Review

Getting Value from Pulp and Paper Industry Wastes: On the Way to Sustainability and Circular Economy

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Abstract: The pulp and paper industry is recognized as a well-established sector, which throughout its process, generates a vast amount of waste streams with the capacity to be valorized. Typically, these residues are burned for energy purposes, but their use as substrates for biological processes could be a more efficient and sustainable alternative. With this aim, it is essential to identify and characterize each type of waste to determine its biotechnological potential. In this context, this research highlights possible alternatives with lower environmental impact and higher revenues. The bio-based pathway should be a promising alternative for the valorization of pulp and paper industry wastes, in particular for bioproduct production such as bioethanol, polyhydroxyalkanoates (PHA), and biogas. This article focuses on state of the art regarding the identification and characterization of these wastes, their main applied deconstruction technologies and the valorization pathways reported for the production of the abovementioned bioproducts.

Keywords: bioethanol; biogas; pulp and paper industry; polyhydroxyalkanoates; wastes valorization

1. Introduction

The current climate concerns, which are a consequence of industrialization, population growth, and the modification of consumption patterns, demand a reduction in fossil fuels utilization and waste generation [1,2]. The circular economy model proposes the reuse and the recycling of resources instead of the dominant linear economic strategy of “take, make and dispose”, reducing the environmental impact [3,4]. The circular economy model corresponds to a closed cycle within a zero-waste approach. Its implementation would lead to several benefits, including: (i) a reduced requirement of virgin materials and primary raw materials; (ii) increased use of renewable resources instead of non-renewable ones; (iii) the minimization of the waste generated [5]. Additionally, by establishing a cyclical model, the costs associated should be curtailed with environmental legislation and taxes, reducing waste management expenses and the dependence on imports. Consequently, the price volatility of commodity markets will decrease [5,6].

Following this approach, residual biomass and sub-products derived from industrial processes can be considered possible raw materials with a high potential to produce energy and other value-added products [1,3,5]. In 2004, to push for this transition, the European Union (EU) stipulated a target of 70% reusing and recycling wastes by 2030, prioritizing its reintegration into the value chain. Simultaneously, landfills started to be abolished [7]. Despite its low efficiency, the incineration of wastes for energy recovery is still a common practice in the EU, and the opportunity for valorization using other routes...
is lost. Moreover, the risk of releasing and emission persistent organic pollutants is increased [7,8].

For these reasons, sub-products or wastes of lignocellulosic biomass (LCB) origin are perfect candidates to serve as feedstock to produce fuels, chemicals, and materials, according to the biorefinery concept [2,9]. The successful conversion of LCB into added-value products depends on the effective deconstruction and identification of precursors with potential for further bioprocessing [10].

The pulp and paper industry is one of the world’s largest industries and is undoubtedly the major consumer of woody biomass [11,12]. About 146.5 million cubic meters of wood were estimated to be consumed by the European pulp and paper industries in 2020 [13]. Nowadays, the social and legislative pressure on the transition to the green economy in this specific industrial field is high. As a result, companies increasingly seek opportunities to invest in new technologies and adjust their technological processes within the biorefinery and circular economy concepts [14]. Around 11 million tons of waste are estimated to be generated by the pulp and paper industry annually in Europe alone. Different types of wastes are generated in pulp and paper mills along the process stages, comprising mainly wood residues (bark, sawdust, fines, rejects), spent pulping liquors, and sludge. Due to the complexity of these wastes, a deep knowledge of their chemical and structural composition is essential to achieve the fractionation needed to obtain value-added compounds [15].

This work intends to review the developed processes within the circular economy concept to convert wastes from the pulp and paper industry into added value bioproducts. One of the most popular bioproducts is bioethanol, and the different processes for its production will be reviewed. On the other hand, less studied bio-based products, but still very innovative and promising, are polyhydroxyalkanoates (PHA). Furthermore, considering the versatility of anaerobic digestion, biogas production was proposed as an alternative to close the loop, focusing on the circular economy model.

2. Wastes Resulting from Each Step of Pulp and Paper Processing: Composition and Potential for Valorization

During the pulp and paper processing, high volumes of water are consumed, and different waste streams are generated. The accurate determination of the chemical composition of waste streams is challenging since it depends on several factors, including wood source, manufacturing processes, the chemicals used, the operational conditions, the type and grade of final products or the wastewater treatment techniques [16–19]. The chemical composition is essential to envisage the possible routes for the valorization of each waste. Even for energetic purposes through thermochemical pathways, namely combustion and gasification, the knowledge of lignin and extractives’ content is fundamental since it is related to the calorific value [20].

This section identifies the different wastes obtained during the various steps involved in the pulp and paper production, and some of the typical and emergent applications are discussed. The pulp and paper processes are organized into the following steps: wood preparation, pulping, papermaking, and wastewater treatment, as described in Figure 1. Concerning the chemical characterization of wastes, most of the examples found in the literature are related to the Eucalyptus globulus. The popularity of this wood source for pulp and paper production is related to the high forest productivity coupled with the high cellulose and low lignin contents, which results in a high pulping yield [13,18,21–23].
Figure 1. Simplified flowsheet of the wood preparation, pulping, papermaking process and wastewater treatment processes.
2.1. Wood Preparation

Typically, wood preparation comprises harvesting, debarking, chipping, and screening processes [24].

2.1.1. Harvesting

The first step in pulp processing, wood harvesting, occurs in the forests, generating branches and stumps as wastes. In general, these wastes are left in the forest for soil nutrition or are forwarded to the pulp and paper sites for power generation in the biomass boiler [25–27].

Branches

In 2016, about 44 tons of branches were estimated to be generated per 100 tons of produced pulp [26]. Branches derived from *E. globulus* are mainly constituted by glucose and xylose, corresponding to about 47.0% and 15.1% (dry weight), respectively. In terms of lignin, this accounted for up to 25% [26]. Recently, Fernandes et al. [13] characterized *E. globulus* branches, accounting for a cellulose and hemicelluloses content of 41.3% and 22.3%, respectively. Klason lignin represented 17.9%, while ashes and extractives have a similar fraction of around 10.0% [13]. However, there is a scarcity of studies regarding the chemical composition of these wastes, derived from other wood sources and their possible valorization routes, turning them into a good opportunity for researchers to find feasible processes for converting branches into profitable applications within the circular economy concept.

Stumps

The stump involves the near-the-ground stem and the roots, constituting the basal part of the tree [28]. The chemical composition (oven-dry mass) of *E. globulus* stumps revealed about 67% carbohydrates, 24.8% lignin and 15% extractives [20]. Pinto et al. [29] also reported the characterization of the same wood source, with a monosaccharides fraction accounting for about 46.6% (27.7% glucose, 14.9% xylose, 0.8% galactose, 0.3% arabinose, 0.2% rhamnose), lignin 29.6% and extractives 12.9%. Compared to wood, the stumps usually have a higher concentration of extractives, which may have a negative impact on the subsequent pulping and bleaching operations [30].

The thermochemical conversion for bioenergy was already proposed for stumps [20,31]. This technology is based on the controlled heating and/or oxidation of biomass, encompassing pyrolysis, gasification, and combustion steps [32]. However, further studies are still needed to evaluate the consequences of applying combustion and gasification to this feedstock, namely operational problems due to extractives and characterization of solid by-products generated. This latter issue is fundamental to understanding if the resulting ashes could be incorporated into soils to minimize the effects caused by the removal of the stumps from the fields [31].

2.1.2. Debarking

The debarking is crucial since high bark content in wood leads to extended cooking times and increases the requirements for bleaching chemicals, negatively impacting the quantity and quality of the pulp produced [33,34].

Bark

Bark corresponds to about 11–15% (oven-dry mass) of the stem [21,34,35]. It is estimated that about 100–300 kg of bark is generated per ton of dry pulp produced [35]. In general, bark has a lower concentration of carbohydrates and lignin than wood, resulting in a higher content of ash and extractives [21,36]. However, a wide range of values for each parameter was found in the literature, which can be related to various factors, including geographic location, type of soil, tree age, climate and even the sampling method [18,19]. According to Neiva et al. [21], the polysaccharides fraction represented about 61.14% (oven-dry basis) of *E. globulus* bark, with glucose and xylose being the majority compounds, accounting for 37.47 and 15.21%, respectively. To a lower extent,
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lignin, extractives and ashes represented 21.86, 9.86 and 5.37%, respectively. Gomes et al. [37] also found a significant content of polysaccharides, 67.17% (oven-dry basis), 24.42% of lignin and a minimal content of extractives (2.04%) and ashes (2.63%). Pinto et al. [26] showed that E. globulus bark is composed by 41.0% of glucose, 12.3% of xylose, 28.9% of lignin, 8.9% of ashes and only 2.0% of extractives. In contrast, spruce bark contained lower polysaccharides content (41.7%), higher lignin (35.8%) and similar extractives (4.5%) and ashes (3.6%) fraction. A similar composition was reported by Frankó et al. [38].

The bark is commonly used for energy and steam production in the pulp and paper industry or even just left in the forest for soil nutrition [21,27]. Despite being a straightforward approach, bark incineration has a low economic return, generating problems related to fouling and corrosion due to the high ash content and environmental concerns [18,39]. Other applications already explored for bark include the production of wooden panels, the absorption of pollutants, and animal bedding [39]. Some authors have already studied the effect of bark incorporation into the pulping process reporting economic advantages for the pulping mill [36,40,41]. Nevertheless, an additional step before the pulping process may be fundamental to reduce the content of ashes and extractives, for a viable process yield. From a biorefinery perspective, sequential pre-extraction steps could also recover extractives, which have high added value applications in the food and pharmaceutical industries [13,20,28]. Several authors have focused on the recovery of extractives from E. globulus bark by supercritical fluid extraction [42–44]. Furthermore, research showing that E. globulus bark is an appropriate source of high-value triterpenic compounds was already published [27,45].

In the last years, research focused on more profitable valorization routes, namely for the production of biochar, bio-oil, and syngas, the extraction of bioactive compounds, the production of nanoparticles and fermentable sugars, among others [18,46]. The carbohydrates’ fraction of bark can be converted into a wide range of chemicals, including furans, sugar alcohols, and polyols, which can be employed to produce sweeteners, adhesives, and others [18,21]. To fully exploit the bark, the extraction of the polyphenolic fraction should be performed before converting the carbohydrates. Due to its anti-inflammatory, antioxidant, antimicrobial, and antibacterial properties, the polyphenolic fraction has the potential for high-added-value applications in food, cosmetics, and pharmaceutical industries [18,21,47]. Even though the many possible routes for the valorization of bark, with a market share estimated to grow continuously, most of the applications previously mentioned are not yet implemented at an industrial scale [39]. In fact, heterogeneous structure and diverse chemical composition are the two main challenges, making processes even more complex when compared to wood and constituting an obstacle to designing a universal technology for its valorization [18,39].

2.1.3. Chipping and Screening

The chipping process converts wood into smaller pieces. The wood chips are then submitted to a screening operation to ensure an optimum size for pulping processes [33,34]. On the screening, the wood chips are categorized according to their size. Oversized pieces must be re-chipped, whereas undersized chips should be rejected, but they still have the potential to be further valorized [48]. These small fibers are regularly designated by sawdust [34,49].

Sawdust

Currently, sawdust is commonly used for energy generation by the pulp and paper industry [50]. Other applications include manufacturing fiberboards and particle boards [15,51,52] and the production of pellets, a significant renewable solid fuel [51–53]. The small size of sawdust does not allow its use for pulping due to overprocessing [48]. Pinto et al. [26] showed that E. globulus sawdust is composed of 48.4% glucose, 13.9% xylose and 27.7% lignin, 1.1% ashes and 1.1% extractives. No considerable divergences were found for Eucalyptus grandis sawdust, accounting for polysaccharides fraction up to 50% and
lignin for about 30.3%. However, a negligible amount of ashes were detected (0.8%), while extractives represented 5.3% [48].

Due to its high polysaccharides content [54], sawdust is an attractive resource for microbial bioprocesses manufacturing biofuels, chemicals and materials [50]. Typically, there are no requirements for mechanical pretreatment before its conversion into bio-based products due to its small size [55]. Sawdust was already successfully applied in several processes, including its direct liquefaction to produce bio-oils [56], the production of xylooligosaccharides [57], nanofibrillated cellulose [58,59], activated carbons [60,61], and lightweight insulating bricks [62].

Therefore, most of the wastes derived from wood preparation are typically combusted for heat and power generation, resulting in a huge amount of fly ash. Fly ash is mainly composed of minerals, such as iron oxide, silica, and alumina. Moreover, it contains metal oxides, namely the oxides of sodium, calcium, magnesium, potassium, sulfur, and titanium [35]. Most of the ash is still landfilled [63]. Alternative applications that have been studied include the use of fly ash as binder, soil amendment, cementitious material, and absorbent [35,63].

2.2. Pulping Processes

The main aim of the pulping process is to convert wood into a fibrous mass designated by pulp [24]. Mechanical or chemical cooking methods can be applied, originating pulps with different properties and applications [24,34]. Chemical pulping is the most widely used process, representing up to 70% of the total pulp produced globally [64,65].

Typically, the chemical pulps are obtained after feeding the wood chips to the digester with the cooking liquor, aiming to perform LCB delignification. After cooking, the pulp is redirected to the washing unit to remove all impurities, namely cooking chemicals and dissolved organic compounds. There are two leading chemical pulping technologies, the sulfite and the kraft processes. From the former, the resulting waste stream is denominated sulfite spent liquor (SSL), and from the latter, black liquor (BL) [24,66]. Finally, the pulp is forwarded to be bleached and dried in different operational units.

2.2.1. Sulfite Process

The sulfite process is a flexible method, being operated at different pH values and is typically categorized according to the pH range of operation: acid bisulfite (pH 1–2), bisulfite (pH 3–5), neutral sulfite (pH 6–9), and alkaline sulfite (pH 10–13) [65]. Typically, the operating temperature ranges between 130 °C and 180 °C. In this process, the sulfur dioxide (the basic pulping reagent) is combined with a pulping base, usually Na⁺, Ca²⁺, Mg²⁺, or NH₄⁺ [65]. Mg²⁺ is the most common base used in the sulfite process since it leads to better penetration with cooking chemicals, resulting in a more uniform cooking process. Moreover, chemical recovery systems have been developed to regenerate pulping base and sulfur dioxide from SSL [66–68]. The main drawbacks of the sulfite process, compared to kraft pulping, are the higher cooking time, higher sulfur dioxide losses and the shorter range of wood species allowed for pulping [18].

Spent Sulfite Liquor (SSL)

SSL is a highly acidic and dark brown liquid by-product resulting from the sulfite process [67]. Its composition depends on the operational conditions, and the type of monosaccharides relies on the wood species used in the cooking process: softwood spent sulfite liquor (SSSL) predominantly contains hexoses, while hardwood spent sulfite liquor (HSSL) is mainly composed of pentoses [65]. Free monomeric sugars released from hemicelluloses hydrolysis are readily available in SSL, representing a clear advantage for microbial bioprocessing. Compared to LCB wastes, the utilization of SSL avoids the requirement of a previous extensive pretreatment and subsequent hydrolysis for bioprocessing [69]. Lignosulphonates and sugars are the major SSL components and are
recognized as promising raw materials for added-value products. SSL also contains extractives and volatile compounds, such as acetic acid, furfural, and methanol [67]. Marques et al. [68] quantified the major components of HSSL derived from *E. globulus*, namely lignosulfonates (ca. 46% of liquor dry matter) and sugars (ca. 25%). Xylose was the predominant sugar (ca. 68%), but galactose, glucose, rhamnose, arabinose and mannose were also identified. Moreover, acetic acid and furfural were also detected, and are considered potential inhibitors for further bioprocessing [68]. Compared to HSSL, SSSL from spruce (*Picea abies*) contained a slightly higher amount of lignosulfonates and mannose (ca. 43% wt) was the major sugar followed by xylose, galactose, glucose and arabinose [65].

SSLs are produced in large amounts, around 90 billion liters annually worldwide [70]. Typically, SSL is concentrated in multi-effect evaporators with water recovery followed by burning for energy production and chemicals recovery [64]. However, more promising alternatives for the valorization of SSL were developed, namely the recovery of lignosulfonates [67,71,72] and the production of several added-value products like xylitol, bioethanol, furfural, hydrogen, and PHA [73–77]. Other alternatives include the valorization of acetic acid, methanol, succinic acid, and vanillin, which were also reviewed [77].

The valorization of SSL has a well-established market for decades, using lignosulfonates as binders (pelletizing of animal feed, ceramics, dust control, fertilizers), dispersants (ceramics, dyes, pigments), emulsifiers (asphalt, inks, waxes), concrete plasticizing agents or adhesives [18,78–81]. Most of these applications rely on the good water-solubility of lignosulfonates [81].

### 2.2.2. Kraft Process

Kraft pulping promotes the reaction of an aqueous solution containing NaOH and Na₂S (commonly designated by white liquor) with the lignin present in wood at a temperature between 150 and 175 °C, pressure ranging from 7 to 12 bar, and pH values between 13 and 14 [18,24,34,82,83]. Currently, kraft pulping is the dominant chemical process worldwide, corresponding to 91% of chemical pulping and 75% of all pulp produced [18,84,85]. Kraft process widely replaced the sulfite pulping process due to the possibility of using a higher diversity of wood species, originating pulp with better quality properties, and providing a more efficient recovery of energy and chemicals [65,82,86,87]. Kraft pulp mills are designed to be self-sustainable, and in some cases, surplus energy is produced [24,84]. Compared to sulfite pulping, the main disadvantage of kraft pulping is its lower selectivity and yield [66], and the odorous emissions caused by sulfur compounds, which must be controlled due to environmental issues [18,24].

#### Black liquor (BL)

BL is one of the main sub-products of the kraft pulping process with the potential for valorization [18]. This by-product is a highly alkaline, viscous and brown colored liquid, resulting from the high lignin content [67]. About 10 tons of BL are estimated to be generated per ton of pulp produced, accounting for an annual global production of about 1.3 billion tons [18]. In general, BL is mainly composed of lignin (about 25 to 45% wt), saccharinic acids (25–35% wt), formic and acetic acid (10% wt) and extractives (3–5% wt). In minor amounts, it also contains methanol and inorganic elements (mainly sodium and sulfur). Compared to SSL, BL contains a negligible amount of sugars, hindering its bioprocessing [67,85,88]. The composition of BL varies considerably depending on the cooking process conditions and the origin of the wood [89].

Typically, the BL is evaporated to recover water, and the concentrated stream is burned in a recovery boiler for energy production and cooking chemicals recovery [84,90–92]. However, the technical lignin is a promising building block for producing a wide range of chemicals, contributing to fulfilling biorefinery sustainability requirements and overall economic feasibility [93,94]. LignoBoost® and LignoForce™ commercial technologies are already a reality in some pulping mills, allowing the recovery of kraft
lignin from BL by precipitation [90,93,95–97]. Some applications that have been explored include polyurethane foams, polylactic acid, resins, binder to replace bitumen in asphalt mixtures, among others [93,98]. Nevertheless, most of these applications require kraft lignin modifications to improve its potential as a starting material for chemical and polymer synthesis. There are still some technical barriers due to the structural complexity and heterogeneity of lignin [94]. Moreover, kraft lignin is water-soluble at high pH only and precipitates after dilution or lowering of the pH [81].

During the chemical recovery cycle of BL, inorganic wastes containing different minerals are generated, including green liquor dregs, calcite mud, and slacker grits. Dregs have been applied for correcting soil acidity, fertilizer and wastewater treatment. Due to the calcium carbonate composition, grits and lime mud have used as replacement of calcareous raw materials in construction sector. Moreover, lime mud has been used as a soil remedial agent or fertilizer [35].

2.3. Papermaking Process

The papermaking process can be divided into five main stages: (a) stock preparation, (b) web formation, (c) press, (d) drying, and (e) finishing. This process can be described as a continuous dewatering operation to increase the dry content of the paper web until the end of the process [49,66]. The main aim of the stock preparation consists of obtaining fibers to match the requirements of the papermaking process with the desired properties and quality of the final product. Therefore, stock preparation involves several operations, namely refining and blending additives, aiming to improve the paper’s strength and optical properties [49,66]. The pulp suspension is transformed into a continuous sheet during the web formation through a uniformly distributed flow into the machine direction. This step allows for a high moisture reduction by about 80–85% [49,66]. The press section aims to remove water by applying mechanical pressure. In the drying section, the residual moisture present in the paper sheet is removed by heating, achieving a dryness ranging between 90 and 98% [49,66]. The last step, commonly designated as finishing, includes the transformation operations, namely calendaring, winding, sheeting, and packaging [49,66]. During this stage, a large volume of wastewater is generated [99].

2.4. Wastewater Treatment

Large volumes of wastewater are generated during several pulp and paper operations, namely wood preparation, pulp washing and bleaching and paper manufacturing [99–102]. The properties of wastewater derived from each process stage are highly dependent on the type of raw material, pulping process, the recirculation of effluent and the amount of water used. Due to the presence of complex organic and inorganic compounds, several methods have been employed for industrial wastewater treatment [99].

Pulp and Paper Mill Sludge

The spent biomass and residual organic material remaining after wastewater treatment, designated by pulp and paper mill sludge (PPMS), are a significant source of waste derived from the pulp and paper industries [15,102]. It is estimated that from one ton of paper produced, about 40–50 kg of sludge (dry basis) are generated. In general, the wastewater from a pulp mill is subjected to primary and secondary wastewater treatments, from which are generated the respective PPMSs that correspond to about 70% and 30% of the total sludge generated, respectively [16]. The primary treatment removes the suspended solids [87] through sedimentation and floatation [102]. The resulting, primary PPMS is rich in fillers, such as calcium carbonate, and titanium dioxide, and screen rejects, such as fines fibers [102–104]. In terms of chemical composition, primary PPMS comprises mainly 45–60% wt of carbohydrates (mostly xylan), 35–50% wt of inorganic matter (ashes, mostly calcium carbonate) and lignin (5–20% wt) [105].

Secondary PPMS is the residue with the highest microbial content resulting from the biological treatment of wastewater [102,106]. The microbial populations developed in
these systems use organic matter as substrate for oxidation to carbon dioxide, water, and growth, originating more microbial biomass [16,102]. For this reason, the secondary PPMS is often designated as waste activated sludge, biosludge or biological sludge [102]. The two PPMSs differ in the organic content, ash content and heating value and are often combined to facilitate their handling, forming the so-called “mixed PPMS” [102,104,106,107].

Typical applications of PPMS comprise landfilling, composting, incineration or combustion [102]. However, these applications have low economic value and raise severe environmental and sustainable issues [15,102]. The utilization of PPMS should be a target for the circular economy due to the potential negative costs resulting from its disposal, that account for about 60% of the wastewater treatment operating costs [104,108,109]. Furthermore, increasingly strict environmental restrictions are being imposed on pulp and paper industries contributing to higher disposal costs [104,110,111]. Since 1986, sewage sludge for land applications has been restricted in the EU. The EU Directive (86/278/EEC) defined specific requirements concerning the quality of sludge, the soil for application, the loading rate, and the crops that may be grown on the treated lands [112]. Alternatively, PPMS has been used for energy recovery through combustion, pyrolysis, direct liquefaction, anaerobic digestion for biogas production, and bioethanol production [15,102]. Another promising application includes the integration of sludge in materials, such as biocomposites, bioplastics, cement and asphalt [102].

3. Deconstructing Residues for Further Valorization through Bioprocessing

The complexity of residues from the pulp and paper industry generally requires the use of deconstruction technologies before their valorization. These technologies are crucial to improving bioprocessability through promoting the accessibility of hydrolytic agents to the lignocellulosic matrix or reducing/neutralizing the inhibitors present. The selection of the appropriate technology depends on the following factors: the type of raw material, energy requirements, operational conditions, environmental impact, inhibitory compounds released, and cost-effectiveness [15,113,114].

For the residues deriving from wood preparation (branches, stumps, wood, bark and sawdust), categorized as LCB, two main steps are generally required before bioprocessing, namely, pretreatment and hydrolysis [23,115–118]. However, to minimize the harmful effect of the inhibitors, some detoxification technologies are required [116,119]. For the pulp and paper mill sludge resulting from wastewater treatment, some pretreatments were performed, focusing essentially on the improvement of sugars hydrolysis yields. In general, these pretreatments include de-ashing operations [105,120].

3.1. Residues from Wood Preparation

3.1.1. Lignocellulosic Biomass Pretreatments

LCB is mainly composed of a complex network of cellulose (33–54%), hemicelluloses (11–37%) and lignin (17–32%) [121]. This composition varies substantially according to the species, genera, weather, soil fertility, among others [115]. Due to the recalcitrance of LCB and to ensure the access of hydrolysis agents to cellulose and hemicelluloses, lignin separation needs to be promoted before further bioprocessing [115]. The pretreatment step represents a big challenge, mainly due to the complex and organized morphological structure of LCB that determines the intrinsic characteristics such as recalcitrance and heterogeneity of residues [122]. Moreover, the physicochemical properties of LCB are highly dependent on the origin of biomass and influence the performance, yield, and type of products generated during the pretreatment [123,124]. An efficient pretreatment should avoid the degradation of sugars. Depending on the selected pretreatment, the separation of each LCB fraction into three streams for further valorization can also be promoted, contributing to the economic feasibility [113,125–127]. For all reasons abovementioned, designing a unique pretreatment that generates low concentrations of inhibitory
compounds and is simultaneously efficient and economical is rather complex [116]. This complexity can be confirmed by several recent review papers describing the different pretreatment methods applied to the LCB [113,128–130].

Since the kraft pulping process allows for the separation of lignin, Pinto et al. [26] assessed its performance in branches, sawdust, and bark from E. globulus. Using the conventional pulping process as a pretreatment step for residues can signify a new paradigm for the pulp and paper industry. Besides being a well-established technology to produce pulp, this is an alternative with relatively low investment costs and risks since the necessary process units already exist in pulping mills [84]. Among all the wastes tested from wood preparation, branches were demonstrated to be the best source of polysaccharides due to the higher pulp yield [26]. However, there is a scarcity of studies related to the branches, namely their chemical composition, possible pretreatments, and valorization routes. Stumps typically contain a significant amount of contaminants, including soil and sand. Therefore, caution is crucial during collecting, handling, and processing to avoid contamination [20]. Sometimes, an additional cleaning step may be required [20,30]. Regarding bark, the use of a pretreatment step has been extensively studied [18]. The main pretreatments employed were kraft pulping and hot water extraction (HWE) [26,40,41,131,132]. Besides these two processes, steam explosion (SE) was also extensively applied to sawdust [48,50,59,133–135]. Other tested alternatives included mechanical refining, microwave irradiation, organosolv, and soda pulping [48,50,135].

3.1.2. Hydrolysis of Polysaccharides

After the appropriate pretreatment, the hydrolysis process converts the polysaccharides from cellulose and hemicelluloses into monosaccharides for further microbial conversion to added-value products [116,117]. The hydrolysis process can be catalyzed mainly by acids or enzymes [115,136].

Acid hydrolysis can be carried out by using sulfuric acid diluted (0.5–1.5%) or concentrated acid (30–70%) [115,116]. Despite the low cost of this method, it presents problems of security and corrosion. Furthermore, during this process, some inhibitors, such as furfural, acetic acid, and phenolic compounds, may be formed that hinder biological processes [105,137].

Enzymatic hydrolysis (EH) presents several advantages over acid hydrolysis, such as higher efficiency, lower corrosion and security issues. Moreover, it releases a lower amount of microbial inhibitors. Furthermore, this method is considered eco-friendly due to milder reaction conditions (45–55 °C and pH 4–5) and the biodegradability of enzymes [121]. Cellulose and hemicelluloses are hydrolyzed by cellulases and hemicellulases systems, respectively [116]. Cellulases attack β-1,4 glycosidic bonds of cellulose, generating glucose. Hemicelluloses are more susceptible to hydrolysis than cellulose due to their amorphous and branched nature [136,138]. However, the degradation of hemicelluloses requires complex systems of xylanases and accessory enzymes due to the different types of linkages in their chains [116,139]. Xylose, galactose, mannose and arabinose are the main monosaccharides released [82,136]. The slow rate of the EH can be a result from the inhibition of cellulase activity caused by the presence of several compounds, namely lignin and xylan [121]. Besides the non-productive binding of cellulases to lignin and hemicelluloses, EH is also inhibited by soluble carbohydrates (glucose, cellobiose, oligosaccharides derived from hemicelluloses) and soluble aromatic compounds (e.g., phenolics) present in hydrolysis slurry [140]. Some promising strategies to overcome this problem include the production of enzymes with enhanced catalytic activity and the optimization of the operating conditions [121,122]. Even with some costs decreasing, the cost of the commercial enzymatic consortia is another main bottleneck of this process, hindering the scale-up [121]. Therefore, some strategies have been proposed to improve the economic feasibility of this process, namely operation with high solids loading content and fed-batch [121,141]. High gravity technology that applies high
substrate loadings has economic and environmental benefits. However, this approach could increase the level of inhibitors in reaction broth, decreasing the hydrolysis rate by cellulases and the growth rate of the microorganisms. Furthermore, high substrate loading increases the viscosity, hindering the mass transfer phenomena, and increases mixing power and impeller speed [142–144]. Few studies were found describing the EH of wood-derived wastes. Asada et al. [133] compared the EH performance of sawdust and residues resulting from extractions with water and methanol of steam-exploded sawdust. The SE pretreatment was performed at 45 atm for five minutes resulting in the highest glucose yield (81%) during the EH step, producing 27.6 g L\(^{-1}\) of glucose from 50 g L\(^{-1}\) of residue. Guigou et al. [48] subjected sawdust from \(E.\) grandis to several combined pretreatments to fractionate biomass for further valorization. Firstly, the sawdust was pretreated by autohydrolysis at 170 °C and 40 min. After this first step, three assays with an additional pretreatment were performed: mechanical refining, kraft pulping, and soda pulping. According to the results reported, all additional pretreatments positively affected the EH efficiency. The highest EH efficiency of 95 ± 2% was obtained for the autohydrolysis followed by kraft pulping (140 min, 2.7% active alkali) [48]. Kemppainen et al. [145] studied the fermentability of the spruce bark subjected to three pretreatments: SE, HWE, and in combination (HWE+SE). Both HWE and the sequential pretreatment led to a similar hydrolysis yield of 63% after using cellulases supplemented with β-glucosidase and pectinase. The information concerning integrated configurations (such as SSF) is detailed in the corresponding section.

3.2. Residues from Pulping Processes

From the point of view of residues valorization, as abovementioned, the presence of monomeric sugars represents a high competitive advantage of SSL [69]. The main challenge associated with SSL bioprocessing is the presence of some degradation products, such as acetic acid, furfural and low molecular weight lignosulfonates, that inhibit microbial metabolic activities [53,77,146,147]. The detoxification of SSL is a way to reduce these inhibitory effects focused on improving its bioprocessability through the neutralization and/or removal of the inhibitors [116,119]. Noteworthy, these processes are time-consuming and may lead to loss of sugars incurring additional costs [117].

The pretreatment of SSLs is usually focused on the removal of these inhibitory compounds and the separation of lignosulfonates and sugars fractions. SSL purification and fractionating were already studied using ion exchange resins [147,148]. Alternatively, biological methods are generally considered more environmentally friendly than typical detoxification methods, namely due to minimal chemicals demand and milder operational conditions [149,150]. A successful improvement in fermentability of HSSL was reached by Pereira et al. [119], after promoting its biological detoxification by \(P.\) variotii NRRL-1115, using a sequential batch reactor.

3.3. Residues from Wastewater Treatment

Some examples of pretreatments applied to primary PPMS included hot air oven, electrohydrolysis and steam explosion [151]. For secondary PPMS, pretreatments mostly tested are hydrothermal, ultrasounds and chemical processes [151]. Veluchamy and Kalamdhad [152] reviewed the main pretreatments employed to PPMS reported in the literature. A similar summary was presented by Kumar et al. [151], who reviewed the pretreatments performed before submitting different types of PPMS to anaerobic digestion, aiming to boost methane production. Furthermore, the significant amount of ashes from sludge, mainly calcium carbonate (CaCO\(_3\)), may hinder the bioconversion process leading to a low product concentration due to the irreversible binding of enzymes to ash [102,103,105,153]. Some strategies to overcome this limitation were studied, namely through ash removal [153,154]. Kang et al. [120] showed that de-ashing primary PPMS allowed a reduction in the enzyme dosage of about 30%. The challenge of the de-ashing operation is related to the conservation of the carbohydrates fraction, whereas keeping
the ash content low enough to ensure the fermentability of the materials [120]. Mendes et al. [105] tested several pretreatments for primary PPMS, namely acid neutralization through the addition of chemical agents, such as EDTA, CH₃COOH, HNO₃, HCl, H₂SO₄, or spent acid (a residual stream from the pulp and paper mill). The authors also evaluated a sequence of washing cycles with reused water as an alternative. Finally, the CO₂ bubbling was also assessed. For EH assays, only the primary PPMS pretreated with HCl and spent acid was tested using 35 FPU g⁻¹ carbohydrates of commercial Celllic CTec2 or Accellerase 1500. The authors demonstrated that Celllic CTec2 was the most suitable enzymatic consortium for producing cellulosic sugars from primary PPMS, regardless of the pretreatment technology or initial carbohydrate content. Untreated primary PPMS provided conversion yields lower than 20% after 24 h. The EH with Celllic CTec2 using an initial carbohydrate concentration of 46 g L⁻¹ of primary PPMS pretreated with HCl has resulted in a concentration of glucose and xylose of 33.1 g L⁻¹ and 7.3 g L⁻¹, respectively, corresponding to the highest EH yield of 88% [105]. Dey et al. [155] submitted primary PPMS (previously subjected to sequential steam explosion and sodium hydroxide pretreatments) to fed-batch EH with 18% (w w⁻¹) of total solids loading (7% followed by 6% and 5% (w w⁻¹)). The experiment was conducted at 50 ºC, 300 rpm, two liter working volume and an enzymatic loading of 158 FPU g⁻¹ total solids. After 60 h, a maximum glucose and xylose concentration of 79.56 g L⁻¹ and 8.65 g L⁻¹ were attained, respectively. Authors also concluded that the addition of the overall enzymatic consortium at the beginning benefited the overall performance and solids loading higher than 18% (w w⁻¹) did not boost the release of sugars [155]. Recently, Arthur et al. [156] accomplished considerable savings in overall enzyme dosages by applying cellulase recycling strategies in PPMS ethanol fermentation. The performance of simultaneous saccharification and fermentation (SSF) configuration was maintained during consecutive experiments by recycling either the enzyme-containing supernatant or whole broth with no requirements for enzyme separation methods. This approach could represent considerable cost savings for the overall process [156].

4. Getting Value from Wastes: Production of Bioethanol, PHA and Biogas

The residues generated by the pulp and paper industry have the potential to be converted into bioproducts after suitable deconstruction technologies. Several products were successfully obtained by microbial conversion, namely bioethanol, biomethane, biohydrogen, succinic acid, and PHA [157]. Among them, bioethanol, PHA and biogas are some of the most promising, and the current state of their production from wastes derived from the pulp and paper industry is discussed in this section.

4.1. Bioethanol

Currently, one of the main applications for anhydrous bioethanol in the EU is, as biofuel, blended with gasoline in different proportions [136,158,159]. Additionally, ethanol is recognized as a promising building block for the chemicals platform and is utilized as a commodity in the cosmetic and pharmaceutical industries [64,136,158,160].

Cellulosic bioethanol is a second generation biofuel since its production does not interfere with the food chain and is one of the main alternatives to the first generation, obtained from food crops [158,160,161]. To promote the use of second generation biofuels, the EU established Renewable Energy Directive II, which defined a target of at least 3.5% of transportation fuels derived from advanced biofuels in 2030 [140,162–164]. Moreover, the EU set out targets to limit the share of first generation biofuels to 7% by 2030 [162,163].

Currently, bioethanol production can follow different configurations. The first configuration developed was the separate hydrolysis and fermentation (SHF). The main advantage of SHF is the operation of each step can be optimized separately. However, during EH, the accumulation of monosaccharides, namely glucose, often causes product inhibition, which is a significant drawback [125]. Then, to overcome this limitation, the
SSF configuration, with both saccharification and fermentation steps in a single reaction vessel, was proposed [11,116,165]. This approach avoids enzymatic inhibition since the monosaccharides formed during hydrolysis are immediately fermented into ethanol. This configuration is more economically attractive since it reduces operation time and requires less equipment [116,165]. However, the SSF process requires a compromise between the optimal working temperature to maximize the enzymatic activity, usually between 45 °C and 60 °C, and the suitable temperature for the ethanol-producing microbial strains in the range of 25–35 °C [166,167]. Some authors have already upgraded this configuration to simultaneous saccharification and co-fermentation (SSCF), aiming to consume both hexoses and pentoses. For that, a recombinant or natural C5 fermenting yeast is required. Alternatively, a consortium of microorganisms can be used [168,169].

Another emerging configuration is the consolidated bioprocessing (CBP), which integrates all the stages for the conversion of LCB into ethanol in a single step, including microbial enzymes production, hydrolysis, and fermentation. In this configuration, genetically engineered ethanologenic yeast strains are required to avoid the need for the addition of exogenous enzymes [11,165,169]. Moreover, this configuration reduces the number of unit operations and, consequently, the maintenance and capital costs [166]. However, the conversion efficiency is still low and it is a time-consuming process (from three to twelve days), hindering its application on a commercial scale [115,170].

Several residues from the pulp and paper industry were already tested for bioethanol production. These studies are summarized in Table 1, referring to the feedstock, pretreatment, configuration, microorganism, as well as the main process parameters, such as ethanol concentration and productivity.

4.1.1. Bioethanol Production from Sawdust

Guigou et al. [48] subjected sawdust from *E. grandis* to several combined pretreatments to fractionate biomass for further valorization. Firstly, the sawdust was pretreated by autohydrolysis, and after that, three additional pretreatments were evaluated: mechanical refining, kraft pulping, and soda pulping. Following a pre-saccharification and simultaneous saccharification and fermentation (PS-SSF), the best results were achieved for the combination of autohydrolysis and soda pulping, which provided the highest ethanol yield of 85 ± 1%, with a maximum ethanol concentration of 58 ± 3 g L⁻¹ and a productivity of 1.2 ± 0.3 g L⁻¹ h⁻¹ [48]. These results are summarized in Table 1.

4.1.2. Bioethanol Production from Bark

Regarding the conversion of *E. globulus* bark into bioethanol, studies are scarce (Table 1). Recently, Amândio et al. [132] assessed the bioethanol production from *E. globulus* bark previously submitted to kraft pulping through SHF configuration. The maximum ethanol concentration of 50.8 ± 0.5 g L⁻¹ was achieved using Ethanol Red® (*Saccharomyces cerevisiae* yeast) after 20.5 h, corresponding to the productivity of 2.48 ± 0.02 g L⁻¹ h⁻¹ and 81.0 ± 0.6% of the theoretical yield (0.511 g ethanol g⁻¹ sugars) [132].

Gomes et al. [37] tested the fermentability of the hydrolysate obtained from solids derived from hydrothermal pretreatment of *E. globulus* bark. Two different strategies were attempted for bioethanol production: SSF and PS-SSF. The highest ethanol production (about 38 g L⁻¹) was achieved through the PS-SSF approach, with a solids loading of 17.5% and nutrient supplementation, with a conversion efficiency of 73% of the theoretical yield and a productivity of 0.52 g L⁻¹ h⁻¹ [37].

Kemppainen et al. [145] studied the SSF configuration using spruce bark previously pretreated through HWE and HWE+SE. For bark consistency of 15%, a maximum ethanol concentration of 21.0 g L⁻¹ and yield of 66.4% was attained from HWE+SE spruce bark. HWE spruce bark achieved only a slight reduction in performance [145].

Frankó et al. [38] studied the use of mixtures of woodchips with different ratios of spruce (*Picea abies*) bark as the substrate for bioethanol production through both
configurations, SHF and SSF. Regardless of the bark content, SSF proved to be the most efficient considering the overall efficiency of the process. Overall, the mixture with the bark content of 30% (dry matter) provided the highest ethanol yield, 76.8% and 77.5% for SHF and SSF, respectively. The SSF process attained ethanol concentrations from 20.9 g L\(^{-1}\) to 45.8 g L\(^{-1}\) for the proportions of bark from 100–0% (only bark-free spruce woodchips), respectively. Therefore, an increase in the bark proportion negatively affected the ethanol conversion yield and resulted in higher extractives and ash contents than wood chips [38]. It is worthwhile mentioning that due to the lower carbohydrates content of bark, the production of ethanol that could be expected, per dry ton metric of bark, would be lower than for wood [36].

4.1.3. Bioethanol Production from SSL

SSL from hardwood (HSSL) was the object of several studies focused on assessing its fermentability since it is a waste already enriched in monosaccharides, especially in xylose, although with some lignin derivatives [76,127,171]. Nigam [172] studied bioethanol production from HSSL of *E. globulus* by *Scheffersomyces stipitis* Y-7124 after boiling and overliming with Ca(OH)\(_2\) as a detoxification step. The gradual adaptation of *S. stipitis* to HSSL coupled with the fermentation step carried out using microaerophilic conditions (an oxygen transfer rate of two mmol O\(_2\) L\(^{-1}\) h\(^{-1}\)) proved to be efficient strategies, providing an ethanol concentration of about 20 g L\(^{-1}\), with a productivity of 0.44 g L\(^{-1}\) h\(^{-1}\) and a yield of about 82% [172].

Xavier et al. [147] achieved the best fermentation yield (96%) and productivity (1.22 g L\(^{-1}\) h\(^{-1}\)) for the ion-exchange purified HSSL at pH 5.8. A maximum ethanol concentration of about 8.1 g L\(^{-1}\) was attained, a value slightly lower than the operation at pH 7.0 [147].

By using a bio-detoxified HSSL by *S. stipitis* NRRL Y-7124, Pereira et al. [119] achieved a maximum concentration of 2.4 g L\(^{-1}\) after 28 h, corresponding to an ethanol yield of 47%. Later, Pereira et al. [173] successfully improved ethanol production (4.60 g L\(^{-1}\)) by using an evolutionary engineering strategy to adapt *S. stipitis* NRRL Y-7124 to 60% (v v\(^{-1}\)) HSSL [173]. The stable isolate *S. stipitis* Cs showed higher resistance to inhibitors than the parental strain and better performance in a two-stage aeration fermentation strategy with 60% of HSSL [74]. This approach allowed one to achieve an ethanol concentration of 12.2 g L\(^{-1}\), corresponding to an ethanol efficiency of 74.4%, with no requirements for the detoxification step [74]. Table 1 summarizes all these studies.

4.1.4. Bioethanol Production from Pulp and Paper Mill Sludge (PPMS)

Several studies regarding PPMS valorization for bioethanol production were already published (Table 1). Mendes et al. [174] compared two different approaches for ethanol production from PPMS: SSF batch and SSF fed-batch operation modes. The Novozymes commercial consortium (NS 22192) was used for the EH and the *S. cerevisiae* ATCC 26602 yeast for the fermentation step. SSF batch process was reported to achieve the best results, presenting higher ethanol productivity, 0.78 g L\(^{-1}\) h\(^{-1}\) instead of 0.52 g L\(^{-1}\) h\(^{-1}\) and a slightly higher ethanol concentration, 41.7 g L\(^{-1}\) instead of 39.7 g L\(^{-1}\) for fed-batch [174].

Mendes et al. [105] tested the hydrolysates derived from primary PPMS, composed of 82–85% of glucose and 15–18% of xylose, with two different yeasts, *S. stipitis* and *S. cerevisiae*. The PPMS was previously submitted to hydrolysis with HCl and spent acid. Regardless of pretreatment, the highest ethanol production was achieved by *S. stipitis*. Fermentation of primary PPMS pretreated with HCl produced an ethanol concentration of 10.5 g L\(^{-1}\), while pretreated with spent acid resulted in about 8.5 g L\(^{-1}\). In both cases, the ethanol yield was 76.5% [105].

Kang et al. [175] submitted primary PPMS to SSF and SSCF configurations. The SSF was carried out with *S. cerevisiae* ATCC-200062 strain, while in the SSCF, the recombinant *Escherichia coli* ATCC-55124, with the ability to ferment xylose, was used together with *S. cerevisiae*. Ethanol concentrations of 25.5 g L\(^{-1}\) and 32.5 g L\(^{-1}\) were reported for SSF and SSCF in batch, respectively, corresponding to theoretical yields of 74.5% and 95.8%. Fed-
batch assays allowed significantly higher ethanol concentrations of 45.0 g L\(^{-1}\) and 42.0 g L\(^{-1}\) for SSF and SSCF to be reached, but with lower yields of 70% and 68%, respectively. Despite the high ash content of primary PPMS, it could be successfully converted to ethanol. Nevertheless, the high ash content limited operation at a high solids loading, resulting in low product concentration.

To overcome this constraint and improve the process yield, Kang et al. [120] tested the fermentability of de-ashed primary PPMS. The authors showed that de-ashing of primary PPMS allowed a considerable reduction in the enzyme dosage and, simultaneously, improved ethanol production, achieving a concentration of 24.7 g L\(^{-1}\) and 30.3 g L\(^{-1}\), corresponding to 72.8% and 73.6% of the theoretical yield for SSF and SSCF, respectively. The fed-batch strategy boosted ethanol production to 47.8 g L\(^{-1}\) and 60 g L\(^{-1}\) for SSF and SSCF, respectively [120].
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Pretreatment</th>
<th>Configuration</th>
<th>Enzymatic Consortium</th>
<th>Hydrolysis Efficiency (%)</th>
<th>Microorganism</th>
<th>[Ethanol]$_{max}$ (g L$^{-1}$)</th>
<th>Prod ethanol (g L$^{-1}$ h$^{-1}$)</th>
<th>Yethanol (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eucalyptus sawdust</td>
<td>Autohydrolysis + soda pulping</td>
<td>PS-SSF</td>
<td>Cellic Ctec2</td>
<td>N.A.</td>
<td>S. cerevisiae PE-2</td>
<td>58 ± 3</td>
<td>1.2 ± 0.3</td>
<td>85 ± 1</td>
<td>[48]</td>
</tr>
<tr>
<td>E. globulus bark</td>
<td>Kraft</td>
<td>SHF</td>
<td>Cellic Ctec2</td>
<td>N.R.</td>
<td>Ethanol Red®</td>
<td>50.8 ± 0.5</td>
<td>2.48 ± 0.02</td>
<td>81.0 ± 0.6</td>
<td>[132]</td>
</tr>
<tr>
<td>E. globulus bark</td>
<td>Hydrothermal</td>
<td>PS-SSF</td>
<td>Cellic Ctec2</td>
<td>N.A.</td>
<td>Ethanol Red®</td>
<td>38.03 ± 0.33</td>
<td>0.52</td>
<td>73.14</td>
<td>[37]</td>
</tr>
<tr>
<td>Spruce bark</td>
<td>HWE+SE</td>
<td>SSF</td>
<td>Cellic Ctec2</td>
<td>N.A.</td>
<td>S. cerevisiae VTT-B-08014</td>
<td>21.0</td>
<td>N.R.</td>
<td>66.4</td>
<td>[145]</td>
</tr>
<tr>
<td>Spruce wood chips mixed with bark</td>
<td>SO²-catalysed steam</td>
<td>SSF</td>
<td>Cellic Ctec3</td>
<td>N.A.</td>
<td>Ethanol Red®</td>
<td>34.5 ± 0.4</td>
<td>2.5 ± 0</td>
<td>77.5 ± 1.3</td>
<td>[38]</td>
</tr>
<tr>
<td>HSSL</td>
<td>Boiling + overliming with Ca(OH)$_2$</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>S. stipitis NRRL-7124</td>
<td>20.20 ± 0.43</td>
<td>0.44 ± 0.02</td>
<td>82.00 ± 0.41</td>
<td>[172]</td>
</tr>
<tr>
<td>HSSL</td>
<td>Ion-exchange resins</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>S. stipitis NRRL-7124</td>
<td>8.1</td>
<td>1.22</td>
<td>96</td>
<td>[147]</td>
</tr>
<tr>
<td>HSSL</td>
<td>Biological detoxification by using P. variotii NRRL-1115</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>S. stipitis NRRL-7124</td>
<td>2.4</td>
<td>0.09</td>
<td>47.0</td>
<td>[119]</td>
</tr>
<tr>
<td>HSSL</td>
<td>pH adjustment to 7.0 with KOH followed by aeration</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>S. stipitis C4 isolate</td>
<td>4.60</td>
<td>0.05</td>
<td>32</td>
<td>[173]</td>
</tr>
<tr>
<td>HSSL</td>
<td>pH adjustment to 7.0 with KOH followed by aeration</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>S. stipitis C4 isolate</td>
<td>12.2</td>
<td>0.03</td>
<td>74.4</td>
<td>[74]</td>
</tr>
<tr>
<td>Primary PPMS</td>
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<td>SSF</td>
<td>Enzymatic extract NS 22192</td>
<td>N.A.</td>
<td>S. cerevisiae ATCC 26602</td>
<td>41.7 ± 1.2</td>
<td>0.78 ± 0.03</td>
<td>48.9 ± 1.4</td>
<td>[174]</td>
</tr>
<tr>
<td>Primary PPMS</td>
<td>HCl</td>
<td>SHF</td>
<td>Cellic CTeC2</td>
<td>88</td>
<td>S. stipitis DSM 3651</td>
<td>10.5</td>
<td>0.20</td>
<td>76.5</td>
<td>[105]</td>
</tr>
<tr>
<td>Primary PPMS</td>
<td>Spent acid</td>
<td>SHF</td>
<td>Cellic CTeC2</td>
<td>72</td>
<td>S. stipitis DSM 3651</td>
<td>8.5</td>
<td>0.16</td>
<td>76.5</td>
<td>[105]</td>
</tr>
<tr>
<td>Primary PPMS</td>
<td>N.A.</td>
<td>SSF</td>
<td>Spezyme CP and Novozyme-188</td>
<td>N.R.</td>
<td>S. cerevisiae ATCC-200062</td>
<td>25.5</td>
<td>N.R.</td>
<td>74.5</td>
<td>[175]</td>
</tr>
<tr>
<td>Primary PPMS</td>
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<td>Fed-batch SSF</td>
<td>Spezyme CP and Novozyme-188</td>
<td>N.R.</td>
<td>S. cerevisiae ATCC-200062</td>
<td>45.0</td>
<td>N.R.</td>
<td>70</td>
<td>[175]</td>
</tr>
<tr>
<td>Primary PPMS</td>
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<td>Spezyme CP and Novozyme-188</td>
<td>N.R.</td>
<td>E. coli ATCC 55124</td>
<td>32.5</td>
<td>N.R.</td>
<td>95.8</td>
<td>[175]</td>
</tr>
<tr>
<td>Primary PPMS</td>
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<td>Fed-batch SSCF</td>
<td>Spezyme CP and Novozyme-188</td>
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<td>E. coli ATCC 55124</td>
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<td>N.R.</td>
<td>68</td>
<td>[175]</td>
</tr>
<tr>
<td>Primary PPMS</td>
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<td>Spezyme CP and Novozyme-188</td>
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<td>S. cerevisiae ATCC-200062</td>
<td>24.7</td>
<td>N.R.</td>
<td>72.8</td>
<td>[120]</td>
</tr>
<tr>
<td>--------------</td>
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</tr>
<tr>
<td>Primary PPMS</td>
<td>De-ashing</td>
<td>Fed-batch SSF</td>
<td>Spezyme CP and Novozyme-188</td>
<td>S. cerevisiae ATCC-200062</td>
<td>60.0</td>
<td>N.R.</td>
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<td>[120]</td>
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<tr>
<td>Primary PPMS</td>
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<td>N.R.</td>
<td>73.6</td>
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<tr>
<td>Primary PPMS</td>
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<td>Fed-batch SSCF</td>
<td>Spezyme CP and Novozyme-188</td>
<td>E. coli ATCC 55124</td>
<td>47.8</td>
<td>N.R.</td>
<td>70</td>
<td>[120]</td>
<td></td>
</tr>
</tbody>
</table>
4.2. Polyhydroxyalkanoates (PHA)

PHA are bio-based and biodegradable biopolymers and, consequently, excellent candidates to replace conventional plastics from a sustainable point of view. They are composed of monomeric units known as hydroxyalkanoates, with 3-hydroxybutyrate (HB) and 3-hydroxyvalerate (HV) being the most common [176]. The high diversity of monomers of PHA and all their possible combination allows for a wide range of characteristics, from thermoplastics to elastomers. This possibility raised the attention of different industrial branches, making them suitable for many applications and markets, including in the medical field, and as building blocks for the synthesis of fine chemicals [177].

Several bacteria and archaea synthesize PHA as intracellular carbon and energy storage [176]. This storage occurs under conditions of nutrients’ excess or growth limitations. The accumulated polymers can be depolymerized when the monomers are needed for the biosynthesis of other metabolites or energy generation [177]. Their production is reported by pure cultures or mixed microbial cultures (MMC), microbial populations of unknown composition, like activated sludge from wastewater treatment plants [178]. While pure cultures produce PHA from a diversity of substrates, MMC require a feeding enriched in short chain organic acids (SCOA). Despite the necessity of a preliminary step of acidification of residues, MMC processes do not require sterile conditions. Given such a wide range of producers, PHA production was already tested using several complex substrate sources, like LCB.

As shown in the revision by Al-Battashi et al. [179], LCB is a suitable substrate for PHA production, but its processing often requires preliminary pretreatment and hydrolysis steps. Different types of wastes from the pulp and paper industry were already used as substrates for PHA production, ranging from wood hydrolysates to industrial wastewaters [179]. Table 2 summarizes those studies, referring to the type of carbon source used, the main process parameters, and polymer characteristics.

4.2.1. PHA Production from Residues of Wood Preparation

Dried poplar particles were submitted to HWE pretreatment and subsequent EH by Yin et al. [171]. The hydrolysates produced were used with acetic acid as a co-substrate for PHA production by activated sludge. The highest polymer concentration achieved in the accumulation assays was 2.3 g L\(^{-1}\) of the copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P(3HB-co-3HV)), after optimization of the carbon/nitrogen (C/N) ratio to 33 g g\(^{-1}\) and pH to 8 [171], as shown in Table 2.

Waste poplar biomass was also used as raw material using MMC. After an acidified stream (containing acetic, propionic and butyric acids) production, the MMC was able to accumulate PHA up to a content of 50% of P(HB-co-HV) with a yield of 0.71 g COD PHA g\(^{-1}\) COD [180] (Table 2).

4.2.2. PHA from Lignin

Lignin is a widely studied substrate for PHA production, as reviewed by Xu et al. [181], which is an interesting approach as, although lignin can be extracted and valorized as aforementioned, its characteristics limit processability options. Lignin is regarded as waste in most cases since its toxicity hinders biological processes. So far, all the studies report the use of pure cultures and most reported low productivities compared to other wastes or by-products for PHA production. The most promising results, using lignin from the pulp and paper industry, were reported by Shi et al. [182] (Table 2), where kraft lignin was used as the carbon source for PHA production by Cupriavidus basilensis B-8. In batch assays, a PHA production of 0.13 g L\(^{-1}\) was obtained, but following a fed-batch configuration significantly improved the amount produced, reaching 0.32 g L\(^{-1}\). The maximum PHA accumulation reported was 18.5% cell dry weight (cdw). The
biodegradation of kraft lignin was also successful, with the removal of 41.5% of lignin, 37.7% of total carbon and 43.0% of color after seven days of incubation [182]. Kumar et al. [183] also conducted an exploratory study of PHA production using lignin derivates by a lignin-degrading bacterial strain, *Pandoraea* sp. ISTKB. This bacteria was able to use kraft lignin and accumulated 21% of P(HB-co-HV) after 96 h [183].

### 4.2.3. PHA from Wastewaters

Wastewaters from pulp and paper processing are residues that are hard to process due to high concentrations of complex carbon sources and toxic compounds. For this reason, their treatment before disposal is complex and requires high amounts of energy [184]. Unlike other bioproducts, the valorization of wastewaters from the pulp and paper industry by PHA production by MMC increased in recent years since it is a common ability of microorganisms thriving in activated sludge processes. Furthermore, production by MMC has lower operating costs, which can compensate the wastewaters’ low yields of production. As shown in some of the following studies, this approach can not only produce a valuable biopolymer using low-value substrates, but also works as a wastewater treatment procedure, reducing the organic load of the effluent and degrading toxic compounds before disposal.

To achieve an effective PHA accumulation process by MMC, it is essential to select a culture with a high capacity for accumulating biopolymer by the imposition of adequate reactor conditions, like aerobic dynamic feeding (ADF) or anaerobic/aerobic system (AN/AE). This process should be followed by an accumulation step to maximize PHA production. Since SCOA are the preferred substrates, an initial acidification step to convert the organic matter could be applied in order to increase the amount of organic acids. This configuration is normally designated as a three-step process [185].

Wastewater from fiberboard production was used in a study conducted by Mato et al. [186] using MMC. After converting the wastewater through an acidogenic fermentation process into SCOA, the acidified effluent was used in a batch test to produce PHA by an MMC selected in an aerobic sequential batch reactor (SBR), operated under ADF conditions. Very low storage yields were obtained, with a maximum accumulation of PHA of 25% (cdw). The authors suggested that such results might be due to high concentrations of ammonia in the media, usually known to enhance the bacterial growth process against the storage process. Nonetheless, during the process, a chemical oxygen demand (COD) removal of 80% was achieved, contributing to the biodegradation of the effluent used [186]. The same research group conducted another study with the same wastewater, but this time using an inoculum selected with a SCOA-enriched synthetic medium. This change resulted in a 39% increase in storage yield, suggesting that the selected culture was better adapted to accumulate PHA [187]. Table 2 presents a summary of the results obtained in the studies described below.

Bengtsson et al. [188] used whitewater from a paper mill producing liner and fluting from recycled fibers paper as a substrate for PHA production using a three-step production process with different selection strategies. In both cases, the first step of the process consisted of acidogenic fermentation of the whitewater to produce SCOA to be used as carbon sources by the MMC in the selection step. In this step, ADF and AN/AE were attempted in order to define the best selection strategy. As seen in Table 2, AN/AE enrichment had better productivity of 0.093 (gPHA gbiomass⁻¹ h⁻¹) but both methods led to similar accumulation percentages and yields in terms of YPHA/S (gPHA gCOD⁻¹). Nonetheless, only AN/AE enrichment led to the formation of significant amounts of PHMV, which could improve the polymer properties [188].

Pozo et al. [189] used kraft mill effluents in a batch system for PHA production and evaluated the influence of the MMC origin and the ammonium concentration. Three different sources of inoculum were tested: activated sludge treatment plant; sewage of paper; and kraft pulp mills. The source of the inoculum did not have a significant impact on PHA production, which ranged from 0.10 to 0.14 mgPHA mgCOD⁻¹. The authors also
observed that lower C/N of these types of effluents promoted higher COD removal (80%) but were less beneficial for PHA accumulation [189].

Jiang et al. [178] also studied the feasibility of producing PHA from paper mill wastewater using MMC in a three-step process. The microbial enrichment obtained could accumulate copolymer P(3HB-co-3HV) with a maximum of 77% (cdw) PHA of cell dry weight within five hours. This is the best result reported until now, using effluents from the pulp and paper industry as substrate [178].

Tobella et al. [190] worked with kraft cellulose industry effluents and studied the simultaneous production of PHA and degradation of a toxic compound, 2,4,6-trichlorophenol (2,4,6-TCP), by Sphingopyxis chilensis S37 and Wautersia sp. PZK. Both bacteria were able to synthesize PHA, specifically HB and 3-hydroxyhexadecanoic acid, respectively, using the paper mill effluent. PHA accumulation capacity was not accounted for, but polymer detection by flow cytometry showed that, for S. chilensis S37, 80% of the cells accumulated PHA and 60% of the 2,4,6-trichlorophenol present was degraded. Wautersia sp. PZK had the best results since it thoroughly degraded 2,4,6-trichlorophenol, and more than 90% of the cells accumulated PHA in 72 h [190].

4.2.4. PHA from Spent Liquor

Finally, HSSL was also tested in PHA production by MMC, with the advantage of not requiring any kind of pretreatment. Queirós et al. [191] reported the use of this sub-product for the production of PHB, with a maximum accumulation of 67% (cdw) and productivity of 0.057 gPHA gbiomass\(^{-1}\) h\(^{-1}\), as shown in Table 2. The change to a three-step process seemed to have benefits, with higher biomass concentrations and volumetric productivity. This was an indication that, even though a lower accumulation capacity was reported (22%) for the selection step, this value could increase significantly in the accumulation step [192]. SSL was also tested as a substrate for PHA production by halophilic microorganisms. PHB was identified by fluorescent microscopy on Halorhodospira halophila grown on 6.6% w w\(^{-1}\) dry matter SSL [193].
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Pretreatment</th>
<th>Microorganism</th>
<th>PHA Composition</th>
<th>PHA (%) w w&lt;sup&gt;−1&lt;/sup&gt;</th>
<th>[X] (g L&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>PHA (g L&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Y&lt;sub&gt;PHA/S&lt;/sub&gt; (g&lt;sub&gt;PHA&lt;/sub&gt; g&lt;sub&gt;S&lt;/sub&gt;&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Prod&lt;sub&gt;Vol&lt;/sub&gt; (g&lt;sub&gt;PHA L&lt;sup&gt;−1&lt;/sup&gt; h&lt;sup&gt;−1&lt;/sup&gt;&lt;/sub&gt;)</th>
<th>Prod&lt;sub&gt;SP&lt;/sub&gt; (g&lt;sub&gt;PHA g biomass&lt;sup&gt;−1&lt;/sup&gt; h&lt;sup&gt;−1&lt;/sup&gt;&lt;/sub&gt;)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood particles</td>
<td>HWE + EH</td>
<td>MMC</td>
<td>PHB:PHV (85:15%)</td>
<td>N.R.</td>
<td>N.R.</td>
<td>2.3</td>
<td>N.R.</td>
<td>N.R.</td>
<td>N.R.</td>
<td>[171]</td>
</tr>
<tr>
<td>Waste wood</td>
<td>Hydrothermal + EH</td>
<td>MMC</td>
<td>PHB:PHV (94:6%)</td>
<td>50</td>
<td>6.30</td>
<td>3.15</td>
<td>0.71&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.237</td>
<td>0.029</td>
<td>[180]</td>
</tr>
<tr>
<td>Kraft lignin</td>
<td>N.A.</td>
<td>C. basilensis B-8</td>
<td>P(S3HB):P(R3HB):PHB (98:1:0.4%)</td>
<td>19</td>
<td>3.87</td>
<td>0.74</td>
<td>0.15</td>
<td>0.015</td>
<td>0.004</td>
<td>[182]</td>
</tr>
<tr>
<td>Kraft lignin</td>
<td>N.A.</td>
<td>Pandoraea sp. ISTKB</td>
<td>PHB:PHV</td>
<td>21</td>
<td>0.08</td>
<td>0.02</td>
<td>N.R.</td>
<td>N.R.</td>
<td>N.R.</td>
<td>[183]</td>
</tr>
<tr>
<td>Wood mill effluent</td>
<td>N.A.</td>
<td>MMC</td>
<td>PHB:PHV (46:54%)</td>
<td>29</td>
<td>3.93</td>
<td>1.14</td>
<td>0.23&lt;sup&gt;4&lt;/sup&gt;</td>
<td>N.R.</td>
<td>N.R.</td>
<td>[187]</td>
</tr>
<tr>
<td>Wood mill effluent</td>
<td>N.A.</td>
<td>MMC</td>
<td>PHB:PHV (81:19%)</td>
<td>25</td>
<td>7.88</td>
<td>1.97</td>
<td>0.57&lt;sup&gt;4&lt;/sup&gt;</td>
<td>0.303</td>
<td>0.038</td>
<td>[186]</td>
</tr>
<tr>
<td>Paper mill effluent</td>
<td>N.A.</td>
<td>MMC</td>
<td>PHB:PHV:PHMV (6:47:47%)</td>
<td>48</td>
<td>2.63</td>
<td>1.26</td>
<td>0.11&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.152</td>
<td>0.058</td>
<td>[188]</td>
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<tr>
<td>Paper mill effluent</td>
<td>N.A.</td>
<td>MMC</td>
<td>N.R.</td>
<td>42</td>
<td>2.63</td>
<td>1.10</td>
<td>0.10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>0.244</td>
<td>0.093</td>
<td>[188]</td>
</tr>
<tr>
<td>Kraft mill effluent</td>
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<td>MMC</td>
<td>N.R.</td>
<td>42</td>
<td>N.R.</td>
<td>0.08</td>
<td>0.14&lt;sup&gt;5&lt;/sup&gt;</td>
<td>0.001</td>
<td>N.R.</td>
<td>[189]</td>
</tr>
<tr>
<td>Kraft mill effluent</td>
<td>N.A.</td>
<td>S. chilensis S37</td>
<td>PHB (100%)</td>
<td>42</td>
<td>N.R.</td>
<td>N.R.</td>
<td>0.08</td>
<td>N.R.</td>
<td>N.R.</td>
<td>[190]</td>
</tr>
<tr>
<td>Kraft mill effluent</td>
<td>N.A.</td>
<td>Wautersia sp. PZK</td>
<td>Long chain length PHA</td>
<td>42</td>
<td>3.4</td>
<td>0.75</td>
<td>0.42</td>
<td>0.170</td>
<td>0.051</td>
<td>[192]</td>
</tr>
<tr>
<td>HSSL</td>
<td>N.A.</td>
<td>MMC</td>
<td>PHB:PHV (68:32%)</td>
<td>22</td>
<td>3.4</td>
<td>0.75</td>
<td>0.42</td>
<td>0.170</td>
<td>0.051</td>
<td>[192]</td>
</tr>
<tr>
<td>HSSL</td>
<td>N.A.</td>
<td>MMC</td>
<td>PHB (100%)</td>
<td>67</td>
<td>0.88</td>
<td>0.60</td>
<td>0.77&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.050</td>
<td>0.057</td>
<td>[191]</td>
</tr>
<tr>
<td>HSSL</td>
<td>N.A.</td>
<td>MMC</td>
<td>PHB:PHV (86:14%)</td>
<td>77</td>
<td>N.R.</td>
<td>0.83</td>
<td>0.80&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.083</td>
<td>N.R.</td>
<td>[178]</td>
</tr>
</tbody>
</table>

Table 2. PHA production from pulp and paper wastes.
4.3. Biogas

Anaerobic digestion (AD) is defined as the biological degradation of organic compounds into different end products by a MMC in the absence of oxygen [194]. This process typically consists of four stages: hydrolysis; acidogenesis; acetogenesis; and methanogenesis. During the hydrolysis stage, macromolecules such as cellulose, starch, proteins, and lipids are decomposed into monomers such as sugars, amino acids and fatty acids. These monomers are then converted into C=–C3 based SCOA and alcohols, as well as H2 and CO2 in the acidogenesis stage. SCOA and alcohols are then converted into acetic acid during the acetogenesis stage. Finally, methane is produced through the conversion of acetic acid to CH4 and CO2 (acetoclastic methanogenesis), or the reduction in formic acid, or CO2 to CH4 (hydrogenotrophic methanogenesis), during the methanogenesis [151,195]. Generally, hydrolysis is the rate-limiting step due to the complexity of the feedstocks used. When this is not the case, methanogenesis becomes the limiting step [195,196]. The end product of anaerobic digestion is biogas, composed of methane (50–75%), carbon dioxide (25–50%), hydrogen (5–10%), and nitrogen (1–2%) [194]. The biogas can be combusted to generate heat and/or electricity or upgraded and refined into transportation biofuel. On the other hand, the remaining digestate is still rich in nutrients and can be further valorized into fertilizers or biochar [16].

Given the versatility of AD, its use has been proposed for the valorization of all kinds of feedstocks, from agricultural and industrial residues to municipal solid waste. The pulp and paper industry is also a great candidate for AD. Compared to the conventional biological treatment, the implementation of this process allows for the reduction in the produced wastes simultaneously with the production of biogas [194]. Besides, the ability to handle a high organic loading rate is another advantage of the AD, given the highly concentrated wastewaters produced in the pulp and paper industry [151].

The literature shows that AD is already proven for many pulp and paper industry streams, with varying reactor configurations and operational conditions [151,194,195,197]. Most studies focus on BL [198,199], lignin [200–202], PPMS [203–206], different sources of wastewaters [200,207–209] and condensates resulting from the condensation formed during the concentration of spent liquor [201,202]. Studies with BL report COD removals up to 80%, with maximum methane production of 36.9 μmol mL⁻¹, showcasing the potential of AD for effluent treatment [199]. Biogas production from the degradation of lignin waste streams was tested by several authors [210]. Some of the best results were achieved when wet explosion pretreatment was applied, with 44.4% of the lignin fraction converted to biogas during the anaerobic digestion process after the pretreatment compared to only 12.6% for the non-pretreated counterpart, representing methane yields of 320 and 70 L kg⁻¹ volatile solids day⁻¹ [211]. Similarly, the high recalcitrant nature of PPMS makes the hydrolysis step the bottleneck of AD, and a pretreatment step is often applied [203]. Bayr et al. [205] tested several pretreatment methods and reported a 31% increase in methane yield when a hydrothermal pretreatment (150 °C, 10 min) was applied. AD is particularly interesting for condensate valorization, as these wastes have yet to be applied for other biological processes. For example, using a submerged anaerobic membrane bioreactor, COD removal efficiencies of 93–99% were achieved with a methane production rate of 0.35 L g⁻¹ COD removed and methane content of 80–90% in produced biogas [201]. Still, the characteristics, process conditions and developments of AD of these wastes are already well-reviewed and documented [151,194,197,210,212,213].

Anaerobic digestion is being used for wastewater treatment from pulp and paper mills since the middle of the 80s [214,215]. Most of the studies have been focused on strategies for improving the AD of pulp and paper industry wastes, namely co-digestion with nitrogen-rich wastes for optimum C/N ratios, pretreatment technologies to decrease sludge retention times and remove inhibitors, and bioaugmentation by introducing microbial strains and consortia that can efficiently degrade recalcitrant compounds [151,194,212,213].
The use of forest-based LCB like bark, wood chips, and sawdust generally has slow anaerobic decomposition rates [216]. Nonetheless, some studies showed that AD of a mixture of pretreated pine sawdust and food waste was possible [217] and that the addition of wood chips during the AD of food waste could increase the methane production yield by 640% [218]. Rasi et al. [216] also studied the effect of HWE and pyrolysis on the AD of softwood bark. Their results showed that the cascade processing of the wood, tannins, and polyphenols extraction with hot water, followed by pyrolysis, whose liquid fraction is used in AD, enhances methane production (from 53 and 46 to 99 and 55 mL CH$_4$ g volatile solids added$^{-1}$ of pine and spruce bark, respectively) and creates more value from the same residue [216].

Spent liquor is also not an ideal candidate for AD due to its high content of recalcitrant COD [219,220]. However, some studies showed that dilution, fungal pretreatment, and the addition of hydrogen peroxide enhanced its anaerobic biodegradability, increasing COD removal and methane production over 10 and 15 times, respectively [219,221]. Overall, this reported data shows that AD has a tremendous potential to be integrated into a biorefinery based on the pulp and paper industry.

4.4. Challenges and Future Perspectives for Conversion of Wastes into Bioethanol, PHA, and Biogas

Regarding cellulosic ethanol production, some challenges still need to be overcome. In particular, the low sugar concentrations which can result in reduced ethanol concentrations with high costs associated with the downstream processing [126,161]. Moreover, the presence of toxic compounds and contaminants could inhibit the activity of the fermenting microorganisms. The inability of the most natural microorganisms to ferment both hexoses and pentoses is another limitation [158]. Another major bottleneck hindering large-scale cellulosic ethanol production is the overall production cost, in particular, the cost of the enzymatic consortium, which could represent up to 40% of the minimum selling price of ethanol [156]. Therefore, solid loading optimization during pretreatment and enzymatic hydrolysis steps, onsite production of enzymatic consortium and integration of process steps are the main critical domain topics for further research [222]. Following a co-production strategy within a multi-product biorefinery could be a potential alternative to offset the high capital and production costs, improving competitiveness and representing extra revenues [37,164]. Some authors have studied some possibilities, namely the integration of the production of cellulosic ethanol with xylooligosaccharides [37,223,224] PHA [225], among others.

Current research shows that PHA production from wood industry wastes is a good possibility, especially when considering the combined biodegradation of those effluents. This technology development can be applied to pulp and paper to treat wastewaters and other waste streams and contribute to waste management implementation since their valorization routes are very limited. The circular economy pushing for technical cycle solutions could be applied by using them as suitable feedstocks for PHA production. Regardless of its potential, there are still some challenges that need to be overcome before scaling up and process optimization. Some authors reported limitations with oxygen mass transfer when using paper mill effluents, microbial inhibition from compounds present in the waste streams used and some inorganic compounds precipitation, which could stimulate biofilm formation and cause problems in the PHA extraction [178,191]. Further research should focus on overcoming these challenges and increasing PHA productivities to implement a wood waste-based PHA production process.

Concerning the anaerobic digestion, despite being already a reality for wastewater treatment in the pulp and paper industry, there is still scope for improvement. The main challenges are related to feedstock variability responsible for process performance fluctuation, low process efficiency and lower product quality [215]. Besides the calorific value of biogas being lower than natural gas, it is highly dependent on many operating conditions, including feedstock composition, temperature, retention time, among others.
Biogas could contain impurities (such as nitrogen gas, oxygen, carbon monoxide and ammonia) responsible for corrosion and toxicity [215].

Overall, waste-based bioprocesses presented some challenges related to the intrinsic heterogeneity of feedstock. For that reason, the process should be flexible enough to ensure the quality of the final product, regardless of the variations in the process feed [164]. Moreover, the multi-product biorefinery seems to be a potential alternative to stimulate economic feasibility. The employment of this concept in existing pulp and paper mills could significantly reduce transport, disposal, infrastructure and energy costs, with the possibility of an additional revenue stream. Finally, government policies and financial de-risking by investment incentives could also support the employment of these technologies at the commercial scale, which must be economically competitive with the existing alternatives [222].

5. Conclusions

The valorization of wastes and residues derived from pulp and paper mills by integrating them within a biorefinery concept is a promising approach. Some benefits include increasing revenues, expanding the portfolio of products, and boosting market opportunities. The pulp and paper industry already has well-established industrial facilities, logistics, and services, which is a competitive advantage for implementing an integrated biorefinery. Furthermore, this integration can reduce production costs, contributing to a more competitive market for bio-based products. The three products chosen, bioethanol, PHA, and biogas, illustrate how these residues can be treated and, at the same time, valorized, closing the loop proposed by the circular concept. However, the feasibility of these processes depends on several factors, namely availability and transport of feedstock, technology readiness level of the available techniques, capital and operation costs, industrial plant capacity, revenues, and others. The assessment of the techno-economic impact of the modifications to be implemented in the existing pulp and paper processes is crucial. The selection of the valorization route for each residue will depend on the economic assessment and the life-cycle analysis, opting for the most feasible, sustainable, and profitable alternative.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

ADF Aerobic dynamic feeding
AN/AE Anaerobic/aerobic system
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>Anaerobic digestion</td>
</tr>
<tr>
<td>BL</td>
<td>Black liquor</td>
</tr>
<tr>
<td>C/N</td>
<td>Carbon/nitrogen ratio</td>
</tr>
<tr>
<td>Cdw</td>
<td>Cell dry weight</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>CBP</td>
<td>Consolidated bioprocessing</td>
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<tr>
<td>EH</td>
<td>Enzymatic hydrolysis</td>
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<tr>
<td>[Ethanol]$_{\text{max}}$</td>
<td>Maximum ethanol concentration (g L$^{-1}$)</td>
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<td>EU</td>
<td>European Union</td>
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<tr>
<td>HB</td>
<td>3-hydroxybutyrate</td>
</tr>
<tr>
<td>HSSL</td>
<td>Hardwood spent sulfite liquor</td>
</tr>
<tr>
<td>HV</td>
<td>3-hydroxyvalerate</td>
</tr>
<tr>
<td>HWE</td>
<td>Hot water extraction</td>
</tr>
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<td>LCB</td>
<td>Lignocellulosic biomass</td>
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<tr>
<td>MMC</td>
<td>Mixed microbial cultures</td>
</tr>
<tr>
<td>P(3HB-co-3HV)</td>
<td>Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)</td>
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<tr>
<td>PHA</td>
<td>Polyhydroxalkanoates</td>
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<tr>
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<td>Volumetric productivity (g$_{\text{ethanol}}$ L$^{-1}$ h$^{-1}$)</td>
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<td>Prod$_{\text{sp}}$</td>
<td>Specific productivity (g$<em>{\text{PHA}}$ g$</em>{\text{biomass}}^{-1}$ h$^{-1}$)</td>
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<tr>
<td>Prod$_{\text{VOL}}$</td>
<td>Volumetric productivity (g$_{\text{PHA}}$ L$^{-1}$ h$^{-1}$)</td>
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<td>Pre-saccharification and simultaneous saccharification and fermentation</td>
</tr>
<tr>
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<td>Pulp and paper mill sludge</td>
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<tr>
<td>SHF</td>
<td>Separate hydrolysis and fermentation</td>
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<td>Sequential batch reactor</td>
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<td>Simultaneous saccharification and co-fermentation</td>
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<tr>
<td>SSF</td>
<td>Simultaneous saccharification and fermentation</td>
</tr>
<tr>
<td>SSSL</td>
<td>Softwood spent sulfite liquor</td>
</tr>
<tr>
<td>SE</td>
<td>Steam explosion</td>
</tr>
<tr>
<td>SSL</td>
<td>Sulfite spent liquor</td>
</tr>
<tr>
<td>Y$_{\text{ethanol}}$</td>
<td>Ethanol yield (g$<em>{\text{ethanol}}$ g$</em>{\text{substrate}}^{-1}$)</td>
</tr>
<tr>
<td>Y$_{\text{PHA/S}}$</td>
<td>PHA yield (g$<em>{\text{PHA}}$ g$</em>{\text{substrate}}^{-1}$)</td>
</tr>
</tbody>
</table>

**References**


