Chapter 1
Introduction to Lignocellulose-based Products

Akram Zamani

Abstract Lignocellulosic materials are naturally designed composites that play crucial roles in the survival of plants. Considering their broad availability, there is a general agreement on the replacement of a major part of fossil-derived fuels and chemicals with lignocellulosic products. Additionally, some products are solely prepared from lignocelluloses and have no fossil-based equivalent. Several chemical, enzymatic, and thermal treatments are available to fractionate the lignocelluloses to their constituents, i.e., cellulose, hemicellulose, and lignin. Once separated, they are employed for the production of a wide variety of products. Pulp and paper, textiles, and nanocellulose are produced directly from cellulose. Cellulose may undergo chemical modifications to prepare cellulose derivatives. Hemicelluloses are used as a source of films, coatings, and hydrogels. Cellulose and hemicelluloses are hydrolyzed to sugars. Biofuel production from lignocellulosic sugars is among the most attractive routes. The consumption of ethanol, biobutanol, biohydrogen, biomethane, and biodiesel not only reduces the need to fossil fuels but also controls the environmental pollutions resulted by fossil fuels. Organic acids, polysaccharides, microbial biomass, and single cell proteins are other valuable products of fermentation of lignocellulosic sugars. Moreover, these sugars can be chemically converted to some other important chemicals, i.e., furfural, hydroxymethyl furfural, and levulinic acid. Xylitol is produced from hemicellulosic xylose by both chemical and biological methods. Lignin has a high potential for the production of several products including fuels, aromatics, carbon fiber, activated carbon, fillers, adhesives, resins, and dispersants. This chapter presents a brief overview of importance, applications, and production processes of different lignocellulosic products.

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1.1 Introduction

Amazing micro- and macro-structure of the plants cell wall, i.e., lignocellulosic materials, is the key factor for plants survival. During the growth of plant cells, multilayer cell wall is formed around their plasma membrane which protects the plant cells against mechanical, chemical, and microbial stresses (Taherzadeh and Jeihanipour 2012). Lignocellulosic materials are mainly composed of cellulose (35–50 %), hemicellulose (15–35 %), and lignin (10–35 %). The concentration of the mentioned components varies with plant types. For example, higher concentrations of lignin are found in higher plants, whereas lower lignin is present in annual plants (Azadi et al. 2013). Cellulose, hemicellulose, and lignin have very close interactions with each other in the cell wall. This results in a unique three-dimensional structure of cell wall. The presence of a high number of OH groups on the cellulose chain, polymer of glucose, makes this biopolymer susceptible for formation of strong hydrogen bonds. This ends with formation of high crystalline cellulose micro-fibrils in plant cell wall. Cellulose micro-fibrils are surrounded by hemicellulose (a heteropolymer of five and six carbon sugars) and lignin (a complex polymer of phenolic compounds). The high crystallinity of cellulose is crucial for exhibition of a high mechanical strength by plant cell wall. Lignin and hemicellulose protect the cellulose against microbial and chemical attacks. Moreover, the hydrophobic nature of lignin shields plant cells against moisture loss and death due to drying. The lignocellulosic biomass, the direct product of photosynthetic reactions by plants, is indeed the most abundant renewable material in the world (Karimi et al. 2013; Taherzadeh and Jeihanipour 2012; Xu et al. 2013).

Besides the critical function of lignocellulosic materials in plants life, they have a potential to play a significant role in development of modern sustainable societies as they have been introduced as a widely available feedstock for the production of energy and chemicals. Annually, several million tons of lignocellulosic materials are produced in the form of forest trees, grasses, and agricultural residues (Skog and Stanturf 2011). Dependence of human life to lignocellulosic materials goes back to several thousand years ago where human used wood as a source of energy (by direct burning) as well as construction materials. By discovery of fossil fuels, especially petroleum, the consumption of lignocellulosic materials as a source of energy was declined namely in the developed countries. However, limited sources of fossil fuels as well as serious environmental concerns arise from the unlimited consumption of these sources have returned the attentions to lignocellulosic materials in recent years. Indeed, lignocellulosic materials will be one of the most important sources of energy and materials in the future (Ma et al. 2012). Thanks to clever design and build up of lignocellulosic materials in the nature, we have access to huge amounts of these materials with low costs. Nowadays, the strategic goal in several developed and underdeveloped countries is to have a sustainable society by employing lignocellulosic materials as a source of material and energy.

There are two perspectives for application of lignocellulosic materials in the human life:

- Direct consumption.
- Conversion to secondary value-added products.

High-quality wood is still a major component used as a construction material for houses and furniture in many countries (Cambria and Pierangeli 2012). Getting the benefit of high nutritional values, many of agricultural residues are nowadays directly used as animal feed (Walker and Kohler 1981). Additionally, lignocellulosic biomass is still used for heat generation through the direct combustion in several rural areas. However, what can have a significant impact on the reduction of environmental concerns is indirect application of these materials as feedstock for the production of energy careers and chemicals. In this indirect route, chemical, thermal, and biological approaches are employed to convert lignocellulosic materials to several value-added products (Menon and Rao 2012). In this road, physicochemical properties of individual constituents of lignocellulosic materials are considered for creation of new materials. For example, high-strength fibers and textiles are produced from cellulosic fraction of lignocellulosic materials. For such applications, the component with the desired properties (cellulose in this example) should be purified from its complex in lignocellulosic materials and used for different applications. On the other hand, the decomposition of different components of lignocellulosic materials has opened up several opportunities for the production of new chemicals. Biofuels and several other chemicals are some examples which are categorized in this group. In an ideal biorefinery, the goal is complete fractionation of lignocellulosic biomass to several value-added products (Garver and Liu 2014).

In this chapter, an overview of different products which can be obtained from cellulose, hemicellulose, and lignin through biological and chemical routes is presented (Fig. 1.1).

1.2 Products Derived from Cellulose and Hemicellulose

Polysaccharides, i.e., cellulose and hemicellulose, make up 45–80 % of lignocellulosic biomass (Azadi et al. 2013). Taking into account the enormous amounts of existing low-cost lignocellulosic materials, e.g., forest residues, agricultural wastes, and a major part of municipal solid wastes, considerable amounts of these polysaccharides are annually produced which can be employed for preparation of several products. Cellulose- and hemicellulose-based products can be categorized into two groups. The first group refers to the products which are directly obtained from these biopolymers. Paper, textiles, cellulose derivatives, packaging films, and superabsorbent materials are a few examples of such products. In contrast, the process of production of second groups of products goes through a hydrolysis step in which polysaccharides are converted to their building blocks, i.e., simple six and

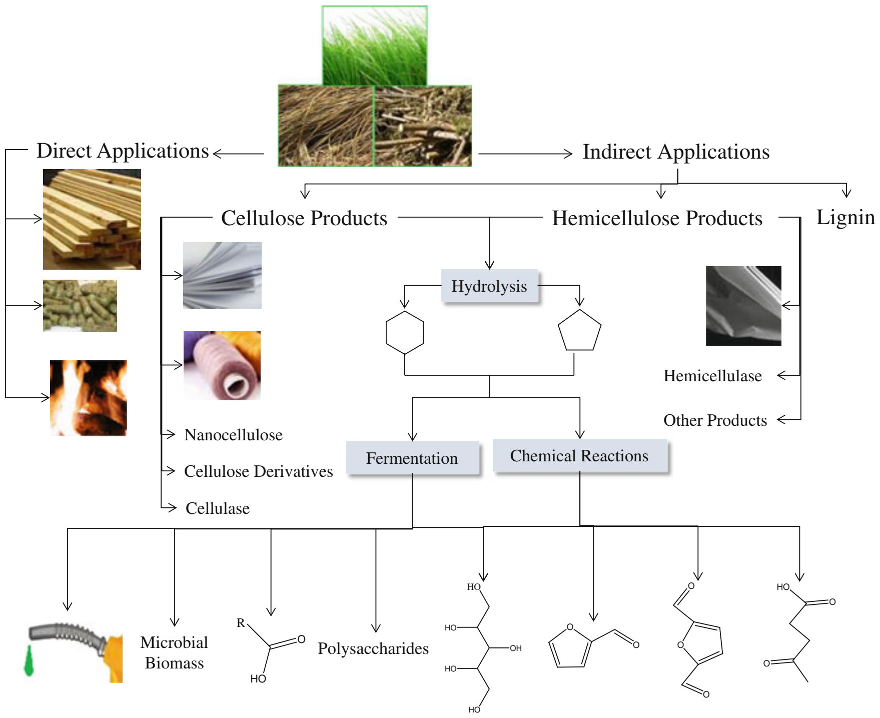

Fig. 1.1 Different products obtained from lignocellulosic materials

five carbon sugars. Sugars and all of their derivatives belong to this group. Different thermal, chemical, and biological approaches are employed for conversion of lignocellulosic sugars to final products (Rødsrud et al. 2012; French et al. 2000).

1.2.1 *Products Directly Obtained from Cellulose*

1.2.1.1 Pulp and Paper

Indeed, pulp and paper are the most well-known products obtained from lignocelluloses. Although before 1800s cotton and linen rags were the only resources for paper production, woody biomass is nowadays the dominant source (90 % of total production). The process of paper production from wood chips has seven major steps of pulping, washing, beating, blending with additives, fiber mat formation, water drainage, and drying (Shmulsky and Jones 2011).

The pulping is referred to mechanical, thermal, or chemical processes in which cellulose fibers are separated from their complex mixture in lignocellulosic materials. The progress of lignin and hemicellulose removal from the cellulosic fibers (pulp) is the key factor determining the quality of the final product. The obtained pulp is then washed to remove the impurities. Due to presence of low amounts of lignin in the produced pulp, the pulp color is brown. The unbleached pulp is a suitable raw material for applications where color is not important, e.g., for paper bag production. However, for writing and book papers, the pulp should be bleached to remove or lighten the remaining lignin. After the polishing step, to enhance the strength of the paper, the cellulose micro-fibrils are mechanically flattened and disentangled. This step is called beating or refining. Afterward, the pulp is mixed with different additives such as starch and clays to increase the bond strength and brightness, respectively. Finally, a thin mat is formed using the pulp. The pulp slurry is poured onto a horizontal screen, the water drains away and the mat is remaining on the screen. The mat is finally dried and used for different applications (Hocking 2005; Shmulsky and Jones 2011; Young et al. 2003). The whole process of paper production from woody materials is illustrated in Fig. 1.2.

It should be mentioned that during the pulping process, lignin and hemicelluloses are mainly separated leaving a product with high cellulose purity. The separated lignin and hemicelluloses can subsequently be used for different purposes as discussed in the coming sections.

1.2.1.2 Fibers and Textiles

Cellulosic fibers typically contribute to over 40 % of different textiles used for clothing, home furnishing, and different industrial applications. Cotton, , and are the most important cellulosic textiles in terms of production volume. Although the

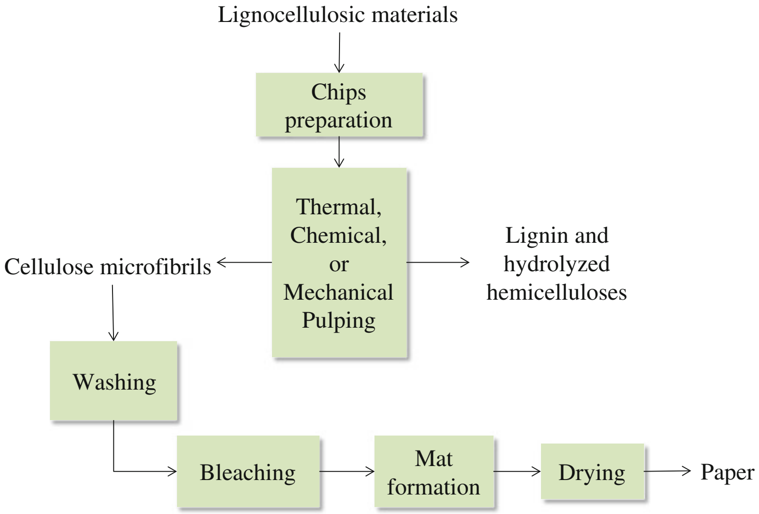

Fig. 1.2 The overview of paper production process from lignocellulosic materials

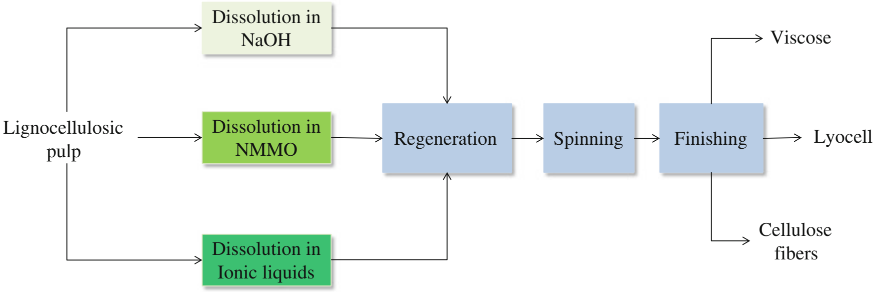

Fig. 1.3 Production of cellulosic fibers from lignocellulosic materials

seeds of gossypium plant are the only recourses for cotton production, viscose and lyocell textiles can be produced from lignocellulosic materials. The latter textiles are produced via a process including dissolution of cellulosic fraction of lignocellulosic pulp in a solvent, regeneration of cellulose, spinning of fibers, and finishing. The solvents used for preparation of viscose and lyocell are sodium hydroxide solution and N-Methyl morpholine-N-Oxide (NMMO), respectively (Mather and Wardman 2010; Perepelkin 2007; Wilkes 2001). Recently, application of ionic liquids as more efficient solvents compared to NaOH and NMMO has been proposed for production of cellulose fibers (Moniruzzaman and Ono 2012). A schematic of cellulosic fiber production process from lignocellulosic pulp is presented in Fig. 1.3.

1.2.1.3 Nanocellulose

Besides extensive application of cellulose for the production of paper and textiles for a very long time, some new aspects of application of cellulosic fraction of lignocellulosic materials, in nano-scale, have been recently proposed. Getting the benefit of inherent properties of cellulose, e.g., high hydrophilic nature and potential for chemical modifications together with unique properties of materials at nano-scale, namely extremely large surface areas, nanocellulose exhibits outstanding sole characteristics. Nanocellulose has been produced from pure cellulose as well as the cellulose available in wood and agricultural residues (Dufresne 2008).

The process of production of nanocellulose from lignocellulosic materials usually includes two major steps of cellulose purification and nanocellulose formation. In the purification step, a process similar to pulping is performed to remove lignin and hemicellulose from cellulose. Accordingly, lignin and hemicellulose removal is accompanied using chemical or enzymatic reagents together with mechanical treatment. The product of this step is subjected to a bleaching process to remove the remaining lignin and produce a purified cellulose pulp. This is then subjected to a process called fibrillation where cellulosic fibers are transferred to nanocellulose. Originally, fibrillation was performed through extensive mechanical share to disintegrate the large cellulose fibers and liberate cellulose nanofibers. However, this is nowadays performed in commercial scale by passing of cellulose–water suspensions through mechanical homogenizers under very high pressure drops. Besides homogenization, cryocrushing can also be employed for fibrillation. In this method, the cellulose slurry is quickly frozen in liquid nitrogen and the frozen sample is subjected to very high share forces. The presence of ice crystals exert extremely high pressures and result in cellulose rupture and nanocellulose liberation. Additionally, some modified types of grinders have been used for cellulose fibrillation in which the cellulose suspension is placed between two grind stones (one static and one rotating) and nanocellulose is formed (Dufresne 2008; Eichhorn et al. 2010; Klemm et al. 2011; Rebouillat and Pla 2013; Siró and Plackett 2010).

All types of mechanical forces for nanocellulose generation suffer from the bottleneck of very high energy consumption (higher than 25,000 kWh/ton product). This negatively affects the economy of nanocellulose production. Therefore, recently pretreatment steps have been suggested to reduce the energy consumption during the fibrillation. The pretreatment of cellulose with acid (HCl or H_2SO_4) or cellulosic enzymes considerably reduce the energy consumption in subsequent mechanical fibrillation process (Klemm et al. 2011). Figure 1.4 represents the major steps performed during the nanocellulose formation process.

Although there is not a long time since nanocellulose has been introduced, different applications are known for this material today. Several features such as very high tensile strength and stiffness, high viscosity, film and foam forming properties, very high barrier characteristics, possible surface modifications, hydrophobicity, and high biocompatibility of nanocellulose have made this biomaterial an ideal choice for different purposes. Most commonly, nanocellulose is used as reinforcement in nanocomposites. In biomedical industry, nanocellulose is used in wound dressing, artificial skins, implants, bandages, face masks, artificial blood vessels, supports for drug delivery, cell and enzyme carriers, and cosmetic tissues. In food industry, it is widely used as thickeners, flavor carriers, and suspensions stabilizer. In other industries, nanocellulose can be used in different forms such as foams, membranes, filters, coatings, adhesives, packaging and sealing materials, superabsorbent, and nonwoven materials (Dufresne 2008; Eichhorn et al. 2010; Klemm et al. 2011; Rebouillat and Pla 2013; Siró and Plackett 2010).

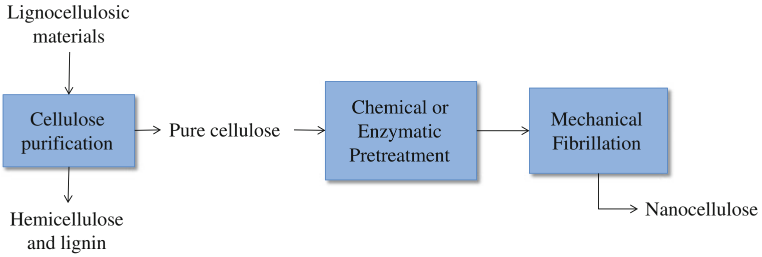

Fig. 1.4 The production of nanocellulose from lignocellulosic materials

1.2.1.4 Cellulose Derivatives

Today, besides direct application of cellulose, different derivatives of this biopolymer are also used in various sectors. Presence of three hydroxyl groups on each building block of cellulose chain creates a high potential for chemical modification of cellulose. Cellulose derivatives are commonly produced through esterification or etherification reactions (Majewicz and Podlas 2000). These reactions are traditionally performed in heterogeneous phase. However, due to difficulties in control of the reactions at heterogeneous conditions, many studies have been dedicated to perform the cellulose modification reactions in a homogenous phase where cellulose is dissolved in an appropriate solvent and the reaction takes place in the solution (Blanchi et al. 1997).

Among the wide variety of cellulose derivatives, cellulose acetate, carboxymethyl cellulose, cellulose nitrate, methyl cellulose, and hydroxyethyl cellulose are the most important ones in terms of production volume. Cellulose derivatives have versatile applications in preparation of coatings, films, membranes, and absorbents. Moreover, they are employed as additives to enhance the characteristics of food, pharmaceuticals, and cosmetics (Majewicz and Podlas 2000; Bidgoli et al. 2014; Barba et al. 2002; Toğrul and Arslan 2003).

1.2.2 Products Obtained Directly from Hemicelluloses

Although cellulosic-based products are commercially used for a very long time, application of hemicellulosic polymers for different purposes has recently got a high attention. One reason for the latter discovery of hemicellulosic characteristics and its wide application may be extensive degradation of hemicelluloses during the course of most cellulose purification processes. For example, when lignocellulosic materials are subjected to pulping process, the strong chemical environment leads to considerable hydrolysis of hemicelluloses to sugars and their degradation products (Spiridon and Popa 2008). Therefore, hemicellulosic polymers are not recovered in nearly all industrial pulping and fiber formation processes.

However, in order to get the benefit of the whole polysaccharide fraction of lignocellulosic materials, i.e., hallocellulose, hemicelluloses should be recovered prior to the harsh treatments. Strong interaction of hemicelluloses with cellulose and lignin renders the easy liberation of hemicelluloses during the extraction processes. Several approaches have been proposed for effective recovery of hemicelluloses. Most commonly, alkali treatments are used for effective extraction of hemicelluloses (Peng et al. 2012; Spiridon and Popa 2008). However, the extracted hemicelluloses are usually contaminated with significant amounts of lignin. On the other hand, hemicelluloses are considerably deacetylated during the course of alkali extraction. Employment of alkali peroxide pretreatment significantly enhances the purity of extracted hemicellulose with respect to lignin contamination (Peng et al. 2012; Spiridon and Popa 2008). Organic solvent treatment, especially treatment with dimethyl sulfoxide, not only effectively extracts the hemicelluloses but also does not alter the structure of these polymers (Hansen and Plackett 2008; Peng et al. 2012). Mechanical treatments, including ultrasonication and extrusion, and thermal treatments including microwave irradiation enhance the performance of hemicellulose chemical extraction process (Sedlmeyer 2011; Peng et al. 2012). Although hemicelluloses are nowadays commercially extracted and used for different purposes, there is still active research aiming at improvement of the hemicelluloses extraction process to achieve a material with desired properties.

Nowadays, different applications of hemicelluloses are known in food, medical, and cosmetic industries. Emulsifying, stabilizing, and binding properties are among the important characteristics of hemicelluloses in different applications (Spiridon and Popa 2008). Additionally, hemicelluloses have shown promising potential in the enhancement of immune system in human body (Peng et al. 2012). Moreover, hemicelluloses exhibit excellent film-forming properties. Currently, hemicelluloses are commercially applied as packaging films and coatings for food products. However, researches are still conduced to improve the oxygen and water vapor barrier properties of the films and coatings (Hansen and Plackett 2008). The production of hydrogels from hemicelluloses in combination with other biopolymers such as chitosan is another recently proposed use for hemicelluloses. The obtained hydrogels have a high potential to be used in biomedical applications, e.g., drug delivery systems (Hansen and Plackett 2008; Sedlmeyer 2011).

Because of relatively short-term research on hemicellulose-based products compared to that of cellulose, new routes may be investigated in the future suggesting new aspects for application of hemicellulosic polymers.

1.2.3 Lignocellulosic Enzymes

In the nature, degradation of lignocellulosic materials is performed through the simultaneous action of several different enzymes specifically cellulases, hemicellulases, and ligninases. Cellulases are usually referred to a group of enzymes that act synergically on crystalline cellulose and hydrolyze it to glucose. Moreover, hemicelluloses catalyze the hydrolysis of hemicelluloses to their building blocks, i.e., five and six carbon sugars. In contrast, ligninase promotes depolymerization of the complex structure of lignin (Martins et al. 2011). Interestingly, several applications for these enzymes have been recognized in different industries. Among different lignocellulosic enzymes, cellulases are the most important group such that the need for these enzymes shares 8 % of the total demand for different enzymes in the world (Acharya and Chaudhary 2012).

Microbial cellulases are nowadays broadly used in food, textile, and paper processing (Acharya and Chaudhary 2012; Martins et al. 2011). A new application for cellulases has recently got increasing attentions in parallel to the growth of second generation of biofuels from lignocellulosic materials. The enzymatic hydrolysis of cellulose by cellulases is one of the most important and challenging steps in production of biofuels, e.g., ethanol, from lignocellulosic materials. Nowadays, one of the major bottlenecks of lignocellulosic ethanol production is high cost of cellulases. Therefore, there is an increasing demand for production of cellulases with lower costs and higher activities (Hahn-Hägerdal et al. 2006; Percival Zhang et al. 2006; Quinlan et al. 2010).

Pure cellulose as well as lignocellulosic materials can be employed as a substrate for the production of cellulases. Although several fungal and bacterial strains are able to produce different levels of cellulases, nowadays, cellulases are industrially produced using fungal strains specifically *Trichoderma* spp (Fig. 1.5). This is because of the high cellulases production ability of fungi and less complexity and easier recovery of the fungal cellulases compared to the bacterial ones (Acharya and Chaudhary 2012; Martins et al. 2011; Quinlan et al. 2010; Quiroz-Castañeda et al. 2011).

The Danish company, Novozymes, as the largest enzyme producer, has succeeded to significantly reduce the cellulases cost and enhance its activity in recent years (Acharya and Chaudhary 2012; Quinlan et al. 2010). However, the enzyme production industry still needs to pave the way to achieve lower prices and higher activities to meet the requirements for lignocellulosic ethanol production.

The production of cellulases by fungi can be performed both in solid state and submerged fermentations. Although the submerged fermentation is industrially used for production of cellulases, solid-state fermentation is expected to be a competitive method getting benefit of a number of advantages including lower working volumes, higher productivities, higher concentrations, and easier recovery and purification of the enzymes (Acharya and Chaudhary 2012; Martins et al. 2011).

Although the fungal cellulases are nowadays industrially dominant, bacterial cellulases have been the subject of several researches in recent years. Compared to

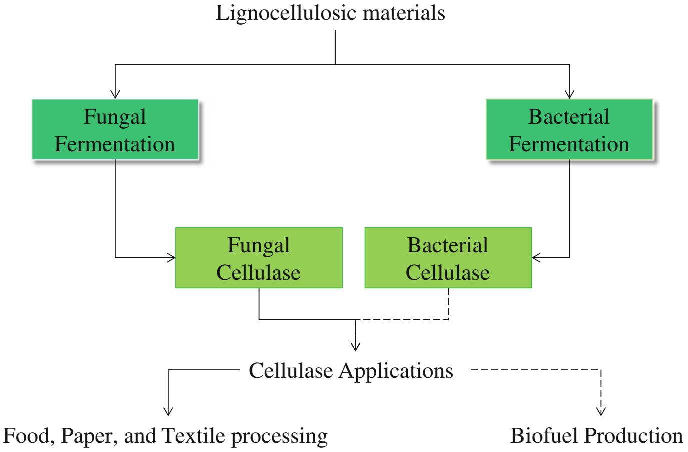

Fig. 1.5 Production of microbial cellulases and their current and future applications

fungi, bacteria generally have a higher growth rate. Moreover, especial strains of cellulase-producing bacteria are enormously resistant to environmental stresses and can withstand extreme conditions of temperature and pH. More complex structure of bacterial cellulose may result in increased synergy and effectiveness (Sadhu and Maiti 2013). Even though promising results have been achieved in this area, there is still a long way until bacterial cellulases get enough commercial impacts (Fig. 1.5).

1.2.4 Products Obtained Through the Hydrolysis of Cellulose and Hemicellulose

Although cellulose and hemicellulose are directly employed for the preparation of different polymer-based products, a wider range of products are obtained through hydrolysis of these polysaccharides. Once cellulose and hemicellulose are cleaved to their building blocks, i.e., simple sugars, they can either be used directly or converted to a broad spectrum of secondary products. Conversion of sugars to the end products can be performed through chemical, thermal, and biochemical methods.

1.2.4.1 Lignocellulosic Sugars

Glucose is the sole building block of cellulose, while hemicelluloses are composed of different five and six carbon sugars (e.g., xylose, mannose, and glucose). These sugars are released in hydrolysis reactions. Generally, hemicelluloses are much more susceptible to different hydrolytic agents compared to cellulose. For example, because of hydrolysis of hemicelluloses during the pulping process, usually 15–22 % of total sugars are available in the liquor of pulping processes where cellulose remains almost unchanged (Taherzadeh et al. 2003). This sugar mixture can be employed for the cultivation of different microorganisms and biosynthesis of different fermentation products (Helle et al. 2008). However, unlike hemicelluloses, the cellulosic fraction of lignocelluloses cannot be easily hydrolyzed (Karimi et al. 2013).

Very high crystallinity along with high protection by lignin and hemicelluloses hinder the chemical and enzymatic hydrolysis of cellulose. Therefore, for the efficient production of glucose from cellulose, a pretreatment step is needed prior to enzymatic or chemical hydrolysis. Up to now, several physical, chemical, and biological treatments have been proposed for enhancement of cellulose saccharification. Although there is a general agreement that pretreatment is a key step toward profitable production of some strategic fermentation products from lignocelluloses, e.g., ethanol, however, up to now, no unique pretreatment is available, which is optimized for all types of lignocellulosic materials (Karimi et al. 2013; Menon and Rao 2012; Taherzadeh and Jeihanipour 2012; Taherzadeh and Karimi 2008b; Xu et al. 2013). Different leading pretreatment techniques and their performance are discussed in detail in Chap. 3 of this book.

At ideal conditions, pretreatment removes lignin and hemicellulose from cellulose and reduces its crystallinity. The ready to digest pretreated cellulose can be either subjected to chemical (e.g., by acid) or enzymatic hydrolysis to liberate glucose. The enzymatic hydrolysis of cellulose is usually ended with a much higher conversion yield compared to chemical hydrolysis, e.g., by acid (Taherzadeh and Karimi 2007a, b). However, high price of enzyme is a major limiting factor. Details of different aspects of enzymatic hydrolysis are thoroughly discussed in Chap. 4.

The sugars obtained from lignocellulosic materials can be potentially recovered, purified, and used as pure sugars; however, since the purification is difficult, they are usually converted to other products through chemical and biological reactions. This is probably due to the fact that the production of edible sugars from other sources such as sugar beet, sugar cane, and starch is much easier and safer than production from lignocellulosic materials (Sjöman et al. 2008; Aguedo et al. 2013). Therefore, lignocellulosic sugars are usually converted to other value-added products.

It is worth mentioning that due to the recalcitrance of lignocellulosic materials and high costs of pretreatment and enzymatic hydrolysis steps; there is still a long way until these processes become widely commercial (Gnansounou and Dauriat 2010; Klein-Marcuschamer et al. 2010).

1.2.4.2 Products of Lignocellulosic Sugars Obtained by Biological Reactions

Numerous biological products can be obtained in fermentation processes where microorganisms consume sugars as carbon and energy sources. Therefore, lignocellulosic materials can be potentially employed as low cost and widely available substrates for production of a very broad range of bio-products. Some of the most important examples of these products are biofuels, organic acids, microbial biomass, proteins, and polysaccharides. A brief overview of production process as well as applications of these materials is discussed in this section.

Biofuels

Currently biofuels are the most strategic products which can be obtained from lignocellulosic materials. The limited resources for fossil fuels as well as irreparable negative side effects of these fuels on the environment dictate the necessity of biofuels. Production of biofuels from lignocellulosic materials is referred to as the second generation of biofuels which was proposed as a solution for food–energy conflict resulted by the first generation, i.e., the production of biofuels from edible sugars and starches (Zhu and Zhuang 2012; Menon and Rao 2012).

Annually, considerable amounts of lignocellulosic materials are produced which are regarded as waste materials and have no especial applications. Agricultural residues such as rice and wheat straws are examples of these waste materials. These materials can be employed as a low-cost feedstock for the production of biofuels

(Hahn-Hägerdal et al. 2006; Taherzadeh and Karimi 2008b). Different aspects of biofuel production from waste materials are presented in Chap. 2.

The overall process for the production of biofuels from lignocellulosic materials consists of three major steps, i.e., the pretreatment of feedstock, saccharification of polysaccharides through enzymatic, chemical, or microbial routes, and fermentation of sugars to biofuels by microorganisms (Fig. 1.6) (Karimi et al. 2013). The most well-known biofuels are bioethanol, biomethane, biobutanol, and biohydrogen.

Saccharomyces cerevisiae and *Mucor indicus* are among the best microorganisms for ethanol production. The former is nowadays the industrial ethanol producer (only from hexoses), while the later has recently been introduced as an alternative which assimilate both hexoses and pentoses and produce ethanol with high yields (Karimi and Zamani 2013). Indeed, ethanol is the most important biological product in terms of the volume of production. Although there are a high number of large scale ethanol production companies in the world and this product is extensively used in the transportation section, research about production of this valuable biofuel from low-cost feedstock, i.e., lignocellulosic waste materials, is still a very hot topic (Taherzadeh and Karimi 2008a). Different aspects of ethanol production from lignocellulosic materials are thoroughly discussed in Chap. 5 of this book.

Colestridium acetobutilicum is the famous microorganism that ferments sugars to a mixture containing acetone, butanol, and ethanol with approximate ratio (w/w) of 3, 6, and 1 (Ni and Sun 2009). Butanol can be used as a biofuel which has a higher heating value and miscibility with gasoline in car engines than ethanol. Similar to ethanol, industrial butanol production processes were originally developed based on sugar and starch feedstocks. However, the employment of lignocellulosic materials is expected to improve the economy of butanol production process (Tashiro et al. 2013). The production of butanol from lignocellulosic materials is the subject of Chap. 8.

For both ethanol and butanol, lignocellulosic materials can be either hydrolyzed by chemical or enzymatic catalysts to obtain fermentable sugars. Then, the appropriate microorganism converts the sugars to the biofuels. The process of biomethane production from lignocellulosic materials is different from that of ethanol and butanol production. A consortium of several hundreds of microorganisms works together to convert lignocelluloses to this biofuel. The first group of these microorganisms hydrolyzes the polysaccharides. After the hydrolysis reactions, three groups of microorganisms subsequently perform acidogenesis, acetogenesis, and

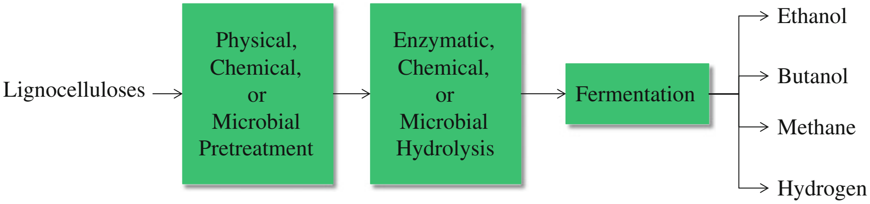

Fig. 1.6 The production of biofuels from lignocellulosic materials

methanogenesis reactions. The final product is a mixture of methane and carbon dioxide which is called biogas (Taherzadeh and Jeihanipour 2012). Biogas production from lignocellulosic materials is described in detail in Chap. 6.

Hydrogen can also be produced from lignocellulosic materials via a process comparable to that of biogas. Hydrogen is produced in a process called dark fermentation. In this process, anaerobic microbial consortiums hydrolyze the feedstock and convert it to hydrogen (Sigurbjornsdottir and Orlygsson 2012; Brynjarsdottir et al. 2013; Lo et al. 2011). Details of this process are presented in Chap. 7.

Although ethanol, butanol, methane, and hydrogen can be obtained as the final products of fermentation processes, biodiesel, the other commercially important biofuel, can also be produced from lignocellulosic materials but not through the pathway shown in Fig. 1.6. Because of limited amounts and high price of oil resources, especially edible oils, the conventional biodiesel production process from plant oils currently has faced crucial problems. Therefore, the production of oils by microorganisms, single cell oils, has got growing attentions. Among different possible feedstocks for single cell oil production, lignocellulosic sugars have been highly recommended because of low cost and wide availability (Zeng et al. 2013). Different oleaginous microorganisms can be employed for single cell oil production. Several yeast and fungi have been reported to store considerable amounts of lipids in their body during their growth phase. For example, *Trichosporon fermentans*, *Rhodotorula glutinis*, and *M. indicus* have been reported to contain 40, 29, and 24 % lipids in their biomass (Karimi and Zamani 2013; Yousuf 2012). Oil production is performed through the aerobic cultivation of oleaginous fungi. Microbial oil can be extracted by mechanical forces or appropriate solvents. The obtained microbial oil should be subjected to a process called transesterification where the oil molecules (triglycerides) are reacted with methanol in the presence of a catalyst which is usually a base (e.g., NaOH and KOH) or acid, and consequently methyl esters (biodiesel) and glycerol are formed (Fig. 1.7). The obtained biodiesel can be used as an alternative to fossil diesel in the car engines (Galafassi et al. 2012; Yousuf 2012).

Process of biodiesel production from lignocellulosic materials still paves the preliminary steps toward industrialization. Costly pretreatment and hydrolysis processes are among the bottlenecks of this process.

Microbial Biomass and Proteins

Lignocellulosic hydrolysates have also been employed for cultivation of different microorganisms, and the obtained microbial biomass has been used for different purposes, e.g., as a source of animal feed. Different fungal strains such as *Rhizopus oryzae*, *Rhizomucor pusillus*, and *M. indicus* have been successfully cultivated on lignocellulosic hydrolysates and spent sulfite liquor. The obtained biomass has shown superior characteristics for being used as a fish feed (Taherzadeh et al. 2003;

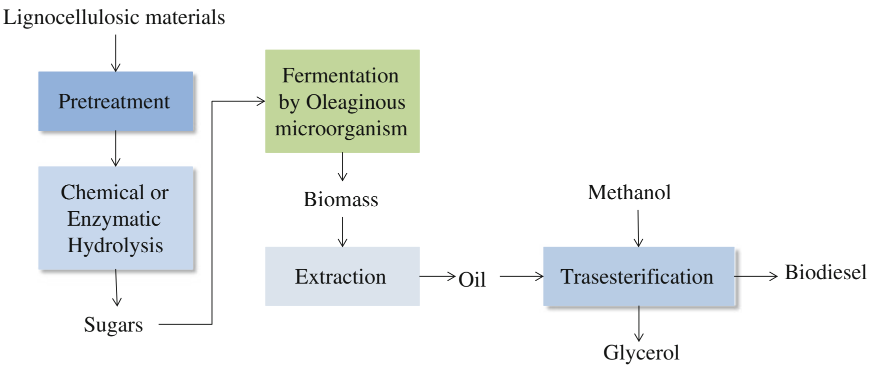

Fig. 1.7 Production of biodiesel from lignocellulosic materials

Lennartsson et al. 2009, 2011; Ferreira et al. 2013). Moreover, the obtained fungal biomass is shown to have a high potential for heavy metal removal from wastewaters (Karimi and Zamani 2013; Rouhollahi et al. 2014).

Integration of the first and second generation of bioethanol, where zygomycetes and ascomycetes fungi are cultivated on a mixture of lignocellulosic hydrolysates and the residue of ethanol production process (from starch) has been recently proposed. The employment of the fungi not only enhances the ethanol production yield but also improves the quality of distiller's dried grains and soluble (DDGS), the byproduct of ethanol process, for being used as an animal feed (Lennartsson et al. 2014).

Proteins comprise around 50 % of the microbial biomass. Lignocellulosic sugars can be fermented to prepare single cell proteins, which have very high nutritional values (Ferreira et al. 2013; Chandel et al. 2012).

Organic Acids

Nowadays organic acids allocate a big part of the market of biological products. Different microorganisms produce various organic acids such as citric, lactic, gluconic, itaconic, kojic, succinic, and acetic acids during their growth phase. Like any other fermentation product, the employment of vastly abundant and low-cost feedstock such as lignocellulosic materials may significantly enhance the large scale production of organic acids.

Citric acid

Citric acid is one of the most important organic acids in terms of production volume. This versatile acid has numerous applications especially in food, pharmaceutical, and cosmetic industries. Biological processes for the production of citric acid are generally more favorable than chemical routes, and today 99 % of food grade citric acid is obtained via fermentation processes. *Aspergilus niger* is the most applied industrial strain for citric acid production (Max et al. 2010).

Nowadays, the commercial substrates for citric acid production are sugars and starchy materials which usually have high costs. Moreover, because of the growing demand for this acid in different industries, its annual production is continuously rising. Therefore, lignocellulosic materials have been considered as an alternative feedstock for citric acid production. Different strains of *A. niger* usually do not display a high potential for hydrolysis of polysaccharides present in lignocellulosic materials. As a result, similar to biofuels, the production of citric acid should be carried out through pretreatment, enzymatic hydrolysis, and fermentation steps (Singh Dhillon et al. 2011).

Co-cultivation of a cellulase-producing microorganism such as *Trichoderma reesei* and *A. terreus* together with a citric acid-producing microorganism such as *A. niger* and *Yarrowia lipolytica* has been suggested for direct conversion of lignocellulosic materials to citric acid. In this process, the cellulosic fraction of the substrate stimulated the cellulase production. Then, the obtained cellulase hydrolyzes the cellulose to glucose which is finally converted to citric through the fermentation (Liu et al. 2014).

The employment of some especial strains of *A. niger* with cellulase synthesis ability, in the presence of a co-substrate such as sucrose and an alcoholic stimulator such as methanol, is another proposed approach for direct production of citric acid from lignocellulosic materials (Bari et al. 2009). Genetic modification of a more conventional *A. niger* strain to achieve a strain with high ability for cellulose hydrolysis has also been performed for production of citric acid from pure cellulose (Watanapokasin et al. 2007).

Moreover, the employment of lignocellulosic materials for citric acid production in solid-state fermentation systems has recently received high attentions. In such systems which are more favorable for citric acid production in operational and economical points of view, lignocellulosic materials are not only used as a substrate but also as a support to avoid wash out the acid-producing microorganism (Bari et al. 2009; Grewal and Kalra 1995; Khosravi-Darani and Zoghi 2008).

Despite considerable research and promising results, the production of citric acid from lignocellulosic materials has not still come to the commercial market.

Lactic acid

Lactic acid is another organic acid which is broadly used in food, cosmetics, pharmaceutical, leather, textile, and other chemical industries. The production of polylactic acid, as a promising substitute for synthetic plastics, is a new application which has increased the need for this acid.

Nowadays, around 90 and 10 % of lactic acid production is performed through biological and chemical routes, respectively. The chemical method has a limited potential for expansion, and therefore increased demand for lactic acid should be supplied through fermentation processes. Higher production volumes dictate the need for a low cost and widely available feedstock for the replacement of current sugar and starchy substrates. Similar to citric acid, lignocellulosic materials have been considered as suitable alternative substrates for lactic acid production (Hofvendahl and Hahn–Hägerdal 2000).

Different strains of lactic acid bacteria as well as *Rhizopus* fungi are among the well-known microorganisms for lactic acid production (Hofvendahl and Hahn–Hägerdal 2000; Zhang et al. 2007). The production of lactic acid from lignocellulosic materials can be considerably improved if pentose-fermenting microorganisms are employed. Unfortunately, many strains of lactic acid bacteria are not able to ferment pentose sugars, a major building block of hemicellulose. To overcome this limitation, screening of lactic acid bacteria as well as genetic modification of the available strains has been performed (Ou et al. 2011; Hofvendahl and Hahn–Hägerdal 2000). *Rhizopus* fungi have the ability for fermentation of both pentoses and hexoses to lactic acid. Additionally, they have some other advantages such as lower nutrient requirement and more valuable biomass compared to the bacteria (John et al. 2009; Zhang et al. 2007).

The process of lactic acid production from lignocelluloses comprises three main steps of pretreatment, hydrolysis, and fermentation. Although this process still has not came to the industrial scale, several researches have been performed aiming at improvement of the economy of this process. Performing the hydrolysis and fermentation processes in one single stage (simultaneous saccharification and fermentation) (John et al. 2009), employment of membrane bioreactor to carry out continuous fermentation and product purification by electrodialysis (Neureiter et al. 2004), and employment of thermo-tolerant and genetically modified bacterial strains with high lactic acid productivity (Ou et al. 2011) are among the attempts for enhancement of the yield of lactic acid production.

Succinic acid

Succinic acid, another important organic acid, is the precursor of several chemicals used in food, chemical, and pharmaceutical industries. Several specialty chemicals (e.g., detergents, surfactants, chelators, and corrosion inhibitors), additives (e.g., pharmaceutical intermediates, food ingredients, and flavor additives), and commodity chemicals (e.g., adipic acid, fumaric acid, and esters) are nowadays produced from succinic acid (Akhtar et al. 2014; Borges and Pereira 2011; Li et al. 2011; Liu et al. 2013).

Although succinic acid is produced through a petrochemical process, nowadays there is increasing attentions for biological production of this acid where sugar and carbon dioxide are employed as raw materials. Using lignocellulosic substrates as a feedstock has been proposed for improvement of profitability of the biological production of succinic acid. Separate as well as simultaneous saccharification and fermentation of lignocellulosic materials has been successfully evaluated for the production of this acid while the latter is more preferred because of lower enzyme consumption and higher succinic acid productivity (Akhtar et al. 2014).

There are several succinic acid-producing microorganisms which are able to ferment glucose. However, there are limited strains that can consume several carbon sources including hexoses and pentoses. *Actinobacillus succinogenes* is among those microorganisms (Borges and Pereira 2011). Generally, xylose uptake by succinic acid producer is delayed due to the presence of glucose. Therefore, a recombinant strain of *Eschercia coli* has been developed which can simultaneously ferment both glucose and xylose available in the hydrolysate of hemicelluloses (Akhtar et al. 2014; Borges and Pereira 2011; Liu et al. 2013).

Similar to citric, lactic, and succinic acids, lignocellulosic materials have also been recommended as alternative raw materials for biological production of other acids such as acetic, gluconic, itaconic, and kojic acids. A general overview of organic acid production from lignocellulosic materials is presented in Fig. 1.8.

Polysaccharides

Polysaccharides are the other group of products can be obtained from lignocellulosic sugars through in vivo biological reactions. A general outline of the process for production of these biopolymers is shown in Fig. 1.9. Chitosan, xanthan, bacterial cellulose, and microbial polyesters are among the most important polysaccharides which can potentially be produced from lignocellulosic materials.

Chitosan

Chitosan is one of the cationic biopolymers with superior characteristics such as antimicrobial activity, metal-binding capacity, and gel- and film-forming characteristics. This biopolymer has a number of current and potential applications namely

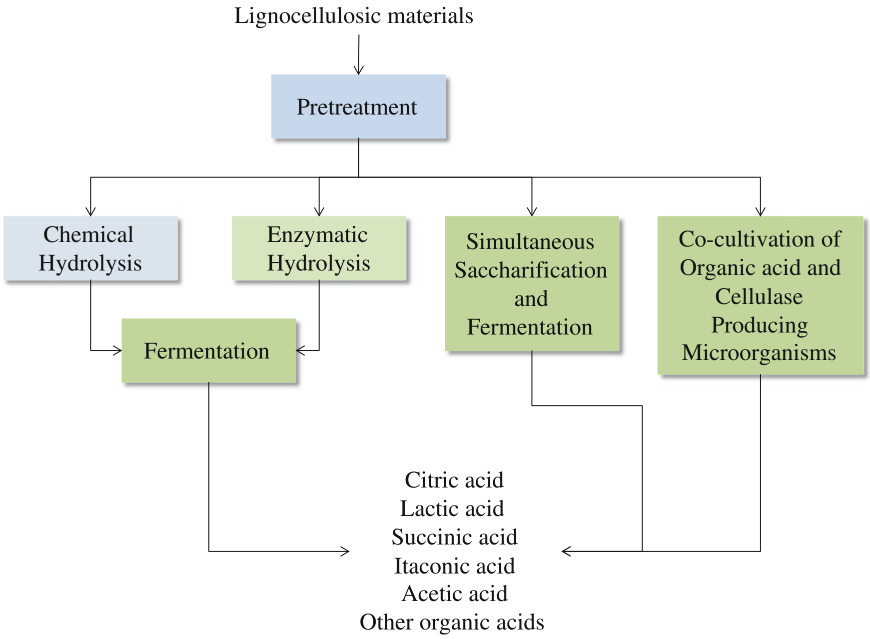

Fig. 1.8 Outline of organic acid production from lignocellulosic materials

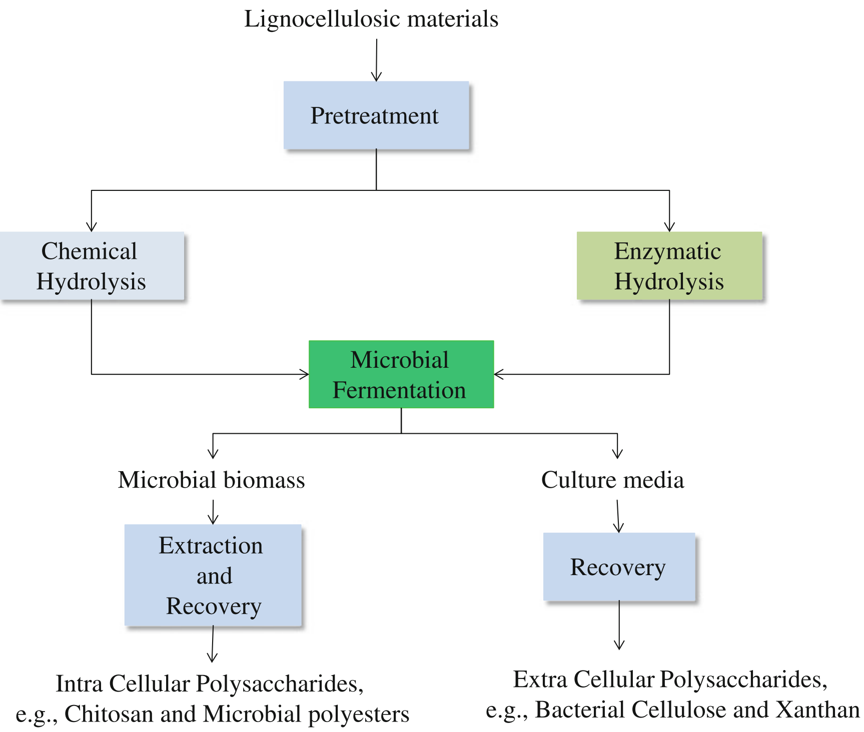

Fig. 1.9 Production of polysaccharides from lignocellulosic materials

in food, medical, cosmetic, agricultural, paper, and water treatment industries (Zamani 2010).

Nowadays, chitosan is commercially produced from shellfish wastes through chemical deacetylation. However, due to environmental drawbacks of the existing process, attentions have been paid to the production of this polysaccharide by fermentation processes. Chitosan biosynthesis takes place in a family of fungi called zygomycetes. Chitosan is produced during the fungal growth and stored in cell wall. Zygomycetes fungi are usually able to consume different five and six carbon sugars. Therefore, hydrolysates of lignocellulosic materials seem to be a suitable low-cost feedstock for chitosan production by fermentation (Karimi and Zamani 2013; Zamani 2010; Zamani et al. 2010; Millati et al. 2005; Asachi et al. 2011).

Interestingly, some strains of these fungi which store considerable amounts of chitosan in their cell wall have been recognized as efficient ethanol producers with comparable yield and productivity to that of industrial *S. cerevisiae*. *M. indicus*, *Mucor hiemalis*, and *R. oryzae* are examples of these strains (Heidary Vinche et al. 2012; Karimi et al. 2005, 2006; Lennartsson et al. 2009; Millati et al. 2005, 2008). Therefore, current researches about the production of ethanol from lignocellulosic materials by zygomycetes fungi are directly connected to chitosan production.

In other words, using zygomycetes fungi, all lignocellulosic sugars are efficiently consumed and ethanol with high yield is obtained as the main product, while chitosan is produced as a valuable byproduct. This method has been introduced as one of the promising routes for industrialization of the process of lignocellulosic ethanol (Karimi and Zamani 2013). So far, bench- and pilot-scale studies have resulted in hopeful results (Lennartsson et al. 2011); though much more is needed to be done before industrialization. Once chitosan is synthesized in the fungal cells, appropriate extraction process should be employed for its extraction and recovery (Zamani et al. 2010; Naghdi et al. 2014).

Xanthan

Xanthan is another broadly used biopolymer which can be produced from lignocellulosic sugars. Unlike chitosan, xanthan is an extracellular product which is commercially produced by *xanthomonas* bacteria. Indeed, the process of production of this exopolysaccharide was one of the earliest industrial biological processes. Because of unique rheological characteristics, xanthan gum has several applications in food, cosmetic, petroleum, and paper industries (Palaniraj and Jayaraman 2011).

Some attempts for improvement of the economy of xanthan production process are performed through the searching for alternative substrates with lower cost and higher availability. Accordingly, lignocellulosic hydrolysates have been considered as a suitable feedstock for xanthan production. However, the rate of xylose uptake by the famous xanthan producer, i.e., *Xanthomonas campestris*, is not as high as that of glucose. It has been reported that xanthan produced from acid hydrolysates of lignocelluloses has higher stability toward changes of temperature, pH, and ionic strength compared to xanthan produced from glucose. Xanthan is directly dissolved in the culture medium after biosynthesis and therefore can be recovered by precipitation (Gunasekar et al. 2014; López et al. 2004; Woiciechowski et al. 2004; Zhang and Chen 2010).

Bacterial cellulose

The third biopolymer which can be produced from lignocellulosic materials is bacterial cellulose. The employment of plant cellulose and hemicelluloses to produce bacterial cellulose has recently got significant attentions. Compared to plant cellulose, bacterial cellulose exhibits several unique features such as nano-structure and higher purity, crystallinity, degree of polymerization, water binding capacity, tensile strength, and biocompatibility. Getting benefit of these features, new applications are continuously proposed for bacterial cellulose in food, pharmaceutical, cosmetic, paper, biomedical, electronic, paint, coating, and membrane industries. However, novel applications can be commercialized only if bacterial cellulose is produced with high volume and low costs (Huang et al. 2014).

The product of sugar fermentation by *Acetobacter xylinum* is bacterial cellulose which is formed as an insoluble layer above the liquid cultivation medium of the bacterium. Costs of sugars have a considerable effect on the total cost of bacterial cellulose production. Therefore, using lignocellulosic sugars, obtained by chemical or enzymatic hydrolysis, considerably improve the economy of the process. Recovery of bacterial cellulose is easier than that of chitosan and xanthan since this biopolymer is already formed as an insoluble layer which is easily collected and washed to remove the bacterial cells, e.g., by alkali solutions (Cavka et al. 2013; Chen et al. 2013; Guo et al. 2013; Hong and Qiu 2008; Hong et al. 2011).

Microbial polyesters
Microbial polyesters, classified as polyhydroxyalkanoates, are other big group of biopolymers that are produced by fermentation processes. Low concentrations of some nutrients together with excess amounts of carbon source lead to the formation of intracellular granules of microbial polyesters by several bacterial strains. There is a very high potential for the replacement of synthetic plastics by polyhydroxyalkanoates if these biopolymers can be broadly produced with reasonable prices (Pan et al. 2012).

Fortunately, many of polyester-producing microorganisms consume xylose even better than glucose, and therefore lignocellulosic hydrolysates seem to be ideal substrates for production of these biopolymers. The production of microbial polyesters from lignocellulosic materials is usually performed in two steps of hydrolysis (chemical or enzymatic) and fermentation. Recombinant strains of *E. coli* have been also developed with the ability to hydrolyze hemicelluloses (namely xylan) and convert the obtained xylose to microbial polyesters. After fermentation, polyesters are separated and purified by extraction from microbial biomass using suitable solvents (Lee and Na 2013; Zhang et al. 2013; Salamanca-Cardona et al. 2014).

Xylitol

Xylitol is a five-carbon sugar alcohol which has got growing attentions in food and pharmaceutical industries. The most important characteristics of xylitol are strong sweetness with lower calorie and higher tolerance by diabetic people compared to sucrose (Parajó et al. 1998).

Although, the present industrial production of xylitol is performed through the chemical hydrogenation of the dominant hemicellulosic sugar, i.e., xylose, high production costs limit the growth of applications of this sugar. In contrast, biological conversion of xylose to xylitol has the potential to be performed at high volumes. In this method, microorganisms directly uptake the xylose from lignocellulosic hydrolysates, and therefore the costly xylose purification step, that is needed in the chemical process, is omitted. Several bacteria, filamentous fungi, and yeasts can perform the biotransformation of xylose to xylitol. Different strategies such as entrapment of xylitol-producing microorganisms, cell recycling, fed batch cultivation, and using metabolically engineered cells have been suggested for improvement of the yield and hence the economy of xylose production by fermentation (Carvalho et al. 2005; Chandel et al. 2012; Cheng et al. 2010; Granström et al. 2007; Sjöman et al. 2008; Su et al. 2013; Wang et al. 2013).

Up to now, the chemical conversion of xylose is still used for production of xylitol; however, recently, some research-based companies try to commercialize the biotechnological production method. Once xylitol is produced by fermentation, it can be recovered by crystallization from lignocellulosic hydrolysates (Martínez et al. 2007).

1.2.4.3 Products of Lignocellulosic Sugars Obtained by Chemical Reactions

Although the biological conversion of sugars to value-added products is generally preferred especially because of lower environmental impacts, some important chemicals are nowadays obtained by chemical conversion of lignocellulosic sugars. A brief overview of the process for the production of these materials is described in this section. Some of lignocellulosic-based products are prepared in the course of dehydration of sugars under acidic conditions, usually at high temperatures. Furfural, hydroxymethyl furfural, formic acid, and levulinic acid are among the most important examples of these products (Fig. 1.10) (Peng et al. 2011).

Furfural

Furfural is a colorless oily organic liquid with almond odor which turns to yellow color upon air exposure. A wide range of applications are industrially known for furfural including solvents (e.g., for petroleum refining) and precursors for production of different chemicals (e.g., furfuryl alcohol and tetrahydrofuran) (Peng et al. 2011).

Nowadays, furfural is mainly produced from pentoses available in hemicellulosic hydrolysates through the cyclic dehydration reactions. These reactions are usually catalyzed by sulfuric acid. The possibility of extensive dehydration of furfural after formation in the reaction mixture, which leads to considerable reduction of furfural yield, is among the major drawbacks of this process. Therefore, in industrial furfural production processes, a high pressure steam is injected to the reactor to heat up the reaction mixture and at the same time strip the formed furfural and remove it from the reaction mixture (Fig. 1.11). This noticeably avoids unwanted side reactions. Annually, around 300,000 ton of furfural is produced by this method in batch and continuous processes (Peng et al. 2011; Agirrezabal-Telleria et al. 2014).

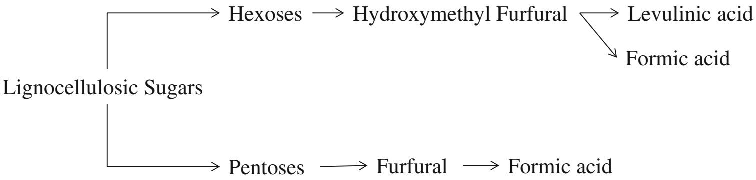

Fig. 1.10 Acid-catalyzed dehydration of sugars to new products

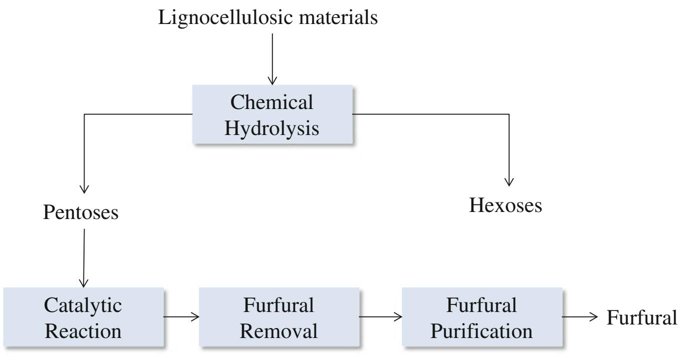

Fig. 1.11 Production of furfural from lignocellulosic materials

Despite presence of a fully developed industrial process for furfural production, extensive research is still conducted primarily to improve the process conditions toward higher yields and to find new catalysts with better performance than that of sulfuric acid. Accordingly, performing the acid-catalyzed dehydration of pentoses in hemicellulosic solvents (instead of aqueous solutions) (Campos Molina et al. 2012), using two-phase (aqueous-organic) solvent system for simultaneous removal of furfural after formation (Peng et al. 2011), removal of furfural from the reaction mixture by supercritical carbon dioxide (Gairola and Smirnova 2012), and hydrothermal conversion of pentoses at high pressures and temperatures (Gairola and Smirnova 2012) are among the new suggested processes for improvement of the process yield. Besides, supplementation of sulfuric acid with salts, e.g., NaCl, using other mineral acids as catalyst, and conducting the furfural formation reaction in heterogeneous phase employing solid catalysts such as $CrCl_3$ and zeolites have been proposed to enhance the catalyst performance and reduce the downstream purification costs (Zhang et al. 2014; Yoo et al. 2012; Agirrezabal-Telleria et al. 2014).

The production of furfural from lignocellulosic sugars is the only accepted method for industrial production of this versatile material. The economy of this process is expected to be greatly enhanced when the results of the above-mentioned researches are applied in industrial scale. Furfural is usually purified from the reaction mixture by azeotropic distillation.

Hydroxymethyl Furfural

Hydroxymethyl furfural (HMF) is one of the most important derivatives of lignocellulosic hexoses obtained by chemical dehydration. This is a very high potential intermediate which can be converted to high-quality fuels, resins, adhesives, composites, binders, solvents, monomers, and pharmaceuticals (Peng et al. 2011).

A number of different catalysts including organic acids, inorganic acids, salts, ion exchange resins, zeolites, and Lewis acids accelerate the dehydration of hexoses to HMF (Peng et al. 2011). Generally, dehydration of fructose to HMF is performed very easily. In contrast, direct conversion of glucose to HMF requires especial types of catalysts, and this conversion is performed in two steps of isomerization of glucose to fructose and conversion of fructose to HMF. It should be mentioned that from economical point of view, glucose is a more preferred substrate for HMF production than fructose (Ståhlberg et al. 2010; Mascal and Nikitin 2010). Therefore, considerable attentions have been paid to enhance the yield and rate of reactions of HMF production from glucose. Accordingly, attempts for finding new effective catalytic systems, e.g., lanthanide catalysts, incorporation of other solvents, e.g., ionic liquids, and using bi-phasic solvents have shown promising results in production of HMF from glucose (Ståhlberg et al. 2010, 2011; Choudhary et al. 2013; Bali et al. 2012; Agirrezabal-Telleria et al. 2014; Mascal and Nikitin 2010).

However, more research is still needed to be conducted before commercialization of HMF production from lignocellulosic sugars. It should be mentioned that prolonged reaction times lead to conversion of HMF to another value-added chemical, i.e., levulinic acid.

Levulinic Acid

Levulinic acid is a five-carbon chain fatty acid which has a ketone carbonyl and an acidic carboxyl group. Levulinic acid has a very high potential for synthesis of alternative fuels, fuel additives, solvents, dyes, flavoring agents, and different resins (Peng et al. 2011).

The most well-known method for production of levulinic acid is degradation of hexoses in the presence of mineral acids. As mentioned in the previous section, HMF is formed as an intermediate in this process. Biofine process which was developed by Biofine Corporation is an improved process for production of levulinic acid with considerably higher yield compared to traditional methods. In this process, a continuous system with two reactors is used for production of levulinic acid (Fig. 1.12) (Bozell et al. 2000).

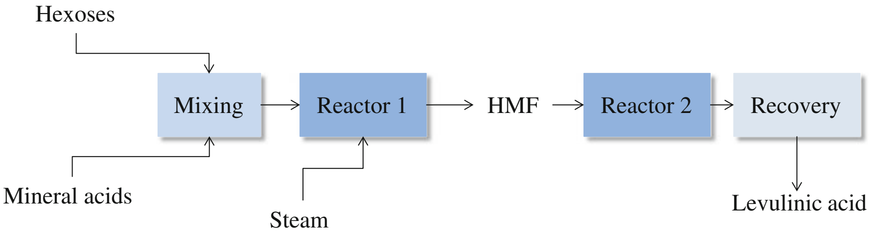

Fig. 1.12 Production of levulinic acid from hexoses

In this system, hexoses are fed to the first reactor where they are converted mainly to HMF in the presence of 1.5 % mineral acid. HMF is continuously removed using steam and fed to the second reactor. The residence time in the first reactor is rather short (15–25 s), while the reaction occurs at 210–230 °C. Longer residence times (15–30 min) as well as lower temperatures (145–230 °C) are applied in the second step to convert HMF to levulinic acid (Bozell et al. 2000).

Although using mineral acids as catalyst efficiently convert sugars to levulinic acid in this economically feasible process, alternative catalysts have also been evaluated for the production of levulinic acid. Accordingly, transition metal chlorides have shown a high catalytic activity in this reaction. Chromium chloride is among the best catalysts recommended for production of levulinic acid. Application of chromium chloride has the advantage of easier separation and recovery of catalyst, since it is partially dissolved in the reaction medium (Chang et al. 2007; Galletti et al. 2012; Bozell et al. 2000; Mascal and Nikitin 2010).

As levulinic acid can be easily produced from lignocellulosic sugars with high yields and low costs, new researches are more concentrated on the production of new value-added chemicals from this material.

Xylitol

As mentioned in Sect. Xylitol, the production of xylitol by fermentation has not yet come to the industrial market. Therefore, nowadays the only industrial method for xylitol production is chemical reduction of xylose obtained from lignocellulosic materials (Peng et al. 2011). An overview of the industrial process is shown in Fig. 1.13.

It should be emphasized that the purification of xylose from hemicellulosic hydrolysates is a crucial and costly step in this process. A combination of ion exchange chromatography and activated carbon treatment is used to remove dissolved salts, charged degradation products, and color from the hydrolysates. However, the presence of other sugars in the hydrolysates which are not removed

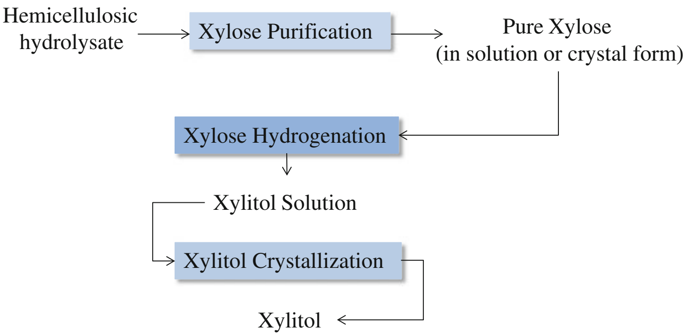

Fig. 1.13 Chemical production of xylitol from xylose

by chromatography is a problem for this process. Different metal-based catalysts (Pt, Ru, Pd, and Ni) have been proposed to assist the hydrogenation of xylose to xylitol. Most commonly nickel-based catalysts are used for the production of xylitol. This process is performed at relatively high temperatures and pressures (80–130 °C and more than 40 bar, respectively) (Peng et al. 2011).

1.3 Products Derived from Lignin

Besides cellulose and hemicellulose, lignin is another main part of lignocellulosic materials. Despite abundant resources of lignin in the nature, its application has not been developed as broadly as cellulose and hemicelluloses. The main reason for the limited applications is very complex chemical structure of lignin. Lignin has a cross-linked macromolecular structure of phenylpropanoid monomers. These monomers have the same phenylpropanoid skeleton but different degrees of oxygen substitution on the phenyl ring (one, two, or three hydroxyl or methoxyl groups which are referred to as hydroxyphenyl (H), guaicyl (G), and syringyl (G) monomers, respectively). The share of each monomer varies depending on the plant type and growing conditions. Therefore, generally lignins not only exhibit a very complex structure but also show a very wide diversity. This makes the development process of lignin-based products very difficult (Doherty et al. 2011; Silva et al. 2009).

However, appreciated amounts of lignin are available in lignocellulosic materials, and therefore it is the main byproduct of the industries which are based on cellulose, hemicelluloses, and their derivatives. Additionally, if the biofuel production from lignocellulosic materials comes to the commercial market, huge amounts of lignin will also be produced as an unavoidable byproduct of such industries.

Therefore, the employment of lignin as a source of energy and materials is among the important goals for improvement of the economy of cellulose- and hemicelluloses-based industries. Because of very high heating value of lignin, compared to polysaccharides, traditionally, this material is directly burned in the paper making facilities to produce electricity and steam. However, lignin has a much higher potential for the production of value-added products as well as energy which may not be obtained from other biological materials. Therefore, although direct combustion of lignin improves the economy of pulp and paper industry, it is not the most reasonable way for lignin application in the future (Azadi et al. 2013; Silva et al. 2009).

Recently, besides direct burning, lignin has got other small- and big-scale applications. Different applications are designed based on the lignin characteristics. It should be mentioned that lignin purification process significantly influences the lignin properties. Many of purification processes lead to cleavage of several bonds on lignin macromolecular structure. Therefore, the purified lignin does not exhibit exactly the same characteristics as it does in original form in plant cell wall (Doherty et al. 2011; Lora 2008).

Generally, lignin purification method is categorized into two groups: (a) the methods in which lignin is dissolved and removed from cellulose and (b) the methods in which cellulose is dissolved and lignin is recovered as insoluble fraction. It is worth mentioning that due to rather instable nature of hemicelluloses, these polysaccharides are usually dissolved and sometimes hydrolyzed during the lignin purification processes (Azadi et al. 2013; Doherty et al. 2011).

All pulping processes (Fig. 1.14) are belong to the first group while some pretreatments of lignocelluloses, such as pretreatment with cellulose solvents, as well as dilute acid hydrolysis of lignocellulosic materials are examples of the second group. Sulfite, kraft, and soda lignins which are, respectively, obtained in sulfite, kraft, and soda pulping processes are nowadays commercially available sources of purified lignin (Lora 2008; Azadi et al. 2013; Doherty et al. 2011; Silva et al. 2009; Baurhoo et al. 2008).

The sulfite process is used for preparation of pulp from woody biomass. In this process, wood chips are treated in aqueous solutions of bisulfite or sulfite salts (Na, Mg, Ca, or NH_4 salts) at 140–170 °C. In this process, several complex reactions take place resulting in dissolution of lignin, hydrolysis of hemicelluloses, and recovery of cellulose. The spent sulfite liquor obtained in this process contains hemicellulosic sugars and the dissolved lignin. The sulfite lignin, lignosulfonate, contains high amounts of sulfur (4–8 %) and is soluble in almost full range of pH (Lora 2008; Doherty et al. 2011).

Before recovery of sulfite lignin, it is worth to employ hemicellulosic sugars, e.g., for cultivation of microorganisms. These sugars have been used for cultivation of different zygomycetes fungal strains to achieve fungal biomass which can be

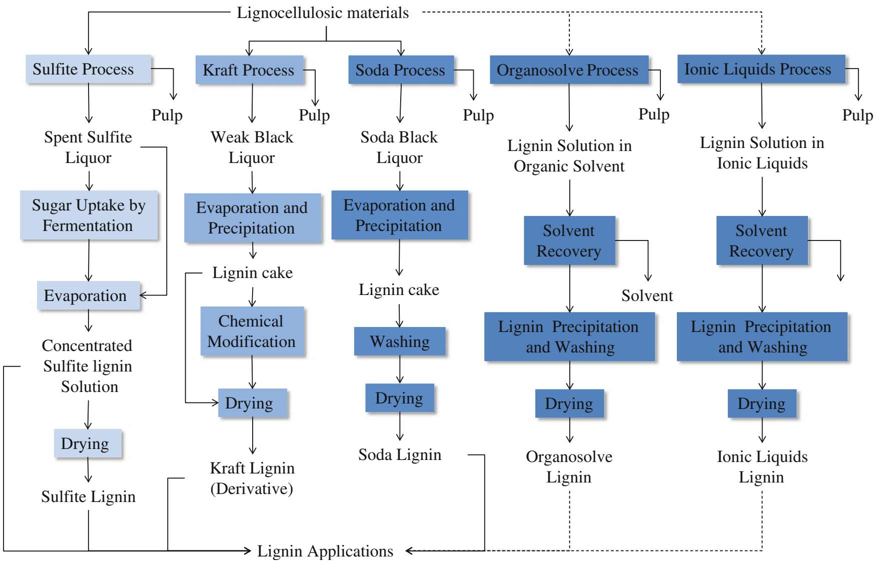

Fig. 1.14 Lignin recovery and purification during different pulping processes

used as a source of fish feed, fungal chitosan, and fungal oil (Helle et al. 2008; Taherzadeh et al. 2003; Zamani et al. 2010; Lora 2008). After consumption of sugars, spent sulfite liquor is evaporated to obtain concentrate sulfite lignin. This can either be used directly or further be dried to get a powder form (Fig. 1.14) (Lora 2008).

Sulfite lignin is used as a dispersant in concrete, gypsum wallboards, agrochemicals, dyes, bitumen, pigments, and drilling fluids for oil recovery. Moreover, it is used for several binding applications, e.g., in animal feed, fertilizers, refractory materials, and phenol-formaldehyde resins. Crude spent sulfite liquor can also be utilized for soil stabilization and control of dust. Furthermore, sulfite lignin is used for production of vanillin, a flavor agent and an intermediate of pharmaceutical products, through a catalytic oxidation reaction (Lora 2008; Silva et al. 2009).

Although the sulfite process was the main method of pulping in the past, discovery of more efficient pulping processes, such as kraft process, led to the replacement of this method. Currently, only 10 % of the pulp is obtained by sulfite method. However, it is important to know that recovery of lignin in new pulping processes has not as broadly applied as the sulfite process. Therefore, today, still a significant part of the commercially available lignin is sulfite lignin (Azadi et al. 2013; Doherty et al. 2011; Lora 2008).

Kraft pulping process is nowadays the most commonly used method of pulping. In this method, wood is treated with sodium hydroxide and sodium sulfide to remove lignin and hemicelluloses. The obtained pulp has enhanced characteristics compared to the pulp obtained in sulfite process (Fig. 1.14) (Hocking 2005; Lora 2008).

Despite wide application of kraft process, only a small portion of the kraft lignin is recovered, and the rest is directly burned to balance the costs of the pulping process. On the other hand, several researches are conducted to find alternative ways for kraft lignin utilization which can compete the burning process in economical point of view. Kraft lignin is recovered from the weak black liquor of pulping process by precipitation as low pH. The lignin can either be dried directly or chemically modified (e.g., by sulfonation or amination) prior to drying (Fig. 1.14) (Lora 2008).

Although the kraft lignin is commercially available at low volumes, it has already got several applications in different industries. For example, kraft lignin can be used as a dispersant for dyes and agrochemical products. It can also be employed to enhance air entrainment in mortar and concrete giving a microstructure to these products. Application of kraft lignin as an expander in lead–acid batteries has also been reported. Another interesting proposed application of this lignin is asphalt emulsifier where lignin stabilizes the asphalt at a very broad range of temperature. Kraft lignin has also shown antioxidant and UV protection activities. In addition, the production of dimethyl sulfoxide has been reported (Azadi et al. 2013; Doherty et al. 2011; Lora 2008).

The sulfite and kraft processes have been mainly developed for woody feedstock. In contrast, soda (or alkali) process has been proposed for pulp production from annual plants. Annual plants provide only 5 % of total world pulp production.

These plants usually have lower lignin contents compared to wood and are delignified using only sodium hydroxide solutions. The dissolved alkali (soda) lignin is recovered by acid precipitation (Azadi et al. 2013; Doherty et al. 2011; Lora 2008).

Absence of any sulfur reagent during the course of pulping process leads to the recovery of a sulfur-free lignin. Therefore, soda lignin is much more similar to native lignin than sulfite and kraft lignins. This similarity provides the opportunity for some new applications of soda lignin. For example, soda lignin has shown promising performance for the replacement of fossil-based phenol, e.g., in phenol-formaldehyde resins. Additionally, soda lignin is a better choice for animal health and nutrition products compared to sulfite and kraft lignin. Moreover, soda lignin has shown interesting activity for replacement of antibiotics (Doherty et al. 2011; Lora 2008).

In addition to the sulfite, kraft, and soda processes, currently some new pulping methods have been proposed which are called organosolv processes (Fig. 1.14). Although none of these methods have been broadly commercialized yet, they have a high potential for being used for pulping in the future. The organosolv treatments are performed using a low boiling point organic solvent such as ethanol and methanol in the presence or absence of acidic catalysts to dissolve lignin. In this processes, hemicelluloses can be hydrolyzed to their sugars while cellulose is remained intact. Prior to lignin recovery, the solvent is recovered by evaporation. Then, the organosolv lignin can be precipitated by pH alteration and recovered. Since relatively low structural changes occur on lignin during these processes, organosolv lignin has been recognized as one of the most suitable lignins for production of lignin-based materials (Doherty et al. 2011; Sarkanen et al. 1981).

Organosolv methods are very effective not only for pulp production but also for biofuel production from lignocellulosic materials. As mentioned in Sect. Biofuels, a pretreatment step is necessary prior to hydrolysis of lignocellulosic materials for biofuel production.

Organosolv pretreatments are among the most promising methods for pretreatment of lignocellulosic materials, e.g., for ethanol production (Lai et al. 2014; Azadi et al. 2013). Therefore, in both pulp and biofuel industries, organosolv processes are expected to improve the economy of the whole process.

Organosolv methods are not the only new proposed solutions for improving the efficiency of pulping process and obtaining of a high-quality lignin. Currently, considerable attentions have been paid to separation of lignin using ionic liquids. Early investigations indicate that ionic liquids may play an important role in lignin purification in the future because of low boiling point, high efficiency in lignin dissolution, and very high recovery (Prado et al. 2013b; Pu et al. 2007).

As mentioned earlier, pulping processes are not the only methods of lignin purification. Dilute acid hydrolysis of lignocellulosic materials at elevated temperatures results in the hydrolysis of cellulose and hemicellulose. The intermediate products of carbohydrates hydrolysis are sugars while the end products are furfural, HMF, levulinic acid, and formic acid. Lignin and ash contents of the substrate are recovered as a solid residue called char. Char has a very high heating value (26 MJ/kg) and is mostly used for heat generation (Azadi et al. 2013).

Applications of lignin are not limited to the fully developed ones and continuously new aspects and opportunities are reported getting benefit of the sole structure of lignin in the nature. Indeed, lignin is the only material with biological origin which is composed of aromatic residues. Therefore, this can be considered as the sole feedstock for replacement of fossil-based aromatics (benzene, toluene, and xylene). Ideally, depolymerization of lignin would end up with formation of lignin aromatic constitutes which can be employed as substitutes for fossil-based aromatics. However, up to now, there is no optimized depolymerization process which result in high selectivity and yield for a certain component. However, it has been reported that even partial depolymerization of lignin and subsequent product separation, based on, e.g., boiling point, may be economically feasible. This is due to the fact that the obtained bulk grade aromatics also have a high potential for different applications, e.g., high-quality liquid fuel production. Although extensive studies have been conducted aiming at development of appropriate methods of lignin depolymerization for aromatic formation, there is much to be done to achieve this goal. Therefore, the production of aromatics from lignin is considered to be a very long-term objective (Azadi et al. 2013; Nanayakkara et al. 2014; Prado et al. 2013a).

Meanwhile, lignin can be employed in some other new applications. The production of carbon fiber, activated carbon, polymer fillers, resins, and adhesives from lignin have got considerable attentions in recent years. On the other hand, lignin can be completely converted to syngas (a mixture of mainly hydrogen and carbon mono-oxide) through well-designed gasification processes. The obtained syngas can be either directly combusted in gas turbines to create heat and electricity or be converted to methanol and Fischer–Tropsch fuels. Furthermore, syngas can be upgraded to pure hydrogen (Azadi et al. 2013).

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