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Alternative Raw Materials for Pulp and Paper Production in the Concept of a Lignocellulosic Biorefinery

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Abstract

The main source of cellulosic fibre used for pulp and paper production comes from wood, while non-wood fibres are used to a lesser extent. However, a renewed interest exists in the use of non-woody raw materials due to their abundance as source of low-cost fibres and because they are sometimes the only exploitable source of fibres in certain geographical areas, mainly in developing countries. Moreover, the great variety of characteristics, fibre dimensions and chemical composition of these alternative raw materials give them a great potential to produce different types of papers. On the other hand, the pulp and paper industry is an excellent starting point for the development of lignocellulosic biorefineries, possessing the necessary technology and infrastructure as well as extensive experience in lignocellulosic biomass transformation. Since its beginnings, the pulp and paper industry has been practicing certain aspects of the biorefinery concept, generating the energy necessary for the production of cellulosic pulp from the combustion of lignocellulosic waste and black liquors, recovering the chemical reagents used and generating high value-added products (e.g. tall oil) together with cellulosic pulp. However, the evolution of the pulp and paper industry to a lignocellulosic biorefinery requires technological innovations to make bioenergy and new bioproducts available alongside traditional products.

Keywords: alternative raw material, agricultural residues, annual plant (vegetables), pulp, paper, biorefinery

1. Introduction

Several successful industrial factories based on alternative raw materials for pulp and paper production already exist nowadays [1, 2]. Lignocellulose is the major structural component of plants and is by far the most abundant type of earthly biomass [1, 3]. It mainly consists of cellulose (40–60%), hemicellulose (10–40%) and lignin (15–30%), with minor amounts of extractives, proteins and inorganic compounds [1, 3]. Lignocellulose components can be found in both woody (e.g.

spruce, pine, eucalypt, poplar, etc.) and non-woody biomass, the latter including vegetables (e.g. bamboo, tagasaste, kenaf, abaca, etc.) and agriculture residues from harvesting and pruning operations (e.g. barley straw, wheat straw, orange tree pruning, olive tree pruning, etc.) and from agro-food industry [e.g. bagasse, empty fruit bunches from oil palm (EFB), etc.]. Cellulose is a linear and highly ordered polymer of cellobiose (D-glucopyranosyl β -1,4-D-glucopyranose), whereas hemicellulose represents a family of branched carbohydrate polymers containing both pentoses (e.g. xylose, arabinose) and hexoses (e.g. galactose, mannose, glucose) and showing often uronic acids (e.g. glucuronic acid) and acetyl moieties as sidechain groups [1, 3]. By contrast, lignin is a three-dimensional network buildup of dimethoxylated (syringyl, S), monomethoxylated (guaiacyl, G) and non-methoxylated (p-hydroxyphenyl, H) phenylpropanoid units, derived from the corresponding p-hydroxycinnamyl alcohols, which give rise to a variety of subunits including different ether and carbon-carbon bonds [4].

The main non-food use of lignocellulosic biomass is the production of cellulosic pulp from which a wide range of products can be obtained, highlighting the production of paper. At the beginning of the 1990s, there was the conviction that the arrival of new information technologies would reduce the consumption of paper; however the data of world consumption of paper and cardboard revoke this idea as it went from 240 million tonnes in 1990 to 413 million tonnes in 2016, of which 77.3 million tonnes are consumed in Europe [5]. In the past, the raw materials used in the manufacture of paper were herbaceous biomass such as flax, cotton, bamboo and cereal straw. It was not until the middle of the nineteenth century when woody materials began to be used, mainly due to the increased demand for paper because of the emergence and increased use of printing. Today, most of the cellulosic fibers used come from wood species, mainly hardwoods and softwoods [1, 2, 6]. Nevertheless, in recent years there has been an increase in consumer awareness of the need to preserve the environment, which is why they demand a more ecological production of paper, both in the use of raw materials and in manufacturing processes. With the same purpose, government bodies devote economic and human resources to research into alternative raw materials to conventional ones. For these reasons, a large number of studies on the use of non-woody materials, including agriculture residues and vegetables as alternative source for cellulosic pulp production, have emerged in recent years [1, 7–14].

Some of the advantages of using non-woody raw materials can be mentioned: (i) in developing countries with scarce forest resources, non-woody biomass provides an effective alternative to importing wood, paper, or cellulosic pulp. In these countries, there may be a large area devoted to food crops, which would provide considerable amounts of agricultural residues and agro-food industries [1, 15]; (ii) non-woody biomass increases the added value of agri-food crops by taking advantage of their residues (traditionally used for burning or agricultural amendments) to obtain a product in great demand such as paper [1, 15]; (iii) production of special papers, whose most suitable raw materials are certain vegetable alternatives to conventional woods [1, 16]; and (iv) since the morphological characteristics of the fibers and the chemical composition of the non-woody species are very varied, a wide range of papers can be obtained by properly selecting and/or mixing these raw materials [1, 14].

2. Availability of raw materials

The availability of raw materials is very important when approaching the industrial facility for the production of cellulosic pulp. Availability is related to

the production and location of the various lignocellulosic materials that can be used for the intended purpose. In the case of agricultural residues from harvesting and pruning operations, it can be said that they are very abundant in Spain. Specifically, it is estimated that the production of the most important agricultural residues, due to their abundance, such as cereal straw, sunflower stalks, vine shoots, cotton stems, olive, orange and peach tree pruning and vegetable and other similar crop wastes, represents about 50 million tonnes per year, with Andalusia contributing with more than 20% [1, 17].

Due to its abundance, it seems that the most recommended agricultural residue for the manufacture of paper pulp is cereal straw since it represents almost 20% of the agricultural residues considered in 2007, and the technology used in its collection is fully developed [1, 17–19]. Regarding the waste from the agri-food industry used for the production of cellulosic pulp, the bagasse from the extraction of sugar cane and waste from the palm oil industry (EFB) should be highlighted [20].

With regard to alternative vegetables for cellulosic pulp production, they can be classified in three groups: (i) plants of wild nature such as bamboo, different types of cane, esparto grass, etc. [21]; (ii) plants from plantations with industrial uses, such as sorghum, abaca, sisal, jute, hemp, kenaf, flax, etc. [7, 22]; and (iii) other plants, mainly herbaceous species, grasses and legumes, which produce high biomass yields when grown in intensive plantations (tagasaste, *Leucaena* spp., etc.) [23–25].

3. Storage of lignocellulosic materials

The prolonged storage of lignocellulosic raw materials is always necessary in the pulp and paper industry. In the case of raw materials that are harvested only at a specific period of the year, the storage is even more important. Therefore, these raw materials must be collected in order to meet the annual needs of a factory, so that it operates all year round, with the consequent better use of installed capacity. On the other hand, many alternative lignocellulosic materials are more easily deteriorated due to their non-woody special properties, such as straws, herbaceous vegetables, etc., mainly if they contain high percentages of humidity. In fact, of all the factors that influence the storage of this type of sources, the most relevant is the residual humidity. Given that these materials do not require too rigorous conservation, as they are not intended for food, the rule of allowing slightly higher humidity than the “Caurie safety” humidity obtained by adjusting the experimental data on equilibrium humidity and relative humidity of the environment of the adsorption isotherms to the Caurie equation can generally be adapted. Applying this standard and observing the experimental adsorption isotherms, it appears that wheat straw, vine shoots and cotton stems can be well conserved in environments with relative humidity below 60–70%, while other agricultural residues such as olive tree pruning or sunflower stems require lower values [26]. On the other hand, it has been verified that the recommended maximum relative humidity values, according to the standard followed in this work, coincide with those obtained experimentally when storing the different agricultural residues considered in environments with different relative humidity for 10 or 12 months. As the chemical composition of these agricultural residues is considered as well as their fibrous structure does not differ so much from other agricultural residues such as wastes from agro-food industries, forestry residues and vegetable materials in general, the above conclusions can be extended to all these alternative lignocellulosic materials.

4. Characterization of lignocellulosic materials

Theoretically speaking any plant containing a reasonable amount of fibres can be used as a raw material for pulp and paper production. In practice, this is not the case. Besides the abundance of the plant, a steady supply and many other requirements are necessary. The fibre content of the plant is important. The plant contains in addition to fibres many non-fibrous cells, e.g. parenchyma cells. Fibres themselves vary much in different plants regarding their length, width, fine structures or microstructures, as well as their chemical composition. In one and the same plant, there are different types of fibres. The same fibre type is not equal in dimension but contains a spectrum of different dimensions. For this reason, one speaks of “average fibre length”. The length of the fibre is one of the most important parameters affecting paper strength [1].

Chemical characterization, which gives rise to the percentages of the main chemical constituents of lignocellulosic materials (generally cellulose, hemicellulose, lignin, as well as extractives and ash), is of great interest since it can indicate their possible applications for obtaining cellulosic pulps, in terms of the most suitable process to follow and the type of pulp that can be obtained. In this characterization, the contents of holocellulose, lignin, α -cellulose, hemicellulose, and extractives in water, 1% soda and ethanol-benzene and ash are determined as the most important. For this chemical characterization, TAPPI test methods, including TAPPI T 204 om-88, TAPPI T 211 om-93, TAPPI T 222 om-88 [27], and NREL analytical methods (National Renewable Energy Laboratory NREL/TP-510-42168) are usually employed [28].

When comparing the results obtained by different authors, a good concordance is generally observed for each specific material. Sometimes discrepancies appear that can be attributed to the different procedures used as well as to the different origins and varieties of the raw materials considered. For example, the chemical characterization results obtained for rice straw were analysed and compared with (i) some agriculture residues from harvesting and pruning operations and from agro-food industry (e.g. olive tree pruning, wheat straw, sunflower stems, sorghum stems, bagasse, vine shoots, and cotton stems); (ii) some vegetables (e.g. *Leucaena colinsi*, *Leucaena leucocephala*, *Chamaecytisus proliferus*, *Retama monosperma*, *Phragmites* spp., *Arundo donax*, *Prosopis juliflora*, and *Paulownia fortunei*); and (iii) softwoods (pine) and hardwoods (eucalyptus) [23, 29]. From this comparison it could be deduced that:

- The value of the hot water soluble content of rice straw (7.3%) is lower than that of the rest of agricultural residues, except for bagasse and cotton stems; it is higher than the values found for the vegetables considered, except for *P. fortunei*, and higher than the values for pine and eucalyptus.
- The value of soda extractives at 1% of rice straw (57.7%) is higher than the values corresponding to the rest of agricultural residues and vegetable considered, as well as those of pine and eucalyptus.
- The content of ethanol-benzene extractives in rice straw (0.56%) is lower than that of the materials considered: agricultural and agro-food residues, vegetables, pine and eucalyptus.
- The ash content of rice straw (9.2%) is higher than the values presented by the rest of agricultural residues and much higher than the values of pine and eucalyptus.

- The holocellulose content of rice straw (60.7%) is similar to the value found for olive tree pruning and lower than the values found for the rest of the agricultural residues considered, as well as those of the alternative vegetables considered and those of pine and eucalyptus.
- The content of α -cellulose of rice straw (41.2%) is lower than the values presented by the cotton stems, *L. colinsi*, *L. leucocephala*, *C. proliferus*, *R. monosperma*, pine and eucalyptus; higher than the values corresponding to olive tree pruning, wheat straw, *Phragmites*, *P. fortunei*, *Prosopis juliflora*; and similar to the values of the other species considered.
- The lignin content of rice straw (21.9%) is similar to the values corresponding to the cotton stems, *L. leucocephala* and *R. monosperma*; lower than the values found for *Phragmites* spp., *A. donax*, *P. fortunei* and pine; and higher than those of the other species considered.

In the same way, following the same example of rice straw, the experimental data on its physical characterization, which determines the size of its fibers, are compared with those of other lignocellulosic materials such as wheat straw, sunflower stalks, vine shoots, cotton tree stalks, olive tree pruning, sorghum stalks and pine and eucalyptus woods. After a biometric analysis with the rice straw studied, it is concluded that the length of its fibers (1.29 mm) is similar to that corresponding to the stems of sorghum, superior to those of the other agricultural residues considered and to that of eucalyptus but inferior to that of pine.

In summary, it can be stated that the alternative non-woody materials under consideration have acceptable chemical and physical characteristics for the production of pulp and paper [30].

5. Cellulosic pulp production

The manufacture of cellulosic pulp consists of the separation of cellulose fibers, which are cemented by the middle wall, composed mainly of lignin using physical or chemical methods [1, 2, 6]. In order to obtain cellulosic pulps from alternative non-woody materials, different chemical classical processes have been used (using chemical reagents such as soda, sodium sulphate and sodium sulfite) and organosolv (using organic solvents). In general, non-woody raw materials have a less density and more porous structure and, also in most of the cases, less lignin content, which means less energy and chemical requirements for fibre separation during pulp production. In addition, they have shorter growth cycles, reaching maturity faster than wood species, and in many cases the pulp yields obtained are higher [30].

5.1 Classical pulping processes

5.1.1 Soda pulping

Soda pulping is the oldest pulping processes known and consists of subjecting raw materials, cut and conditioned, to a cooking process with a given concentration of sodium hydroxide, at a specific temperature and cooking time, depending on the quality of the pulp to be obtained (chemical or semi-chemical) and the characteristics of the raw materials used [1, 2, 6]. A recovery of reagents and purification of black liquors is finally carried out. Each of these sections of the process can group

together different operations. Thus, for example, in the preparation of the raw material, a debarking is carried out in the case of woody plants or pith is removed in the case of some vegetables (e.g. sunflower stalks), a cutting or reduction in size to produce chips or flakes, a cleaning to remove impurities, and so on. In the pulping section, the operations of impregnation of the raw material, cooking or delignification to separate lignin, washing of the solid fraction resulting from cooking and draining of the same to eliminate the fluid used in the washing can be integrated. In the same way, the sections of reagents recovery and purification of residual black liquors are made up of different operations.

Soda pulps have been obtained from different alternative raw materials, specially agriculture residues such as wheat straw [31], sunflower stalks [32, 33], vine shoots [34], olive tree pruning [35], sorghum stalks [36, 37], tagasaste [24], EFB [20, 38], *H. funifera* [39] and rice straw [29, 38, 40], obtaining different yields depending on the conditions of soda concentration, temperature and cooking time used. Soda pulping has also been carried out using additives such as anthraquinone and parabenzoquinone, which accelerate the delignification process and stabilize carbohydrates, improving the yield of the process with respect to the conventional “soda” process when operated under the same working conditions. Assays have been carried out using wheat straw, olive tree pruning, rice straw and EFB. For rice straw and EFB, pulps have also been obtained using KOH in aqueous solutions [20, 40].

Miao et al. [22] also analysed the composition of the hemp root bast (HRT) to further subject it to a process of soda pulping and bleach it with an elemental chlorine free (ECF) bleaching sequence. These authors conclude that HRT is a suitable raw material to make paper obtaining a pulp with high viscosity and brightness (893 mL/g and 85.52% ISO, respectively). González et al. and Marrakchi et al. [41, 42] also applied soda pulping to orange tree wood and *Stipa tenacissima* stems, respectively. The first ones studied the influence of operational variables in both pulping and pulp beating (temperature, 155–185°C; time, 40–90 min; soda concentration, 10–16%; and number of PFI beating revolutions, 0 to 3000) on the yield and on the pulp refining degree as well as the physical properties of resulting paper sheets. These authors found an optimum compromise as regards operating conditions (170°C, 40 min, 13% soda concentration and 2700 number of PFI beating revolutions), obtaining a pulp with tensile index, burst index and tear index of around 59.11 Nm/g, 4.10 kN/g and 2.79 mNm²/g, respectively; these values deviate from their maximum values in 5.8, 2.2, and 1.4%, respectively. The pulp yield under these operating conditions is 43.9%; the refining degree is of 39.5°SR with the advantage of an increased drainability in paper production. These conditions involve a lower temperature, time, soda concentration and refining than those required to maximize the studied paper properties; so it is possible to save energy, chemicals and capital for industrial facilities. On the other hand, Marrakchi et al. [42] analysed the composition and fibre characteristics of the *S. tenacissima* stems and of its corresponding soda unbleached and bleached pulps. They conclude that the properties of *S. tenacissima* fibers are intermediate between those of non-wood and wood plants and are most often close to those of eucalyptus fibers. After studying a refining process and characterizing paper sheets obtained, these authors demonstrate the high potentiality of this non-wood species for papermaking applications.

5.1.2 Kraft pulping

The pulp obtained by this procedure is usually called Kraft (strong) if used for raw papers or “sulphate” if they are going to receive a further bleaching, although

both denominations are used indistinctly. The name “sulphate” is due to the fact that it is the sodium sulphate, and not the sodium sulphide, the reagent that is replaced, although the real agent that acts during the reaction is the sulphide that is generated in the recovery treatment of residual black liquors [1, 2, 6]. The process can be divided into two parts: the first is the obtaining of the pulp, and the second is the recovery of the chemical reagents used from black liquors.

According to different authors [1, 2, 6], Kraft pulping process consists of the following stages:

- i. The chips are taken to the reactor where they are cooked with white liquor (dissolution of sodium hydroxide and sodium sulphide), controlling the “liquid/solid” ratio.
- ii. Pulping takes place during the established time, under appropriate pressure conditions.
- iii. The black or residual liquor and the pulp are separated by filtration. The pulp is washed, and the black liquor is sent to the reagent recovery phase.
- iv. Once washed, the pulp goes to the bleaching stage or to the raw paper manufacturing plant.

In the reagent recovery phase, organic compounds dissolved in black liquor are used to produce energy, thus reducing the rate of polluting effluents. The stages of recovery are as follows: (i) concentration of the black liquor in the evaporators; (ii) spraying of the concentrated black liquor in the oven, where the carbon reduces the sodium sulphate to sodium sulphide; (iii) the melted solids are discharged and dissolved in water, resulting in the green liquors; and (iv) the green liquor is sent to the causticizing stage, where the sodium carbonate reacts with the calcium oxide to form sodium hydroxide [1, 2, 6].

Some studies have been carried out to obtain Kraft pulps using alternative materials to traditional wood, including olive tree wood [43], *Cynara cardunculus* L. [44], vine shoots [34], wheat straw [45] and kenaf [46]. Nevertheless, due to the more accessible structure of these materials compared to conventional wood materials, a soda process is usually applied to them, as this process is less pollutant. Thus, as an example, a factorial design of central composition experiments to find equations that relate the characteristics of the pulp and paper sheets with the operation variables have been realized using olive tree pruning [47, 48]. From these studies, it can be concluded that, in order to obtain pulp with suitable characteristics to be bleached to obtain paper and with good mechanical properties in the paper sheets, it is necessary to operate with an active alkali concentration of 25%, at 175°C during 90 min. The paper sheets obtained from olive tree pruning pulps were produced in different degrees of refining and were characterized attending their stretch index, burst index, and tear index. All paper sheets reach between 33 and 39 kN m/kg in the stretch index, between 1.5 and 2 kN/g in the burst index and 0.7–2.5 N m²/g in tear index and not using a high refining degree (<45°SR) [47, 48].

5.1.3 Sulfite pulping

Sulfite pulps are obtained by cooking the lignocellulosic material with a solution of bisulfite and sulfur dioxide [1, 2, 6]. The cooking liquor is obtained by burning sulfur to obtain sulfur dioxide which is absorbed in a base of calcium, magnesium, sodium or ammonium. The most important variables of the “sulfite” process

includes impregnation of the chips with the cooking reagents, dimensions and quality of the chips, temperature, time, pressure, pH of the white liquor, concentrations of sulfur dioxide combined (total and free), “liquid/solid” ratio and raw material used. Several “sulfite” processes have been proposed, including acid sulphite, bisulphite, alkaline sulphite, multistage sulphite, high-yield sulphite, etc., to obtain dissolving pulp [1, 2, 6]. In addition to these variables, it has been proposed to use molybdate or anthraquinone as catalysts, achieving a stabilization of the polysaccharides and an acceleration in delignification.

The sulfite process has been studied for several alternative raw materials but not as much as the soda and Kraft processes. Then, different studies of sulfite process with olive tree [35, 49], sunflower stalk [50], bagasse [51] and wheat straw [52] have been reported.

5.1.4 *Organosolv pulping*

These processes are characterized by the fact that the separation of lignin from lignocellulosic materials is achieved by solubilization with organic solvents, which are subsequently recovered for a new pulping cycle, resulting in a concentrate rich in lignin, from which different by-products can be obtained [53]. Among organic solvents used, alcohols (ethanol, methanol, butanol, etc.) and organic acids (acetic and formic acids) are commonly employed for non-woody materials [1, 2, 18, 24, 34, 54–66]. Nevertheless, acetone and other solvents such as phenol, formaldehyde, ethanolamine, ethylene glycol and ethanol-water have also been used for these alternative raw materials [1, 2, 19, 23, 34, 38, 60, 67–71], demonstrating that these materials can be used for the manufacture of pulp and paper through different processes with acceptable characteristics.

5.1.4.1 *Pulping using alcohols*

These are the most widely used processes due to the selectivity that these solvents contribute to the separation of the lignin and their easy recovery by distillation. In the case of the ethanol process, the influence of the operating variables (ethanol concentration, temperature, time and liquid/solid ratio) on the characteristics of the pulp and paper sheets obtained from different alternative raw materials, including olive tree [62], wheat straw [1, 2, 18], tagasaste [24, 57], sunflower stalk and *P. fortunei* [54, 55] and vine shoots [34], has been studied. As an example, in the case of wheat straw, when pulping is carried out at 200°C, with an ethanol concentration of 75% for 60 min, acceptable good values are obtained for yield (37.6%), holocellulose (88.8%), α -cellulose (46.9%) and lignin (7.2%) [1, 2, 18]. Methanol and butanol have also been used on wheat straw [37, 61].

5.1.4.2 *Pulping using organics acids*

Along with the processes that use alcohols, the processes that use organic acids are the following most used. The most common are those that use acetic acid and formic acid, and different studies have been reported with EFB [58], rice straw [63], jute [66], rapeseed straw [56], cardoon stalk [64], and wheat straw [65].

The pulping of wheat straw with acetic acid and formic acid has been carried out, studying the influence of operation variables on the properties of the resulting pulps. Comparing the results obtained when operating for times ranging between 0.5 and 2 h, at temperatures of 75–125°C and 150–200°C, and with concentrations of 50–100% and 50–80% of the formic and acetic acids, respectively, it is concluded

that to obtain pulp with acceptable holocellulose (88.2%), α -cellulose (40.2%) and lignin (6.4%) contents are more effective than formic acid, operating at 50% concentration, 100°C and 2 h. This fact is mainly due to it requiring less acid and lower working temperature, with the consequent savings in chemical reagents and energy for heating [65].

5.1.4.3 Acetone process

Several studies have been studied with acetone solvent mainly on wheat straw [1, 2, 19, 60, 67]. From these studies it is concluded that it must be operated at 200°C, for 95–100 min and with 55–60% of acetone to obtain high holocellulose and α -cellulose values and low lignin and extractives, although the yield of the pulp is low [60]. To obtain good values of breaking length (3456 m), elongation (1.42%), burst index (1.36 kN/g) and tear index (3.86 mNm²/g) of the paper sheets formed, a temperature of 200°C has to be used. On the other hand, if the brightness has to be high, it has to be operated at 140°C for 1 h with a concentration of 60% acetone [65].

6. Refining of cellulosic pulps

The refining of pulp is an operation that modifies, through the action of mechanical work and in the presence of an aqueous medium, the morphology of the fibres and their physicochemical structure, decisively changing the properties of the paper sheets obtained from the refined pulp [1, 2, 6]. Using a Sprout-Bauer refiner, the influence of refining pulp from different agricultural residues (wheat straw, sunflower stems, vine shoots, olive tree pruning, cotton stems and sorghum stems) on the corresponding pulp and paper sheets was studied [1, 2, 19, 32, 69]. In view of the results, it can be concluded that olive tree pruning pulp must be severely refined to obtain good quality paper, although the maximum values of the ring crush test (RCT) and the tear index are reached for refining grades of 45 and 55°SR, respectively. In the case of EFB soda-anthraquinone pulp, a study has been carried out in a PFI refiner, studying the influence of the cooking variables (soda concentration, temperature and time) and the number of turns in the PFI on the properties of the resulting paper sheets [20]. From this study it is deduced that under some operation conditions, 15% of soda, 170°C, 70 min and 2,400 turns in the PFI, the properties of paper sheets obtained deviate less than 12% from their optimum values (59.6 Nm/g for the traction index, 4.48% for elongation, 4.17 kN/g for the burst index and 7.20 mNm²/g for the tear index), for a degree of refining of 47.5°SR, acceptable for the formation of paper sheets. Under these conditions, reagents, energy and immobilized capital are saved with respect to the maximum values of the operating variables used [20].

7. Bleaching of cellulosic pulps

The bleaching of cellulosic pulps is carried out for the elimination and/or modification of some constituents that add color to the raw pulp, generally using chemical reagents in one or more stages and trying to degrade the cellulose fibers as little as possible [1, 2, 6]. The main light-absorbing substances in the pulps are lignin and resins, so in order to bleach a pulp, these substances must be chemically transformed into a solid state in order to reduce their light absorption characteristics or

be oxidized, reduced or hydrolysed, to make them soluble in aqueous solutions and thus be able to be removed from the pulps.

The need to reduce pollution from bleached pulp mills has led to the study of new bleaching sequences [1, 2, 6], with research focusing in three main directions: (i) bleaching processes with reagents without elemental chlorine (ECF), which consist of the total substitution of chlorinated stages by compounds such as chlorine dioxide (without elemental chlorine), regardless of whether other bleaching agents totally free of chlorine, such as oxygen, hydrogen peroxide, etc., are also used; (ii) bleaching processes with totally chlorine free reagents (TCF), using reagents such as oxygen, hydrogen peroxide and ozone, mainly [72]; and (iii) biological bleaching processes involving microorganisms or enzymes produced by them.

ECF and TCF bleaching processes including enzymatic stages have been studied for different alternative raw materials. It is worth highlighting the TCF processes which have been studied using different chemical reagents individually (hydrogen peroxide, oxygen, ozone, sodium perborate and peracetic acid) or with OZP bleaching sequences (where Z is an ozone stage) [1, 2, 6].

Hydrogen peroxide has been used for the bleaching of Kraft olive tree pruning pulp with a Kappa index of 21, operating at a temperature of 70°C and a consistency of 10%, and following a factorial design of experiments in which the peroxide concentration varies from 1 to 5% and the time from 30 to 210 min, finding that it is recommended to use a low-medium concentration of peroxide (1–3%) and a long time (210 min) [73]. Comparing the results with those of bleached pulps with other reagents, it is concluded that the viscosity of the pulps is higher in the case of peroxide bleached pulps than those bleached with oxygen, ozone or chlorine dioxide. To improve the Kappa index and brightness values of peroxide bleached pulp, it is desirable to combine hydrogen peroxide with oxygen or to use the combination oxygen and ozone [74].

For the bleaching of abaca soda pulp with peracetic acid [75], the influence of the operating conditions on the Kappa index, viscosity and brightness of the pulp and on the breaking length and burst index of the paper sheets was studied. Following a factorial design of experiments, it is concluded that operating at 55°C, with 4.5% peracetic acid for 150 min, a brightness of 79.9% is obtained (only 6.5% lower than the maximum possible) and the maximum possible values for the breaking length (6547 m), burst index (5.0 kN/g) and viscosity (1519 mL/g).

Peracetic acid has also been considered in the bleaching of olive tree pruning, finding that it has to be operated at 55°C for 90 min, a consistency of 10% and an acid concentration of 2.5%, providing good values for brightness and Kappa index and improving the viscosity of the bleached pulp with respect to crude pulp [76].

In the bleaching of abaca soda pulp with sodium perborate [77], the influence of the concentration of reagent (1–5%), temperature (60–80°C) and time (1–2 h) on the characteristics of the bleached pulp and the resulting paper sheets has been studied. It is concluded that in order to obtain pulp with the highest possible values of viscosity (1601 mL/g) and breaking length (5943 m), it is necessary to operate at 60°C, 1% perborate and 60 min, achieving a brightness of 62.7%, only 11.9% below the maximum possible.

For abaca soda pulp, the bleaching processes using hydrogen peroxide, peracetic acid, sodium perborate and the OZP sequence were compared from the point of view of pulp yield and brightness, breaking length and burst and tear indexes of the paper sheets. Overall, the best results are achieved for peracetic bleached pulp (4.5%, at 55°C for 0.5 h), providing little loss of yield (<1%) and some values for breaking length (6.555 m), burst index (4.97 kN/g) and tear index (15.77 mNm²/g), which only decrease, with respect to those of the raw starting pulps, by 7.0, 8.8 and 20.9%, respectively, while brightness (77.4%) increases by 56.7%; with the

additional advantage that by operating at a lower temperature and for less time than in the other bleaching processes considered, energy savings are produced for heating and immobilized capital for industrial installations. The pulp bleached with the OZP sequence has more brightness but loses more yield. Moreover, the characteristics of the paper sheets are worse, and the process requires higher costs of reagent, energy and immobilization [78].

The OZP sequence has been applied to EFB soda-anthraquinone and diethanolamine pulps [79]. For similar Kappa index values for the two pulps (14.2 and 17.3), the paper sheets of the raw soda-anthraquinone pulp exhibit higher values for tensile (25.8 Nm/g), elongation (2.35%), burst index (1.69 kN/g) and tear index (0.50 mNm²/g) and brightness (60.6%) than the diethanolamine pulp, but the latter has a higher viscosity (659 mL/g). When OZP bleaching sequence is used, the diethanolamine pulp exhibits higher viscosity (783 mL/g), and the properties of the paper sheets are similar to or better than those of the soda-anthraquinone pulp: 22.2 as opposed to 20.4 Nm/g for the tensile index, 1.30 vs. 1.42 kN/g for the burst index, 0.71 vs. 0.70 mNm²/g for the tear index and 71.3 vs. 77.5% for brightness [79].

7.1 Biobleaching

It is worth highlighting in this section that apart from xylanases, the use of laccases has been used for the bleaching of alternative raw materials [80–84]. As it is known, these enzymes need a mediator to make the bleaching more effective since thanks to them they are able to oxidize not only the phenolic part but also the non-phenolic of the lignin.

The work of Camarero et al. [80], who apply three different fungal laccases (from *Pycnoporus cinnabarinus*, *Trametes versicolor* and *Pleurotus eryngii*) and two mediators, 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) and 1-hydroxybenzotriazole (HBT) to bleach flax pulp using a TCF sequence (enzymatic stage (L) plus hydrogen peroxide bleaching (P)), is noteworthy. These authors obtain delignification values of up to 90% after hydrogen peroxide bleaching when initial pulp is subjected to the enzymatic pretreatment (L). These results are improved when they apply a P stage under pressurized oxygen, obtaining a pulp with 82% ISO of brightness, and kappa index close to 1. Fillat et al. [81] also bleached flax pulp using natural mediators: syringaldehyde (SA), acetosyringone (AS) and p-coumaric acid (PCA) in combination with the laccase of *P. cinnabarinus* as a pretreatment prior to hydrogen peroxide bleaching stage. All mediators decrease the kappa index and increase the brightness of the bleached pulps after peroxide bleaching especially when SA was used. On the other hand, soda-anthraquinone pulp from orange tree pruning is also bleached by Fillat et al. [82]. In this case three different laccase-mediator systems (LMS) were used as pretreatment to an alkaline extraction plus a hydrogen peroxide bleaching: laccase from *Trametes villosa* (Tv), either in combination with 1-hydroxybenzotriazole (HBT) or with acetosyringone (AS) as natural mediator, and laccase from *Myceliophthora thermophila* (Mt) in combination with AS. The three laccase-mediator systems improve the bleaching sequence, with L-Tv + AS being the LMS that provides the highest delignification and improvement of optical properties. Finally, Martín-Sampedro et al. [83] also bleached soda pulp from olive tree pruning using not only a typical LMS but also adding xylanase jointly or prior to LMS to study the effect of this enzyme on the characteristics of the bleached pulps. The best results are found when both enzymes are applied in the same stage. In these conditions the lowest hydrogen peroxide consumption (63%), kappa index of 11.6 and brightness of 46% ISO are reached. Same authors [84] also bleached pulp from oil palm empty fruit bunches using laccase and xylanase. An enzymatic process with xylanase (X) and/or laccase (L) was incorporated before the alkaline extraction step

(E) and the hydrogen peroxide bleaching (P). Comparing with controls, the LEP sequence results in an improvement of optical properties (colorimetric properties and brightness) and a reduction of the kappa index. When both enzymes (xylanase and laccase) are used jointly, no improvement is detected; however, when the xylanase stage is applied before the laccase stage, the beneficial effects of laccase are boosted. Thus, the XLEP bleached pulp shows a brightness of 60.5% ISO, a kappa index of 5.4 although the hydrogen peroxide consumption increase (77.0 vs. 64.5% and 73.8% for EP and LEP, respectively).

8. Integration of the pulp and paper industry using alternative raw materials into the biorefinery concept

The concept of lignocellulosic biorefinery aims at the integral use of the main components of lignocellulosic raw materials to obtain energy, chemicals and products [85]. The pulp and paper industry is an excellent initial point for the establishment of this concept as it has the best infrastructure for biomass fractionation and conversion and a great deal of practical industrial experience. Then, the classical pulp and paper industry, including Kraft, sulfite and soda technologies, has been applying this concept for a long time as it not only produces paper as the main product (cellulosic fraction) but also recovers the reagents and produces energy from the residual black liquors (lignin-rich fraction) as well as the generation of bioproducts such as tall oils, which are sold to obtain high added value products (e.g. adhesives, detergents, etc.), and lignin for the production of chemicals or materials. In the future, the extraction of hemicelluloses prior to pulping will be included in order to make maximum use of lignocellulosic materials. A general scheme, which will be developed below including also gasification of lignin, is shown in **Figure 1**.

Using the same scheme-work of the pulp and paper industry with classical pulping methods, different organosolv pulping processes have been developed to produce cellulosic pulp and other products from different alternative raw materials such as agriculture residues [53], among them, those employing ethanol such as the Alcell® process for the production of cellulosic pulp, giving value to other biomass fractions, such as high-quality lignin in the residual black liquor with several potential industrial applications, and the Lignol® process, which also extracts lignin, as well as sugars for the production of ethanol, oligomers, furfural and acetic acid. However, one of the disadvantages of these processes lies in the incorporation of both extracts and a part of the hemicelluloses to the residual black liquors. For this reason, the possibility of carrying out a hydrolysis pretreatment of the polysaccharides with the original raw materials prior to organosolv pulping methods, using water at a high temperature (hydrothermal treatment), has been explored [53]. Then, a hydrolysis of the acetyl groups to acetic acid is produced, which acts as a catalyst solubilizing all or part of the hemicelluloses (autohydrolysis) and then resulting in a pretreatment aqueous fraction with oligomers (mainly gluco-oligosaccharides and xylo-oligosaccharides), sugars (glucose, xylose, arabinose), acetic, furfural or 5-hydroxymethyl-2-furfural (HMF) and some lignin. Oligomers are used as food additives or substrate for sugars, after hydrolysis and fermentation (xylose and arabinose could be fermented to ethanol or xylitol); and furfural and lignin derivatives have applications in the chemical industry [86, 87]. The disadvantage of this fractionation is the low selectivity towards cellulose, giving rise to a solid fraction structurally affected, which can limit its later use; but an adequate hydrothermal pretreatment achieves a solid fraction that can be used to obtain pulp and paper by classical or organosolv procedures, whose resistance can be improved using a relevant refining.

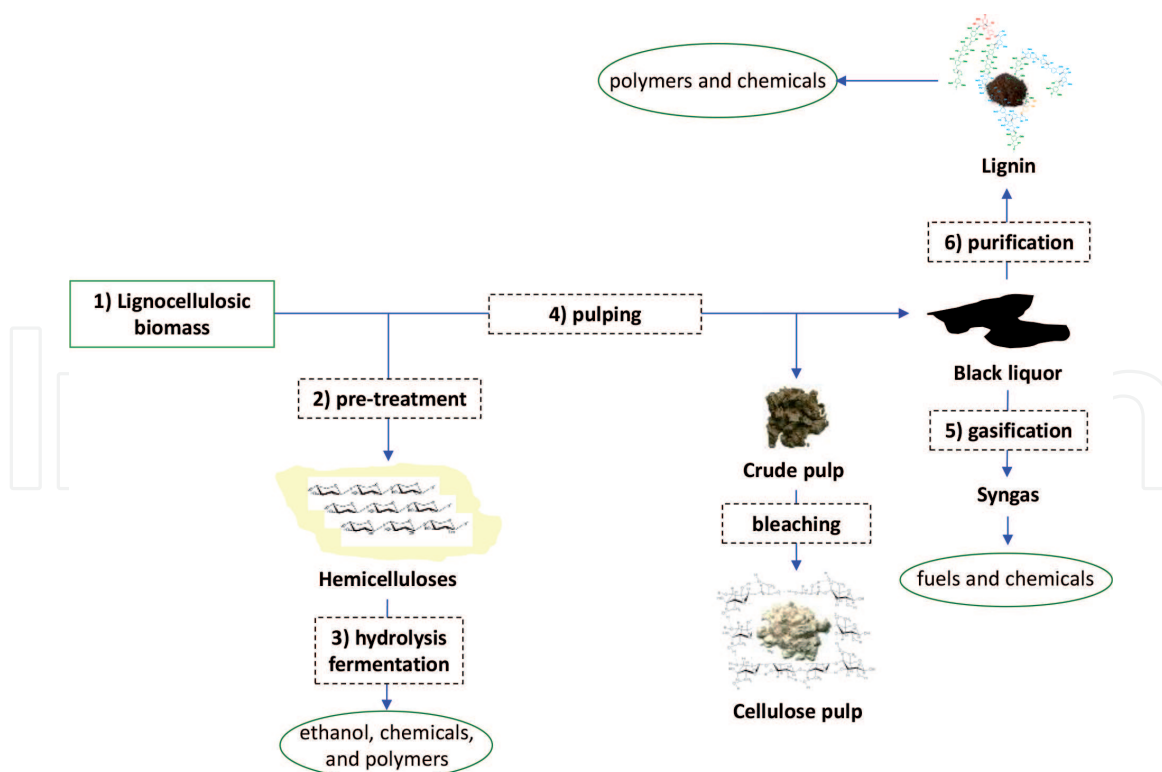


Figure 1.
 Scheme of integration of pulp and paper industry into the biorefinery concept in the future.

In the pulping processes of the solid fraction coming from autohydrolysis or hydrothermal pretreatment, some residual black liquors are obtained, with lignin being the majority component. These liquors, after the separation of water and/or organic solvents used in cooking (which are recycled in the cooking process), are transformed into a concentrate rich in lignin. From these concentrates lignin can be obtained for different uses, and/or it can be subjected to gasification processes with the aim of obtaining high-quality products such as hydrogen, methanol, synthesis gas or dimethyl ether (DME) for motor applications [86–89].

8.1 Hemicellulose isolation by hydrothermal treatments

As commented above, one of the possibilities to convert the classical chemical pulp and paper industry into a biorefinery is to extract a portion of hemicelluloses from lignocellulosic materials prior to pulping, obtaining a liquid fraction enriched in hemicellulosic carbohydrates that can be converted into ethanol and/or chemical products. One of the options for the separation of hemicellulose from lignocellulosic materials is its depolymerization by autohydrolysis, also known as hydrothermal process, which does not require the addition of acids as it is auto-generated in the process [53, 85]. In addition to the process of autohydrolysis itself, the process of steam explosion is very significant (once autohydrolysis has taken place, the mixture undergoes a sudden decompression to produce the vaporization of the water contained in the fibers and the consequent disaggregation of the lignocellulosic matrix), as well as its variants, such as the Rash, Masonite, Iotech, Siropulper and Stake processes [53, 85].

These hydrothermal treatments can be carried out in a very wide range of operating conditions, with the temperature, time, solid concentration and particle size of lignocellulosic materials being the most influential variables [85]. In the case of autohydrolysis, the range of temperatures to treat lignocellulosic materials in an aqueous medium is in the range between 150 and 250°C. Under these conditions, the self-ionization of water generates protons that act as a catalyst for the hydrolysis

of the hemicellulose, reacting among others the acetyl groups (present in the form of esters in the hemicellulosic heteropolymers), which are released in the form of acetic acid. Its contribution to the generation of protons is 1700 to 1,000,000 times greater than that of water, so the contribution of aqueous protons to the hydrothermal process can be neglected once acetic acid has been generated. At the same time, there is total or partial solubilization of hemicelluloses and their conversion with good yields of oligosaccharides and monosaccharides, which can be used for different purposes [53, 85].

Other minor reactions associated with this type of process are the formation of products such as furfural from pentoses and HMF from hexoses; the generation of carbon dioxide by decomposition of carboxyl groups present in uronic acids; the condensation of some unstable molecules that intervene as reaction intermediates; the decomposition under severe conditions of products such as furfural, sensitive to acid concentration; the decomposition of HMF to formic and levulinic acids; and condensation reactions with lignin [90].

Different studies with traditional woody materials such as eucalypt have shown a pre-extraction of hemicellulose prior to pulping process by hydrothermal processes [91–93]. In the same way, these hydrothermal processes have also been applied to alternative raw materials such as paulownia [55], sunflower stems [54], rice straw [71], tagasaste [25] and *H. funifera* [94].

The influence of the temperature (160–200°C) of the autohydrolysis process applied to paulownia on the composition of the resulting solid and liquid fractions has been studied [55]. It is found that the maximum concentrations of glucose, xylose, arabinose, acetic acid, furfural, HMF and oligomers of the resulting liquid fraction correspond to when operating at maximum temperature.

A similar study carried out with sunflower stems concludes that at 190°C the highest values are obtained for the glucose, xylose and arabinose contents of the liquid fraction of the hydrothermal treatment, with a yield of 24.5%, while the yield of the solid fraction, which can be pulping, is 72.5% [54].

In the case of rice straw, the influence of temperature (150–190°C), time (0 to 20 min after reaching the working temperature) and liquid/solid ratio (6:10) on the hydrothermal treatment, on the lignin content, on the yield of the resulting solid fraction and on the composition of the corresponding liquid phase (glucose, xylose, arabinose and acetic acid) was studied [71]. It follows that in order to obtain high values of glucose (1.92 g/L), xylose (3.97 g/L), arabinose (0.99 g/L) and acetic acid (1.96 g/L) concentrations, it is necessary to operate at high temperature (190°C) and low-medium conditions for time (15 min) and hydromodule (9), which allows capital savings by not operating with the maximum time and using the maximum hydromodule value. The yield obtained for the solid fraction is 88.1%, and the lignin content is 24.43%.

Finally, tagasaste wood was submitted to hydrothermal treatment at 175–185°C [25]. Then, a liquor containing a substantially increased amount of oligomers (between 16.6 and 47.7% as percentages with respect to the content of the raw material in each polymer fraction) is obtained. In the case of *H. funifera*, a sulphuric acid-catalysed hydrothermal treatment (170°C, 0, 20 min after reaching operating temperature, 8 liquid/solid ratio, and 0.3% sulphuric acid), gives a liquid fraction containing 4.62% of glucose, 10.56% of xylose, 1.28% of arabinose, and a solid fraction with a solid yield of 57.0%.

8.2 Pulping of the solid fraction from hydrothermal treatment

Hydrothermal treatments under relatively mild operating conditions (temperature and time) do not cause significant alterations in the cellulose. In this way, solid fractions susceptible to delignification or pulping are obtained [53].

The solid fraction of the hydrothermal treatment of paulownia carried out at 190°C was subjected to pulping process with ethanol following a factorial design of experiments [55]. The conclusion of this work is that operating at 180°C for 30 min and an ethanol concentration of 20%, obtained pulp has acceptable values of Kappa index and viscosity, and their corresponding paper sheets have a brightness of 27.4% ISO, a tensile index of 28.87 Nm/g, a burst index of 1.22 kPam²/g and a tear index of 1.23 kNm²/g.

In the case of sunflower stems [54], the solid fraction of a treatment carried out at 180°C is cooked with ethanol (70%, 170°C for 2 h and a hydromodule of 8) giving rise to a pulp with properties (36.3% of pulp yield, 69.1% cellulose, 12.6% hemicellulose, 18.2% lignin, 551 mL/g viscosity, 3.8 km breaking length, 1.23% elongation, 1.15 kN/g burst index and 2.04 mNm²/g tear index) similar to that obtained by the soda process.

The influence of operating conditions (temperature from 160 to 180°C, time from 30 to 90 min and concentration of diethanolamine from 60 to 80%) on the pulping process of the solid fraction obtained from a hydrothermal treatment of rice straw (carried out at 190°C) on the characteristics of the pulp (yield, Kappa index, viscosity and degree of refining) and of the paper sheets obtained from them (length of rupture, elongation, burst index, tear index and brightness) was also studied [71]. It is deduced that it is convenient to operate at 162.5°C, 60 min and 70% of diethanolamine, since paper sheets present characteristics that deviate little from the optimal ones (less than 8% in the worst case), saving chemical reagents, energy for heating and immobilized capital for the installation, when operating with values of time and the concentration of diethanolamine medium and medium-low temperature, with respect to the maximums considered; likewise the values found for the yield and Kappa index deviate less than 14% with respect to the optimal values.

Autohydrolysed tagasaste wood was also submitted to ethanol and soda pulping procedures [25]. The autohydrolysis prior to ethanol pulping increases yields (53–60%); reduces Kappa index (28.8–34.6), but also viscosity (755–857 mL/g); and decreases paper strength (2.97–5.22 kNm/kg). However, applying a refining process to tagasaste pulp is found to improve its strength-related properties more markedly than in soda pulp from the same material (tensile index of 44 kNm/kg). In the case of *H. funifera*, the samples pretreated with sulphuric acid-catalysed autohydrolysis was subsequently submitted to soda, soda-anthraquinone, ethanolamine, ethylene glycol, diethanolamine and diethyleneglycol [94]. In this case, the best pulp of *H. funifera* pulp is obtained by cooking with 10% NaOH and 1% anthraquinone at 155°C for 30 min, exhibiting good values of yield (48.3%), viscosity (737 mL/g), Kappa index (15.2), tensile index (83.6 Nm/g), stretch (3.8%), burst index (7.34 kN/g) and tear index (3.20 mNm²/g). Moreover, the soda-anthraquinone pulps of raw material have better properties than the pulps from solid fraction of hydrothermal treatments.

8.3 Use of residual liquors components obtained during pulping

The valorization of lignin-rich black liquors generated from pulping processes is another transition path from the traditional pulp and paper industry to future biorefineries. Generally, residual lignins from black liquors are used to obtain energy for processing plants, mainly by combustion. However, the aromatic structure of lignin makes it a potential source for the production of new bio-based high-value products and chemicals, increasing the sustainability and competitiveness of this pulp and paper industry [86]. Other different fractions of lignin and compounds such as various polysaccharides present in these black liquors, which may not have

specific applications or their transformation into high value-added products may not be profitable, can also be valorized by gasification process [89].

Pulp and paper industry is estimated that moves around 70 million tonnes of lignin annually [95], of which only just over 1 million tonnes are currently marketed, corresponding to lignosulfonates, and which have an established market for use in various uses such as plasticizers and dispersion agents, whereas Kraft lignins are used in the recovery tanks of products from the paper plants themselves and only market around 100.000 tonnes per year. Finally, only a few hundred tonnes of lignins from the soda process come onto the market each year, although this quantity is expected to rise rapidly to around 10,000 tonnes due to the fact that an increasing number of small paper mills, which use agricultural waste and non-wood species to produce cellulose, are introducing lignin recovery processes as the only way to meet environmental effluent treatment specifications.

8.3.1 Lignin applications

Depending on the biomass feedstock, pulping technology and conditions and isolation procedures, lignin has distinct features that may render them useful for different applications. Purity, molar mass and chemical functionalities are some of the characteristics to take into account [96]. So, a detailed knowledge of lignin structure, composition and purity is required in order to determine its behaviour in different potential applications. In this sense, characterization of residual lignins from Kraft and soda-anthraquinone pulping of agriculture residues such as olive tree pruning [97] and wheat or barley straw [98], as well as vegetables like *L. leucocephala*, *C. proliferus*, and *H. funifera* [99, 100], has been carried out.

Among the different characteristics of lignin, its high heterogeneity is one of the most important, which not only affects its structure but also its high distribution of molecular weights (range from 1.000 to 300.000 Da for the same sample) [101]. Therefore, fractionation is one of the ways of obtaining reactive lignins. The preparation of lignin with a defined molecular weight distribution can be carried out by means of different processes: ultrafiltration, selective extraction with solvents and differential precipitation.

The technique of ultrafiltration and nanofiltration is one of the methods being investigated today, with the dual intention of on the one hand reducing the organic load contained in the digestion solution, for its subsequent reincorporation into the pulping process without the loss of inorganic reagents, and on the other obtaining valuable organic resources for use in the development of high-value-added materials. By means of ceramic membranes capable of filtering the residual liquor until the separation of substances smaller than 1 kDa, low molar lignin fractions (1000 g/mol maximum) are obtained. After suitable purification processes, these lignins have a high phenolic hydroxyl content (and/or acid groups), high reactivity and low processing and handling temperatures. In this way, Toledano et al. [102] propose ultrafiltration as a fractionation process to separate different molecular weight lignin fractions from olive tree pruning organosolv black liquor.

Solvent extraction of lignin can be carried out primarily in two ways. In one case, lignin is extracted by a single solvent or a sequential use of multiple solvents. In the other case, a solvent is used to dissolve lignin and then precipitated using chemical (mainly with acids) treatments. Then, Domínguez-Robles et al. [103] used different proportions of acetone (40 and 60%) in water for lignin fractionation of two different sources (organosolv and soda wheat straw lignins), obtaining different fractions with different molar masses and functional groups. Finally, fractionation of the lignins by differential precipitation consists of extracting

different lignin samples as the pH of the solution is gradually lowered. It is the most commonly used method because the simple addition of a strong acid is sufficient, compared to the high costs of the other two methods. However, it has a disadvantage derived from the formation of colloids during precipitation, which can greatly complicate the filtration process. In this sense, Domínguez-Robles et al. [104] have proposed an acid precipitation of wheat straw lignin from soda black liquor using three different inorganic acids (phosphoric, sulphuric and chloride acids) at three different concentration levels, achieving pH values from 11 to 2.

Different lignin applications have been suggested depending on its properties. Then, poorly degraded lignin is employed as dispersants, surfactants and thermoplastic blends or copolymers [105–107] or as an aromatic compound platform to obtain fine chemicals such as polyols, benzene, xylene, toluene, vanillin, ferulic acid, etc. [87]. In contrast, extensively depolymerized lignin, therefore, with a high phenolic content, is suitable for coating, adhesives and composites [108–111]. In this sense, some examples of lignin valorization from alternative raw materials have been reported. Then, Borrero-López et al. [112] showed the possibility to produce olegels from soda lignin obtained from solid state fermented wheat straw; Tejado et al. [113] assayed soda-anthraquinone flax lignin and ethanol-water wild tamarind lignin to phenol-formaldehyde (PF) resin production; Domínguez-Robles et al. [103] investigated the use of soda wheat straw lignin as natural adhesive for the production of high-density fibre board; and Domínguez-Robles et al. [98] analysed Kraft, soda and organosolv wheat straw lignins as a binder material for electrodes in rechargeable lithium batteries.

8.3.2 Gasification of residual liquors components

Any proportion of the agricultural raw material non-suitable for pulp and paper production, in addition to lignin and other compounds such as various polysaccharides obtained in lignin separation processes, may be converted—via pyrolysis—into several types of fuels and petrochemical substitutes [1, 88].

As commented above, different fractions of lignin and other compounds such as various polysaccharides can be obtained in lignin separation processes. Some of these fractions may not have specific applications, or their transformation into high-value-added products may not be profitable, so they may be suitable for a gasification process [89]. This consists of the partial oxidation of the lignocellulosic residues to obtain carbon monoxide, hydrogen, methane, nitrogen and carbonic anhydride mainly, in proportions that depend on the raw material considered and the conditions of the process. Three types of processes can be distinguished: (i) exothermic, using oxygen or air to obtain carbon monoxide or a mixture of carbon monoxide and nitrogen (lean gas); (ii) endothermic, which use water vapor to obtain carbon monoxide and hydrogen (synthesis gas); and (iii) balanced or mixed, using oxygen and water vapor or air and water vapor to obtain carbon monoxide and hydrogen or a mixture of carbon monoxide, hydrogen and nitrogen.

Gasification gases can be used as fuels or to obtain chemicals. Among the latter, those obtained from carbon monoxide (methyl formate, formamide, formic acid, carbonyls, acrylic acid, etc.) and those obtained from carbon monoxide and hydrogen (ammonia, nitric acid, hydrazine, urea, hydrocyanic acid, aldehydes, explosives, etc.) can be distinguished. For example, pyrolysis of soda *H. funifera* lignin gives a gas mixture containing 1.13% H₂, 31.79% CO and 1.86% CH₄ by weight, whereas gasification of the same sample provides a mixture containing 0.18% H₂, 24.50% CO and 17.75% CH₄, also by weight [39].

9. Conclusions

The availability and concentration of wood in areas of easy access, the elevated fibre content, the cost of transport, the ease of storage as well as the stability of the raw material and its performance during the pulping process have supported the use of the wood in the pulp and paper industry. However, due to the numerous advantages of certain alternative raw materials (low-cost fibers, fast growth, low lignin content and fiber morphology, among others), they have proved to be a viable option as a starting raw material for the production of a wide range of different papers. On the other hand, taking into account the concept of lignocellulosic biorefinery, the pulp and paper industry is a good starting point since from its beginnings it not only produced pulp for paper but also energy. However, this industry needs different innovations to adapt even more to this concept. These innovations include the valorization of the extractives and hemicellulosic fractions through extraction prior to the pulping process, the valorization of black liquors through gasification or purification, the valorization of lignocellulosic waste through gasification or other processes such as saccharification and fermentation and also the introduction of new alternative raw materials to wood, as summarized in this work.

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Conflict of interest

The authors declare no conflict of interest.

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