell, D.J., Haluzok, C., Dadkhah-Nikoo, A. 1989. Biomass fuel characterization, testing and evaluating the combustion characteristics of selected biomass fuels. Bonneville Power Administration, Corvallis, OR.
- Cetin, N.S., Ozmen, N. 2003. Studies on lignin-based adhesives for particleboard panels. *Turk J Agric For* 27:183–189.
- Crespo, J.E., Balart, R., Sanchez, L., Lopez, J. 2007. Mechanical behaviour of vinyl plastisols with cellulosic fillers. Analysis of the interface between particles and matrices. *Int J Adhesion Adhesives* 27:422–428.
- Danielson, B., Simanson, R.. 1998. Kraft lignin in phenol formaldehyde resin. Part 1. Partial replacement of phenol by kraft lignin in phenol formaldehyde adhesives for plywood. *J Adhesion Sci* 12:923–939.
- Das, S., Malmberg, M.J., Frazier, C.E. 2007. Cure chemistry of wood/polymeric isocyanate (PMDI) bonds: Effect of wood species. *Int J Adhesion Adhesives*. 27: 250–257.
- Demirbas, A. 1991. Fatty and resin acids recovered from spruce wood by supercritical acetone extraction. *Holzforschung* 45:337–339.
- Demirbas, A. 1997. Calculation of higher heating values of biomass fuels. *Fuel* 76:431–434.
- Demirbas, A. 1998. Determination of combustion heat of fuels by using non-calorimetric experimental data. *Energy Edu Sci Technol* 1:7–12.
- Demirbas, A. 2000. Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Convers Mgmt* 41:633–646.
- Demirbas, A. 2001. Biomass resource facilities and biomass conversion processing for fue and chemicals. *Energy Convers Mgmt* 42:1357–1378.
- Demirbas, A. 2002. Fuel characteristics of olive husk and walnut, hazelnut, sunflower and almond shells. *Energy Sources* 24:213–219.
- Demirbas, A. 2003. Fuelwood characteristics of six indigenous wood species from Eastern Black Sea Region. *Energy Sources* 25:309–316.
- Demirbas A. 2004. Combustion characteristics of different biomass fuels. *Prog Energy Combust Sci* 30:219–230.
- Demirbas A. 2006. Production and characterization of bio-chars from biomass *via* pyrolysis. *Energy Sources Part A* 28:413–422.
- Demirbas, A. 2008a. Biodiesel: A Realistic fuel alternative for diesel engines. Springer, London.
- Demirbas, A. 2008b. Heavy metal adsorption onto agro based waste materials: A review. *J Hazard Mat* 157:220–229.
- Demirbas, A., Güllü, D., Caglar, A., Akdeniz, F. 1997. Determination of calorific values of fuel from lignocellulosics. *Energy Sources* 19:765–770.
- Demirbas, A., Kucuk, M.M. 1993. Delignification of *Ailanthus altissima* and spruce *orientalis* with glycerol or alkaline glycerol at atmospheric pressure. *Cellulose Chem Technol* 27:679–686.
- Demirbas, A., Ucan, H.I. 1991. Low temperature pyrolysis of black liquor and polymerization of products in alkali aqueous medium. *Fuel Sci Technol Int* 9:93–105.
- Elliott, D. 1999. Prospects for renewable energy and green energy markets in the UK. *Renewable Energy* 16:1268–1271.
- El-Saied, H., Nada, A.M.A., Ibrahim, A.A., Yousef, M.A. 1984. Waste liquors from cellulosic industries. III. Lignin from soda-spent liquor as a component in phenol-formaldehyde resin. *Angew Makromol Chem* 122:169–181.
- Fengel, D., Wegener, G. 1983. In *Wood chemistry, ultrastructure, reactions*, Chap 7, p. 326. Walter de Gruyter, Berlin.

- Freudenberg, K., Neish, A.C. 1968. Constitution and biosynthesis of lignin. Springer, New York.
- Fridleifsson, I.B. 2003. Status of geothermal energy amongst the world's energy sources. *Geothermics* 32:379–388.
- Garcia-Valls, R., Hatton, T.A. 2003. Metal ion complexation with lignin derivatives. *Chem Eng J* 94:99–105.
- Gardziella, A., Pilato, L.A., Knop, A. 2000. Phenolic resins: Chemistry, applications, standardization, safety and ecology. Springer, New York.
- Glasser, W.G., Sarkanen, S. (eds.) 1989. Lignin: Properties and materials, American Chemical Society, Washington, DC.
- Goldemberg, J., Coelho, S.T. 2004. Renewable energy – Traditional biomass vs. modern biomass. *Energy Policy* 32:711–714.
- Goldstein, I.S. 1981. Organic chemical from biomass, CRC Press, Boca Raton, FL.
- Haag, A.P., Geesey, G.G., Mittleman, M.W. 2006. Bacterially derived wood adhesive. *Int J Adhesion Adhesives* 26: 177–183.
- Haag, A.P., Maier, R.M., Combie, J., Geesey, G.G. 2004. Bacterially derived biopolymers as wood adhesives. *Int J Adhesion Adhesives* 24: 495–502.
- Hamelinck, C., Faaij, A. 2006. Outlook for advanced biofuels. *Energy Policy* 34:3268–3283.
- Hashem, A., Akasha, R.A., Ghith, A., Hussein, D.A. 2007. Adsorbent based on agricultural wastes for heavy metal and dye removal: A review. *Energy Edu Sci Technol* 19:69–86.
- He, G., Yan, N. 2005. Effect of moisture content on curing kinetics of pMDI resin and wood mixtures. *Int J Adhesion Adhesives* 25: 450–455.
- Hergert, H.L., Pye, E.K. 1992. Recent history of organosolv pulping, *Tappi Notes-1992 Solvent Pulping Symposium*, pp. 9–26.
- Hoyt, C.H., Goheen, D.W. 1971. Lignins—Occurrence, formation, structure and reactions. Wiley-Interscience, New York.
- IPCC. 1997. Greenhouse gas inventory reference manual: Revised 1996 IPCC guidelines for national greenhouse gas inventories. Report Vol. 3, p. 1.53, Intergovernmental Panel on Climate Change (IPCC), Paris, France (available from: [www.ipcc.ch/pub/guide.htm](http://www.ipcc.ch/pub/guide.htm)).
- IPCC. 2007. Intergovernmental Panel on Climate Change (IPCC) fourth assessment report, Working Group III (available from <http://www.ipcc.ch>).
- Jain, R.K. 1992. Fuelwood characteristics of certain hardwood and softwood tree species of India. *Biores Technol* 41:129–133.
- Jain, R.K., Singh, B. 1999. Fuelwood characteristics of selected indigenous tree species from central India. *Biores Technol* 68:305–308.
- Karaosmanoglu, F., Aksoy, H.A. 1988. The phase separation problem of gasoline-ethanol mixture as motor fuel alternatives. *J Thermal Sci Technol* 11:49–52.
- Kartha, S., Larson, E.D. 2000. Bioenergy primer: Modernised biomass energy for sustainable Development. Technical Report UN Sales Number E.00.III.B.6, United Nations Development Programme, 1 United Nations Plaza, New York, NY 10017, USA.
- Knop, A., Pilato, L.A.. 1985. Phenolic resin chemistry, application and performance, future directions. Springer, Heidelberg.
- Knop, A., Scheibm W. 1979. Chemistry and application of phenolic resins. Springer, Berlin.
- Kopf, P.W., Little, A.D. 1991. Phenolic resins. In *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 18.
- Kuznetsov, S.A., Kuznetsov, B.N., Aleksandrova, N.B., Danlov, V.G., Zhizhaev, A.M. 2005. Obtaining arabinogalactan, dihydrate quercetin and microcrystalline cellulose using machanochemical activation. *Chem Sustain Develop* 13:261–268.
- Larson, E.D. 1993. Technology for fuels and electricity from biomass. *Annual Rev. Energy Environ.* 18:567–630.
- Leite, J.L., Pires, A.T.N., Ulson de Souza, S.M.A.G., Ulson de Souza, A.A. 2004. Characterisation of a phenolic resin and sugar cane pulp composite. *Brazilian J. Chem. Eng.* 21:253–260.
- Li, K., Geng, X., Simonsen, J., Karchesy, J. 2004. Novel wood adhesives from condensed tannins and polyethylenimine. *Int J Adhesion Adhesives* 24:327–333.

- Liu, Y., Li, K. 2007. Development and characterization of adhesives from soy protein for bonding wood. *Int J Adhesion Adhesives* 27:59–67.
- Lorenz, L.F., Christiansen, A.W. 1995. Interactions of phenolic resin alkalinity, moisture content, and cure behavior. *Ind Eng Chem Res* 34: 4520–4523.
- Lubin, G. 1969. *Handbook of fiberglass and advanced plastics composites*. Van Nostrand Reinhold, New York.
- Mantanis, G.I., Young, R.A., Rowell, R.M. 1995. Swelling of compressed cellulose fiber webs in organic liquids. *Cellulose* 2:1–22.
- Mohan, D., Pittman, C.U., Jr., Steele, P.H. 2006. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels* 20:848–889.
- Morrison, R.T., Boyd, R.N. 1983. *Organic chemistry*, fourth ed., Chap. 24., 960, Allyn and Bacon, New York.
- Murphy, H., Niitsuma, H. 1999. Strategies for compensating for higher costs of geothermal electricity with environmental benefits. *Geothermics* 28:693–711.
- Pérez, J.M., Rodríguez, F., Alonso, M.V., Oliet, M., Echeverría, J.M. 2007. Characterization of a novolac resin substituting phenol by ammonium lignosulfonate as filler or extender. *BioRes* 2:270–283.
- Ragland, K.W., Aerts, D.J., Baker, A.J. 1991. Properties of wood for combustion analysis. *Biores Technol* 37:161–168.
- Reddy, S.S., Kotaiah, B., Reddy, N.S.P., Velu, M. 2006. The removal of composite reactive dye from dyeing unit effluent using sewage sludge derived activated carbon. *Turkish J Eng Env Sci* 30:367–373.
- Rydhholm, S.A. 1965. *Pulping Processes*. Wiley-Interscience, New York.
- Saga, K., Yokoyama, S., Imou, K., Kaizu, Y. 2008. A comparative study of the effect of CO<sub>2</sub> emission reduction by several bioenergy production systems. *Int Energy J* 9:53–60.
- Sarkanen, K.V., Ludwig, C.H. (eds.) 1971. *Lignins: Occurrence, formation, structure and reactions*, Wiley, New York.
- Sellers, Jr., T. 1993. Modification of phenolic resin with organosolv lignins and evaluation of strandboards made by the resin as binder. PhD Thesis, The University of Tokyo, Japan.
- Shafizadeh, F. 1982. Introduction to pyrolysis of biomass. *J Anal Appl Pyrolysis* 3:283–305.
- Shafizadeh, F. 1985. In *Fundamentals of thermochemicals biomass conversion*. In: Overend, R.P., Milne, T.A., Mudge, L.K. (eds.). Elsevier Applied Science, New York.
- Sheehan, J., Dunahay, T., Benemann, J., Roessler, P. 1998. A look back at the U.S. Department of Energy's aquatic species program – Biodiesel from algae. National Renewable Energy Laboratory (NREL) Report: NREL/TP-580-24190. Golden, CO.
- Tewfik, S.R. 2004. Biomass utilization facilities and biomass processing technologies. *Energy Edu Sci Technol* 14:1–19.
- Theander, O. 1985. In: *Fundamentals of thermochemical biomass conversion*. In Overend, R.P., Mile, T.A., Mudge, L.K. (eds.). Elsevier Applied Science, New York.
- Tillman, D.A. 1978. *Wood as an Energy Resource*, Academic Press, New York.
- Timell, T.E. 1967. Recent progress in the chemistry of wood hemicelluloses. *Wood Sci Technol* 1:45–70.
- UNDP (United Nations Development Programme). 2000. *World Energy Assessment. Energy and the challenge of sustainability*.
- Weimer, P.J., Koegel, R.G., Lorenz, L.F., Frihart, C.R., Kenealy, W.R. 2005. Wood adhesives prepared from lucerne fiber fermentation residues of *Ruminococcus albus* and *Clostridium thermocellum*. *Appl Microbiol Biotechnol* 66:635–640.
- Wenzl, H.F.J., Brauns, F.E., Brauns, D.A. 1970. *The chemical technology of wood*. Academic Press, New York.
- Wooten, A.L., Sellers, T., Tahir, P.M. 1988. Reaction of formaldehyde with lignin. *Forest Products J* 38(6): 45–46.
- Yesil, Z.D., Karaoglanoglu, S., Akyil, M.S., Seven, N. 2007. Evaluation of the bond strength of different composite resins to porcelain and metal alloy. *Int J Adhesion Adhesives* 27:258–262.



- Young, R.A. 1986. Structure, swelling and bonding of cellulose fibers. In *Cellulose: Structure, modification, and hydrolysis*, pp. 91–128. Wiley, New York.
- Ysbrandy, R.E., Sanderson, R.D., Gerischer, G.F.R. 1992. Adhesives from autohydrolysis bagasse lignin. Part I. *Holzforschung* 46:249–252.
- Zanzi, R. 2001. Pyrolysis of biomass. Dissertation, Royal Institute of Technology, Department of Chemical Engineering and Technology, Stockholm.
- Zanzi, R., Sjöström, K., Björnbom, E. 1996. Rapid high-temperature pyrolysis of biomass in a free-fall reactor. *Fuel* 75:545–550.

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