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An Integrated Approach for Added-Value Products from Lignocellulosic Biorefineries

Vanillin, Syringaldehyde, Polyphenols
and Polyurethane



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Preface

This book is a result of more than 25 years of research on lignin valorization at the Laboratory of Separation and Reaction Engineering (LSRE), now Associate Laboratory LSRE-LCM at the Department of Chemical Engineering, Faculty of Engineering of the University of Porto (FEUP).

It all started with an invitation of Roberto Cunningham, coordinator of Subprogram IV (Biomass as source of chemicals and energy) of CYTED (Iberian-American Program on Science and Technology for Development), to join project IV.2 “Transformation of lignin on high-added value products” directed by Alberto Venica. The project involved partners from Spain, Portugal, and Latin-American countries.

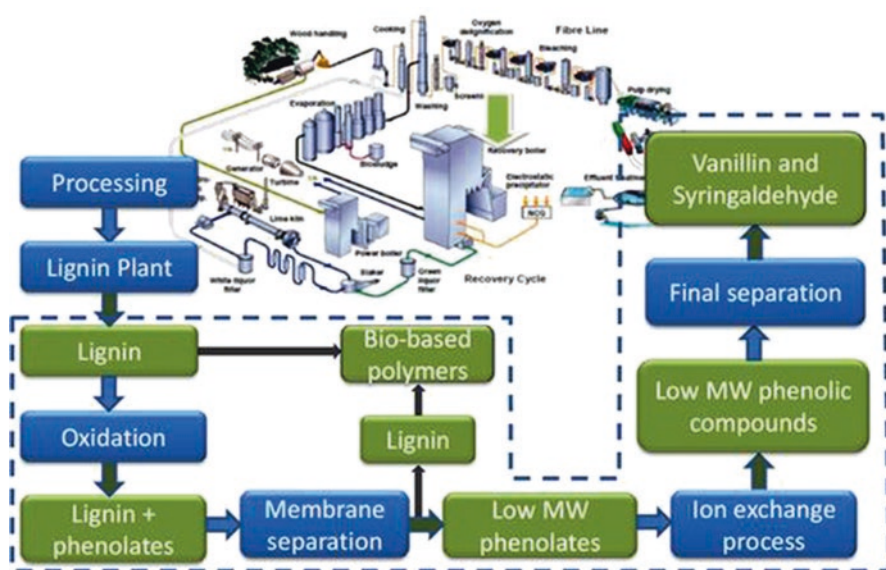
My task was to produce vanillin from lignin by oxidation and another partner, Mary Lopretti from Uruguay, was using a biochemical route to get vanillin out of lignin. This was in 1990. By chance a Brazilian student applied for a PhD – Álvaro Luiz Mathias from UFPR in Curitiba. He took the subject and started lignin oxidation studies in a Büchi batch reactor. He was more trained in analytical chemistry, and we went to the pulp mill in Cacia of Portucel processing *Pinus pinaster* at that time (now it belongs to The Navigator Company and processes only *Eucalyptus globulus*), took samples of black liquor, and isolated lignin for the oxidation studies aiming at producing vanillin. Alvaro Mathias defended his PhD in 1993 “Production of vanillin from lignin: kinetics and process study.”

At that time, I got a Human Capital and Mobility grant from European Union allowing me to hire some postdocs, and Claire Fargues from Nancy (now at IUT d’Orsay) joined this research program. From this research some publications appeared: Fargues et al. 1996 (Kinetics of vanillin production from kraft lignin oxidation, *Ind Eng Chem Res* 35, 28–36); Mathias et al. 1995 (Chemical and biological oxidation of *Pinus pinaster* lignin for the production of vanillin, *J Chem Tech Biotechnol* 64, 225–234); Mathias and Rodrigues 1995 (Production of vanillin by oxidation of pine kraft lignins with oxygen, *Holzforschung* 49, 273–278).

The next step was to make the lignin oxidation process continuous, and a laboratory reactor was built using a structured packing from Sulzer. This was done in the PhD thesis of Daniel Araújo “Development of a process for vanillin production

from kraft black liquor” (2008) and published in *Catalysis Today* 147, S330–S335 (2009); *Catalysis Today* 105, 574–581 (2005); and *ChERD* 88, 1024–1032 (2010).

In the meantime, the idea of an integrated process to produce vanillin from the black liquor was being tackled step by step. First using model compounds membrane separation of lignin/vanillin mixture was studied by Miriam Zabkova (now at VULM, Slovakia) and Eduardo Borges da Silva (now at Novozymes, Curitiba, Brazil) and then ion exchange to convert low molecular weight sodium vanillate in vanillin. The whole integrated process was published in *ChERD* 87, 1276–1292 (2009) where degraded lignin was also used to produce polyurethanes. An integrated process to produce vanillin and lignin-based polyurethanes from kraft lignin is sketched below. The contribution to the field of polyurethane materials in LSRE-LCM is being conducted by Prof. Filomena Barreiro, presently at the Polytechnic Institute of Bragança. This was the topic of the PhD of Carolina Cateto (2008), now at ExxonMobil (Belgium).



Flow sheet of the integrated process in an industrial unit

In 2009, Dr. Paula Pinto joined the laboratory LSRE and was engaged in various biorefinery projects with industry: Bioblocks with The Navigator Company and another project with a USA company both in lignin topic, and BIIPP (Biorrefinaria Integrada na Industria de Pasta e Papel) in polyphenols from eucalyptus bark. During her stay at LSRE two PhD theses were concluded: Carina Costa “Vanillin and syringaldehyde from side streams of pulp & paper industries and biorefineries” (2017) and Inês Mota “Fractionation of syringaldehyde and vanillin from oxidation of lignin” (2017).

During this period various advances were achieved to produce vanillin and syringaldehyde from lignin. A radar tool (Costa et al. 2015, “Radar tool for lignin classification on the perspective of its valorization,” *Ind Eng Chem Res* 54 (31), 7580–7590) was developed to characterize and screen lignins for the production of vanillin and syringaldehyde. Detailed studies on membrane fractionation and adsorption/desorption were done in view of the final objective: Costa et al. 2018 (“Lignin fractionation from *E. globulus* kraft liquor by ultrafiltration in a three stage membrane sequence,” *Sep. Pur. Tech* 192, 140–151), Pinto et al. 2017 (“Separation and recovery of polyphenols and carbohydrates from *Eucalyptus* bark extract by ultrafiltration/diafiltration and adsorption processes,” *Sep Pur Tech* 183, 96–105), Mota et al. 2016 (“Successful recovery and concentration of vanillin and syringaldehyde onto a polymeric adsorbent with ethanol/water solution,” *Chem Eng J* 294, 73–82), and Pinto et al. 2016 (“Performance of side-streams from eucalyptus processing as sources of polysaccharides and lignins by kraft delignification,” *Ind Eng Chem Res* 55 (2), 516–526).

Paula Pinto left LSRE-LCM and joined the R&D center RAIZ of The Navigator Company in 2016 followed by Inês Mota in 2017.

The work now continues with three PhD students. Elson Gomes started in 2015; his thesis looking at fractionation of membrane permeate by adsorption separating acids, aldehydes, and ketones (Gomes et al. 2018, “Fractionation of acids, ketones and aldehydes from alkaline lignin oxidation solution with SP 700 resin,” *Sep Pur Tech* 194, 256–264) and the final step (crystallization) of the integrated process; Filipa Casimiro hired in 2016 is dealing with the oxidation of species resulting from lignin oxidation, and Carlos Vega-Aguilar (Costa Rica) started his PhD in 2017 on the production of dicarboxylic acids from lignin.

The book is organized in five chapters. Chapter 1 deals with “Chemical pulp mills as biorefineries,” providing an overview of delignification industrial processes, integration of new biorefining processes in pulp industry, characterization and classification of lignins using a radar tool, and bark composition and products from bark. Chapter 2 addresses an “Integrated process for vanillin and syringaldehyde production from kraft lignin.” It starts with lignin oxidation in batch reactor and then in a continuous structured packed bed reactor. Separation processes (membrane, ion exchange, and adsorption/desorption) are detailed next to separate the low molecular weight phenolics from the degraded lignin and recovery. Chapter 3 is about “Polyurethanes from recovered and depolymerized lignins.” After an overview of strategies and opportunities, the use of lignin as such is discussed and then the lignin use after chemical modification is analyzed in particular the case of production of polyurethanes. Chapter 4 deals with “Polyphenols from bark of *Eucalyptus globulus*” including composition of polar extracts and extraction of polyphenols followed by fractionation of ethanolic extracts. Chapter 5 presents “Conclusions and future perspectives.”

Acknowledgments

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Contributions from other PhDs and post-docs (Álvaro Mathias, Claire Fargues, Daniel Araújo, P. Sridhar, Carolina Cateto, and Elson Gomes) are also acknowledged.

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Chapter 1

Chemical Pulp Mills as Biorefineries



Abstract Forest-based biorefinery is a multiplatform unit converting lignocellulosic biomass into several intermediates and final products according to different transformation pathways. Among intermediates and final products, cellulose, lignin, biofuels, and simple sugars stand out as commodities, while some general examples of specialties are flavoring agents, intermediates for chemical synthesis, and building blocks for polymers. Most of these specialties come from further conversion of commodities via different conversion and separation routes. Similarly, to a refinery, these units start with a complex and multicomponent matrix (crude oil versus biomass) and its fractionation and conversion into a variety of products which will serve as feedstock to another industrial step. Different levels of conversion platforms can be considered in a single biorefinery, from high production (low price) to small production for a specific market (high price).

Pulp industry has been recognized as the leading industrial sector in biorefining since a long time ago due to the raw materials and to the integrated production of pulp (cellulose) and energy, mostly provided by burning lignin of the black liquor. In a more extended sense, pulp and paper industry is an example of realistic circular (bio)economy implementation, considering energy cycle, water recycle in the process, and chemical recovery cycle and on-site production. In the following sections, a general overview about chemical pulping will be given. The most common side stream and chemical recovery processes will be addressed along with the main steps for integration of biorefinery processes in pulp mills. Finally, recent advances of lignin end uses and new perspectives will be presented.

Keywords Pulp mills · Biorefineries · Lignin characterization · Delignification process · Radar tool · Kraft pulping · Sulphite pulping · Kraft lignin · Lignosulfonates · Organosolv · Bark

1.1 General Overview: Delignification Industrial Processes

Mechanical pulping and chemical pulping are the two main industrial processes for fiber separation, leading to materials with different properties for different end uses. Mechanical processes have a high energy demand, and fiber separation is achieved by mechanical force and softening the middle lamella lignin (Popa 2013). Chemical pulping is required for removing lignin from lignocellulosic matrix leading to the cellulosic fiber separation with minimum of mechanical force – delignification – and, therefore, this section is focused on these processes. This is the principle of pulping technology by chemical processes. However, nowadays, delignification has a broad sense, and the general concept has been applied to different types, rates, and extents of delignification in biorefining processes.

In pulping chemical processes, lignin is cleaved, and new charged groups are introduced leading to dissolution of lignin/lignin fragments in the pulping liquor, while the polysaccharide-rich fraction remains as a cake and proceeds for washing and bleaching stages. However, delignification has a limited selectivity for lignin; therefore, a fraction of initial carbohydrates, in particular the hemicellulose, is also dissolved in pulping liquor and lost. Pulping is stopped at a predefined level of residual lignin content in pulp in order to avoid further pulp yield decrease due to carbohydrate degradation. In general, chemical pulp fibers are more flexible than mechanical ones, leading to a better paper formation and giving good strength properties to chemical pulp. Kappa number is the parameter used for estimating the residual content of lignin in the pulp and the delignification degree.

Kraft Pulping

The first alkaline process developed for pulp production from wood is attributed to Burgess and Watt in 1851, known as the soda process. The introduction of sulfides into pulp production was patented in 1870 by Eaton, but the first kraft process was implemented only in 1885 in Sweden (Sjöström 1993). About 90% of the global chemical pulp is produced by kraft process. This process uses, as active reagents, sodium sulfide and sodium hydroxide. It is applicable to almost all wood species, resulting in high yields and pulps with better physico-mechanical properties compared to other processes and is therefore known as the “kraft process” (“kraft” stands for “strong” in German and Swedish). One of the disadvantages of this process is, besides the emission of malodor compounds, the dark color of pulp. However, the development of bleaching techniques in the 1940s has enabled the production of white cellulosic pulps of superior quality leading to the consolidation of kraft process. It is currently the dominant pulping chemical process in the world (90% of pulp production) (Popa 2013), being applicable to a wide variety of wood species with efficient regeneration of chemicals and energy (Clayton et al. 1983; Gullichsen 1999; Minor 1996; Ek et al. 2009; Sjostrom 1981).

The debarked wood logs are converted to woodchips and sieved, selecting the chips with the appropriate dimensions to assure uniform delignification at the digester. In the continuous process, the wood chips are pre-vaporized to facilitate

impregnation and are introduced into the kraft digester with white liquor. White liquor, or pulping liquor, is composed of sodium hydroxide, NaOH, and sodium sulfide, Na₂S. The ions OH⁻ and hydrogen sulfide HS⁻ are the species that react with lignin during kraft pulping. The concentration of these chemicals is usually expressed in equivalent amounts of Na₂O, being effective alkali, active alkali, and sulfidity the most important parameters of white liquor. The active alkali concentration depends on the active alkali charge and also on the liquor-to-wood ratio. To produce bleachable pulp grades from hardwoods, the active alkali charge required ranges from 17% to 19% NaOH, while for softwood higher charge is required, usually between 20% and 25%. At higher values, for a fixed temperature, the delignification rate increases. In general, the initial active alkali concentration is 40–60 g/L NaOH for kraft pulping. White liquor includes also salts inactive in pulping process, such as sodium sulfate (Na₂SO₄) and sodium carbonate (Na₂CO₃), coming from chemical recovery cycle (referred later in this section). The sulfidity strongly influences the pulping rate and process selectivity, and it is expressed as the percent ratio between sodium sulfide and active alkali. The sulfidity ranges between 25% and 35% for the cooking of hardwoods and 35–40% for softwoods. Pulping temperature is in the range 160–175 °C and pressure 7–12 bar (Gullichsen 1999; Sjostrom 1981). Pulping is stopped by extracting the liquor containing the dissolved material, referred to as black liquor, and then washed, removing the uncooked chips and other fragments, obtaining the raw pulp. After that, impurities such as shives and dirt are removed in the screening process, and then the pulp can be bleached or used for the manufacture of paper or board. The black liquor and the washing water are then introduced in the recovery circuit: diluted black liquor is evaporated, and the concentrated stream is burnt at the recovery boiler for energy production from dissolved organic compounds and recovery of inorganic compounds. The resulting stream (smelt) results in green liquor which is converted to white liquor by causticizing, at the chemical circuit (Clayton et al. 1983; Gullichsen 1999; Ek et al. 2009). A simplified scheme of this sequence of processes is presented in Fig. 1.1. The pulp yield is approximately 50%, depending on the wood and conditions used (Gullichsen 1999). For each ton of pulp produced, about 10 tons of weak black liquor, containing between 1.2 tons and 2.0 of dry solids, are generated.

Kraft pulping operations are highly integrated, and the recovery process is one of the most relevant advantages assuring the sustainability of this process (Sect. 1.2). However, the recovery boiler capacity is limited, hampering the increase of pulp production. Therefore, some mills have been considering the removal of part of black liquor from the circuit, or organic material dissolved in black liquor, and, therefore, gaining some additional pulp production capacity. At the same time, several efforts have been made to get marketable kraft lignin product in order to cover the capital and operational expenditure, since burning is a very limited solution for lignin. Some companies have been designing and building their own lignin isolation processes, and there are commercial solutions for this purpose in the market, being already operational (Sect. 1.4.3).

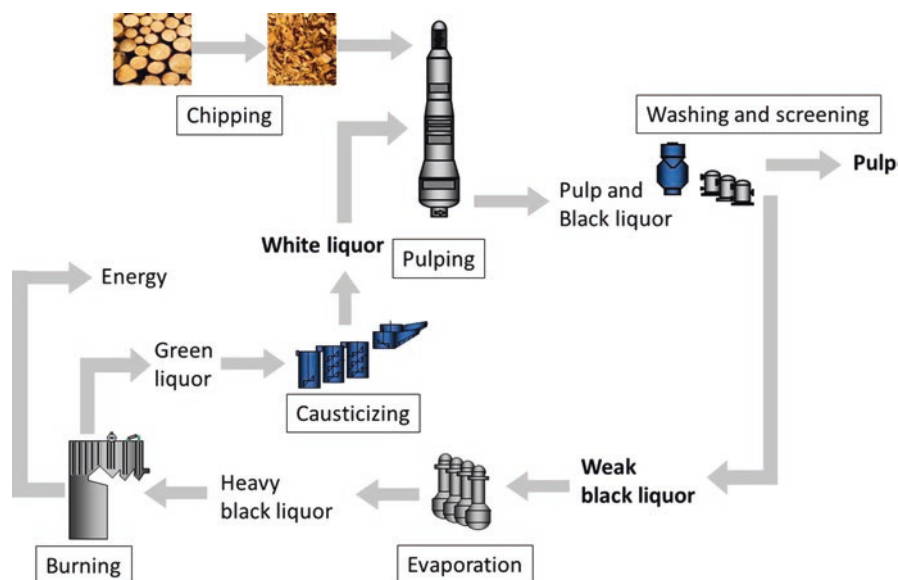


Fig. 1.1 Sequence of processes in kraft pulping

Sulfite Pulping

Sulfite pulping was developed and patented by the American chemist Benjamin Chew Tilghman in 1867. Acid sulfite pulping was the dominant pulping process until the 1940s, when it was succeeded by kraft cooking. Some modifications to the process were introduced, mainly in the 1950s and 1960s, replacing calcium by magnesium, sodium, or ammonium, giving rise to a more flexible process, extending it to different raw materials, and producing different pulps. The dominant cationic base in the process is magnesium. The sulfite pulping is referred to in different ways depending on the pH range used. In an acid medium, depending on the pH range, the process is named bisulfite acid (pH 1–2) or simple bisulfite (pH 3–5). In both cases, the active agents are H^+ and HSO_3^- . Neutral sulfite process operates at pH range of 6–9, and the active agents are HSO_3^- and SO_3^{2-} , while alkaline sulfite has a pH 10–13.5 with SO_3^{2-} and OH^- . The acid process produces dissolving pulp for textiles and pulp for newsprint or tissue, while pulps from neutral and alkaline sulfite are applied mainly for corrugated medium and package grades.

As compared with kraft pulp, cooking cycle is long, and it is not suitable for all wood species. However, acid sulfite pulp is brighter and can be used without bleaching to produce some printing paper grades. The main disadvantage of this process as compared with kraft one is the sulfite spent liquor due to the high sulfur dioxide loss and the unfeasibility of chemical recovery (Popa 2013). However, lignosulfonates have nowadays an established market being used mainly as dispersants in cement admixtures and dye solutions and binder for pelleting animal feed and for dust control, among others, thus creating an additional driving force for this process, besides pulp. Borregaard LignoTech is one of the world leaders of

lignosulfonate-derived products, including vanillin flavor produced by oxidation of softwood lignosulfonates. Other player in the lignosulfonate market is Tembec, with an annual production capacity of 225,000 metric tons (Tembec 2002), recently acquired by Rayonier Advanced Materials (Rayonier Advanced Materials 2018). Burgo Group (Tolmezzo mill) is also a lignosulfonate producer, stating a wide range of applications (Burgo Group 2013).

1.2 Side Streams and Current Recovery Cycles of Chemicals and Energy in Typical Mills

Black liquor is the main side stream of kraft pulping, containing about one half of the wood content together with spent pulping chemicals. At the final stage of pulping, black liquor is separated from cooked woodchips, and pulp washing waters are collected together with main stream, giving rise to the weak black liquor. About 10 tons of weak black liquor is generated per ton of pulp produced, containing between 12% and 20% of total solids. Weak black liquor is evaporated to reduce the water amount to about 15%. The resultant stream, heavy (or concentrated) black liquor, is then injected into the recovery boiler, the most important component of the kraft recovery cycle. This process makes pulp production self-sustaining for energy and almost sufficient for pulping chemicals. Figure 1.2 summarizes the main steps of the kraft recovery process. Black liquor is one of the fifth most important fuels in the world: globally over 1.3 billion tons/year of weak black liquor is produced. This represents about 200 million tons of dry solids to recover 50 million tons of cooking chemicals and simultaneously producing about 700 million tons of high-pressure steam (Reeve 2002).

The recovery cycle is briefly described. At recovery boiler the organic content of the black liquor is burned producing heat, which is then recovered by heat exchangers and simultaneously takes place the first stage for chemical recovery. The heavy black liquor is injected; the organic material burns at 1000 °C, while other fraction burns onto the porous char bed under reducing conditions. In the char bed, sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2S) are the main chemicals generated from the sodium and sulfur (mainly sodium sulfate, Na_2SO_4) coming with the black liquor. Sodium carbonate and sodium sulfide are the two major components of the smelt. Smelt (the mixture of molten salts) flows out of the boiler and is brought to the dissolving tank producing the green liquor. The recovery in modern mill is higher than 90%. Makeup sodium sulfate can be added to compensate losses in pulping, which in average are between 10 and 20 kg per ton of pulp. The green liquor is then clarified, removing insoluble components (dregs), and goes to the causticizing plant. At this stage, sodium carbonate reacts with quicklime (CaO) in the presence of water producing sodium hydroxide (NaOH) (conversion nearly 90%). Sodium hydroxide and sodium sulfide are the active components of the white liquor for the delignification reactions, and it is returned to the digester for reuse in

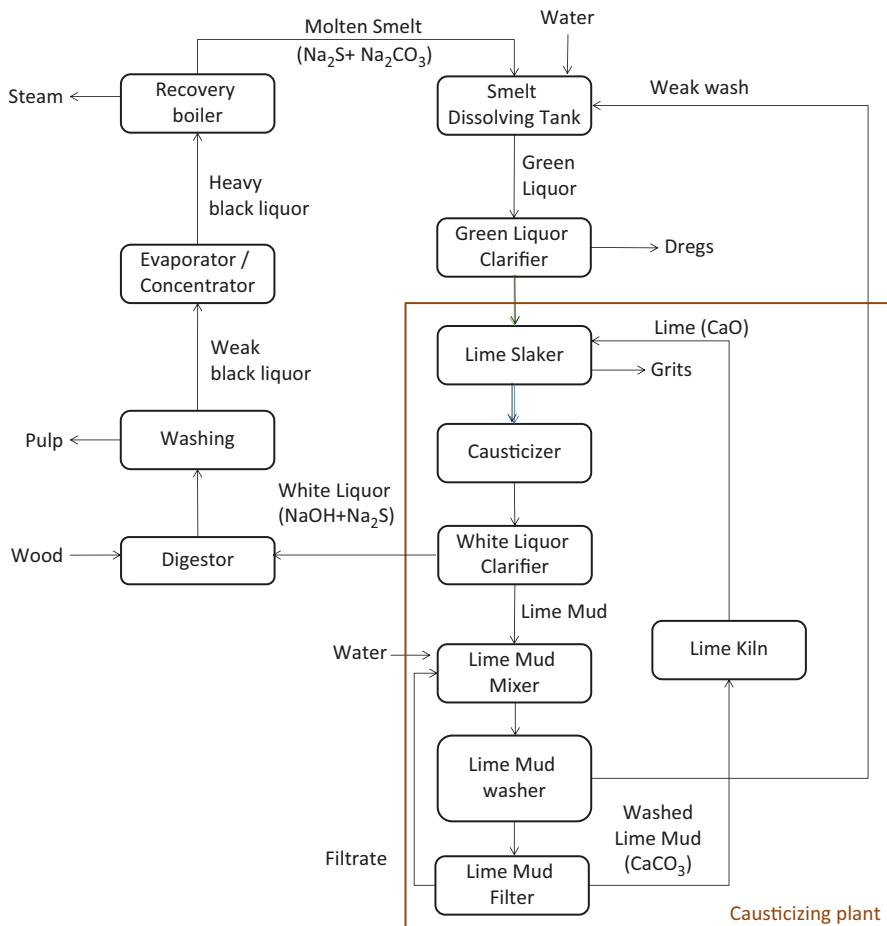


Fig. 1.2 Simplified flowsheet of the kraft pulping chemical recovery process

pulping. The CaCO_3 (slaked lime) resulting from causticizing is washed to reduce Na losses and sent to the lime kiln to regenerate CaO for reuse (Fig. 1.2).

Methanol is generated in the kraft cooking process. It comes from the delignification reactions, being washed out and then condensated at the evaporation plant and then often distilled in one or two distillation columns to produce a water-free methanol stream. The methanol stream contains various organic sulfur compounds and therefore has an unpleasant odor. Usually methanol is used as a support fuel for burners.

The bark and other forest biomass such as sawmill resulting from wood processing into fines and primary sludge and secondary sludge coming from effluent treatment are also considered side streams. Although not all of the forestry biomass coming from dedicated forest plantations is available for collecting (due to access and transport limitations and soil sustainability issues), there is an important source

of lignocellulosic material that can be integrated into different value chains, generating products, materials, and bioenergy. The bark (produced in bole debarking process, being about 10% on wood basis) and forest biomass are currently burned at thermal boilers for energy production for using at mill site, and the surplus is introduced in the electrical grid. However, the potential of these solid side streams is well known as source of bioactive compounds, polysaccharides, and even lignin (Pinto et al. 2016). Primary and secondary sludge and sawdust are produced in lower quantities as compared with bark/forest residues. There are several opportunities for their applications such as fertilizers or as energy source as well. The strategy for their valorization is quite dependent on the particular company, being the landfill disposal the last choice for most of them for environmental and economic reasons.

1.3 The Integration of New Biorefining Processes in Pulp Industries

Forest-based industry is historically centered on pulp and energy production. Pulp and paper companies are mature commodity industries. However, several developments have been changing this paradigm, leading these companies to invest more in R&D activities and innovation and in a stepwise increase of business areas and product portfolio.

Biorefining and related processes have been considered and planned from a long time ago. Myerly and co-workers have published in 1981 the “Forest Refinery” (Myerly et al. 1981) giving their perspective based on up-to-date developments. In this paper, the authors have made a brief state of the art about biomass conversion to products, defending that “...we would get greater flexibility for its use if we were to refine biomass into cellulose, hemicellulose, and lignin cuts, preserving the integrity of each to the maximum degree possible. These pure intermediates could then be converted to highest value.” From this perspective comes up that pulp industry is already a biorefinery converting forest material to bio-based products (pulp). Moreover, conventional kraft industry produces renewable energy from lignin and recovers pulping chemicals to be reintroduced in the process, while sulfite industry produces also lignosulfonates. Authors already mentioned other bio-based products already in the market at that time such as vanillin and turpentine, highlighting also the great potential to be exploited. Since then, massive scientific and technological progresses were made, and, nowadays, some pioneer industries have been extending their portfolio to other bio-based products, with several successful examples of biorefineries.

The pulping industry has a quite privileged position to gradually move into a forest biorefinery. This sector has the logistic, knowledge, and operational and industrial systems to be at the front head of the forest-based bioeconomy. Some companies have already moved to biorefinery activity. One of the world’s most advanced forest-based biorefinery is Borregaard, producing lignin products, especially

cellulose, vanillin, and bioethanol for several economic sectors, from cosmetics to construction. Other pulp and paper industries in Europe and in the world are moving to bioproducts and advanced biofuels. Some examples of this new trend are the Stora Enso, UPM, and Domsjö in Europe and Suzano and Fibria in South America. In this case, the recent acquisitions of the Canadian company Lignol and the new company, Fibria Innovations, are some examples of development or integration of technology in pulp and paper companies focused on bioproducts.

Figure 1.3 presents examples of biorefining pathways integrated in pulping industry. In this scenario, after chipping, wood goes to the pulp mill, and other forestry biomass comes into the pre-extraction and purification sector. This sector could be a unit dedicated to extract and fractionate bioactive compounds or hemicelluloses. The solid residue left after extraction is then introduced in the pretreatment/hydrolysis unit. At this stage, depending on the material and the previous type of process, a pretreatment (partial or complete delignification or steam explosion, among others, to liberate the fiber material) followed by hydrolysis could be considered. The final result should be sugar solutions and lignin. Lignin is also resulting from wood pulping process. Sugars and lignin can be further converted, in independent routes, to advanced fuels, chemical building blocks, polymers, or other products in the same site or in other value-added industries. Examples of products from sugars are ethanol, lactic acid, furfural, and hydroxymethylfurfural, while lignins can be converted to advanced fuels, phenolic resins, polymers, bio-based materials

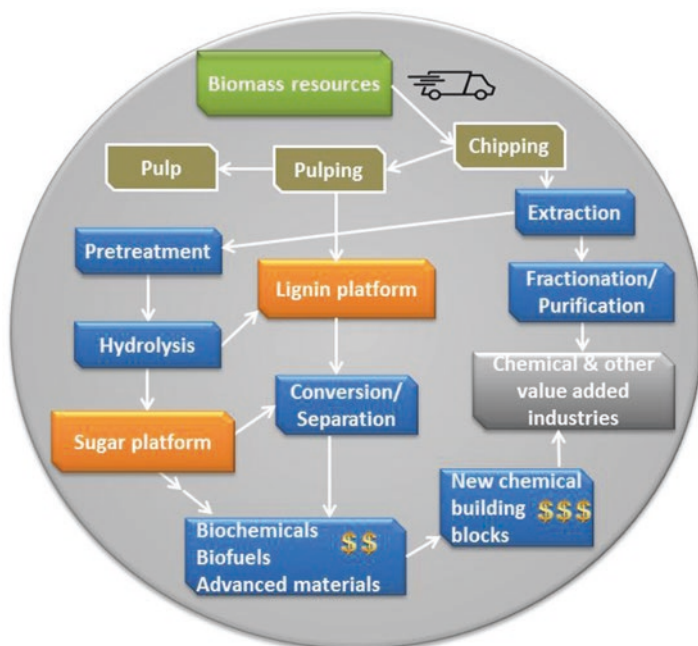


Fig. 1.3 Integration of new biorefining possible pathways in pulp industries