# Chapter 2
Structure of Lignocellulosic Biomass

Abstract Lignocellulosic materials consist mainly of three polymers: cellulose, hemicellulose, and lignin. These polymers are associated with each other in a hetero-matrix to different degrees and varying relative composition depending on the type, species, and even source of the biomass. The relative abundance of cellulose, hemicellulose, and lignin are inter alia, key factors in determining the optimum energy. Structural and compositional features of lignocellulosic biomass are presented in this chapter.

Keywords Lignocellulosic material · Polymers · Cellulose · Hemicelluloses · Lignin · Biomass · Structure · Composition

Plant biomass consists mainly of three polymers: cellulose, hemicellulose and lignin along with smaller amounts of pectin, protein, extractives and ash. The composition of these constituents can vary from one plant species to another. Hardwoods for example have greater amounts of cellulose, whereas wheat straw and leaves have more hemicellulose (Table 2.1). The ratios between various constituents within a single plant vary with age, stage of growth, and other conditions. These polymers are associated with each other in a heteromatrix to different degrees and varying relative composition depending on the type, species, and even source of the biomass (Carere et al. 2008; Chandra et al. 2007; Fengel and Wegener 1984). The relative abundance of cellulose, hemicellulose, and lignin are inter alia, key factors in determining the optimum energy conversion route for each type of lignocellulosic biomass (Mckendry 2002). Lignocellulosic feedstocks need aggressive pretreatment to yield a substrate easily hydrolyzed by commercial cellulolytic enzymes, or by enzyme producing microorganisms, to liberate sugars for fermentation. Cellulose is the main constituent of plant cell wall conferring structural support and is also present in bacteria, fungi, and algae. When existing as unbranched, homopolymer, cellulose is a polymer of beta-ᴅ-glucopyranose moieties linked via beta-(1,4) glycosidic bonds with well documented polymorphs (Fig. 2.1). The degree of polymerization of cellulose chains in nature ranges from 10,000 glucopyranose units in wood to 15,000 in native cotton. The repeating unit of the cellulose chain is the disaccharide

Table 2.1 Cellulose, hemicellulose, and lignin contents in lignocellulosic biomass
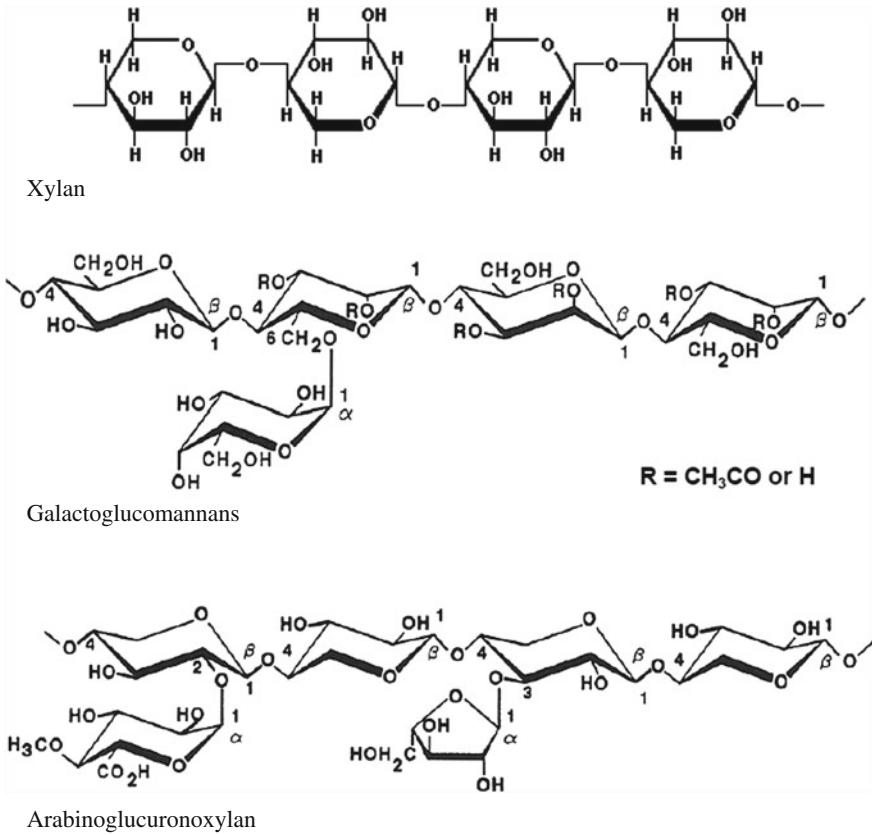
|	Cellulose	Hemicellulose	Biomass
Hardwoods	40–55	24–40	18–25
Softwoods	45–50	25–35	25–35
Wheat straw	30	50	15
Corn cobs	45	35	15
Grasses	25–40	35–50	10–30
Switchgrass	45	31.4	12
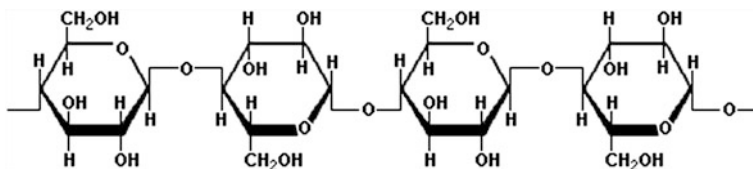
Fig. 2.1 Structure of cellulose

cellobiose as oppose to glucose in other glucan polymers (Desvaux 2005; Fengel and Wegener 1984). The cellulose chains (20–300) are grouped together to form microfibrils, which are bundled together to form cellulose fibers. The long-chain cellulose polymers are linked together by hydrogen and van der Waals bonds, which cause the cellulose to be packed into microfibrils. Hemicelluloses and lignin cover the microfibrils. Fermentable D-glucose can be produced from cellulose through the action of either acid or enzymes breaking the beta-(1,4)-glycosidic linkages. In biomass cellulose is present in both crystalline and amorphous forms. Crystalline cellulose contains the major proportion of cellulose, whereas a small percentage of unorganized cellulose chains form amorphous cellulose. Cellulose in its amorphous form is more susceptible to enzymatic degradation. The cellulose microfibrils are mostly independent but the ultrastructure of cellulose is largely due to the presence of covalent bonds, hydrogen bonding and Van der Waals forces. Hydrogen bonding within a cellulose microfibril determines 'straightness' of the chain but interchain hydrogen bonds might introduce order (crystalline) or disorder (amorphous) into the structure of the cellulose (Laureano-Perez et al. 2005).

Hemicellulose is the second most abundant polymer containing about 20–50 % of lignocellulose biomass. It is not chemically homogeneous like cellulose (Fig. 2.2). Hemicellulose has branches with short lateral chains consisting of different types of sugars. These monosaccharides include pentoses (xylose, rhamnose, and arabinose), hexoses (glucose, mannose, and galactose), and uronic acids (4-O-methylglucuronic, D-glucuronic, and D-galactouronic acids). The backbone of hemicellulose is either a homopolymer or a heteropolymer with short branches linked by beta-(1,4)-glycosidic bonds and occasionally beta-(1,3)-glycosidic bonds. Also, hemicelluloses can have some degree of acetylation, for example, in heteroxylan. Hemicelluloses have lower molecular weight compared to cellulose and branches with short lateral chains that are easily hydrolysed (Fengel and

Fig. 2.2   Structure of hemicelluloses

Wegener 1984; Saha 2003). Hemicelluloses are found to differ in composition. In agricultural biomass like straw and grasses, hemicelluloses are composed mainly of xylan while softwood hemicelluloses contain mainly glucomannan (Fig. 2.2). In many plants, xylans are heteropolysaccharides with backbone chains of 1,4- linked beta-D-xylopyranose units. In addition to xylose, xylan may contain arabinose, glucuronic acid, or its 4-O-methyl ether, acetic acid, ferulic and p-coumaric acids. Xylan can be extracted easily in an acid or alkaline environment while extraction of glucomannan requires stronger alkaline environment (Balaban and Ucar 1999; Fengel and Wegener 1984). Among the key components of lignocellulosics, hemicelluloses are the most thermo-chemically sensitive (Hendricks and Zeeman 2009; Levan et al. 1990). Hemicelluloses within plant cell walls are thought to 'coat' cellulose-fibrils and it has been proposed that at least 50 % of hemicellulose should be removed to significantly increase cellulose digestibility. Nevertheless, severity parameters should be carefully optimized to avoid the formation of hemicellulose degradation products such as furfurals and hydroxymethyl furfurals
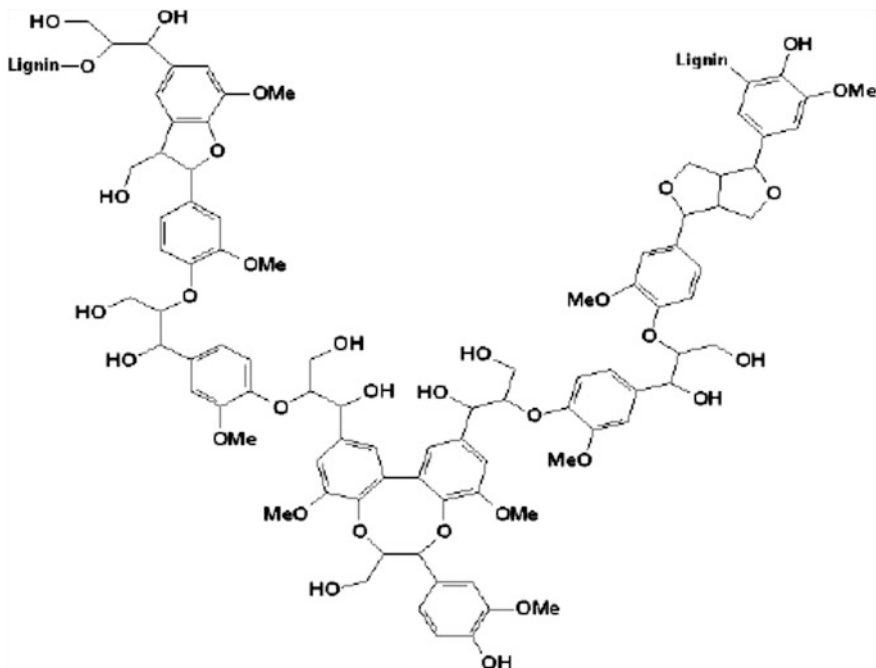
Fig. 2.3 Structure of lignin (complex cross-linked polymer of aromatic rings). Based on Walker (2010)

which have been reported to inhibit the fermentation process (Palmqvist and Hahn-Hägerdal 2000a, b). For this reason, pretreatment severity conditions are usually compromised to maximize sugar recovery and depending upon what type of pretreatment method is used hemicellulose could be obtained either as a solid fraction or a combination of both solid and liquid fractions (Chandra et al. 2007).

Lignin is the third most abundant polymer in nature. It is a complex, large molecular structure containing cross-linked polymers of phenolic monomers (Fig. 2.3). It is present in plant cell walls and confers a rigid, impermeable resistance to microbial attack and oxidative stress. It is present in the primary cell wall and imparts structural support, impermeability, and resistance against microbial attack. Three phenyl propionic alcohols exist as monomers of lignin. These are:

– Coniferyl alcohol (guaiacyl propanol)
– Coumaryl alcohol (p-hydroxyphenyl propanol)
– Sinapyl alcohol (syringyl alcohol).

Alkyl-aryl, alkyl-alkyl, and aryl-aryl ether bonds link these phenolic monomers together. In general, herbaceous plants such as grasses have the lowest contents of lignin, whereas softwoods have the highest lignin contents (Table 2.1) (Hendricks and Zeeman 2009). Lignin is generally accepted as the 'glue' that binds the different

Table 2.2 Mechanisms of pretreatment

Physical effects
Disrupt the higher order structure
Increase surface area, chemical or enzyme penetration into plant cell walls
Chemical effects
Solubility
Depolymerization
Break crosslinking between macromolecules

components of lignocellulosic biomass together, thus making it insoluble in water. Lignin has been identified as a major deterrent to enzymatic and microbial hydrolysis of lignocellulosic biomass because of its close association with cellulose microfibrils (Avgerinos and Wang 1983). Chang and Holtzapple (2000) showed that biomass digestibility is increased with increasing lignin removal. In addition to being a physical barrier, the harmful effects of lignin include:

– Nonspecific adsorption of hydrolytic enzymes to "sticky" lignin;
– Interference with, and non-productive binding of cellulolytic enzymes to lignin-carbohydrates complexes;
– Toxicity of lignin derivatives to microorganisms.

Different feedstocks contain different amount of lignin that must be removed via pretreatment to enhance biomass digestibility. The lignin is believed to melt during pretreatment and coalesces upon cooling such that its properties are altered; it can subsequently be precipitated (Brownell and Saddler 1987; Converse 1993; Lynd et al. 2002). Delignification (extraction of lignin by chemicals) causes the following effect:

– Biomass swelling
– Disruption of lignin structure
– Increases in internal surface area
– Increased accessibility of cellulolytic enzymes to cellulose fibers.

Although not all pretreatments result in substantial delignification, the structure of lignin may be altered without extraction due to changes in the chemical properties of the lignin. The pretreated biomass becomes more digestible in comparison to the raw biomass even though it may have approximately the same lignin content as non-pretreated biomass. Table 2.2 shows the mechanism of pretreatment.

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