CONTENTS

1

From Biomass, Broadly Defined, to Electrochemical Feedstocks

Definition and Availability

In the biosphere, that portion of the earth in which life exists, the energy of the sun drives the biological cycle. *See* Figure 1 (*1*). Through photosynthesis, plants grown on land or in water reduce carbon dioxide to form organic matter (e.g., carbohydrates) and molecular oxygen. Coombs (*2*) estimates that the overall practical maximum efficiency of conversion

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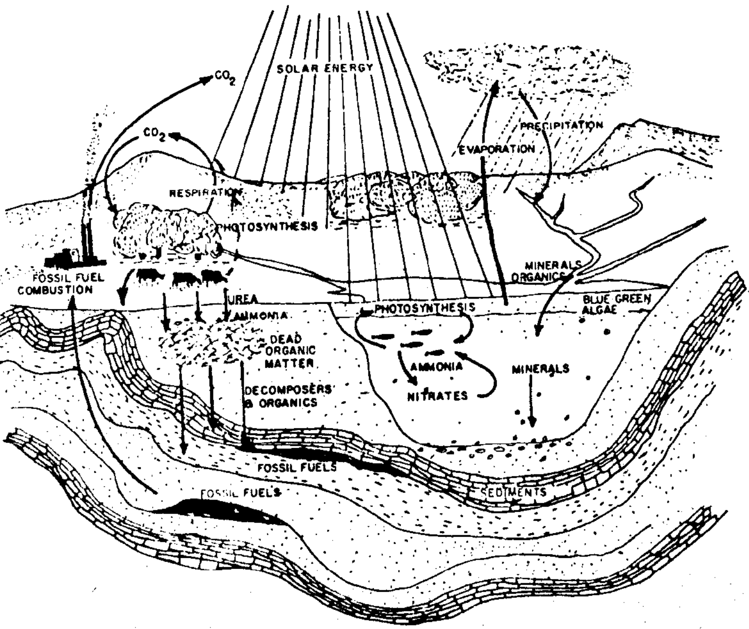

Figure 1. The primary cycles of the biosphere. (Reproduced with permission from Ref. 1. Copyright 1980, Marcel Dekker, Inc.)

of solar energy into fixed carbon compounds is approximately 5.6% for a prolonged period of time for terrestrial species. In practice, however, lower conversion efficiencies (0.1–2%) are observed because conversion by terrestrial species depends, in part, on climate, solar insulation, and species. Higher conversion efficiencies are found for aquatic biomass. Unlike vascular plants, aquatic biomass (e.g., algae) do not develop large amounts of nonphotosynthetic secondary tissue that require respiration energy.

The organic matter produced in the photosynthetic process has several uses: foodstuff for the animal kingdom; structural materials for housing, paper, and fiber-related products; and, to a lesser extent in industrialized countries, energy from combustion processes. The organic matter, or its decomposition products, is transformed by heat, pressure, and time into the fossil fuels that are burned to generate electricity or transformed into chemicals and into liquid fuels for vehicular propulsion. Whereas the availability of such fossil resources as petroleum, natural gas, coal, oil shale, tar sands, and peat is finite, many sources of chemicals and energy are renewable because they are part of the sun-driven biological cycle (Figure 1). The continued use of fossil materials may pose environmental problems. Biomass offers minimal environmental effects because of its low sulfur and nitrogen content; many types also have very low ash.

A strict definition of the term biomass refers to materials produced by plants grown on land or in water (*3*). In a broader sense, however, biomass can be defined as the result of direct photosynthesis (terrestrial and aquatic plants) as well as indirect photosynthesis. This definition enables us to include the recurring by-products of life processes (animal residues) and our civilization (municipal solid wastes, sewage, and industrial wastes) (*4*). The major types of biomass sources are agriculture, silviculture, aquaculture, residues, and wastes (*5*). In Table I, we give examples of the various types of biomass now being used in food production and in the forest-products industry. Other types of biomass that can be developed (*5*) are also shown; these alternatives will be discussed in the next section.

In the past decade, we have become more aware of the dependence of the United States (and many other countries) on importation of liquid fuels, of the finite nature of our fossil fuel reserves, and of the possible environmental and technological problems that can arise as a result of the use of such resources (*6–8*). This awareness has led the scientific community (in part, through government programs) to search for alternative sources of chemicals, fuels, and energy. Recently, in the United States, decreased prices of imported oil and financial constraints have limited, individually as well as nationally, the implementation and continuing research and development of alternative fuels. This limitation has also affected many energy conservation initiatives. However, continuing investigation is still necessary if we are to realize an energy-secure future that utilizes all of the vast energy resources of this country (with proper attention to the regional character of the many resources). The same consideration applies to other countries; in some areas (e.g., Brazil), the development of alternative fuels based on renewable resources is a reality (*9–14*). Hall et al. (*15*) addressed many alternative ways to utilize renewable resources for energy in developing countries. In References 5 and 16–40, we find examples of recent conferences and publications that discuss the conversion of renewable resources to chemicals, fuels, and energy.

The quantities of biomass annually produced worldwide, compared to the present oil production, are shown in Table II (*2*). Consult McClure and Lipinsky (*5*) for a detailed resource assessment of the various types of biomass. For the utilization of biomass through its conversion into fuels, chemicals, and energy, figures of availability are important; for a broad definition of biomass, very approximate values (U.S. data) are shown in Table III (*43–47*). This table compares the amount of biomass

Table I.
Types of Biomass Sources (5)

Sources	*Climate*	*Type*	*Products*	*Examples*
Agriculture	Temperate	Carbohydrate producing	Starch based	Grains (corn, wheat, oats, and barley)
				Tuber (potatoes)
			Sugar based	Root (sugar beet)
				Stalk (sweet sorghum)
		Oil bearing	Oils from seeds	Peanut, soybean, and sunflower
			Latex	Milkweed
		Lignocellulosic		Cotton, alfalfa, and clover
	Tropical and subtropical	Carbohydrate producing	Starch based	Grains (rice)
				Tuber (cassava)
			Sugar based	Sugar cane
		Oil bearing	Oils from seeds	Castor oil, jojoba, and oiticica
			Latex	Guayule
		Lignocellulosic		Kenaf and Johnson grass
Silviculture	Temperate	Hardwoods	Timber and plywood	Oak, aspen, poplars, and maple
		Softwoods	Pulp	Southern pine and Douglas fir
	Tropical and subtropical	Oil bearing	Natural rubber	*Hevea brasiliensis*
		Lignocellulosic	Timber and pulp	Eucalyptus, teak, and mahogany
Aquaculture		Fresh, brackish, or marine water		*Spirulina* (high protein) and *Chlorella* and *Scenedesmus* (lipid producing)
Residues		Crop		
		Forest (logging)		
		Wood products (mills)		
		Animal		
Wastes		Food processing		
		Municipal (solid)		
		Sewage		
		Industrial		

Table II.
Annual World Biomass Production (2)

Production Sources	*Metric Tons*
Net primary production (organic matter)	2×10^{11}
Forest production (dry matter)	9×10^{10}
World's wood consumption	$7–8 \times 10^{8}$
Cereal	
As harvested	1.5×10^{9}
As starch	1×10^{9}
Root crops	5.7×10^{8}
As starch	2.2×10^{8}
Sugar crops	1×10^{9}
As sugar	9×10^{7}
Present oil production	2.8×10^{9}

Table III.
Approximate Amounts of Biomass Processed in the United States, Approximate Area Used in Their Production, and By-products and Residues Generated (1977–79) (*44, 45, 47, 51–53, 67*)

	Production (millions dry metric tons/year)	
Source	*Crop*	*Residue*
Forest[a]	250	105[b]
Paper products	100	50
Structural products	150	15
Thinnings from stand improvements and mortality and excess over harvest	—	77
Agriculture[c]	420	310
Grain	215	303
Oilseed	41	34
Green crops	153	—
Fruits and vegetables	13	—
Forage	750	130
Wastes and Residues		
Urban and municipal solid waste	—	136
Industrial wastes	—	100
Municipal sewage	—	15
Manure	—	175
Food processing residues (major)	—	20

[a]Uses about 720 million acres.
[b]Residues left on the forest after harvesting.
[c]Uses 310–350 million acres.

processed, the approximate area utilized for the production of the major types of terrestrial biomass, and the amounts of generated by-products and residues. Full utilization of these biomass resources is unlikely. Depending on the type of residue, however, approximately 10% (grains) to 50% (municipal solid wastes) could be converted to fuels and chemicals. One conservative estimate of the total biomass potentially available in the United States for energy conversion is about 700 million dry tons/year (*47*). Higher estimates have been made by the Office of Technology Assessment (*see* Ref. 45). Agricultural residues are seasonal and crop residue can be a significant source of plant nutrients and soil conditioner (*1, 47–50*) (*see* Figure 2A). How much agricultural residue can be safely removed on a sustainable basis without causing serious land erosion or loss of nutrients is an area of current assessment. When we consider wood residues, we include sawdust and bark from sawmills (which are burned in part to generate electricity and heat for processing), logging wastes such as tree tops and branches, dead and diseased trees, tree stumps, and thinnings from timber-stand improvements (*43, 51*).

Increased use of logging residues depends on the cost, which includes collecting, transporting, and processing. Removal of dead and diseased trees, downed materials, and growth in excess of harvest will also depend on the accessibility of the resources. In Figure 2B, we show a comparison of the geographic availability of agricultural and forestry residues in the United States (*43*).

The potential of major food processing wastes as a source of cellulose for enzymatic conversion processes is assessed in Reference 53.

Because of the cost of collection, transportation, and disposal, the accumulation of municipal solid wastes (MSWs) is a continuing problem for cities and towns (*20–22, 34, 36, 47*). MSW, therefore, is available at very low cost. The separation of the cellulosic fraction from these wastes, however, may be expensive (*34, 36*). In general, MSW contains, by weight, approximately 21–53% paper and 24% garbage and yard wastes. Metals, ceramics, glass, and rocks, items that can be easily separated from the lignocellulosic components, comprise about 19%. In addition, approximately 5% plastics and rubber and 15% miscellaneous materials can be found. Integrated schemes (which include the separation and recycling of the metals and glass) for MSW reclamation that utilize the cellulosic fraction have been proposed (*44, 54–56*). Conversion of the cellulose to glucose and then to ethanol, coupled with the production of single cell protein is one of the proposed schemes (*54, 55*). Other schemes involve the conversion of the lignocellulosic fraction into carbon monoxide, hydrogen, carbon dioxide, methane, and oils by pyrolysis (*56, 57*) or gasification (*58*). Economics of conversion are a function of

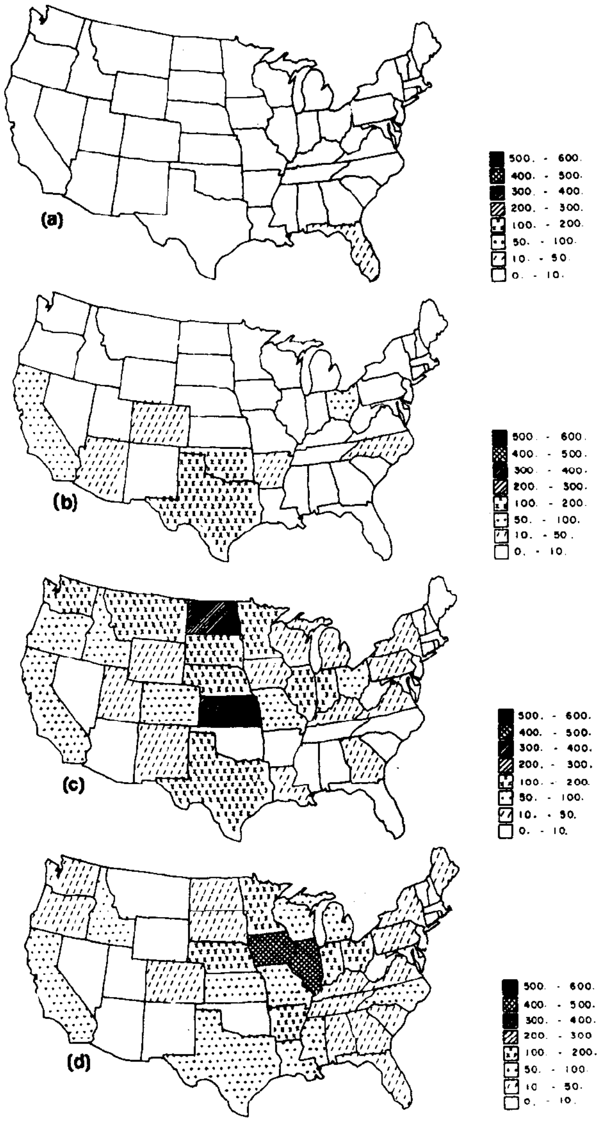

Figure 2A. Agricultural crop residues in winter (a), spring (b), summer (c), and fall (d), expressed as energy equivalents (10^{12} Btu). (Reproduced with permission from Ref. 43. Copyright 1981, Plenum.)

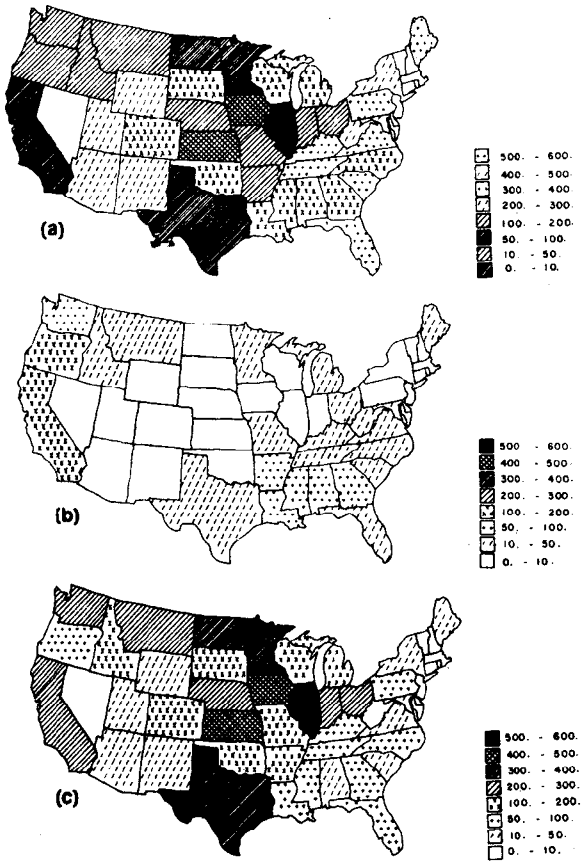

Figure 2B. Agricultural residues (a), forestry residues (b), and total residues (c) by state in energy equivalents (10^{12} Btu). (Reproduced with permission from Ref. 43. Copyright 1981, Plenum.)

the price of the delivered waste. The major processes of conversion of biomass to chemicals are discussed in a later section.

Examples of Strategies in the Development of Biomass for Chemicals, Fuels, and Energy

Previously we referred to the utilization of the by-products of biomass processing of wood, agricultural products, municipal wastes, and of processing associated with present industrial practices. Several other strategies have been proposed for the production of selected types of biomass. As these approaches are still under development, estimates of their potential impact are more uncertain. These strategies include expansion of the biomass lipid-producing capabilities (terrestrial and/or aquatic); aquatic biomass with fresh, brackish, or saline waters; and silvicultural farming and tree crops.

Expansion of the Biomass Lipid-Producing Capabilities. The fats and oils industry in the United States (production and imports) presently handles about 9 million tons of vegetable oils (mainly soybean oil) as well as an equal amount of animal fats, industrial oils, and marine animal fats. About two-thirds of the production is applied to food. Growth in nonfood oil production may be possible through the use of currently available crops (*60*) or through the development of new oil-bearing seed crops (*61*) or new oil-bearing whole plants (*62–64*), both from aquatic or terrestrial origin. The use of currently available crops and the development of new oil-bearing seed crops, including the development of products from the oils, have been investigated by the Agricultural Research Service of the U.S. Department of Agriculture. Approximately 7500 species of wild plants have been analyzed for oil content, protein content, and fatty acid composition, as well as other parameters. About 50 plant species have been identified that contain 60–70% oil in their seeds (*65, 66*). Some of these crops may not be suitable for American agriculture, but may be excellent sources of heat and cooking energy in developing nations where firewood and other energy sources are not readily available (*61–67*). For expansion of these types of biomass in the United States, agricultural land that is mainly devoted to the production of food would be used (*see* Table III).

Farmland constitutes approximately 1000 million acres, of which 470 million acres are available as cropland. Presently, 310–350 million acres are used per year to produce food. According to Princen (*68*), who estimates that 60–80 million acres of cropland could generate all of the petrochemicals for the United States, the total cropland could be increased to about 560 million acres. In addition, other types of land that are not suitable for agriculture should be used to generate fuels. These areas include arid regions, wetlands, strip-mined regions, and areas in which the growing season is short. The U.S. Department of Agriculture (*67*) considers approximately 228 million acres as marginal lands, although a large discrepancy exists between references on the types of land and their amounts. Numbers are cited to give an approximate idea of the areas involved and what they could represent for biomass production and conversion. These estimates are probably low (*45*).

Examples of hydrocarbon-producing plants are jojoba (*Simmondsia chinensis*) and guayule (*Parthenium argentatum*), which may be grown in arid land (*69, 70*). Guayule could serve as a source of natural rubber, which is now imported from Southeast Asia. In addition to polyisoprene [poly(2-methyl-1,3-butadiene)], other chemical compounds have been found. Details on the chemical composition of other hydrocarbons in guayule can be found in Reference 71, and Reference 5 gives the detailed general composition of jojoba and guayule.

Because of their high hydrocarbon content, some new-world plants have attracted the attention of researchers. One example is *Euphorbiae*, which is related to the rubber tree (*Hevea brasiliensis*). *Euphorbiae* sp. are tapped to produce a white milky latex that is rich in polyisoprene, from which natural rubber is made. The hydrocarbon-like fractions of these species contain reduced carbon compounds (other than polyisoprene) that can be used directly as a liquid fuel. Several hundred herbaceous plants of the *Euphorbiaceae* family have been screened for their oil and polyisoprene contents (*69*), and *Euphorbia lathyris* was identified as a potential hydrocarbon-producing herbaceous crop (*69, 70, 72*). Reference 62 contains reviews of this concept, sometimes referred to as a *petroleum plantation*. The large potential fuel value of these crops is estimated; fuel can be obtained both as plant-produced hydrocarbons and as alcohol derived from the carbohydrate fraction of these plants. Estimates of 117,000 MJ/harvest year have been made for *Euphorbia lathyris* (*72*).

Aquatic Biomass. Plants grown in water provide another source of biomass feedstocks. These plants range from algae to macrophytes. Often, plants we consider as possible biomass feedstocks for conversion into chemicals or fuels are viewed as a nuisance, as weeds. One example is the water hyacinth (*Eichhornia crassipes*), an emergent aquatic species that grows very rapidly in the southeastern United States' waterways, often choking them. In the Disney World project in Florida, yields of water hyacinths of 25 dry t/acre·year have been demonstrated. In this region, these species are excellent feedstock candidates for the production of chemicals and fuels.

Microalgae have high production yields (high overall efficiency for sunlight conversion), but their collection for use is a difficult problem, one which is being addressed. Macroalgae have lower production yields but are easier to harvest (more economical with present technology) for further conversion. In both types of algae, the low lignin content allows easy conversion to fuels and chemicals by microorganisms or by other methods. More frequent harvests are necessary with aquatic biomass, however, than with terrestrial plants. References 75 and 76 review in detail the physiology and biochemistry of the algae. Reference 77 updates the production and use of algal biomass.

The first consideration in the use of algal biomass is its food value or high protein content (approximately 30–65% of the dry weight). Mexico and a number of countries in Asia produce this cellular biomass for use as feed (*77*). Another important use of algal biomass growth is for the treatment of wastewater. Microalgae provide the dissolved oxygen content required to meet the biological oxygen demand of municipal wastewater systems. In most wastewater treatment stations, the microalgae are not harvested. Thus, such use could be coupled with controlled harvesting and growth of the algal mass for the production of fuels and chemicals.

Another important potential use of certain types of algal biomass derives from their ability to produce high yields of lipids by regulating media conditions for growth. During and after World War II, researchers found that algae of the *Chlorella* genus could contain 30–86% of their dry weight as lipids. Many other microalgae belonging to the genera *Chlorella*, *Euglena*, *Scenedesmus*, *Micractinium*, and *Spirulina*, as well as others, also produce high lipid yields. The yields of algae produced are presently in the range of 20–30 dry t/acre·year.

Finally, microalgal wastewater treatment for the removal of noxious metals and organic compounds (such as pesticides and herbicides) could be coupled with the production of extracellular chemicals. A variety of hydrocarbons (e.g., amines, organic acids, organic aldehydes, and terpenes) can be secreted by algae (*77*).

These areas are still the subject of research in the United States and other countries. Whereas the feasibility of microalgal production for food has been shown, the feasibility of microalgal production for fuels is still in question because of high carbon dioxide consumption and possible light limitation. (*See* References 78–83 for more discussion.) Aquatic biomass can very likely play an important role in the generation of chemical feedstocks; these species can certainly become more significant sources of food. One of the most important features of some types of aquatic biomass is the ability to grow in brackish waters. In the United States, about 36 million hectares of surface area contain saline ground water (i.e., contain over 3000 ppm of salt) (*84*). Better understanding of the mechanisms of production of lipids and extracellular chemicals will lead to adequate species selection for implementing the use of these types of biomass (*84–88*).

Silvicultural Farming and Tree Crops. Many researchers in the field of biomass have investigated silvicultural farming (*89–91*). Silvicultural farming is the production of wood exclusively for its fuel or feedstock value at a higher rate than by conventional silviculture techniques. The goal in this intensive farming is high tonnage per planted unit area in a short growth cycle (4–7 years). The quality standards for the wood are therefore different from those for the wood grown for the production of lumber and pulp; a juvenile type of wood is produced in this intensive type of farming. At present, intensive tree farming is in the experimental stage.

Various candidate species have been suggested. Many of the most attractive candidates belong to the *Populus* genus, including aspen (*Populus tremuloides*), hybrid poplars, and various cottonwoods. Other candidates include the red alder and eucalyptus (*92, 93*). These plantations are characterized by short rotation, close spacing (to achieve full solar utilization during the rotation period), mechanized planting and harvesting, and intensive management. The costs of collection, handling, and transporting biomass are minimized in this concept. The energy output/input ratio for these systems needs periodic reassessment because of changing economic conditions. Because a monoculture is used, careful disease and pest control are also required. In several examples, 10,000 acres of hardwoods have successfully been grown on a less than 10-year rotation (*89–91*). Reference 94 provides a discussion of the economics of short-term rotation as compared to longer rotation times.

Tree crops are another largely unrecognized approach (*95*). In this concept, annual production of pods, seeds, or fruits that contain fermentable sugars would be used. The crop can be used for energy production (e.g., ethanol) while the trees continue accumulating wood. Examples of tree crops are the honeylocust (*Gleditsia triacanthos*), a variety of berries, and the Chinese tallow tree (*Sapium sebiferum*). *See* Reference 95 for more information on this subject.

The Composition of Biomass

As indicated by our definition, biomass exists in many various forms. However, if we consider the conversion of the main structural biomass components into chemicals, only a few natural polymers need to be considered. This situation is particularly applicable to woody biomass and to agricultural residues. Chemically, wood is a mixture of polymers integrated into various structures into which lower-molecular-weight compounds are dispersed (*96*).

The major form of terrestrial biomass is trees—seed-bearing plants (*Spermatophytae*)—that are subdivided into gymnosperms and angiosperms. The softwoods (conifers) belong in the first category, and the hardwoods (deciduous trees) belong in the second. Many thousands of hardwood species are known; the majority of this species are found in the tropical regions. Approximately 520 species of softwood are known.

Different types of plant cells, both living and dead, compose plant biomass materials. The structure and the composition of these cells vary depending on the location in the plant and on the plant species. Examples of living cells are those in the green leaves (composed of proteins, water, and a small amount of cellulosic cell wall materials), and a very small fraction of cells in the woody tissue, the parenchyma cells. The majority of the cells in the woody tissue are dead prosenchyma cells, which consist of several cell wall layers as well as intercellular material—the middle lamella. A schematic representation of the fine structure of wood fibers for a hardwood and a softwood is shown in Figure 3A. The microfibrils of cellulose are embedded in a matrix of hemicelluloses and lignin; these three natural polymers are the main components of the plant cell wall (approximately 95%). Whereas the first two polymers—the cellulose and the hemicelluloses—are carbohydrates, the lignin is an irregular polymer consisting of *n*-propylbenzene (phenylpropane) units. Figure 3B exemplifies the approximate distribution of these three

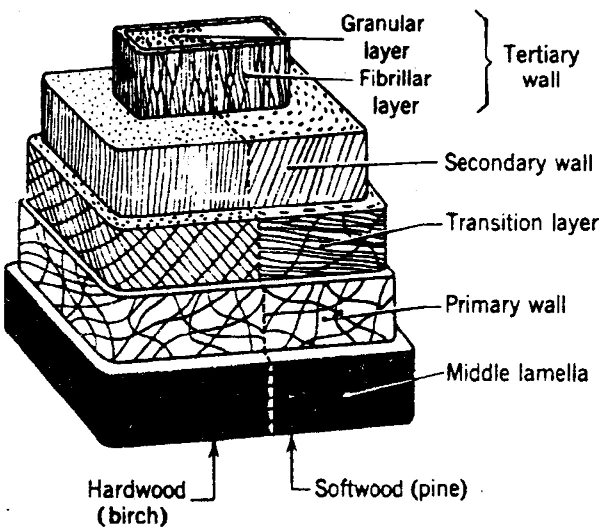

Figure 3A. Model of the fine structure of hardwood (left) and softwood (right) fibers. (Reproduced with permission from Ref. 99. Copyright 1975, R. E. Krieger Publ. Co.)

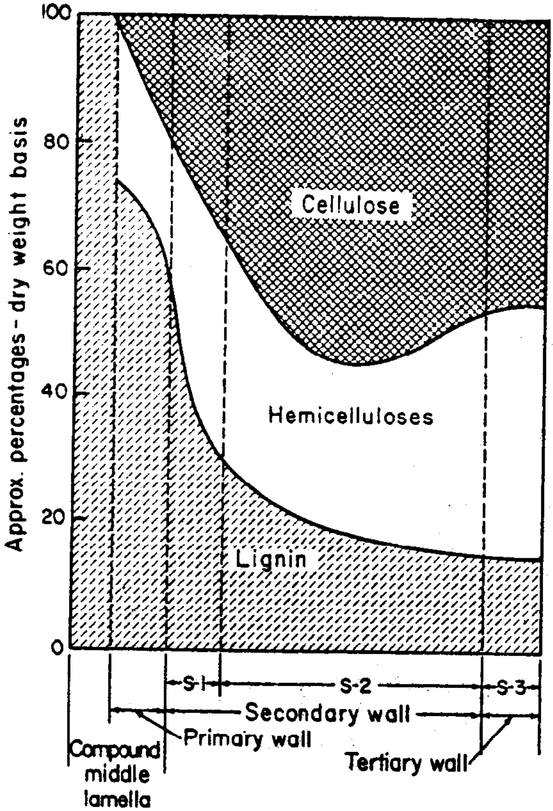

Figure 3B. Approximate distribution of polymeric constituents in the cell wall of Douglas fir (97).

polymers in the cell wall of a softwood (Douglas fir). Lignin is present in high concentration in the outer layers to provide structural rigidity, stiffening, and cementing of the fibers; its concentration decreases towards the inner wall. In contrast, the cellulose content is low in the primary cell wall and increases in the secondary cell wall. The hemicelluloses are present in all cell wall layers with a higher percentage in the inner layers. In addition to these structural materials, some classes of compounds can be found in smaller amounts (approximately 5%); these classes, which are extractable with appropriate solvents, are called extractives. Examples are the lipids and hydrocarbons (terpenes), which are soluble in ether, and various types of phenolic compounds and carbohydrates, which may be soluble in benzene, alcohol, or water. The leaves and the bark generally contain more extractives and less cell wall materials than the wood and woody tissues. *See* References 96–100 for more detailed information on the structure of wood. Such knowledge is important for a deeper understanding of the utilization of the various components of biomass. Sjostrom (*98a*) presents an excellent introduction to wood and its chemistry.

Compared to wood, agricultural residues have one major different characteristic; the diameter of the stem cannot be increased significantly through additional growth. These stems do not have the concentric organization of trees. Some stems have a hollow core, such as the stem of cereal grains or straws; in others, such as cornstalk and bagasse, the stem is solid. In general, the stems consist of parenchymous material through which vascular bundles pass longitudinally. Four categories of cells are found in wheat straw: fibers (about 50%), parenchyma (about 30%), epidermis (about 15%), and vessels (about 5%). Cornstalks and bagasse contain equal proportions of fibers and parenchyma cells. The fine structure of grass fibers is similar to that of wood fibers. Grass fibers are composed of a primary wall and distinct, secondary wall layers. The fraction of fibers in grasses is similar to that in hardwoods, but the quantity of nonfiber cells is much higher. Agricultural residues have a higher ash content than temperate-zone woods, which contain approximately 0.2–1% ash; some tropical woods can contain 4–5%. For most straws, the ash content will vary from 2 to 10%; in cornstalks the ash content is only 1–2% (*5*, *101*).

In this monograph we are mainly concerned with the chemical components of biomass and how to transform them into organic chemicals and fuels. Prior to defining those types that are candidate feedstocks for electrochemical transformations, we will discuss the most important chemical components of biomass: carbohydrates, lignins, fatty acids, and other components.

Table IV presents the major components of a variety of hardwoods and softwoods. The data presented refer to mature trees. The composition of wood in less-mature trees—juvenile wood—is generally higher in lignin and lower in cellulose. The composition of other than normal wood is also different. For softwoods, the lignin content will be higher and the cellulose content will be lower, whereas for hardwoods, the lignin content will be lower and the cellulose content will be higher. Consult References 98 and 99 for more detailed composition of these types of wood. Table V compares the chemical composition of wood species with agricultural residues, aquatic species, wastes, and residues.