Chemical Pretreatments of Wood Chips Prior to Alkaline Pulping - A Review of Pretreatment Alternatives, Chemical Aspects of the Resulting Liquors, and Pulping Outcomes

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The chemical industry is being forced to evaluate new strategies for more effective utilization of renewable feedstocks to diminish the use of fossil resources. In this literature review, the integration of both acidic and alkaline pretreatment phases of hardwood and softwood chips with chemical pulping is discussed. Depending on the pretreatment conditions, high-volume sulfur-free fractions with varying chemical compositions can be produced. In case of acidic pretreatments, the major products include carbohydrates (mono-, oligo-, and polysaccharides), whereas under alkaline (*i.e.*, aqueous NaOH) pretreatment conditions, the sulfur-free fractions of aliphatic carboxylic acids, lignin, and extractives are primarily obtained. All these fractions are potentially interesting groups of compounds and can be used in a number of applications. Finally, the effects of pretreatments on pulping are also considered. Although it is believed that there are important advantages to be gained by integrating this type of renewable raw material-based production, in particular, with kraft pulping, sulfur-free pulping methods such as soda-AQ and oxygen/alkali delignification processes are also briefly discussed.

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INTRODUCTION

Sustainable economic growth requires safe, environmentally friendly, and sustainable resources for industrial production (Hardy 2004; Kamm and Kamm 2004; Sánchez and Cardona 2008; Amidon *et al*. 2011). Due to the depleting resources of fossil fuels, increased concern of global warming, and increased demand for energy and materials, fossil carbon sources, such as petroleum and natural gas, must be replaced by renewable raw materials. Chemicals, biofuels, and biocomposites manufactured from renewable resources, such as forest and agricultural biomass, have been considered to be the most promising alternatives for replacing traditional raw materials (Goldstein 1981; Sinsky 1983; Stevens 2004; Carvalheiro *et al*. 2008; Cherubini 2010; Dautzenberg *et al*. 2011; Alén 2011; Liu *et al*. 2012a,b; Viikari *et al*. 2012). While the needed energy production can be based on various alternative production systems (wind, solar, hydropower, biomass, nuclear fission, and fusion), the production of materials, such as chemicals, polymers, and fuels, mainly depends on biomass. For these reasons, different biorefinery processes integrated with modern pulp and paper mills have gained great interest, especially during the last few decades (Kamm *et al*. 2006; Ragauskas *et al*. 2006;

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Huang *et al*. 2010; Walton *et al*. 2010a; Alén 2011; Marinova *et al*. 2014). This approach includes the modification of a conventional pulp mill to incorporate elements of an integrated forest biorefinery (IFBR) mill (van Heiningen 2006; Hämäläinen *et al*. 2011; Baijpai 2012; Resalati *et al*. 2012; Moshkelani *et al*. 2013). It has been estimated (Connor 2007) that in North America there are approximately 200 chemical pulp mills and high-yield pulp mills that could also economically host biorefineries. There are also another 100 large, nonintegrated paper mills with heat and energy sinks large enough to support a biorefinery. Internationally, it has been estimated that there are over 450 pulp and paper mills and another 400-500 nonintegrated paper mills that are sound potential sites for biorefineries.

As such, conventional chemical pulp mills can be considered as typical examples of chemical/thermochemical biorefineries utilizing different technological innovations to fractionate and convert woody biomass into a wide range of products, such as cellulose, extractives-derived by-products, lignin-based materials, hemicelluloses, and many other minor products (Herrick and Hegert 1977; Alén 1990; Kamm *et al*. 2006; Huang *et al*. 2010; Chirat *et al*. 2012; Sanglard *et al*. 2013; Benali *et al*. 2014; Leskelä *et al*. 2014). However, it can be concluded that modern pulp mills could serve as a promising platform for even more efficient use of wood and other lignocellulosic materials. A modern IFBR approach could include the opportunity to produce not only the main product (pulp fiber), but also value-added green chemicals, such as fuel grade ethanol, as well as cellulose and hemicelluloses together with their derivatives; this could include low-volume/high-value lignin/extractives-based fine chemicals, thus resulting in an enhanced utilization of feedstocks with the simultaneous increase in profitability and decrease in greenhouse gas emissions (Mendes *et al*. 2009; Mansoornejad *et al*. 2013; Martin-Sampedro *et al*. 2014). In addition to the more efficient use of pulp woods, the analogous processing of agricultural and forest residues could be considered as well. This approach could result in the improved use of energy and raw materials with the simultaneous increase in profitability and expansion of the product portfolio of mills.

One of the most promising biorefinery techniques is based on the various chemical pretreatment processes by which wood chips can be treated and partially solubilized under varying conditions (pH, temperature, and treatment time) prior to delignification (Carvalheiro *et al*. 2008; Marinova *et al*. 2009; von Weymarn 2011; Chirat *et al*. 2012; Galbe and Zacchi 2012; Cordeiro *et al*. 2013; Behera *et al*. 2014; Gomes *et al*. 2014). Different pretreatments of lignocellulosics produce carbohydrates- and lignin-containing hydrolysates, which can be further converted into desired chemicals, biomaterials, or biofuels (Kamm and Kamm 2004; Sánchez and Cardona 2008; Alvira *et al*. 2010; Zhu and Pan 2010; Chiaramonti *et al*. 2012; Mood *et al*. 2013; Silva-Fernandes *et al*. 2015). In addition, using various pretreatments, it is possible to increase the reactivity of feedstock material, leading to enhanced pulping performance and recovery of potential by-streams (lignin and hydroxy acids) (Hendriks and Zeeman 2009; Kumar *et al*. 2009; Zhu *et al*. 2010). However, in each case, a general prerequisite for finding a realizable design concept is that the presence of all the feedstock constituents is taken into account when planning target-oriented economic processes for the manufacture of useful products. Hence, the main principle is to maximize the value of lignocellulosic biomass and, conversely, to minimize the production of waste.

Biomass pretreatment technology plays an important role in the modern forest industry and in other biorefinery concepts based on lignocellulosic feedstocks (Mosier *et al*. 2005; Carvalheiro *et al*. 2008; Yoon *et al*. 2008; Yoon and van Heiningen 2008).

Chemical pulp mills use large quantities of both softwood and hardwood feedstocks to produce cellulosic pulp. However, the chemical pulping process is rather unselective, and a significant part of raw wood material is dissolved during delignification into the cooking liquor ("black liquor"), which is burned in the recovery furnace for the recovery of cooking chemicals and the production of energy. This dissolved organic fraction contains, in addition to carbohydrate-derived degradation products (aliphatic carboxylic acids), the degradation products of other significant wood polymeric component lignin, together with minor amounts of extractives. The low heating value of carbohydrates and their degradation products, compared to that of lignin, encourages the partial removal of these constituents by different pretreatment stages prior to the main pulping stage (Tunc and van Heiningen 2008a,b; Al-Dajani and Tschirner 2010; Pu *et al*. 2011; Vila *et al*. 2011; Chirat *et al*. 2012; Liu *et al*. 2012c; Martin-Sampedro *et al*. 2014). Lignocellulosic material (LCM) feedstocks are transformed into three major output streams (cellulose, hemicelluloses, and lignin) together with their degradation products by chemical, physical, and biological pretreatments (Duff and Murray 1996). These materials can be processed further into various value-added end products, such as bioethanol for energy purposes, polymeric composites, or different biochemicals (Gírio *et al*. 2010; Alvira *et al*. 2010; Agbor *et al*. 2011; Liu *et al.* 2011b; Rodríguez-López *et al*. 2012).

Several pretreatment processes and technologies have been suggested for the fractionation and recovery of valuable components from LCMs (Sánchez and Cardona 2008; Tunc and van Heiningen 2008a,b; Kumar *et al*. 2009; Zhu *et al*. 2010; Song *et al.* 2011; Si *et al*. 2015). Biomass pretreatments change the structure of LCMs and remove structural constituents from the feedstocks, making the pretreated materials more accessible for further fractionation and conversion techniques, such as alkaline pulping (Yang and Wyman 2004; Hendriks and Zeeman 2009; Gírio *et al.* 2010). The alteration of wood structure can include the removal of lignin and hemicelluloses, reduction of the crystallinity of cellulose, and increasing the porosity of the LCMs. In addition to the pretreated wood material, carbohydrate-rich hydrolysates are formed (Mok and Antal 1992; Garrote *et al*. 2001; Song *et al*. 2008; Li *et al*. 2010).

Pretreatment processes must meet several requirements. The process must be efficient enough to improve the formation of free carbohydrates (mono-, oligo-, and polysaccharides), which can be further hydrolyzed to fermentable sugars or used as polymers, but at the same time, the production of high quality pulp must be preserved. The degradation and loss of carbohydrates and formation of inhibitory substances, which can disturb subsequent hydrolysis and fermentation processes, must be avoided. Finally, the process must be cost effective. In this review, the following three basic chemical pretreatment processes are discussed (the total amount of material removed is typically in range 15 to 25% of the initial feedstock):

- Hot-water extraction,
- acidic extraction, and
- alkaline extraction.

Other possible pretreatments (left out from this review) include, for example, physical (milling, grinding, *etc*.), enzymatical/biological, and some chemical/physicochemical (ammonia fiber explosion (AFEX), carbon dioxide explosion, organosolv, ionic liquids, *etc.*) pretreatments.

HOT-WATER EXTRACTION

Water is a unique solvent for any industry. It has a relatively high boiling point for its mass, a high dielectric constant, a high polarity, and a highly hydrogen-bonded structure (Ramos *et al*. 2002; Smith 2002; Krogell 2015). However, the properties of water are dramatically altered as the temperature and pressure are raised and the hydrogen-bonded lattice is disrupted due to the increasing thermal motion of the water molecules (Yu *et al*. 2008). Between 100 °C and 374 °C, heated water can have a permittivity very similar to that of typical organic solvents, making the organic non-polar compounds more soluble in water (Wiboonsirikul and Adachi 2008). The increased diffusivity characteristics, the reduced viscosity, polarity, relative permittivity, and surface tension together with enhanced solvent properties towards organic solutes allow more efficient mass-transfer reactions from solid samples (such as wood) compared to the extractions conducted under ambient conditions. Low surface tension and low viscosity promote better penetration of water into the matrix particles, thus enhancing the extraction. Low surface tension between water and the matrix permit better contact of solutes with water, and as the surface tension of water is decreased, the solvent cavity is easily formed, allowing the solute to dissolve more quickly in the solvent. In addition to these physical properties, the enhanced solvent properties of water can be related to the increased vapor pressures and accelerated thermal desorption of the compounds. As a solvent, water is cheap, non-flammable, non-toxic, abundant, easily disposable, and environmentally friendly; thus, it has a great potential to replace commonly used organic solvents.

Hot-water extraction (HWE) conducted at 50 to 100 °C has been used for a long time to extract organic components at the atmospheric pressure from solid sample matrices (Willför and Holmbom 2004; Kronholm *et al*. 2007). However, the extracted compounds have usually been relatively polar and readily soluble in water at these low temperatures. Pressurized hot-water extraction (PHWE, often known also as sub-critical water extraction, superheated water extraction, extraction with water at elevated temperatures and pressures, and near critical water extraction) has become a popular green extraction method for several compounds present in many different biological matrices (Vegas *et al*. 2004; Amidon and Liu 2009; Kim *et al*. 2009; Teo *et al*. 2010; Singh *et al*. 2014). PHWE is typically performed at the temperatures above 100 °C and below 374 °C (the critical temperature of water). The enhancement on the extraction efficiency of PHWE can be attributed to improvement in the solubility and mass transfer effect, and to increased disruption of surface equilibria (Teo *et al*. 2010; Kilpeläinen *et al*. 2013; Penttilä *et al*. 2013; Kilpeläinen 2015). The PHWE has the ability to recover and dissolve both polar and non-polar components from biological matrices, which makes this method an interesting alternative for fractionation of LCMs. Such compounds as phenolic, polycyclic aromatic compounds, oils, and proteins have all been extracted from environmental samples by PHWE. However, within the context of IFBR processes, the main emphasis of the PHWE has often been focused on the production of various hemicelluloses-derived carbohydrate fractions (Kilpeläinen *et al*. 2012).

Several factors, such as temperature, pressure, extraction time, and the analyte characteristics affect the efficiency of PHWE (Wiboonsirikul and Adachi 2008; Teo *et al*. 2010; Kleen *et al*. 2011; Hanim *et al*. 2012; Borrega *et al*. 2013a,b; Krogell *et al*. 2015; Krogell 2015). Other parameters include the flow rate, the type of reaction vessel, and the use of varying modifiers and additives. Temperature is the main parameter affecting the physicochemical properties of water and the efficiency of PHWE (Kronholm *et al*. 2007).

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When the temperature is increased, the solute-matrix interactions caused by van der Waals' forces, hydrogen bonding, and dipole attractions of the solute molecules and active sites of the sample matrix are disrupted. The thermal energy overcomes the cohesive (solute-solute) and adhesive (solute-matrix) interactions by decreasing the activation energy required for desorption (Richter *et al.* 1996). Pressure has only minor effects on the extraction recoveries during PHWE, as raising the pressure has only minor effects on the relative permittivity and solvent strengths of liquid water. During PHWE, a certain minimum pressure is required to maintain the water in a liquid state at the treatment temperatures (100 to 374 °C). In addition, since water has to be efficiently pushed through the sample, some samples may require higher extraction pressures. Extraction time is strongly dependent on the treatment temperature, on the desired extraction yield, and on the nature of the sample matrix components (Kronholm *et al.* 2007). By increasing the treatment temperatures (*i.e.*, more energy is provided), the treatment times can be decreased and *vice versa*.

PHWE can be carried out from several minutes to several hours, depending on used temperature and type of the used sample (Kronholm *et al.* 2007). Sample characteristics, such as the chemical composition of physical nature of the matrix, porosity, surface to volume ratio, size, and mass have a great influence on PHWE efficiency (Kronholm *et al.* 2007; Wiboonsirikul and Adachi 2008; Kleen *et al.* 2011; Krogell 2015). Extraction efficiency, rate, and recovery of various analytes can be greatly increased by increasing the porosity and the surface to volume ratio of the sample. In addition, PHWE efficiency varies according to whether the analytes are deposited in, adsorbed on, or chemically bonded to the sample matrix.

PHWE performed with LCMs is often called autohydrolysis (Garrote *et al.* 1999a,b; Carvalheiro *et al.* 2008; Al-Dajani *et al.* 2009; Testova *et al.* 2009,2011). Autohydrolysis technology covers a wide range of treatments, including water- and steam-based processes (Garrote *et al.* 1999a,b; Li *et al.* 2005). On an industrial scale, autohydrolysis is applied to the production of dissolving pulps based on the pre-hydrolysis kraft process (PHK) (Leschinsky *et al.* 2009a,b; Schild *et al.* 2010). During the first part of the autohydrolysis, catalytical hydronium ions come solely from the water autoionization reactions (Zumdahl and Zumdahl 2007). Hydronium ions act as a catalyst, especially during the early hydrolysis reactions of LCMs, leading to selective cleavage of the glycosidic linkages and in particular the acetyl groups of the hemicelluloses (Garrote *et al.* 2001; Chen *et al.* 2010; Liu 2010).

In the second stage of the autohydrolysis, hydronium ions coming from acetic and uronic acids start acting as catalysts in autohydrolysis (Garrote *et al.* 1999a,b; Carvalheiro *et al.* 2008). The contribution of hydronium ions originating from organic acids is higher than that from water autoionization catalyzing the hydrolysis of the linkages between hemicelluloses and lignin (Chua and Wayman 1979; Wayman and Chua 1979; Bujanovic *et al.* 2012), as well as the hydrolysis of the glycosidic bonds of the carbohydrate chains, resulting in chain degradation and reduced molar masses (Lai 2001; Kamerling and Gerwig 2007; Leschinsky *et al.* 2008a,b; Li and Gellerstedt 2008; Borrega *et al.* 2011a,b).

Depending on the severity of treatment conditions (temperature, treatment time, and pressure), autohydrolysis can result in the formation of mono-, oligo-, and polysaccharides (up to 60 - 80% of the total dissolved organics) (Gullón *et al.* 2012; Lehto *et al.* 2014a,b) and dissolved lignin, together with a variety of their degradation products (Sears *et al.* 1971; Nabarlatz *et al.* 2004; Paredes *et al.* 2008; El Hage *et al.* 2010). The benefits of the autohydrolysis process over the acid pretreatments are that corrosion

problems are limited, no waste sludges are generated, economic and operational costs are low, and cellulose is not significantly degraded under the applied conditions (Garrote *et al.* 1999a,b; Lei *et al.* 2010; Xiao *et al.* 2011). The disadvantage of autohydrolysis process is that it is not specific, and various side processes take place during the treatment, leading to hydrolysates with very complex chemical compositions that need further processing (Garrote *et al.* 2003; Vázquez *et al.* 2005; Leschinsky *et al.* 2009a,b; Gütsch and Sixta 2011).

Determining a relationship between the materials removed from LCMs by autohydrolysis and the process variables, such as temperature and time, is essential in order to predict optimal operation conditions for the production of the desired lignocellulosic products and allow a comparison of operations carried out at different temperatures and times (Tunc and van Heiningen 2009). One such operational parameter is the so-called pre-hydrolysis factor (P-factor), which combines the effect of treatment time with the applied temperature in one parameter, similar to the H-factor for kraft cooking (Brasch and Free 1965; Sixta *et al.* 2006; Pedersen and Mayer 2010; Saukkonen *et al.* 2012a). This single variable can then be used as a tool for estimating and comparing autohydrolysis processes with different temperatures and time. When the activation energy for the cleavage of glycosidic bonds of the carbohydrate materials in wood is coined with the P-factor concept (Lin 1979), Equation 1 can be employed for the P-factor concept (Sixta *et al.* 2006; Gütsch *et al.* 2012),

$$P = \int_{t_0}^{t} \frac{k_{H,(T)}}{k_{100°C}} dt = \int_{t_0}^{t} exp\left(40.48 - \frac{15,106}{T}\right) dt, \qquad (1)$$

where *t* is reaction time in hours, *T* is temperature in Kelvins, and *k* is a rate constant. The activation energy used in Eq. 1 is 125.6 kJ/mol. Typical autohydrolysis pretreatment times range from minutes to several hours, depending on the wanted outcomes (*i.e*., molecular properties of the dissolved hemicelluloses and lignin, formation of unwanted degradation products, and pulping properties of the pretreated wood)

Besides the conventional autohydrolysis, microwave-assisted HWE has been used for extraction of hemicelluloses with high yield from spruce chips (Lundqvist *et al.* 2002,2003). This treatment strongly shortens the required extraction time, since in this case heating the water to the desired temperature is extremely fast. However, the microwave-assisted extraction is difficult to up-scale and can be considered rather expensive.

In addition, surface active agents or surfactants as additives have been used for facilitating the diffusion of hemicelluloses out from the wood matrix and preventing unspecific adsorption of cellulase enzymes to lignin as well as for improving the solubility and removal of lignin from the wood matrix (Kristensen *et al.* 2007; Wei *et al.* 2011). The use of surfactants in autohydrolysis is mainly aiming at the enzymatic degradation of cellulose and hemicelluloses to manufacture of ethanol and other value-added products.

ACIDIC PRETREATMENTS

Acidic pretreatments of LCMs are usually performed with some common organic (Tunc *et al.* 2014) or mineral acids, such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3), or trifluoroacetic acid (F_3CCO_2H, TFA), of which H_2SO_4 is the most commonly used acid (Carvalheiro *et al.* 2008; Marzialetti *et al.* 2008). Acidic pretreatment is often combined with other hydrolysis techniques, such as enzymatic hydrolysis, which

would proceed too slowly without the pretreatment (Uçar 1990). The main aim of these hydrolysis combinations is usually the production of hydrolysate containing fermentable sugars, which can be further processed into various biochemicals, such as bioethanol (Cara *et al*. 2008). Acid hydrolysis has been utilized as a pretreatment method for numerous lignocellulosic feedstocks, such as agricultural wastes (Binod *et al*. 2010; Romero *et al*. 2010; Talebnia *et al*. 2010; Rocha *et al.* 2014; Singh *et al*. 2014), but also for woody biomass (Söderström *et al*. 2003; Jensen *et al*. 2010; Wei *et al*. 2012). The pretreatment time and temperature are strongly dependent on the concentration of the used acid and on the wanted outcomes. Increasing the acid concentration can be used to shorten the needed pretreatment time and to lower the treatment time, and *vice versa*. However, typical treatment times in acidic pretreatments range from minutes (even seconds) to few hours.

However, the removal of constituents from LCMs by acidic hydrolysis techniques involves complex physical changes and chemical reactions that are related to the complexity of the feedstock material itself (Harris *et al.* 1984; Niemelä and Sjöström 1988b). For this reason, the hydrolysates are chemically rather complex. They contain a mixture of various carbohydrates (Garrote *et al*. 1999a,b; Carvalheiro *et al*. 2008; Al-Dajani *et al*. 2009; Teo *et al*. 2010) and a minor amount of other organics, including aliphatic carboxylic acids ("volatile acids", *i.e*., acetic and formic acids) (Tunc and van Heiningen 2011), "acidic" carbohydrate degradation products (furans, *i.e*., 2-furaldehyde or furfural (FF) and 5-(hydroxymethyl)furfural (HMF)), as well as heterogeneous fractions of lignin- and extractives-derived materials (Larsson *et al*. 1999). All these non-carbohydrate materials may be regarded as harmful substances, especially when considering the biochemical utilization of carbohydrates in hydrolysates, and usually some kind of purification or detoxification of acidic hydrolysates is required (Delgenes *et al*. 1996; Olsson and Hahn-Hägerdal 1996; Palmqvist and Hahn-Hägerdal 2000a,b; Nilvebrandt *et al*. 2001). Several purification possibilities, such as solvent extraction (Cruz *et al*. 1999; Garrote *et al*. 2003; Vázquez *et al*. 2005; Moure *et al.* 2006; Parajó *et al*. 2008), resin treatment (Nilvebrandt *et al*. 2001; Conde *et al*. 2008; Schwartz and Lawoko 2010), and membrane assisted filtration (such as ultrafiltration) (Mänttäri *et al*. 1997; Bhattacharya *et al*. 2005; Pizzichini *et al*. 2005; Vegas *et al*. 2006; Sjöman *et al*. 2008) have been proposed for production of detoxified substrates for subsequent fermentation processes.

Among the acidic pretreatments, processes conducted with diluted mineral acids have been the most favored applications for industrial purposes, mainly due to the minor corrosion problems caused by the used diluted acid combined with reasonably high carbohydrate yields dissolved from LCMs (Carvalheiro *et al*. 2008; Yang and Wyman 2009). Compared to the concentrated acid hydrolysis, which is very expensive method due to the significant challenges and costs in both operational and equipment design, dilute acid hydrolysis generates lower amounts of degradation products and significantly fewer corrosion problems in hydrolysis tanks and pipes. Although concentrated acid hydrolysis processes have the advantage of operating at low or medium temperatures, leading to the reduction of operating costs (Gírio *et al*. 2010), the type of used equipment needs to be resistant to an extremely corrosive environment. Special attention must be paid to the recovery of the used acid and to the neutralization of the solution. These requirements are the key challenges that must be overcome to keep the concentrated acid pretreatments economically viable.

Dilute acid hydrolysis has been used primarily for the removal of hemicelluloses from LCMs, leaving the cellulose fraction more amenable for further treatments (Gírio *et*

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al. 2010; Lenihan *et al.* 2010). Dilute acid hydrolysis can result in the recovery yields up to 95% of the theoretical amounts expected from hemicellulose-derived fragments, depending on the applied pretreatment conditions (*i.e.,* temperature, treatment time, and acid concentration). The solid residue from the dilute acid hydrolysis contains mainly cellulose and lignin, which can be subjected to further processing, such as chemical pulping or enzymatic hydrolysis (Parajó *et al.* 1993,1994; Fredrick *et al.* 2008).

In addition to the concentrated and dilute acid hydrolysis, pretreatments conducted with extremely low acid (ELA) additions can be used to hydrolyze LCMs under very low acid concentrations (< 0.1%) and at high temperature (as high as 220 °C) (Ojumu *et al.* 2003; Ojumu and Ogunkunle 2005). The advantages of the ELA hydrolysis process (resembling pretreatments conducted with pressurized hot water (PHW)) include limited corrosion effects, leading to the need for cheaper standard grade stainless steel equipment, instead of using expensive high nickel alloy. For this reason, significant cost advantages can be achieved in the equipment and operational design (Kim *et al.* 2001; Gurgel *et al.* 2012). In addition, a process using ELA qualifies as a 'green technology' because it has only minimal environmental effects. Recent advances in the process design have brought ELA processes into a position where it can compete on par with the enzymatic hydrolysis processes in the overall process economics.

The acid-catalyzed hydrolysis of glycosidic linkages in polysaccharides and the cleavage of α- and β-aryl ether bonds in lignin are the primary degradation reactions that occur when LCMs are treated in acidic media (Sjöström 1993; Brunow *et al.* 1999; Vuorinen and Alén 1999; Ishii and Shimizu 2001; Sakakibara and Sano 2001; Sixta *et al.* 2006; Lange 2007; Wang *et al.* 2012). The hydrolytic reactions are often accompanied by further chemical reactions, such as dehydration, degradation, and condensation reactions. Acid hydrolysis of the glycosidic linkage involves an initial protonation of the glycosidic oxygen, followed by decomposition of the resulting conjugate acid to the cyclic carbonium ion (Vuorinen and Alén 1999; Ishii and Shimizu 2001; Lange 2007). After the rapid addition of water, free carbohydrate is liberated. The alternative mechanism involves a protonation of the ring oxygen atom to form a conjugated acid, followed by a ring opening to give an acyclic carbonium ion (Sixta *et al.* 2006). After this stage, the addition of water to the protonated hemiacetal leads to the hydrolysis and to a liberation of a free monosaccharide. Hydrolysis process is affected by the physical structures and conformation of the carbohydrate components and the nature and concentration of the used acid. Due to the amorphous nature, different ring structures, and carbon atom configurations, hemicelluloses degrade faster under acidic conditions than cellulose.

In addition to the hydrolytic reactions, the acidic treatment of carbohydrate-containing materials produces different degradation products originating from pentoses and hexoses (Li *et al.* 2005; Zeng *et al.* 2010; Liu *et al.* 2013b). From pentoses (such as xylose), the main degradation product formed under acidic conditions is FF (Qi and Xiuyang 2007; Agirrezabal-Telleria *et al.* 2013,2014; Liu *et al.* 2014; López *et al.* 2014). From hexoses, which are more stable than pentoses under acidic conditions, the primary degradation product is HMF. However, HMF can be further degraded to formic and levulinic acids (Marzialetti *et al.* 2008; Zeng *et al.* 2010).

Acidic degradation of lignin proceeds mainly *via* the cleavage of α- and β-aryl ether linkages (Sakakibara and Sano 2001). The acidic cleavage reactions of the bonds linking the lignin precursors together into a web-like structure entails several reaction routes and mechanisms, and they yield a wide variety of different intermediates and end products. The

reaction routes and formed products are dependent on the nature of the lignin and on the presence and the abundance of different bonds linking the lignin monomers together.

ALKALINE PRETREATMENTS

Alkaline extraction of pulp wood chips prior to pulping can be considered as one promising and well integrated biorefinery process combined with an existing industrial alkaline pulping process (Yoon *et al*. 2011; Luo *et al*. 2012; Stoklosa and Hodge 2012; von Schenck *et al*. 2013; Singh *et al*. 2014). Alkaline pretreatment can shorten the cooking times and lower the need for alkali charge of the subsequent pulp cooking process. Also, alkaline pulping liquors, such as white and green liquors, can be used for pretreatments as such (Ban *et al*. 2003a,b, 2004; Ban and Lucia 2003, 2005; Ban *et al*. 2009; Walton *et al*. 2010a; Wu *et al*. 2010; Yoon and van Heiningen 2010; Gonzalez *et al*. 2011; Jun *et al*. 2012; Meng *et al.* 2014; Kim *et al.* 2015; Wang *et al.* 2015). Pretreatments conducted with white and green liquors utilize proven technologies for the sophisticated recovery of all the used chemicals at a very high efficiency, and they can be easily integrated into existing pulp mill operations (Jin *et al*. 2010). For this reason, no additional operational equipment is needed for the production of pretreatment chemicals.

Alkaline pretreatment is chemically similar to kraft pulping, in which acetyl groups, uronic acids, hemicelluloses, and lignin are partly removed. For this reason, it increases the porosity, reactivity, and accessibility of the remaining feedstock towards, for example, chemical pulping, and enzymatic hydrolysis (Minor and Springer 1993; Hu *et al*. 2008; McIntosh and Vancov 2010; Ju *et al*. 2011; Chen *et al.* 2013; Kallioinen *et al*. 2013). The mechanism of the alkaline hydrolysis has been suggested to be the saponification of the intermolecular ester bonds crosslinking hemicelluloses and lignin (Sun and Cheng 2002). Particularly, alkyl aryl linkages of lignin are readily cleaved under alkaline conditions, facilitating enhanced dissolution of lignin (Park and Kim 2012).

When compared to hot-water and acidic pretreatment methods, mild alkaline pretreatments have advantages, as they generally maintain the yield and quality of the produced pulp and cause minor sugar degradation (Al-Dajani and Tschirner 2008; Chen *et al*. 2012; Jun *et al*. 2012; Sim *et al.* 2012; Huang and Ragauskas 2013a,b). The difference between acidic and alkaline hydrolysis lies in the nature of the extracted carbohydrates (De Lopez *et al*. 1996). Whereas the acidic hydrolysis conditions often produce significant amounts of monosaccharides from LCMs, the extraction under alkaline conditions produces oligosaccharides and polysaccharides (Jiang *et al*. 2014; Lehto and Alén 2013, 2015a). Furthermore, carbohydrates are susceptible to further degradation under alkaline conditions, leading to significant formation (up to 60-70% of the dissolved organic material) (Lehto and Alén 2013, 2015a) of various degradation products, such as monocarboxylic and dicarboxylic hydroxy acids, together with volatile acids, such as acetic and formic acids (Niemelä 1990a,b; Sjöström 1991).

Alkaline pretreatment processes are often conducted at low temperatures (below 100 °C) and pressures, and they can be carried out even at ambient pressure (Hu *et al*. 2008). On the other hand, the treatment times are usually long, ranging from hours to even days. The most employed chemicals in alkaline pretreatments of LCMs include NaOH and Ca(OH)$_2$, together with KOH, Na$_2$CO$_3$, and NH$_3$ (Mosier *et al*. 2005; Carvalheiro *et al*. 2008; Alvira *et al*. 2010). Addition of an oxidizing agent (oxygen or H$_2$O$_2$) to an alkaline

pretreatment process can be used to improve the performance of the extraction by favoring the removal of lignin.

Pretreatments performed with NaOH have received the most interest among alkaline pretreatment processes due to their widespread utilization in the course of alkaline pulping (Mosier *et al*. 2005). NaOH causes fiber swelling, increases the internal surface area of cellulose, and decreases the degree of polymerization and crystallinity of wood polysaccharides. These phenomena together promote the cleavage of structural linkages between lignin and carbohydrates and simultaneous disruption of lignin structure (Sun and Cheng 2002; Alvira *et al*. 2010; El Mansouri *et al*. 2011; Bujanovic *et al*. 2012; Mao *et al.* 2012; Xiao *et al*. 2012; Lehto *et al.* 2015). However, the process is quite complicated, involving several reactive and nonreactive phenomena, such as dissolution of non-degraded polysaccharides, peeling reactions, hydrolysis of glycosidic bonds and acetyl groups, and decomposition of dissolved polysaccharides into various degradation products (*i.e*., hydroxy acids) (Mirahmadi *et al*. 2010). The increase in digestibility has been shown to be more enhanced in hardwoods when compared to softwoods. This has been explained by the compositional differences between these two feedstocks, as hardwoods contain a higher proportion of total carbohydrates to lignin compared that for softwoods (Helmerius *et al*. 2010).

In addition to the different carbohydrate to lignin ratios, the types of hemicelluloses also have their effects on alkaline treatments (Helmerius *et al*. 2010). Softwood glucomannans are degraded by the alkaline peeling reactions rapidly under alkaline conditions, while the deacetylated, solubilized oligomeric xylan is more stable due to the 4-*O*-methylglucuronic acid side chains. As xylan is the dominant hemicellulosic component in many commercially utilized hardwoods (such as silver birch, *Betula pendula*), alkaline pretreatment has been found to represent a more suitable extraction method for hardwoods than for softwoods. In addition to the chemical nature of the hardwood hemicelluloses, more open vascular structure of hardwoods renders them more amenable to chemical pretreatments.

CHEMICAL COMPOSITION AND UTILIZATION OF THE PRETREATMENT LIQUORS

Chemical Composition of Pretreatment Liquors

Pretreatment hydrolysates obtained from LCMs under different treatment conditions are complex mixtures containing mainly soluble carbohydrates and other wood-derived components, representing a promising source of renewable raw materials for the production of different biochemicals and biofuels (Kumar *et al*. 2008; Menon and Rao 2012; Lehto and Alén 2013, 2015; Lehto *et al.* 2014a,b). The main purpose of the pretreatment process has often been the recovery of the main hemicelluloses, such as xylan or glucomannan, which can be further processed to desired product applications, for example, *via* fermentation or fractionation processes (Garrote *et al*. 2001; Parajó *et al*. 2008; Song *et al.* 2008). However, in addition to carbohydrates (and depending on the applied pretreatment conditions), especially acidic pretreatment liquors contain a wide variety of "acidic" sugar degradation products (FF and HMF together with "volatile" carboxylic acids such as acetic and formic acids), extractives, and lignin-derived phenolic compounds (Luo *et al*. 2002; Persson *et al*. 2002; Moure *et al*. 2006; Barakat *et al*. 2012; Lehto and Alén 2012, 2013, 2015a; Lehto *et al.* 2014a,b). On the other hand, alkaline

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pretreatments produce significant amounts of various carbohydrates-derived "non-volatile" carboxylic acids, such as hydroxy mono- and dicarboxylic acids (Lehto and Alén 2013, 2015a). Many of these carbohydrates-derived degradation products and non-saccharide compounds are potentially inhibitory to the microorganisms used especially in the fermentation processes, and for this reason further fractionation of the produced hydrolysates is usually necessary (Converti and Del Borghi 1998; Taherzadeh *et al*. 1999; Palmqvist and Hahn-Hägerdahl 2000a,b; Walton *et al*. 2010b; Lehto and Alén 2012). However, these non-saccharide components can also serve as a potential raw material source for the production of many low-volume/high-value components, such as pharmaceuticals.

Fractionation of Pretreatment Effluents

Several fractionation and purification methods have been proposed for the fractionation and production of purified component fractions from pretreatment hydrolysates (Palmqvist and Hahn-Hägerdahl 2000a,b; Moure *et al*. 2006; Peng *et al*. 2012). Such methods as solvent extraction, precipitation with chemicals, chromatographic purification, treatments with adsorption resins (with or without charged groups), and filtration with various membranes have all been used for the fractionation of these complex aqueous mixtures.

Solvent extraction (usually conducted with some common organic solvent, such as ethyl acetate or diethyl ether) is a useful method for removing especially non-saccharide components from lignocellulosic hydrolysates, yielding both a selectively refined aqueous phase containing carbohydrates and a solvent-soluble fraction mainly composed of phenolics and extractive-derived compounds (Cruz *et al.* 1999; Palmqvist and Hahn-Hägerdahl 2000a,b; Garrote *et al*. 2003; Vázquez *et al*. 2005; Moure *et al*. 2005, 2006; Lehto and Alén 2012).

Solvent precipitations performed as single or multistage operations (usually conducted with ethanol, acetone, and 2-propanol) have been successfully employed for the fractionation of carbohydrate components (mainly in their polymeric forms) from lignocellulosic hydrolysates (Kalapathy and Proctor 2001; Vegas *et al*. 2004; Moure *et al*. 2006; Peng *et al.* 2009). In particular, sequential treatments of biomass with hot water and dilute alkali combined with graded ethanol precipitation with increasing alcohol concentrations have been shown to be very effective methods for the fractionation of hemicelluloses from biomass and biomass-derived hydrolysates.

At an analytical level, chromatographic fractionation, such as high-performance anion-exchange chromatography (HPAEC) and size-exclusion chromatography (SEC), have been employed for the production of low-volume, very high-purity hemicellulose fractions from lignocellulosic hydrolysates (Moure *et al.* 2006). In addition, chromatographic techniques have been employed for refining samples prior to structural characterization of the hemicelluloses by a ^{13}C nuclear magnetic resonance (NMR) spectroscopy, matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), and nanospray mass spectrometry (Kabel *et al*. 2002a,b).

Several types of resins and activated charcoals have been used for the purification of plant extracts and lignocellulosic hydrolysates (Miyafuji *et al*. 2003; Canilha *et al*. 2004; Moure *et al*. 2006; Villareal *et al*. 2006; Ou *et al*. 2007; Conde *et al*. 2008; Wickramasinghe and Grzenia 2008; Schwartz and Lawoko 2010; Lehto and Alén 2012). Acrylic, polystyrene-based, and formaldehyde-phenol resins have been used to recover anthocyanins, flavonoids, and hydroxycinnamates from different types of plant extracts.

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Moreover, adsorbent resins have been used to recover and concentrate phenolics from aqueous and synthetic solutions, and ion-exchange (anionic and cationic) resins have been utilized for the purification of lignocellulosic hydrolysates (Nilvebrandt *et al*. 2001; Jeong *et al*. 2014; Trinh *et al*. 2014). Under defined conditions, the adsorption of phenolic compounds can be favored with respect to other compounds (such as carbohydrates) present in the solution. Polymeric resins are highly porous, and a variety of compounds can be adsorbed and desorbed, depending on the polarity of the solvent. Using polar solvents, such as water, resins can absorb organic and non-polar species, whereas in the presence of non-polar solvents, some resins (especially those of acrylic and phenolic nature) exhibit hydrophilic or slightly polar behavior and can adsorb slightly polar species. In the case of ion-exchange resins, anion-exchange resins have been found to be especially effective in removing different types of compounds (phenolics, furan aldehydes, and aliphatic acids) from lignocellulosic hydrolysates (Conde *et al*. 2008).

Membrane-assisted processing of lignocellulosic hydrolysates has gained importance in fractionation of hemicelluloses in particular from aqueous extracts (Moure *et al*. 2006; Vegas *et al*. 2006; Nabarlatz *et al*. 2007; Sjöman *et al*. 2006, 2007, 008; Al Manarash *et al*. 2012a,b; Sainio *et al*. 2013; Ajao *et al*. 2014; Kallioinen *et al*. 2014). In the pulp and paper industry, membrane technology has already been implemented for recycling chemicals, for cleaning process effluents, and for removing impurities from water circulation systems (Mänttäri *et al.* 1997, 2002; Koivula *et al*. 2011, 2012, 2013; Krawczyk *et al*. 2013). Several different membrane filtration processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), have been used in the pulp and paper industry, mainly for concentration and fractionation of spent liquors, to remove color and to treat bleaching effluents (Bhattacharya *et al*. 2005; Pizzichini *et al*. 2005). UF, for example, has been suggested for the recovery of hemicelluloses from the process waters of pulp mills producing thermomechanical pulp (TMP) (Persson and Jönsson 2010). Membrane separation processes can be tailored to meet the wanted degree of purification by choosing the appropriate membranes with convenient membrane weight cut offs (MWCOs) and the right operational conditions, such as applied pressures. The choice of membrane and operating conditions has a considerable impact on the purification efficiency, on the process problems (such as membrane fouling), and the economics of the fractionation process (Mänttäri *et al*. 2000; Persson and Jönsson 2010; Koivula *et al*. 2011; Puro *et al*. 2011).

Fermentation of LCM Hydrolysates

LCM-derived hydrolysates can be fermented with different microorganisms, the aim being at the production of ethanol or other platform chemicals, such as small-size organic acids (Ragauskas *et al*. 2006; Koutinas *et al.* 2008; Sánchez and Cardona 2008; Hörhammer *et al*. 2011; Boucher *et al*. 2014). For fermentation purposes, biomass is converted into sugar solutions, and these substrates are then fermented by case-specific microorganisms to overproduce metabolic products. After purification, the metabolic products could be used as platform molecules for the production of various bulk chemicals through biological/chemical processing routes. Several platform chemicals are already industrially produced *via* fermentation, such as ethanol, citric acid, glutamic acid, lactic acid, and 1,3-propanediol (Viikari and Alén 2011).

However, achieving an economically feasible fermentation process of LCM hydrolysates faces several obstacles affecting the overall efficiency of the bioconversion process. The first problem is that carbohydrate solutions produced with present day

hydrolysis processes are generally very dilute. The second problem is that a large pentosan fraction originating from hemicelluloses cannot be fermented by traditional brewing yeasts. Hexoses can be fermented quite easily to ethanol, whereas work on efficient fermentation of pentoses into ethanol is still in progress (Chirat *et al*. 2009). One of the most profound weaknesses of early efforts to develop effective wood-to-chemicals bioconversion processes has been the lack of organisms capable of fermenting pentose sugars (Delgenes *et al*. 1996; Olsson and Hahn-Hägerdal 1996). As wood hydrolysates are often rich in hemicelluloses-derived pentoses (such as xylose), considerable effort has been subjected towards the isolation and production of microorganisms that can produce fermentation products with high yield from both hexoses and pentoses and that can withstand both the produced fermentation products and the inhibitory compounds present in the hydrolysates (Larsson *et al*. 2001; Katahira *et al*. 2006; Hahn-Hägerdahl *et al*. 2007; Tian *et al*. 2011; Shupe and Liu 2012). Effective pentose fermenting microorganisms (both naturally occurring and recombinant species) have been found among bacteria, yeasts, and fungi. Of the naturally occurring yeasts, *Candida shehatae*, *Pachysolen tannophilus*, and *Pichia stipitis* have been found to be the most promising alternatives for pentose fermentation. Of the genetically engineered yeasts, the recombinant strains of *Saccharomyces cerevisiae* have gained considerable interest (van Maris *et al*. 2006). In addition to genetically engineered yeasts, several bacteria (such as *Escherichia coli*) have been genetically modified and harnessed for ethanol production.

Production of fuel alcohols, such as ethanol or butanol from LCMs, has gained growing global attention during the past few decades (Brandberg *et al*. 2004; Tang *et al*. 2006; Margeot *et al*. 2009; Chin *et al*. 2010; Limayem and Ricke 2012; Sun and Liu 2012; Lee *et al*. 2013). Depletion of fossil resources and growing demands for energy and chemicals have forced industries to search for alternative material sources. Compared with the finite supply of fossil fuels, ethanol produced from abundant and renewable LCMs can play a vital role in achieving sustainable development by reducing greenhouse gas emissions (Xu and Liu 2009). Production of fuel ethanol from LCMs includes the degradation of the lignocellulosic structure to a mixture of fermentable sugars, followed by the fermentation and distillation of the fermentation broth to obtain 95% ethanol (Olsson and Hahn-Hägerdal 1996). The ethanol yield of the process is an important parameter with regards to the process economy, since the costs of raw material and process operation are typically associated with the material passing through the process and not the amount of product manufactured. For producing of fuel ethanol, yeast fermentation is considered to be a mature technology, where future scientific improvements will result only in a minor cost benefit (Duff and Murray 1996). Hexoses are readily fermented by yeasts (such as *Saccharomyces cerevisiae*, also known as Brewer's yeast) (Olsson and Hahn-Hägerdal 1996). In addition to conventional yeast fermentation, certain bacteria are capable of fermenting hexoses to ethanol (Chirat *et al*. 2009).

There are certain advantages when using bacteria instead of yeasts for alcohol fermentation (Chirat *et al*. 2009). During bacterial fermentation, less biomass is generated than in yeast fermentation. For this reason, higher ethanol yields are achieved through the use of anaerobic ethanologenic bacteria, such as *Zymomonas mobilis* or *Zymomonas anaerobia*. In addition to improved yield, the ethanol fermentation by bacteria offers a number of other advantages over the traditional yeast fermentation. Sugar uptake rates and ethanol productivity are generally higher in bacterial fermentation, bacteria have higher ethanol tolerance, and they are less sensitive to low pH and inhibitory compounds found in lignocellulosic hydrolysates. In addition to ethanol, the fermentative production of several

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other alcohols from biomass has been suggested (Felipe *et al*. 1996; Parajó *et al* 1997a,b; Kamm *et al*. 2006; Viikari and Alén 2011). Such alcohols as butanol, xylitol, *n*-propanol, 1,2-propanediol, 1,3-propanediol, glycerol, 2,3-butanediol, and 1,2,4-butanetriol have all been produced by fermentative pathways from lignocellulosic biomass.

Several small-size organic acids produced by fermentative methods are considered to have high "building block potential", either as monomers for the production of novel polyesters and polyamides or as a starting material for a variety of commodity chemicals currently produced petrochemically (Kamm *et al.* 2006). Several carboxylic acids are already produced by fermentative pathways and utilized by industry. Such common organic acids include, for example, lactic, citric, and tartaric acids (Viikari and Alén 2011). Of these, especially lactic acid has gained a great interest, as it can be converted into various chemicals, including acrylic acid, propylene glycol, acetaldehyde, and 2,3-pentanedione (Melzoch *et al*. 1997; Woiciechowski *et al*. 1999; Guo *et al*. 2010).

Lactic acid has a wide range of applications in food, pharmaceutical, and cosmetic industries; in recent years demands for lactic acid have increased due to its application in the manufacturing of biodegradable polymers (poly(lactic acid), PLA) and green solvents (Melzoch *et al*. 1997; Hofvendahl and Hahn-Hägerdahl 2000; Zhang *et al*. 2007; Guo *et al*. 2010). Lactic acid has been commercially produced from fermenting glucose, starch, liquefied starch or sucrose, and it has been estimated that 60 to 80% of the production costs are related to the high cost of substrate raw materials. Thus, using low-cost raw material, such as lignocellulosic biomass, is required for building an economical and sustainable lactic acid industry (Parajó *et al*. 1996).

Considerable efforts have been directed to the search for organisms capable of fermenting lignocellulosic hydrolysates into lactic acid (Guo *et al.* 2010; Abdel-Rahman *et al*. 2011). Many industrial microorganisms producing lactic acid lack the ability to ferment xylose, which is an important component present in lignocellulosic hydrolysates. Therefore, efforts have been made to find wild strains of microorganisms or to genetically engineer such common microorganisms as *Escherichia coli* for the utilization of hydrolysates rich in pentoses. In addition to the complex carbohydrate composition, inhibitory compounds present in lignocellulosic hydrolysates affect the efficiency of the lactic acid fermentation process, as is also the case in alcohol fermentation. Hence, the discoveries of the strains of microorganisms with abilities to not only ferment various sugars, but also to resist fermentation inhibitors, are of great interest to researchers and industry.

In addition to the three most commonly produced acids (lactic, citric, and tartaric acids), the production and exploitation of several other small-size organic acids derived from lignocellulosics has been investigated (Kim *et al*. 2004; Kamm *et al*. 2006; Liu *et al*. 2013a). Such acids as propionic, pyruvic, 3-hydroxypropanoic (3-HPA), butyric, 3-hydroxybutanoic, aspartic, glutamic, succinic, fumaric, malic, and itaconic acids have been highlighted as being potential chemicals produced from LCM feedstocks. Of these, especially 3-HPA, four-carbon diacids (malic, fumaric, and succinic acids), itaconic, aspartic, and glutamic acids have the potential to become economically viable products if low-cost fermentation routes can be developed and scaled up to the industrial level.

Polysaccharide-based Biodegradable Films and Hydrogels

In recent years, various polymeric applications manufactured from LCMs have gained growing attention (Edlund *et al*. 2011; Stevanic *et al*. 2011; Wang *et al*. 2012; Oinonen *et al*. 2013). In this approach, hemicelluloses represent many promising properties

for the manufacture of value-added polymeric composites and blends, which could replace materials currently manufactured from fossil resources or even metals, such as aluminum (Alekhina *et al*. 2014). Natural biopolymers are considered to have many advantageous properties when compared to their synthetic counterparts, as they are abundant, low-cost, biocompatible, nontoxic, biodegradable, and environmentally safe (Peng *et al*. 2011b; Šimkovic *et al*. 2011). Of the several possible hemicelluloses-derived polymeric applications, the manufacture of various polymeric films and hydrogels has garnered the most interest.

Due to their ability to form dense macromolecular networks, hemicelluloses (especially xylans and glucomannans) reveal many promising features for the manufacturing of edible and packaging films, and coatings used in various packaging applications (Bachegul *et al*. 2012; Mikkonen and Tenkanen 2012; Egüés *et al*. 2013; Ruiz *et al*. 2013; Alekhina *et al*. 2014). These bio-based polymers can be used instead of aluminum foil or synthetic polymers, resulting in the decreased carbon footprint of the packaging industry (Oinonen *et al*. 2013; Alekhina *et al.* 2014). Hemicelluloses-derived polymers are hydrophilic, and as such, they demonstrate notable barrier characteristics against oils and fats (Stevanic *et al*. 2011). However, water vapor permeability and oxygen permeability also are crucial properties, especially when considering many food packaging applications (Mikkonen *et al.* 2010). Consequently, modification of the barrier properties of hemicelluloses-derived biopolymers against water and moisture must be significantly improved before they can be considered suitable for various food packaging solutions (Saxena *et al*. 2011; Escalante *et al*. 2012). Such modifications may include several possibilities, such as etherification, esterification, oxidation, and polymerization pathways (Ren *et al*. 2012).

The second class of polymeric application manufactured from hemicelluloses includes the production of hydrogels (Gabrielii *et al*. 2000; Peng *et al*. 2011a; Pohjanlehto *et al*. 2011). Due to the high hydrophilicity, the abundance of hydroxyl groups together with biodegradability, nontoxicity, and responsiveness to environmental stimuli (pH, ionic strength, solvent composition, temperature, as well as electric and magnetic fields) hemicelluloses-derived hydrogels have attracted attention, especially in the manufacture of biomedical product applications, such as controlled drug delivery systems, biological scaffolds for tissue engineering, biosensors, immobilized carriers for the encapsulation of living cells, and barrier materials for regulating biological adhesions (Söderqvist-Lindblad *et al*. 2005; Edlund and Albertsson 2008; Sun *et al.* 2013; Maleki *et al*. 2014). In addition to medical applications, such alternatives as superadsorbents in hygiene products, water treatment, and drying agents have been manufactured from LCM-derived hemicelluloses.

Xylooligosaccharides

Sugar oligomers (especially xylooligosaccharides or XOs) have been found to contain several interesting health effects (such as prebiotic activity), which makes them interesting alternatives for acting as ingredients for functional foods, and replacing commercial antioxidants manufactured *via* chemical synthesis (Kabel *et al.* 2002a,c; Carvalheiro *et al*. 2004; Garrote *et al*. 2004b; Parajó *et al*. 2004; Vázquez *et al*. 2006; Aachary and Prapulla 2010). XOs are used as food ingredients due to their technological properties and health effects (Vázquez *et al*. 2000). The sweetness of dimeric xylobiose is equivalent to 30% of that of sucrose, and the sweetness of other XOs is moderate and possesses no off-taste. XOs are stable over a wide range of pH (2.5 to 8.0) and temperatures (up to 100 °C), which makes XOs promising alternatives, for example, for inulin. This

permits their utilization in many dietary applications, such as low-pH juices and carbonated drinks. For food ingredient purposes, XOs have an acceptable odor, are non-cariogenic and are contain less energy (*i.e.,* are of low-calorie) which means, that they can be incorporated into anti-obesity diets. XOs save insulin secretion from the pancreas and stimulate intestinal mineral absorption. From a nutritional point of view, XOs behave as non-digestible oligosaccharides, which are not degraded in the stomach (Kabel *et al.* 2002c; Vegas *et al.* 2006). XOs can be mixed with other prebiotics to achieve a synergistic effect, or they can be a part of symbiotic preparations together with probiotic microorganisms.

The health effects of XOs are mainly related to their effects on the gastrointestinal flora (Vázquez *et al.* 2000; Kabel *et al.* 2002a,c; Parajó *et al.* 2004; Moure *et al.* 2006; Vázquez *et al.* 2006; Aachary and Prapulla 2010). Tests carried out with humans have demonstrated that beneficial bacteria can utilize XOs as their carbon sources. As ingested xylobiose is not excreted in feces or urine and as XOs cannot be hydrolyzed either by saliva, pancreatin, or gastric juice, the bacterial utilization of the XOs is the only possibility. XOs promote the growth of certain beneficial bacteria (especially *Bifidobacteria* and *Lactobacilli*) in the gastrointestinal tract. Reported advantageous effects of *Bifidobacteria* on human health include such effects as suppressing activity of entero putrefactive bacteria, preventing the formation of detrimental products, such as toxic amines, repression of pathogenic bacteria due to the production of short-chain organic acids, facilitating decreased pH in the gastrointestinal tract, as well as the digestion and absorption of nutrients.

In addition to the enhanced growth of beneficial bacteria, suppression of the growth of some detrimental bacteria (*Clostridium difficile*), which lack the ability of using XOs as a carbon source, has been reported (Vázquez *et al.* 2000; Moure *et al.* 2006; Aachary and Prapulla 2010). The beneficial effects of XOs to gastrointestinal flora are accompanied with the observation that XOs can help to reduce the concentrations of so-called secondary bile acids, which negatively affect the colon and present dose-dependent toxic potential related to mutagenic and tumor-promoting properties that these acids may have. These properties together result in the ability to prevent gastrointestinal infections, to reduce the duration of diarrhea episodes, to maintain the fecal water content within normal levels, and to enhance cecal epithelial cell proliferation. As XOs have been found to contain several positive effects (both cellular and physiological), they fulfill the requirements for prebiotic compounds. XOs are commercially utilized as food ingredients especially in Japan, where about 60 companies use XOs as raw materials.

Utilization of XOs as food additives is by far the most important application discovered for XOs (Vázquez *et al.* 2000; Moure *et al.* 2006; Aachary and Prapulla 2010). XOs can be used in the formulation of so-called functional foods in which XOs are used in combination with, for example, soya milk, nutritive preparations, special preparations for health food for elderly people and children, or as active components of symbiotic preparations. The term "functional food" refers to a food product fortified with added ingredients that can positively affect the consumer's health. As the knowledge and awareness of the links between health, nutrition, and diet is rapidly growing, the markets for functional foods and for their ingredients are quickly expanding. The manufacture of probiotics is growing, but the long-term exploitation of XOs as health promoters is dependent on several factors. The health effects must be scientifically proven with clinical tests, the consumers must be informed and assured of the beneficial effects, markets have to be created, and product quality must fulfill consumer expectations.

In addition to the health effects related to the gastrointestinal tract, several other biological effects have been proposed for the XOs (Vázquez *et al*. 2000; Moure *et al.* 2006; Aachary and Prapulla 2010). Such effects include antioxidant activities, blood and skin related effects, antiallergy, antimicrobial, anti-infection, and anti-inflammatory properties, cytotoxic activity, immunomodulatory action, as well as cosmetic and a variety of other properties. In addition to the biological effects to human health, XOs have been used in phytopharmaceutical and feed applications.

Non-Carbohydrate Components

In addition to the carbohydrates, lignocellulosic hydrolysates contain a variety of non-carbohydrate products originating from lignin, extractives, and initial carbohydrates (Fenske *et al*. 1998; Nilvebrandt *et al*. 2001; Klinke *et al*. 2002,2004; Vázquez *et al*. 2005, Montané *et al*. 2006; Conde *et al*. 2008). As many of these compounds are potentially inhibitory during fermentation processes and because the purity requirements of XOs used in functional foods are high, these components must be fractionated from the hydrolysates. Fractionation can be performed by various common laboratory techniques, such as liquid-liquid extraction performed with suitable organic solvents (*i.e*., ethyl acetate, diethyl ether, various alcohols, and alkenes) or with various adsorption resins (Converti *et al*. 2000; Klinke *et al*. 2004; Zautsen *et al*. 2009; Pienkos and Zhang 2009; Soto *et al*. 2011). However, the non-carbohydrate phenolic component fraction has been shown to contain certain beneficial properties, including antioxidant, antimicrobial, and biological activities, which makes them potentially suitable for food or cosmetic applications (Barclay *et al*. 1997; Lu *et al*. 1998; Cruz *et al*. 2001; Garrote *et al*. 2004a, 2007; González *et al.* 2004; Dong *et al*. 2011; Soto *et al*. 2011). The utilization of the non-carbohydrate fraction could be of scientific and economic interest, fostering an integrated multiproduct process, in which not only carbohydrate fraction, but also non-carbohydrate fraction is commercially utilized.

Phenolic compounds of natural origin containing antioxidant activity exhibit great potential in replacing synthetic compounds (Ogata *et al*. 1997; Cruz *et al.* 2001; Garrote *et al*. 2004a; González *et al*. 2004; Ugartondo *et al*. 2008). Raw LCM is cheap, renewable, and abundant, and the concerns regarding the safety of the synthetically manufactured products and the consumer preferences for natural products make these compounds interesting both commercially and environmentally. Interest in manufacturing natural antioxidants from various sources has grown, and LCMs are a promising source of these components (González *et al*. 2004; Garrote *et al*. 2004a). Many non-carbohydrate components present in lignocellulosic hydrolysates originate from lignin, and thus they are of a phenolic nature. On the other hand, the antioxidant activity of phenolics formed during hydrolysis of LCMs is well known (Cruz *et al.* 2001; Garrote *et al.* 2004a). The antioxidant activity of the compound is dependent on the chemical structure of the compound (Cruz *et al*. 2005; Egüés *et al*. 2012). Lignin monomers and dimers have been shown to be effective antioxidants. Simple benzoic and cinnamic acid-related phenolic acids are absorbed *via* organisms' metabolic pathways and have a role in the antioxidant defense. Esters of phenolic acids are more active than phenolic acids, whereas oligomers and condensed tannins are more active than monomeric phenols.

The mode of action of phenolic components in biological systems seems to be related with the effects to membrane permeability, decreased electron transport through the membranes, and the possible interference of the metabolic synthesis of macromolecules and nucleic acids (Garrote *et al*. 2004a). The inhibitory effect of the phenolic component

is dependent on the size of the molecule but also on the functionality of the compound (Garrote *et al*. 2004a; García *et al*. 2010; Ponomarenko *et al*. 2014). A linear relationship between the number of carbon atoms in an alkyl side chain and antimicrobial activity has been observed. In addition, the presence of different functional groups present in phenolic components has been shown to affect the toxicity of the compound. The inhibitory potential of the functional groups attached to the benzene ring is estimated to increase in the order: COOH > *p*-OH > CHO > CH=CH. A variety of pharmacological and biochemical activities (anticarcinogenic, antiatherogenic, and anti-inflammatory) has been reported for phenolic compounds. Phenolic compounds produced by colonic microflora from flavonoids can have protective activities in the colon, whereas caffeic and ferulic acids are protective against nitrite ions. Ferulic acid esters are active agents in cosmetics, as they contain antioxidant and ultraviolet absorption properties.

ALKALINE PULPING OF PRETREATED WOOD

Industrial pulping refers to processes by which wood or other LCMs are converted into a fibrous end product (*i.e*., pulp) by chemical, mechanical, or by combination of these methods (Alén 2000; Sixta *et al*. 2006). Of these methods, chemical pulping accounts for 70% of the total pulp production, with the sulfate process (*i.e*., kraft process) being the most utilized chemical pulping method worldwide. During chemical pulping, the web-like structure of lignin is degraded, and lignin is dissolved through chemical reactions at elevated temperatures (Prinsen *et al*. 2013). The liberated fibers can then be separated from the cooking liquor, washed, and bleached. However, delignification is not a highly selective process. Simultaneously with the lignin removal, significant parts of the hemicelluloses and some cellulose together with extractives are also degraded. The total yield of cellulosic fiber ranges from 45% to 55% depending on the wood source and the applied pulping process. In addition to pulp, only turpentine and tall oil from kraft pulping and lignosulfonates from sulfite pulping have so far achieved considerable value as by-products, although the recovery of other degraded organics (*i.e*., degradation products of carbohydrates and lignin) could be an interesting alternative to using them as fuel in recovery boilers.

Pretreatment processes have a profound effect on the chemical composition of wood and on the subsequent delignification behavior of the pretreated feedstocks (Borrega *et al*. 2011a,b; Duarte *et al*. 2012; Coelho dos Santos Muguet *et al*. 2013; Huang and Ragauskas 2013a,b; Vila *et al*. 2013; Lehto and Alén 2015a,b,c). In general, autohydrolysis and mild acidic pretreatments have been proposed to enhance the delignification rates of both softwoods and hardwoods when compared to the untreated feedstocks, resulting in savings in the costs of pulping and bleaching chemicals, reduced cooking times, and lower energy demand (Yoon and van Heiningen 2008; Lu *et al*. 2012; Chirat *et al*. 2013; Hamaguchi *et al*. 2013; Runge and Zhang 2013). It has been revealed in previous studies (Reguant *et al*. 1997; Jahan *et al*. 2009; Lu *et al*. 2012; Lehto and Alén 2015b,c) that the kappa number of the produced pulp can be lowered significantly by applying a pretreatment stage prior to pulping. The enhanced delignification of the pretreated wood has been explained by the improved penetration of cooking chemicals caused by the increased pore volume and permeability of the fiber cell wall together with the hydrolytic cleavage of lignin structure, removal of hemicelluloses and their degradation products, and cleavage of LCC bonds. In addition, it has been shown in previous studies (Lehto and Alén 2015b,c;

Lehto *et al.* 2015) that applied pretreatments have a profound effect on the formation of various degradation products originated from lignin and carbohydrates. The content of various aliphatic hydroxy acids was significantly higher in those black liquors originated from pretreated (hot-water extracted) feedstocks. This was assumed to be caused by partial removal of acetyl groups already during the pretreatments, leading to decreased content of acetic acid (*i.e.,* decreased need for its neutralization during cooking) in the corresponding black liquors. Furthermore, higher-molar-mass lignin was found to be dissolving during cooking from pretreated feedstocks, when compared to the reference cooks without pretreatments (Lehto *et al.* 2015). As described earlier in this chapter, this was thought to happen due to the more open structure of pretreated wood, thus enhancing the diffusion of higher-molar-mass lignin from the wood matrix.

Besides positive aspects, negative effects from autohydrolysis and mild acidic pretreatments on pulping and pulp quality also exist (Yoon and van Heiningen 2008; Duarte *et al*. 2011; Saukkonen *et al*. 2012b; Hamaguchi *et al*. 2013; Vena *et al*. 2013a,b; Liu *et al.* 2012d; 2015). The most profound negative effects include the reduced yield of pulp compared to the reference kraft cooks produced without pre-extraction, reduced refining response, and decreased strength (tensile and burst strengths) properties of the produced pre-hydrolysis kraft (PHK) pulps. Alkaline pretreatments in general have only very minor negative effects on modified pulping and pulp quality (Huang and Ragauskas 2013a,b; Johakimu and Andrew 2013; Vena *et al*. 2013a,b)

Applying a pretreatment stage prior to delignification has been extensively used in the manufacture of dissolving pulp. In general, dissolving pulp refers to a cellulose product having very high cellulose content (95% or higher) suitable for manufacturing of various cellulose derivatives, such as cellulose esters and ethers, viscose, and cellophane (Biermann 1996; Sixta 2006). It is known that 85 to 88% of the total dissolving pulp is manufactured from wood by PHK and acid sulfite processes combined with subsequent purification stages, such as hot and cold caustic extraction (HCE and CCE), respectively (Sixta and Schild 2009; Radiotis *et al*. 2011; Sixta *et al*. 2011; Borrega *et al*. 2013a; Wang *et al*. 2014). The PHK process is a variation of the typical kraft pulping process, with the addition of a pre-hydrolysis stage to extract hemicellulose fraction from wood chips prior to cooking (Liu *et al*. 2011b; Saeed *et al*. 2012; Mateos-Espejel *et al*. 2013). The main objective of the drastic manufacturing process is to remove the non-cellulosic carbohydrates (*i.e.*, hemicelluloses) as completely as possible and to produce pulp, containing a low amount (3 to 4%) of hemicelluloses compared to typical paper-grade kraft pulp (10%). Even though the subsequent purification processes (HCE and CCE) cause considerable increases in production costs due to high yield loss and high chemical charges, they are still needed because even small amounts of non-cellulosic polysaccharides may influence the processability and properties of the final product. However, in addition to the production of high-grade dissolving pulp, the PHK process allows the recovery of various organic components (such as acetic acid and carbohydrates) from the pre-hydrolysis liquors (Saeed *et al*. 2012; Ahsan *et al.* 2014).

Kraft Pulping

The most important chemical pulping process used today is the kraft process (Gellerstedt 2001; Dimmel and Gellerstedt 2010). Its advantages include excellent paper strength and permanence, low energy requirements, sophisticated chemical recycle (*i.e*., low chemical costs), and insensitivity to wood species. The disadvantages are low pulp yields (40 to 55% of wood dry solids (DS)), high capital investment costs, brown

unbleached pulp color, high cost of bleaching chemicals, significant amounts of organic components in the bleaching effluents, and strong odors. In conventional kraft cooking, lignin is dissolved with strong alkaline aqueous cooking liquor (*i.e.*, "white liquor") containing mainly sodium hydroxide (NaOH) and sodium sulfide (Na_2S) as active cooking chemicals (Alén 2000; Sixta *et al*. 2006). The reactions occurring during kraft cooking are complex and not fully understood (Alén 2000; Sixta *et al*. 2006; Lapierre 2010). The main active chemical agents in the kraft process are hydroxide (HO^-) and hydrosulfide (HS^-) anions. It is generally known that the HS^- plays an important role in kraft pulping by accelerating delignification through reacting with lignin, whereas carbohydrate reactions are primarily affected by alkalinity (*i.e.*, HO^-). Furthermore, white liquor contains small amounts of Na_2SO_4, Na_2CO_3, $Na_2S_2O_3$, NaCl, and $CaCO_3$, together with other salts and non-process elements. The concentrations of active cooking chemicals are conventionally expressed as active alkali (*AA*; NaOH + Na_2S) and effective alkali (*EA*: NaOH + ½ Na_2S). Both batch and continuous cooking digesters are used in kraft cooking, typical cooking times being 1 to 3 h and temperatures from 150 ℃ to 180 ℃. The overall effect of cooking time and temperature is usually presented by a single numerical value, the so-called H-factor (Vroom 1957). During kraft cooking, roughly half of the wood material is dissolved. The delignification proceeds in three distinct phases (Dimmel and Gellerstedt 2010). The first phase of delignification is characterized as an "extraction phase", during which the selectivity of the delignification is rather low, resulting in the removal from 15% to 25% of the initial lignin, but simultaneously leading to a loss of as much as 40% of the hemicelluloses. As the process continues, delignification is accelerated due to the increasing temperature. During this second phase (*i.e.*, "bulk delignification phase"), the rate of the delignification is controlled by chemical reactions and follows as a first order reaction. The rate of delignification remains high during the bulk delignification stage until about 90% of the initial lignin has been dissolved. The final delignification phase (*i.e.*, "residual delignification") proceeds slowly and the loss of carbohydrates is significantly increased. The selectivity of delignification for kraft pulping is rather low, leading to the degradation of wood polysaccharides already at comparatively low temperatures as the chips come into contact with the cooking liquor (Alén 2000; Sixta *et al*. 2006; Pakkanen *et al.* 2013). As the cooking process proceeds, the white liquor gradually becomes enriched with an extremely complex mixture of degraded lignin, carbohydrate degradation products, and inorganic anions and cations, and is finally converted to black liquor (Alén *et al*. 1984, 1985; Niemelä *et al*. 1985; Niemelä and Sjöström 1986a,b, 1988a; Niemelä 1988a,b,c, 1989, 1990a,b; Alén 2000b; Sixta *et al*. 2006; Hellstén *et al.* 2013).

After cooking, the spent cooking liquor (*i.e.*, black liquor) is separated from the pulp, concentrated to 65–80% dry solids content, and burned in the recovery boiler for the recovery of cooking chemicals and the production of energy (Adams 1997; Vakkilainen 2008). After combustion, the inorganic fraction (*i.e.*, smelt) containing Na_2CO_3 and Na_2S together with a minor amount of Na_2SO_4 is dissolved in water to form "green liquor" (Hupa 1997; Vakkilainen 2008). Green liquor reacts with lime (CaO) in the causticizing stage during which Na_2CO_3 is converted to NaOH, which can be used for white liquor. The efficiency of the chemical conversion and recovery is about 90%; thus, white liquor still contains small amounts of Na_2CO_3 and other sodium salts.

Soda-Anthraquinone Pulping

Kraft process is the dominant pulping method in the world. However, the sulfur compounds formed during kraft process can cause odor problems already at extremely low

concentrations (Martínez *et al*. 1997; Bordado and Gomes 2002, 2003). Alternative pulping methods mainly comprise sulfur-free alkaline processes, usually in the presence of some catalysts, such as soda cooking combined with the AQ catalyst (Biermann 1996; Feng *et al*. 2002a,b; Ban *et al*. 2009; Prinsen *et al*. 2013; Ikeda and Magara 2015). Without the catalyst, sulfur-free alkaline cooking has some disadvantages. When NaOH is the only cooking chemical, the pulping process is slower and yields less and weaker pulp due to the alkaline degradation of carbohydrates, as strongly alkaline cooking conditions decomposes carbohydrates by peeling reactions and alkaline hydrolysis. Soda-AQ pulping is mainly used for delignification of non-wood materials, such as straw, reed canary grass, various agricultural residues, and annual plants (Feng and Alén 2001; Finell and Nilsson 2004; Hedjazi *et al*. 2009). Of the woody materials, hardwoods are generally more suitable for soda-AQ cooking than softwoods. Hardwoods can be delignified with soda-AQ cooking to pulps that present similarly in terms of yield, strength, and bleachability than corresponding kraft pulps. However, due to the possibly carcinogenic effects, European Food Safety Authority (EFSA) (EFSA 2012) and Confederation of European Paper Industries (CEPI) (Anteroinen 2013) have recommended that the utilization of anthraquinone should be decreased.

As a catalyst, AQ can be used in kraft, soda, and alkaline sulfite processes to increase delignification and decrease carbohydrate degradation (Prinsen *et al.* 2013). The general beneficial phenomena caused by AQ include increased delignification rates, improved selectivity, reduced alkali charges, and improved pulp properties (Fengel and Wegener 1989). The chemical mechanism of alkaline AQ pulping is generally well known (Dimmel 1996; Dimmel and Gellerstedt 2010). AQ acts as a redox catalyst, and during the pulping process, its function is twofold. AQ reacts with aldehyde end groups (reducing end groups) present in carbohydrate chains and oxidizes them to alkali-stable aldonic acids with simultaneous formation of anthrahydroquinone (AHQ) (Chai *et al*. 2007). The catalytic cycle is completed by lignin, which reacts with AHQ and oxidizes it back to AQ (Lundquist *et al*. 1981; Venica *et al.* 2008a,b). The reaction between lignin and AHQ induces the cleavage of β-aryl ether linkages *via* a quinone-methide intermediate, leading to adducts prone to fragmentation under alkaline conditions. Simultaneously with the cleavage of β-aryl ether linkages, AHQ is regenerated to AQ. In addition to this reductive reaction pathway, alternative mechanisms for lignin degeneration caused by AQ have been proposed. It has been suggested that γ-CH_2OH end-groups present in lignin side chains are oxidized by AQ to γ-CHO end-groups, leading to side chains susceptible for alkali catalyzed fragmentation, including reverse aldol and β-elimination type reactions. Furthermore, some degradation of C-C bonds (C-α and C-β) can take place.

Oxygen-Alkali Delignification

Oxygen-alkali delignification can be defined as a process that utilizes oxygen in the presence of alkali to remove residual lignin from unbleached pulp before bleaching stage (McDonough 1996; Alén 2000; Susilo and Bennington 2007; Gellerstedt 2010). However, oxygen-alkali delignification is not a selective process; together with the removal of residual lignin, significant degradation of pulp polysaccharides takes place, leading to a formation of a wide range of water-soluble degradation products, such as hydroxy acids, volatile acids, carbohydrates, and methanol (Sjöström 1980; Theander 1980; Alén and Sjöström 1991; Gellerstedt 2001; Laitinen *et al*. 2002; Salmela *et al*. 2008). Because of the non-selectivity, typically 35 to 55% of the residual lignin can be removed before the

selectivity of the process decreases and degradation of carbohydrates start to decrease the properties of the produced pulp (Yang *et al*. 2003; Fu *et al*. 2005; Shin *et al*. 2006).

The reaction mechanism of oxygen-alkali delignification is extremely complex and not fully understood (Alén 2000). Under alkaline conditions, oxygen is an efficient oxidizing agent for organic compounds, resulting in the formation of various reactive oxygen intermediates, such as hydroperoxyl and hydroxyl radicals, hydrogen peroxide, and hydroperoxide anions. The complicated oxidation process of oxygen delignification involves several radical chain reactions, which are combined with various organic compounds mainly originating from lignin, carbohydrates, and some extractives (Starnes Jr. 1980; McDonough 1996; Alén 2000; Akim *et al*. 2001; Kalliola *et al*. 2011). From lignin, oxidative degradation leads to the formation of various aliphatic carboxylic acids *via* different intermediates, such as catechol, quinone, and muconic acids (Kuitunen *et al*. 2011; Rovio *et al*. 2011). As in the kraft process, the main degradation products originating from carbohydrates during oxygen-alkali process include various carboxylic acids.

As some of the reactive oxygen-containing intermediates are non-selective oxidizing agents and can cause significant carbohydrate losses, their formation must be controlled. Especially, hydroxyl radicals are believed to be responsible for a major part of the damages caused to carbohydrates, particularly at higher degrees of delignification. Their formation is catalyzed by various transition metals, such as Fe, Cu, and Mn, which are present in trace amounts in unbleached pulp. Due to this detrimental effect, some additives (such as magnesium sulfate) are usually added to pulp to prevent the function of these transition metals (Starnes Jr. 1980; Alén 2000).

SUMMARY COMMENTS

For several reasons, a more versatile utilization of renewable resources such as wood ("biomass") for the production of green energy (*e.g*., electricity and liquid fuels biodiesel and ethanol) as well as organic chemicals with a higher added value will be essential already in the near future. Although the major constituent of biomass is cellulose, it also contains substantial amounts of other polysaccharides as well as non-carbohydrate constituents (mainly lignin and extractives). The prerequisite for a realizable biorefinery concept is that the presence of all these constituents is taken into consideration when planning target-oriented economic processes for the manufacture of useful products.

Many different driving forces are shaping developments in the forest industry, and these have consequences for its continuity. It is obvious that in pulp production the present manufacture of by-products remains rather limited, presenting chemists with new challenges in developing more effective and flexible processes. In general, it can be concluded that chemical pulping offers many attractive biorefinery possibilities in the form of new by-products originated from various side-streams. One of the most promising approaches is based on the various pretreatments of chips for producing soluble fractions under varying conditions prior to delignification.

In this review, the integrated process alternatives including acidic and alkaline pretreatments of wood chips mainly for producing carbohydrates- and lignin-derived fractions have been briefly discussed. It is obvious that even a partial recovery of chip organics makes already a high volume production possible. One further attraction of this strategy is that such a biorefinery production can be readily integrated with the existing delignification process whose main product, fiber, is already a well-established product.

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The pulp is suitable for versatile utilization in paper or paperboard, and depending on the cooking conditions can be used as dissolving pulp for the production of cellulose derivatives and regenerated cellulose. However, the main prerequisite for pretreatments is that they can be made by causing only slight modifications to the fiber production process. The reason for this is that the pulp industry is capital-intensive and the equipment, once installed must have a long lifetime. Therefore, sweeping changes of any significance in mill process are even in most cases not possible.

The main points illuminated in this review are as follows:

1. Autohydrolysis of wood chips with water offers a promising, economic, and environmentally-friendly tool for recovering carbohydrate-rich materials prior to pulping, thus creating a possibility for more efficient use of wood raw material enabling the production of carbohydrate-based value-added chemicals and other materials. However, in this case, the modification of the pulp mill environment must be optimized to meet the requirements set for the overall process performance.

2. Aqueous pretreatments with an acid addition have also been realized for producing carbohydrate-rich hydrolysates from biomass. The addition of inorganic or organic acid into the pretreatment has a profound effect on the overall process, both in terms of equipment needed, and products formed. In addition, the recycling of the acid is also normally needed.

3. Aqueous alkaline pretreatment can be considered as one of the most attractive alternatives for producing carbohydrates- and lignin-rich hydrolysates within the existing pulp mill environment. This is due to the fact that modern pulping processes are mainly based on alkaline delignification, thus offering a logical integration of the alkaline pretreatment stage with cooking. In addition, opposite to autohydrolysis and acidic pretreatments, alkaline pretreatments have been found to cause generally only minor negative effects on pulp quality.

4. Depending on the process parameters, pretreatment liquors contain a variety of potential raw materials for producing a wide range of biomass-based platform chemicals or utilized, for example, in various polymeric applications. Carbohydrates can be converted into chemicals such as ethanol or carboxylic acids *via* fermentation. Lignin (especially sulfur-free fractions) is suitable for producing many chemicals and chemical mixtures that are currently derived from petroleum-based sources. It is most likely to be used as a bio-based additive to polymers, but also as low-cost carbon fiber, activated carbon, resins ("phenol mixtures") in the plastic industry, and as many other straightforward products without significant modification, including binders, surface or dispersing agents, emulsifiers, and sequestrants. Aliphatic carboxylic acids from alkaline pretreatments form an interesting group of compounds and can be used as single components, or as more or less purified mixtures, in a number of applications. Of this group, formic and acetic acids as well as "lower-molar-mass" hydroxy acids glycolic and lactic acids are already today commercially important chemicals. In addition, "higher-molar-mass" hydroxy acids 3,4-dideoxypentonic, 3-deoxypentonic, xyloisosaccharinic, and glucosiosaccharinic acids (present in their lactone forms) can, for example, be converted into many valuable derivatives by reduction (*i.e.*, production of polyalcohols), oxidation (*i.e.*, production of polycarboxylic acids) or utilization in various polymers, detergents, and emulsifiers (*i.e.*, production of esters). Together with

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these, mixtures containing high-molar-mass lactones of 3,4-dideoxy-pentonic, 3-deoxy-pentonic, xyloisosaccharinic, and glucoisosaccharinic acids, could be advantageously utilized in the preparation of various detergents and emulsifiers (*i.e.*, surfactants).

5. Alkaline pulping of pretreated wood can be performed for producing not only various grades of chemical pulps, but also a wide spectrum of by-products recovered from the black liquor. With this respect, it would be a benefit if sulfur-free delignification is applied. However, in order to maintain the quality of pulp, combining pretreatments with pulping operations must be very finely tuned. This includes carefully determined pretreatment conditions (*i.e.*, temperature, time, and applied additives) , which remove sufficient amounts of organics from wood to make their utilization and refining economically viable, but which simultaneously preserve the quality of fiber. In addition, the changes caused by the pretreatments must be taken into consideration during the subsequent pulping operations, in order to avoid "overcooking" of the material, which could lead to severely decreased strength properties of the produced pulp and lowered yield.

6. Finally, it should be pointed out that the established pulping processes effectively separate, in much the same way as the new biomass processing technology ("reactive fractionation"), most lignin and a significant proportion of hemicelluloses (as such or in the form of aliphatic carboxylic acids) from cellulose, creating a relatively pure fiber and thus, laying a natural foundation to integrated biorefining of wood resources. For this reason, chemical pulping offers many attractive possibilities in the form of new by-products originated from various side-streams.

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