

Lignocellulosic Biorefining Technologies

Edited by
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1

Biorefining of Lignocellulose into Valuable Products

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Lignocellulosic biomass is a major stakeholder in biorefineries. The transformation of biomass into a wide range of fuels, materials, and valuable chemicals is the overall goal of a biorefinery (de Jong and Jungmeier 2015; Chandel et al. 2018). In principle, a biorefinery would exploit hybrid technologies encompassing various fields including bioengineering, agriculture, and polymer chemistry. In a specific biorefinery, the feedstock is fractionated into valuable constituents through extraction, hydrolysis, fermentation, and controlled pyrolysis for the production of fuels, energy, and high-value products such as organic acids, biopigments, biosurfactants, etc. (Erickson et al. 2012; Isikgor and Becer 2015; Lee et al. 2019).

The concept of biomass fractionation into its main components offers myriad benefits to the bioprocessing industries harnessing the various feedstocks. Nevertheless, the advancement and exploitation of lignocellulosic biomass fractionation technologies are still in their infancy in terms of technoeconomic viability (FitzPatrick et al. 2010; Chandel et al. 2018). Hence, fundamental and applied research will be critically required in this field in the coming decades.

Currently, the price of biomass is a major impeding factor in the economic production of fuels and value-added products/chemicals that accounts for up to 40–60% of the overall price (Chandel et al. 2019). For the overall economization of the process with simplicity, process integration is an important necessity. The second-generation biomass together with waste feedstocks are promising sources for the production of value-added products owing to their surplus availability, cost-effectiveness and non-requirement of land with no competition with food crops (Chandel and Silveira 2017). However, the exploitation of lignocellulosic biomasses to generate fuels and valuable chemicals is challenging because of the complexity of pretreatment followed by enzymatic hydrolysis via the synergistic action of cellulases to yield cellulosic sugars which are considered as renewable building blocks (Chandel et al. 2019). Cellulosic sugars can be further converted into a plethora of bio-based products such as alcohols, organic acids, alkenes, lipids, etc. (Lee et al. 2019).

However, the production potential of biochemicals from these agro-residues have not yet been investigated at large scale under biorefinery conditions (Sanford et al. 2016).

Considering the enormous potential of different lignocellulosic biomass types in biorefinery, as mentioned above, we have attempted in this book to explore the high-value biorefining products which can be created using a variety of lignocellulosic biomass as renewable and economically viable resources.

The book contains 15 chapters. Chapter 1 by Ingle et al., which is also the book preface, presents the overall impact of lignocellulose biorefineries in a nutshell in addition to summarizing each chapter's content. Chapter 2 by Ferrand and colleagues is broadly focused on the various bulk and specialty chemicals present in the plant cell wall. Special emphasis has been given to important aspects such as structure, function, and chemical composition of the plant cell wall. In addition, all the promising valuable chemicals and bioactive compounds present in the plant cell wall are discussed in detail. Chapter 3 by Bustos et al. provides details about the different components present in the lignocellulosic biomass and their characterization; different approaches available for processing lignocellulosic biomass into second-generation sugars are also discussed. Sheetal et al. in Chapter 4 focus on the possibilities of utilization of lignocellulosic feedstocks for the production of biohydrogen. It is well known that hydrogen energy, particularly biohydrogen, is gaining a lot of interest as a sustainable and renewable alternative to fast-depleting fossil fuels. It also provides an additional benefit of not emitting any greenhouse gases (GHG), which provides an incentive to all countries struggling to meet the GHG limitations as per the Paris agreement to combat climate change to adopt this clean fuel. Various recent studies have proved that lignocellulosic biomass sources can be used as an alternate feedstock for biohydrogen production as they are abundant, cheap, and eco-friendly.

Chapter 5 by Bhagat and co-authors emphasizes the role of a variety of lignocellulosic biomass in the production of another form of clean energy – biodiesel. In this chapter, the authors briefly discuss the major constituents of lignocellulosic biomass, and the composition and structure of each of the components present in the biomass have been explained. Most importantly, recent advances in the production of biodiesel using lignocellulosic biomass through different fermentation approaches have been discussed. It is forecast that the demand for renewable energy for transportation is likely to grow by 19% till 2023 whereas approximately a 15% rise in biofuel production is expected in the same time period. In this context, biodiesel can be seen as a renewable energy source that can be used for partial or even total replacement of diesel.

Chapter 6 by Kalita et al. covers the production of bioelectricity from lignocellulosic biomass. Electricity is a vital form of energy which plays a significant role in defining human development. On one side, industrial and economic developments are transforming our way of living and therefore demand for electricity demand is continuously growing. However, on the other side, this continuous increase in energy demand leads to fossil fuel depletion and environmental degradation. Therefore, to resolve these issues, more emphasis is now being placed on harvesting sustainable energy from different renewable energy sources like solar, biomass, wind, etc. In this context, the authors have discussed the various options which can be used in the conversion of lignocellulosic biomass into valuable fuels through thermochemical conversion technologies.

As mentioned earlier, biohydrogen, biodiesel, and bioelectricity are important high-value products commonly produced from lignocellulosic feedstocks through different biorefining strategies. Lignocellulosic materials can also be potentially utilized in the production of other valuable products with applications in numerous sectors like food and agriculture, pharmaceuticals, biomedicine, cosmetics, etc. In view of this, various chapters in the present book have a special emphasis on different lignocellulosic biorefining products. In Chapter 7, Machado et al. provide a special focus on the production of biopolymers using different lignocellulosic materials as important sources of carbon, nitrogen, etc. The authors report that production of biopolymers from renewable resources like lignocellulosic feedstocks has been increasing due to environmental, political and economic concerns about conventional plastics utilization. A wide range of biopolymers with many application possibilities can be produced from lignocellulosic biomass, allowing the replacement of many conventional plastics. Therefore, in this chapter, various key aspects including types and properties of biopolymers, different approaches used for biopolymer production, applications of biopolymers, and the advantages and challenges of obtaining biopolymers from lignocellulosic biomass are critically discussed.

In the same vein, Marcelino and co-authors explain the importance of lignocellulosic biomass in the production of biosurfactants in Chapter 8. Biosurfactants are amphiphathic molecules synthesized by microorganisms (bacteria, yeasts, and filamentous fungi) using a variety of lignocellulosic feedstocks as a source of carbon and nitrogen which are essential for the growth of these microorganisms. Biosurfactants have attracted a great deal of attention across the world due to their unique and novel surface-active and/or emulsifying, antimicrobial, and antitumor properties. Important topics including the types, structure, and functions of biosurfactants, fermentation approaches used for biosurfactant production and applications of biosurfactants are critically discussed in Chapter 8.

Chapter 9 by Abdeshahian et al. is focused on the role of lignocellulosic materials in the production of different enzymes. In this chapter, the authors propose that lignocellulosic biomass or wastes from various sources like agriculture, forest, industries, etc. can be employed as promising raw materials in the production of value-added products such as enzymes using various biorefining technologies. Generally, the production of enzymes is carried out by microorganisms through the fermentation process in which organic carbon contents are provided in the form of lignocellulose which is utilized as a nutrient source by fermenting organisms. The utilization of lignocellulosic materials could provide a cost-effective raw material for enzyme production which in turn reduces the enzyme production cost.

Considering the vital role of organic acids in various biological processes, it is the need of the hour to produce different organic acids using simple, efficient, economic, and environmentally sustainable approaches. In this context, lignocellulosic biomass can be used as inexpensive and renewable sources for the production of organic acids. Therefore, de Cárdenas and co-authors in Chapter 10 discuss the production of organic acids using lignocellulosic feedstocks. Moreover, recent advances in the production of different acids using lignocellulosic biomass are discussed in this chapter along with important related factors.

Chapter 11 by Terán-Hilares et al. covers recent advances in the valorization of lignin into value-added products. Lignin is one of the most abundant macromolecules on Earth. It is a complex fraction in biomass composed of various aromatic building blocks which are

cross-linked with different carbon and ether linkages. Lignin has broad scope for valorization to aromatics, polymers, and other value-added materials. However, in spite of the attractiveness of lignin as a natural source for the production of a wide range of products, there are various technological barriers which limit its ubiquitous use at the industrial level. Considering all these concerns, Chapter 11 focuses on the potential of lignin in the creation of various high-value products. In addition, the chemistry of lignin, various approaches for its processing, and economic and environmental concerns associated with lignin valorization are discussed.

Chapter 12 by Moraes and co-authors provides a detailed explanation of pyrolysis and carbonization, which are commonly used methods for the processing of biomass to develop by-products for energy and agriculture. Special emphasis has been given to the thermochemical conversion of agricultural or lignocellulosic biomass to obtain a solid product like biochar.

Chapter 13 by Perez et al. is about the integrated processes for thermochemical conversion of biomass to produce pyrolytic sugars like levoglucosan required for biofuels and other important bioproducts by fermentation. In this chapter, the authors discuss the integrated processes of a biomass thermochemical conversion plant as a subprocess of an autonomous bioethanol plant. Further, they emphasize that such technological alternatives can be inexpensive, eco-friendly, and attractive in a country like Brazil where surplus amounts of sugarcane bagasse are available.

Chapter 14 by Mazuchi is focused on a life cycle analysis of lignocellulosic conversion into value-added products. In order to study the impacts of different materials, products, and processes on environmental sustainability, a life cycle assessment is required so various aspects of such an assessment have been discussed in this chapter.

The last chapter, by Ellamla, covers the most important issues associated with the biorefinery industries. It provides details about the technoeconomic analysis of biofuel production and other important products. As far as biorefinery industries are concerned, a technoeconomic analysis is essential to assess the feasibility of integrating lignocellulosic biomass into various biorefinery products like biofuels and other high-value compounds.

Lignocellulosic Biorefining Technologies is a collection of articles elucidating recent advances in the utilization of a variety of lignocellulosic feedstocks for the production of high-value products including important forms of bioenergy and other industrially important biorefining compounds like biopolymers, biosurfactants, enzymes, organic acids, etc. The text in each chapter is supported by clear, informative tables and figures. Each chapter contains relevant references to published articles, which offer a large amount of primary information and further links to a nexus of data and ideas.

All the chapters in this book have been written by one or more specialists, experts in their field, and are highly informative and detailed. In this way, we would like to offer a rich guide for researchers, undergraduate or graduate students of various disciplines such as agriculture, food science, biotechnology, biofuel and bioenergy industries, and allied subjects. In addition, this book will be useful for those working in various industries, regulatory bodies, and global fuel and energy organizations.

The editors are very grateful to all the contributors for their outstanding efforts to provide state-of-the-art information on the subject matter of their respective chapters. Their efforts will certainly enhance and update the knowledge of readers about lignocellulosic biorefining technologies. We express our sincere thanks to the publishers and authors whose

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We hope that the book will be useful for all readers looking for information on the latest research and advances in the field of lignocellulosic biorefining technologies.

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2

Bulk and Specialty Chemicals from Plant Cell Wall Chemistry

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2.1 Introduction

Plant cell walls are the most abundant renewable resource on our planet, representing 70% of the annual biomass production by land plants worldwide (Pauly and Keegstra 2008). The woody material of plant cell walls comprises three main types of carbon-based polymer – cellulose, hemicellulose, and lignin – which collectively are called lignocellulosic biomass (LG) (Sanderson 2011). However, not only the woody material of plants is being used as a natural source of cellulosic and noncellulosic materials, but also leaves, branches, flowers, algae, seeds, fruits and vegetables, among others (Asgher et al. 2013; Bernaerts et al. 2018). LG biomass can even come from organic wastes or by-products from other industries, contributing to the ecologic cycle that is being demanded around the globe (Ekman et al. 2013; Ofori-Boateng and Lee 2013; Faris et al. 2015; Petkowicz et al. 2017; Ravindran and Jaiswal 2016; Chrysikou et al. 2018).

Despite agricultural practices and various agro-based industries generating huge amounts of LG biomass every year (about 933 million tons), only 2% of this resource is utilized by humans (Pauly and Keegstra 2008; De Bhowmick et al. 2018). This means that a considerable amount of such LG materials is sadly discarded. However, LG biomass is gaining increasing research interest and special importance because of its renewable nature and the great amount of lost resources (Lyu et al. 2018; Oyola-Rivera et al. 2018; Mei et al. 2019; Luo et al. 2019). Furthermore, LG materials can potentially be converted into different high-value products such as biofuels, value-added chemicals, and cheap energy sources for microbial fermentation and enzyme production (Anwar et al. 2014; Naseem et al. 2016; Cao et al. 2018; Ma et al. 2018). Since a great amount of these materials are generated from atmospheric CO₂, water, and sunlight through biological photosynthesis, biomass is considered to be the only sustainable source of organic carbon on Earth. Considering the depletion of petroleum resources, the intensive utilization of fossil fuels and the awareness of global warming, LG biomass appears to be the perfect substitute for petroleum for the

production of fuels and fine chemicals with net zero carbon emission. It also has a low content of nitrogen, sulfur and ash, which results in lower emissions of NO, SO₂ and soot, compared to conventional fuels (Isikgor and Becer 2015; Dhyani and Bhaskar 2018).

From the first generation of biofuels obtained from energy crops to the second generation originated from many types of biomass, many challenges have been overcome. Nowadays, in Europe, more than 220 LG biorefineries are in operation, of which approximately 180 are first generation, while the remainder belong to the second generation (Hassan et al. 2019). Therefore, biorefineries which allow both bioethanol production and co-production of biochemicals are still in expansion, also being an environmentally friendly system to help mitigate global climate change (Chrysikou et al. 2018).

The aim of this chapter is to explore the different value-added chemicals that could be extracted from cell wall polymers and used as platform chemicals or feedstock to obtain high-interest chemicals, pharmaceutical, biomedical or food products. To this end, we will briefly survey the basics of plant cell wall structure and function. After a short description of the chemical composition of the plant cell wall, a detailed overview of the valuable chemicals that can be obtained from LG biomass is given.

This chapter could help chemists, biotechnologists, agronomists, and food technologists to overview the LG biomass reutilization potential in order to obtain the high value added from block units to bioactive products.

2.2 Plant Cell Wall Structure and Function

The plant cell wall is a complex matrix of polysaccharides that provides support and strength, essential for plant cell survival. Polysaccharides perform a great diversity of functions during plant life, including:

- i) supporting the cell membrane and preventing it from bursting
- ii) expanding under turgor pressure at a controlled rate and direction, facilitating and regulating cell growth
- iii) cooperating with adjacent cells under similar turgor pressure to build a mechanically competent 3D tissue with every cell wall maintained in tension (Jarvis 2011)
- iv) protecting against other organisms and environmental stresses.

The cell wall of higher plants is not a uniform structure and is composed of three major layers (Figure 2.1):

- i) the *middle lamella* or lamellum, which is a thin layer of approximately 50 nm thickness sandwiched between the primary cell walls of neighboring cells. The lamellum is the first formed layer that cements the cell walls of two adjacent cells and is composed of calcium and magnesium pectates (Zamil and Geitmann 2017)
- ii) the *primary cell wall*, which lies down the middle lamella, surrounds and protects the cell, contributing to the wall structural integrity, cell adhesion, and signal transduction (McCann and Carpita 2008);
- iii) the *secondary cell wall*, located between the primary wall and the plasma membrane, is produced only in some cells once cell elongation ceases. Secondary walls may be deposited in a number of layers (S1, S2, S3) and are mainly found in tracheary elements

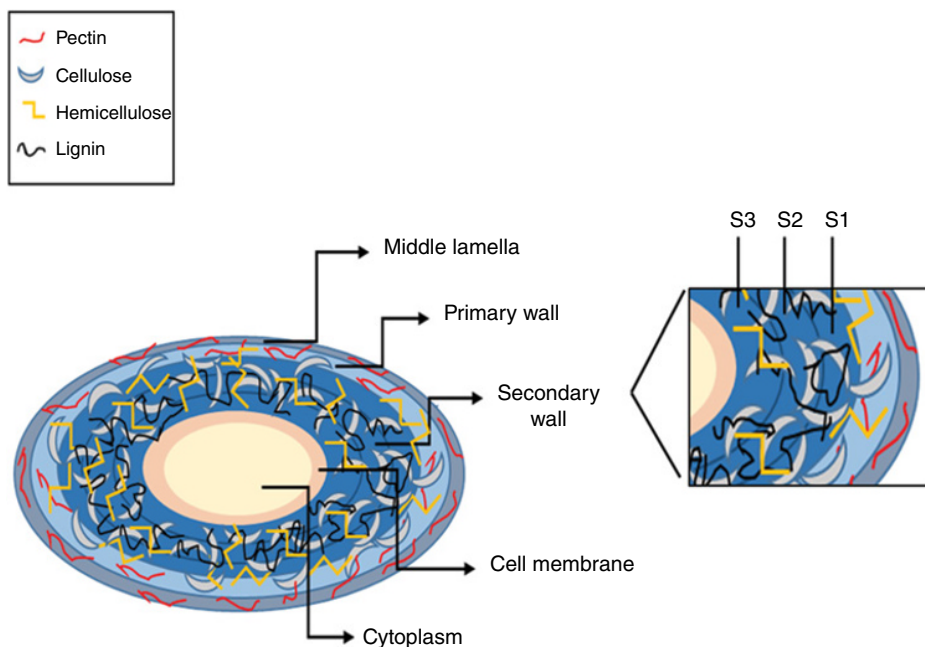


Figure 2.1 Plant cell wall structure and composition.

“tracheids in seedless vascular plants and gymnosperms and vessels in angiosperms” and fibers in the primary xylem and the secondary xylem (wood) (Zhong and Ye 2015).

2.3 Plant Cell Wall Chemical Composition

The plant cell wall is a complex network of cellulosic, hemicellulosic, and pectic polysaccharides and proteins (Altartouri and Geitmann 2015) whose composition depends on plant species and cell type (Davison et al. 2013). However, from a general point of view, they all have a conservative composition involving two phases: a *fibrillar phase*, which acts as the skeleton and is composed mainly of cellulose microfibrils, and a *matrix phase*, which contains a high proportion of noncellulosic polysaccharides that vary in their chemical structures. Structural proteins, glycoproteins, and phenolic components, including lignin, may also be present in the wall matrix (Harris 2006).

The matrix phase of primary walls is almost completely hydrated (65% water), consisting of hemicelluloses and pectins, with some structural proteins (Brett and Waldron 1996). Primary cell walls are usually classified as type I or type II, according to their polysaccharide composition. Type I walls contain cellulose, xyloglucan as the main hemicellulose, and abundant amounts of pectin. These primary walls are present in dicots and noncommelinoid monocots. Type II walls are present in grasses (Poales) cell walls and contain a higher amount of cellulose with negligible percentages of pectin and proteins. The major hemicellulose in type II walls is arabinoxylan (Carpita and McCann 2000).

Secondary walls contain cellulose and arabinoxylan and glucomannans as the major hemicelluloses (Brett and Waldron 1996). In secondary walls, the water in the matrix phase is largely replaced by lignin, making them nearly impenetrable to solutes and enzymes.

2.3.1 Cellulosic Polysaccharides

Cellulose is a major structural component of plant cell walls, which is responsible for mechanical strength. It is a linear polymer of D-anhydro-glucofuranose molecules joined by β -1,4-glycosidic bonds (Figure 2.2) (Alexandridis et al. 2018). Due to their linearity and regular structure, the cellulose molecules associate with each other over large regions, forming bundles of polycrystalline fibers. The degree of polymerization (DP) of cellulose largely depends on the origin and pretreatments applied to the raw LG biomass. DP defines the solubility in water; oligosaccharides having a DP above 13 will probably present some difficulties in forming homogeneous water solutions while oligosaccharides with a DP over 30 become similar to cellulose. Due to the huge amount of hydroxyl groups, cellulose presents an intra- and intermolecular hydrogen bonding network, which makes the crystalline structure robust. To solubilize cellulose polymer, the majority of hydroxyl bonds should break simultaneously. Thus, at mild temperatures, cellulose is insoluble not only in water but also in most typical solvents. Cellulose is one of the most important biomass resources due to its abundance in nature, with the peculiarity of not being included in the human

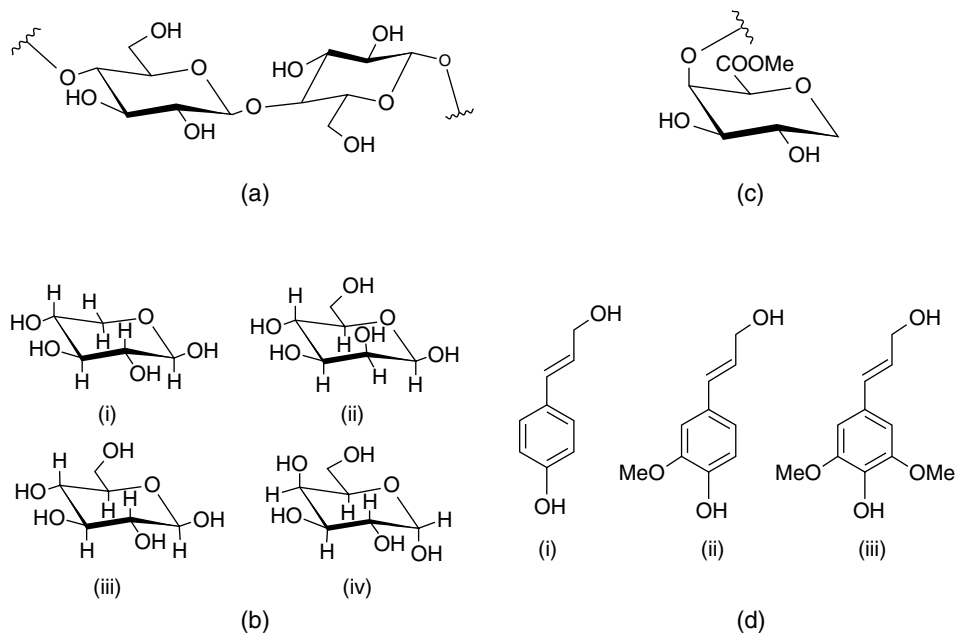


Figure 2.2 Chemical structure of the basic constituents of lignocellulosic biomass. Building blocks of (a) cellulose: β -D-glucopyranose; (b) hemicellulose: (i) β -D-xylopyranose, (ii) β -D-mannopyranose, (iii) β -D-glucopyranose, (iv) α -D-galactopyranose; (c) pectin; (d) lignin: (i) p-coumaryl alcohol, (ii) coniferyl alcohol, (iii) synapyl alcohol.

food chain. Cellulose applications involve paper products, textiles, polymer composites, and chemical precursors of pharmaceuticals, food, drinks, and coatings (Deng et al. 2015b).

2.3.2 Noncellulosic Polysaccharides

Noncellulosic polysaccharides present in plant cell matrix encompass mainly hemicelluloses (d-xylans, d-glucans, d-mannans, etc.) and pectins (d-galacturonans).

2.3.2.1 Hemicellulose

Hemicellulose is the second most abundant polysaccharide after cellulose in plant cell walls, accounting for 15–30% of lignocellulosic biomass by weight (Kapu and Trajano 2014). Although hemicelluloses are found in both primary and secondary cell walls of both monocotyledonous and dicotyledonous plant tissues, greater amounts of hemicellulose in wood and woody biomass than in herbaceous and agricultural biomass have been reported (Vassilev et al. 2012). Among the three main components in biomass, hemicellulose is a promising material to produce value-added chemicals. Hemicellulose consists of a short, highly branched polymer of five- and six-carbon polysaccharide units, such as xylan, mannan, β -glucans, and xyloglucans (Cao et al. 2018; Luo et al. 2019). Compared to cellulose and lignin, hemicellulose has a lower DP (100–200 U). Hemicellulose is more unstable than cellulose and therefore degrades more easily when subjected to heat treatment. Although there are many studies on the conversion of cellulose and lignin, those about hemicellulose conversion are limited.

2.3.2.2 Pectic Polysaccharides

Pectin is one of the most important cell wall polysaccharides, mainly those belonging to vegetables and fruits, and is linked covalently to form a gel matrix, interspacing the cellulose-hemicellulose network in the primary cell wall. It is probably the most complex macromolecule found in nature, as it can be composed of as many as 17 different monosaccharide units containing more than 20 different linkages. Historically, the compound was dubbed “pectic acid” coming from the Greek word $\pi\eta\chi\tau\epsilon\varsigma$, whose translation is *coagulated material*. The name was coined by the French scientist Henri Braconnot, who first isolated pectin from vegetables in 1825 (Yanakieva et al. 2012; Chan et al. 2017). Although a long time has passed since the discovery of pectin, its structural and chemical properties are still the subject of study around the world due to the heterogeneity of this polymer.

Regarding the basic structure, pectin is a heteropolysaccharide predominantly containing galacturonic acid (GalA) residues, an oxidized form of D-galactose (Figure 2.2). The GalA units are linked by ∞ -1/4 galacturonosyl linkages, which are usually interrupted by L-rhamnose units bearing side-chains, which cause a discontinuity in the linear structure of the poly-(GalA) chain. Some of the carboxyl groups on the continuous poly-(GalA) chain of pectin are esterified by methyl groups which generate variation in the degree of methyl esterification (DE). This results in classification as high-methoxyl (HM) pectins, in which DE is greater than 50%, or low-methoxyl (LM) pectins, being lower than 50%. Homogalacturonans (HG), rhamnogalacturonan-I (RGI), and rhamnogalacturonan-II (RGII) are the three main structural classes of pectin. The deposition and the way in which these domains are joined to one another are still a matter of debate. Currently, it is thought

that the polysaccharide regions have covalent bonds and are ionically cross-linked with other pectin strands to form networks that branch throughout the primary cell walls.

The biosynthesis of pectin is known to be complex and our understanding is currently characterized by much speculation (Chan et al. 2016; Adetunji et al. 2017). The diverse properties of pectin at the microstructural and macromolecular levels form the basis for its various food and nonfood applications, including reported health-promoting benefits and bioactivities. The major sources of commercial pectins are citrus wastes (pulp and peel: 85%), and apple pomace (14%), while some specific products may be extracted from sugarbeet pulp (0.5%) (Ciriminna et al. 2015). This is due to the availability of these biomasses and the quality presented by their pectins. Citrus peel and apple pomace are available in large amounts as remainders from juice and essential oil production while sugarbeet pulp is obtained from the sugar industry.

A schematic representation of the composition of the structural elements of cellulose, hemicellulose, lignin, and pectin is given in Figure 2.2.

2.3.3 Proteins and Glycoproteins

There are two groups of cell wall proteins: enzymes and structural proteins. Cell wall enzymes have a broad range of functions, including wall degradation, polymer turnover, wall remodeling, and extension associated with plant growth, development, maturation, and senescence (Waldron et al. 2003). The most abundant structural proteins are the hydroxyproline-rich glycoproteins which comprise several groups, including extensins, arabinogalactan proteins, proline/hydroxyproline-rich glycoproteins, and solanaceous lectins (Cassab 1998; Sommer-Knudsen et al. 1998). It has been proposed that they act as an attachment for lignin and link pectic components (Waldron et al. 2003).

2.3.4 Phenolic Compounds

Two main classes of phenolic compounds are found in plant cell walls: lignin, the most abundant polymer in secondary walls, and simple phenolic esters, such as ferulic acid, which are attached to primary wall polysaccharides (Brett and Waldron 1996).

Lignin is the main component of lignocellulosic biomass, accounting for 15–30% by weight and 40% by energy (Zhang 2018). Less than 2% of the 1.5–1.8 billion tons of industrial lignin waste is used annually, of which lignosulfonate is mainly used as an additive in building materials (Cao et al. 2018). The major source of lignin (kraft lignin and lignosulfonates) is the pulp and paper industry (Mahmood 2014). For the sustainable production of biofuels and bulk chemicals, lignin is considered the second most abundant renewable resource, after cellulose (Agarwal et al. 2018).

In plants, lignin embeds the polysaccharide network of cellulose and hemicellulose like an adhesive that keeps the lignocellulose matrix together, providing strength, rigidity, impermeability, and structural reinforcement to cell walls. The lignin content depends on the plant taxonomy, being most abundant in conifer wood (30%), and 10–15% in grass. All wall layers may accumulate phenolic polymers, namely lignins made of cytosol-synthesized hydroxycinnamoyl alcohols (Voxeur et al. 2015). Despite lignin monomer composition and linkage distribution being extremely variable between species and tissues, only

three types of substituted phenols connected by C—C or C—O bonds form the 3D irregular polymer of lignin (Zhang 2018): p-cumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (noncondensate structure) (Figure 2.2) (Cao et al. 2018). Lignin can be classified as softwood lignin, hardwood lignin, and grass lignin, depending on its origin. Softwood lignin is formed by coniferyl alcohol and trace amounts of sinapyl alcohol-derived units. Hardwood lignin contains both coniferyl alcohol and sinapyl alcohol but in different ratios compared to softwood lignin. Grass lignin contains mainly structural elements derived from p-coumaryl alcohol (Naseem et al. 2016).

Lignin can be separated from lignocellulose by physical, chemical, and biological methods (Hu et al. 2018). The physical method is to break the connection between lignin and cellulose/hemicellulose structures by steam explosion or mechanical grinding (high temperature and pressure), via which lignin with high purity can be obtained (Cao et al. 2018). The biological method is carried out by enzymes under milder conditions, with the aim of destroying the chemical connection between lignin and carbohydrate. Due to high separation efficiency and mild reaction conditions, chemical methods are widely used for industrial production (Cao et al. 2018). Moreover, the production of fine chemical products from lignin can help to reduce the consumption of fossil resources and constitutes one of the environmentally friendly approaches of researchers.

Lignin depolymerization is the most complex, and its utilization for value-added chemicals is a severe challenge compared to cellulose and hemicelluloses. Despite being described as a random construction of aromatic monomers, the scaling of lignin products is the limiting step to obtain valuable chemicals such as phenols, aldehydes, carboxylic acids, alkanes, and arenes (Mei et al. 2019). However, great effort should be directed to this because lignin is the most abundant renewable natural aromatic biopolymer, which can be a sustainable candidate feedstock to produce aromatic chemicals and, in particular, to replace those ultimately derived from petroleum.

2.4 Valuable Chemicals Obtained from Lignocellulosic Biomass

Lignocellulosic biomass is the most abundant renewable material in the world for the production of biofuels (Cai et al. 2017). Bioethanol production via LG feedstock conversion under a biorefinery system appears to be promising in mitigating global climate change involving also the co-production of biochemicals. Thus, in a biorefinery, a wide spectrum of valuable chemical products can be obtained by combining biochemical conversion technologies. LG biomass from crops, paper residues, wood, and solid wastes constitutes a potential sustainable resource for bio-based fuels (Ekman et al. 2013).

As the first step in LG conversion to bioethanol, a pretreatment to remove contaminants and reduce moisture is carried out. Dilute acid pretreatment followed by enzymatic hydrolysis converts LG biomass to fermentable sugars. The fermentation of hexoses and pentoses into bioproducts is then purified by physical treatments, such as distillation or filtration (Borrión et al. 2012; Chrysikou et al. 2018). On the other hand, by using extraction and processing methods, a broad range of functionalized molecules can be released from plants waste: lipids, hemicellulose, bioactives/nutraceuticals, pectin, starch, phytochemicals, phenols, nanoparticles, biodiesel, and activated carbon (Ravindran and Jaiswal 2016).

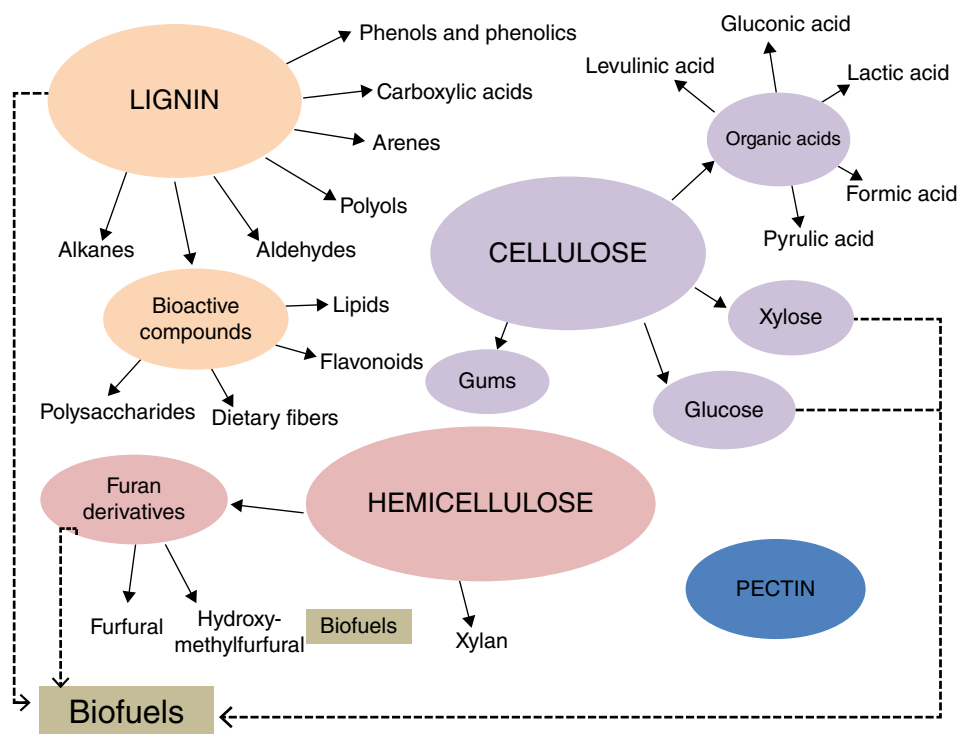


Figure 2.3 Some valuable chemicals obtained from lignocellulosic biomass.

Figure 2.3 shows some of the most common value-added products obtained from lignocellulose sources, while a brief description of the most valuable products obtained from LG biomass follows.

2.4.1 Sugar Alcohols

Producing water-soluble carbohydrates from LG biomass requires cleaving ether bonds in hemicellulose and cellulose chains. Also, the further degradation of the pentose and hexose sugars (xylose, glucose) to insoluble products needs to be carefully inspected. Despite being a high-cost process, the hydrolysis of cellulose to glucose is known to be catalyzed by cellulase enzymes under mild conditions. Mineral acids, such as H_2SO_4 and HCl , can also catalyze the hydrolysis of cellulose to glucose. During the hydrolysis, the β -1,4-glycosidic bonds in cellulose are selectively activated by the Brønsted acids in the aqueous medium. Relatively high yields (30–70%) of glucose can be achieved by using concentrated H_2SO_4 (Deng et al. 2014). However, the problems of corrosion, nonrecyclability, and large amounts of mineral acid wastes make this procedure unattractive. Lutherbacher et al. (2014) proposed the use of biomass-derived γ -valerolactone (GVL) to promote the thermocatalytic saccharification through complete solubilization of the biomass, including the lignin fraction. The overall process, including pretreatment and enzymatic hydrolysis, could be cost-competitive for ethanol production. Oyola-Rivera et al. (2018) recently reported sugar

yields up to 90%, 94%, and 88% for bagasse, plantain peel, and spent barley from brewery production, respectively.

Among the different value-added products obtained, xylose and glucose are the most abundant in the deconstruction of hardwood and softwood (Lutherbacher et al. 2014). These sugars can be converted to many platform molecules for the production of fuels and specialty chemicals using heterogeneous catalysts.

2.4.2 Polyols

Due to its structure, kraft lignin formed by phenyl propanol and aryl-alkyl ether bonding can be a good source of polyols. The multiple hydroxyl groups present in the lignin's structure are essential raw materials for polyurethane production. Also, for polyolefins, polyethylene terephthalate (PET) and polycarbonate production, the plastics can be either replaced or enriched with bio-based components (Brodin et al. 2017). Considering sustainability concerns and the fact that petroleum products are commonly used in the polyurethane industry, bio-based polyols and lignopolyols could be an environmentally friendly solution (Mahmood 2014). Although a bioplastic is characterized by being produced from a renewable source, bioplastics are not necessarily biodegradable. As an example, biopolyethylene (BioPe) is similar to the fossil-based polyethylene and thus is not biodegradable. Hence, plastic biodegradability is determined by the chemical structure rather than origin (Brodin et al. 2017).

2.4.3 Furfural

Furfural (FF), identified by the US Department of Energy (DoE) as one of the top 12 value-added products, has a world market of around 300 000 tons per year. FF is a typical product which could be obtained from hemicellulose in raw biomass and is also a key platform chemical produced in LG biorefineries. The main advantage of FF, as for other block chain compounds, is that it could further be transformed to fuels and useful chemicals. A wide range of products can be derived using FF as starter material, as it is an essential intermediate product in the oil refining, plastics, pharmaceutical, and agrochemical industries. Biofuels can be derived from furfuryl acetate, GVL, levulinic acid, 1,5-pentanediol, bicyclopentane, and furfuryl alcohol resins (diesel/kerosene). On the other hand, as value-added products for the chemical industry, FF can lead to the following derivatives: furan, furfural resins, tetrahydrofurfuryl alcohol, 2-methyl tetrahydrofuran, 2-methyl furan, furoic acid, succinic acid, and 5-hydroxy 2(5H)-furanone, among others (Luo et al. 2019).

2.4.4 Hydroxymethylfurfural

Hydroxymethylfurfural (HMF) is considered a versatile key value-added chemical (or platform molecule) which receives much attention in the petroleum and chemical industries. HMF has a high market value up to USD 300 per kg, depending on the final chemical quality. Currently, commercial production of HMF relies on syrups extracted from energy crops (Yu and Tsang 2017). HMF has excellent chemical reactivity that enables the synthesis of diverse value-added chemical products. In this respect, HMF has been identified as

a primary building block for the production of furanic polyesters, polyamides, and polyurethanes analogous to those derived from the petroleum polymer industry (Pagán-Torres et al. 2012).

Six- and five-carbon carbohydrate derived from biomass need to be transformed into intermediates before being used for biofuel or chemical production (Abou-Yousef et al. 2013). The conversion of biomass-derived carbohydrate into furan derivatives such as HMF and FF is frequently the first step. However, the decomposition behavior of the feedstock depends on the interactions between the cellulose, hemicellulose, and lignin. Thus, diverse HMF yields (2–60%) depend on the substrate composition and conversion systems (Yu and Tsang 2017). Among the carbohydrate sources employed for HMF preparation, fructose is the most popular due to ease of conversion and high selectivity through a simple dehydration reaction. Glucose, cellulose, starch, sucrose, and inulin are also used as starting substances for HMF production (Agarwal et al. 2018). Hydrogenation reactions result in synthesis of the following furan derivatives: 2,5 dimethylfuran, which is a bioderived transportation fuel, 2,5-bis(hydroxymethyl)furan (BHMF) (used in manufacture of polyurethane foam), 2,5-dimethyltetrahydrofuran (used in polyester preparation) and others. Also, HMF acts as an oxidative precursor to prepare FDCA (2,5-furandicarboxylic acid), an alternative intermediate product in PET manufacturing and nylon preparations (van Putten et al. 2013). Also, 2,5-diformylfuran (DFF) finds application in the synthesis of diamine and Schiff bases (Agarwal et al. 2018).

The complexity of cellulose structure causes complete insolubility in aqueous and most common organic solvents. However, in the presence of ionic solutions at suitable conditions, the conversion of glucose to HMF takes place. This is due to the specific properties of ionic liquids, such as very low vapor pressure, no flammability, high thermal and chemical stability, and efficient solvent power for organic and inorganic substances. The solubility of cellulose in ionic liquids is related to its anion, which can dissolve cellulose by disrupting its hydrogen bonds. Thus, the conversion reaction of cellulose to produce HMF passes through three consecutive steps: hydrolysis, isomerization, and dehydration (Abou-Yousef et al. 2013). The hydrolyzation to oligosaccharides is mediated by ionic acids and then to glucose in a short time. Glucose should be isomerized into fructose followed by dehydration of fructose molecules. Conversion of lignocellulose in ionic liquids into the furanic compounds HMF and FF has produced yields up to 52% and 31%, respectively (Zhang and Zhao 2010).

2.4.5 Organic Acids

The high oxygen/carbon ratio feature of cellulose makes it an ideal precursor for the production of organic acids (Li et al. 2018). Under suitable conditions, the lignin phenyl ring can be oxidized to quinones or be cleaved. Because of the instability of benzoquinone structures obtained, they can be oxidized to yield aromatic ring cleavage products, such as dicarboxylic acids (Ma et al. 2018). The conversion of lignin to open chain organic acids has become an area of interest in chemical research. Carboxylic acids also can be derived from lignin co-existing with other products, such as phenols and aldehydes (Mei et al. 2019).

The conversion of carbohydrates into organic acids such as levulinic, gluconic, and formic acid is a promising way to use renewable biomass since it is more cost-effective than