

Review

Pyrolysis and Extraction of Bark in a Biorefineries Context: A Critical Review

Umüt Şen ^{1,*}, Bruno Esteves ² and Helena Pereira ¹

¹ Centro de Estudos Florestais, Instituto Superior de Agronomia, Tapada da Ajuda, 1349-017 Lisbon, Portugal; hpereira@isa.ulisboa.pt

² CERNAS Research Centre, Polytechnic Institute of Viseu, 3504-510 Viseu, Portugal; bruno@estgv.ipv.pt

* Correspondence: umutsen@isa.ulisboa.pt

Abstract: Bark-based biorefineries are estimated to become a trending topic in the coming years, particularly with their adsorbent applications and antioxidant production. While the potential benefits of bark-based biorefineries are well-recognized, it is not known how to develop a bark-based biorefinery considering different unit operations and the potential end products. The characterization and screening of different barks for chemical composition is the initial step in biorefinery development, along with the selection of the relevant conversion processes. This state-of-the-art review provides background knowledge on the pyrolysis and extraction studies of bark as the key conversion operations. The results of recent (2010–2022) bark pyrolysis and extraction studies were critically analyzed for process conditions, product properties, and product yields, as well as a discussion of energy-saving possibilities. A biorefinery scheme was proposed based on these data. The current knowledge gaps were identified and future directions were evaluated, which include the production of charcoals, platform chemicals, and extract profiling for specific applications. The results indicate that barks are particularly rich in hydrophilic extractives with potential antioxidant properties and pyrolysis operations, resulting in functional chars that may be used in value-added applications as adsorbent materials. A biorefinery scheme allows for the production of platform chemicals, antioxidant extracts and biochars from barks while contributing to the reduction of waste and environmental pollution.

Keywords: biomass; biofuels; extractives; fractionation; platform chemicals



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1. Introduction

Bark is defined in plant anatomy as the tissues outside the vascular cambium that externally cover the stem and branches [1,2]. Tree barks are heterogeneous complex solid materials, and they are one of the most important forest by-products available in the field or in the wood-processing industries, potentially reaching an annual amount as high as 400 million cubic meters worldwide [3,4]. The majority of produced bark is not valorized as a resource for value-added products, but rather is disposed of as a waste stream or burned at domestic scale. Only a few barks are converted into value-added products, such as that of the cork oak, where the cork in the outer bark is harvested periodically to produce cork products, namely cork stoppers for the wine industry, valued worldwide [5]. Cork is also used in a number of other applications, including insulation, adsorbents, composites, fillers, cement-replacement materials, etc. [5–8]. Other important industrial barks include birch bark, which is a source of bioactive triterpenoid extractives such as betulin [9], as well as a number of oak and chestnut barks that are utilized for tannin extraction [10]. In former times, willow and poplar barks were extracted to produce salicylates, which are precursors of aspirin [11], which is currently produced from sodium phenolate, a petroleum-based benzene, and CO₂ using the Kolbe–Schmitt process [12] following acetylation with acetic anhydride. The barks of oaks, chestnut, pines, and birch, among other species, are currently being analyzed to produce chemicals and materials. However, many other unused or less known tree barks may have potential economic benefits. According to the latest estimation,

probably less than 100 of the approximately 73,000 different tree species on Earth [13] are currently industrially used, and they are mostly by-products of high-value timber production [3].

The biorefineries and circular bioeconomy concepts were developed to reduce waste, produce sustainable products, and increase the overall efficiency and economy of biomass processing [14,15]. The overall aim is to use biomass feedstocks to produce chemicals, energy and materials, as is the case in conventional petroleum refineries [16]. Barks are considered potential resources to produce sustainable and biodegradable products in a biorefinery approach [17–21]. In order to develop efficient bark-based biorefineries, it is important to characterize the raw material and envisage the specific potential conversion paths. The chemical composition of bark is among the most important parameters for indicating the possible conversion paths, because it shows the content and composition of chemical fractions that will be available during bark conversion, namely ash, extractives, lignin, polysaccharides, and suberin.

Slow pyrolysis is considered the key thermochemical process for converting bark into energy products, because it increases the efficiency of fuel applications and also produces functional biochars that may be used as solid amendment, adsorbent, etc. [3]. The combustion of bark does not increase the net CO₂ release and releases less SO_x emissions into the atmosphere than coal because bark is considered carbon-neutral and contains much less sulfur, thereby contributing less to greenhouse gas emissions compared with coal [10]. Emerging technologies such as biomass gasification can further reduce CO₂ emissions if bark is used as fuel [22]. To increase gasification efficiency, barks may be subject to a previous pyrolysis process such as torrefaction [23], slow pyrolysis [24], or hydrothermal carbonization [25].

The extraction of bark may also be an essential step in biorefinery development, since barks contain many more extractives than wood and other lignocellulosic materials [26]. Bark extracts, often present in substantial amounts and with an outstanding chemical diversity, may therefore be considered for a large range of applications depending on extract yield and composition. Thus, extraction plays an important role in the valorization of bark, and the production of chemicals is an important step in bark-based biorefineries.

While barks are potentially important resources for biorefineries, their systematic conversion through cascade processing encompassing different conversion routes has not been previously analyzed, and the existing studies concentrate usually on a single conversion process. However, a previous study has shown that the conversion efficiency of spruce bark was significantly improved by using an integrated hot water extraction, pyrolysis, and anaerobic digestion process [27]. A successful bark-based biorefinery will therefore require the evaluation of different conversion processes. To achieve this objective, the chemical composition, and particularly the extract profiles, of different barks must be known.

This state-of-the-art review analyzes bark-based pyrolysis studies and extract profiles of different barks, mainly focusing on the period between 2010 and 2022, in order to integrate them into a cascade process for biorefineries. The development of bark-based biorefineries is discussed, the knowledge gaps are identified, and future directions in bark-based biorefineries are proposed.

2. Tree Barks and Biorefinery Research

2.1. Trends in Bark-Based Biorefineries

The first step in the prospective design of a biorefinery is to evaluate the previous studies and trends on the conversion pathways for the target biomass feedstock. A search in the Web of Science (WOS) on the number of publications and research keywords about the lignocellulosic biomass in a biorefinery context is a preliminary phase and has been a common approach in many studies.

It is difficult to estimate the number of studies targeting bark biorefinery by using only the publication titles, because not all have “biorefinery” in the title. Therefore, the

screening for biorefinery studies on barks was conducted using the abstract keywords of “bark” and “waste”, since most biorefinery studies are performed with waste materials. The results show that the number of publications on barks has steadily increased, starting from 25 and reaching 92 between 2010 and 2022 (Figure 1). It is therefore reasonable to expect a higher number of publications on bark conversion in the near future. Therefore, to estimate future trends, a forecast was performed (Figure 1). The forecast indicates that the number of bark-based biorefinery studies will most likely increase, and reach between 173 to 208 by 2035, with a 0.95 confidence level.

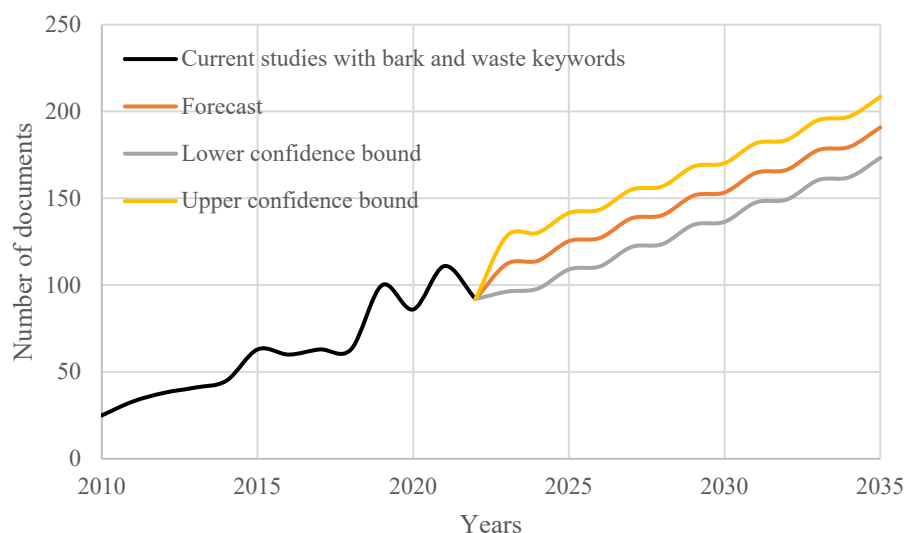


Figure 1. Number of publications in Web of Science using the keywords “bark and waste” in abstracts between 2010 and 2022, and the prognosis of future studies until 2035 with a 0.95 confidence level.

In a second step, using the same approach, abstracts were searched for the terms bark, extraction, and pyrolysis, which resulted in only 28 research items. Considering the low number of co-occurring studies, research titles including bark crossed with pyrolysis or extraction were searched for an extended time frame (1945–2023) and co-occurrence maps were created [28]. These maps show an overview of the studied topics on “bark and pyrolysis” or on “bark and extraction” (Figure 2). The different co-occurring research topics were analyzed, as shown by the different color clusters, and the most-studied topics are represented with larger circles. These maps indicate that studies on bark extraction are more common (310 research items) than on bark pyrolysis (91 research items), with antioxidant production and adsorption applications making up the principal research clusters.

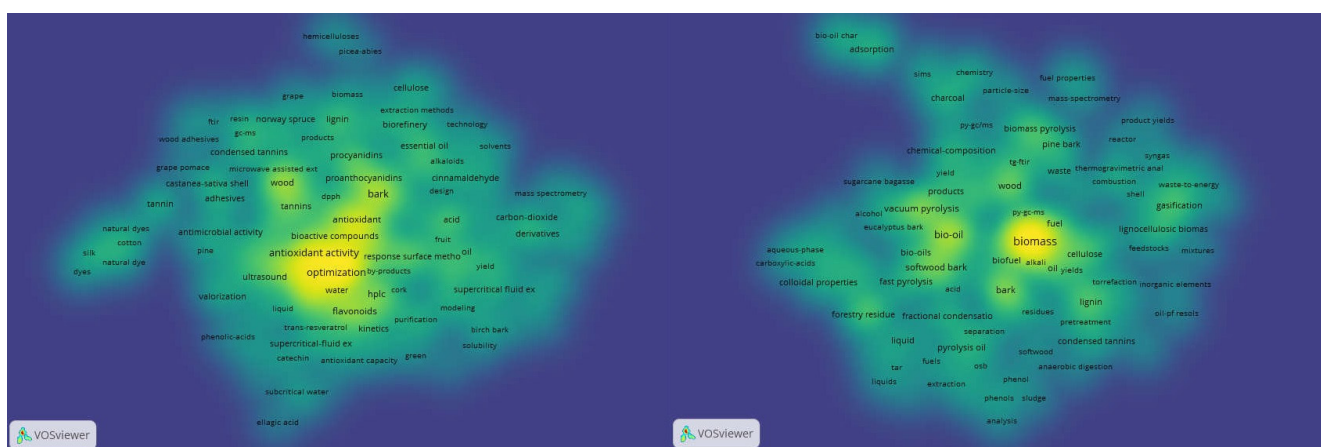


Figure 2. Co-occurrence map of publications with the titles “bark and extraction” on the left, and “bark and pyrolysis” on the right in WOS between 1945 and 2023.

Based on the results of the co-occurrence maps, we deduced that antioxidant production and adsorption applications from barks will be the most important topics in the near future. To estimate future trends, the same forecasting as carried out in Figure 1 was performed, and Figure 3 was created, which shows estimations of the possible development of these topics in the coming years.

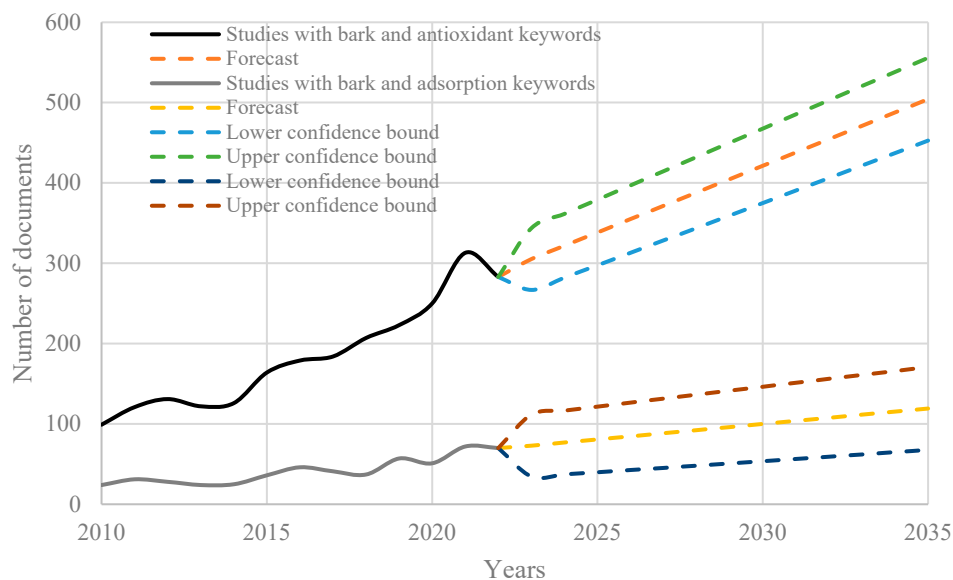


Figure 3. Number of publications in Web of Science using the keywords “bark and adsorption” and “bark and antioxidant” in abstracts between 2010 and 2022.

2.2. Current Bark-Based Biorefinery Applications

The previous section gives information on the development and direction of bark-based biorefineries in the near future. Currently, the application of an integrated biorefinery concept for bark is in its infancy, but recent studies show that its use may be increasing. Therefore, it is important to analyze these works. The bark-based biorefinery studies were performed using barks such as Norway spruce, Scots pine, radiata pine, birch, and aspen, based on a previous screening and evaluation of potentially valuable chemical components including extractives, non-cellulosic polysaccharides (mostly pectin and starch), lignin, cellulose, and suberin [27,29–34] (Figures 4–10). Interestingly, although almost all of these studies considered extraction as the first step, they did not consider a further refinement of extracts. Acetone, hot water, and supercritical CO₂ (scCO₂) extractions were tested for the screening of bark extracts [29,31,32]. The polysaccharide-containing hot water extracts of spruce bark showed immunostimulating activity, suggesting that the extraction of barks may be further refined to obtain bioactive compounds [35].

The non-cellulosic polysaccharides (NCPs), which are rich sources of glucose, arabinose, and galacturonic acids, were obtained from spruce bark with up to 20% yield by using pressurized hot water extraction [36]. The polysaccharide content of barks is lower than that of woods, agricultural wastes, and energy crops [3], but the extraction of NCPs enables the production of functional materials by the addition of other polysaccharide-derived cellulose nanocrystals (CNC) such as NCP/CNC films [20]. The CNCs may be derived from barks [19] or from other lignocellulosic feedstocks [34].

Suberin extraction is another approach in bark biorefineries when the bark has a high content of cork. The application of ionic liquids seems to be a promising method to obtain highly pure suberin [37], which may be used to produce functional materials [31]. Suberin monomers obtained by alkaline hydrolysis may be integrated into biorefineries after purification and polymerization, such as the production of polyepoxy acid [34] as an additive for NCP/CNC films.

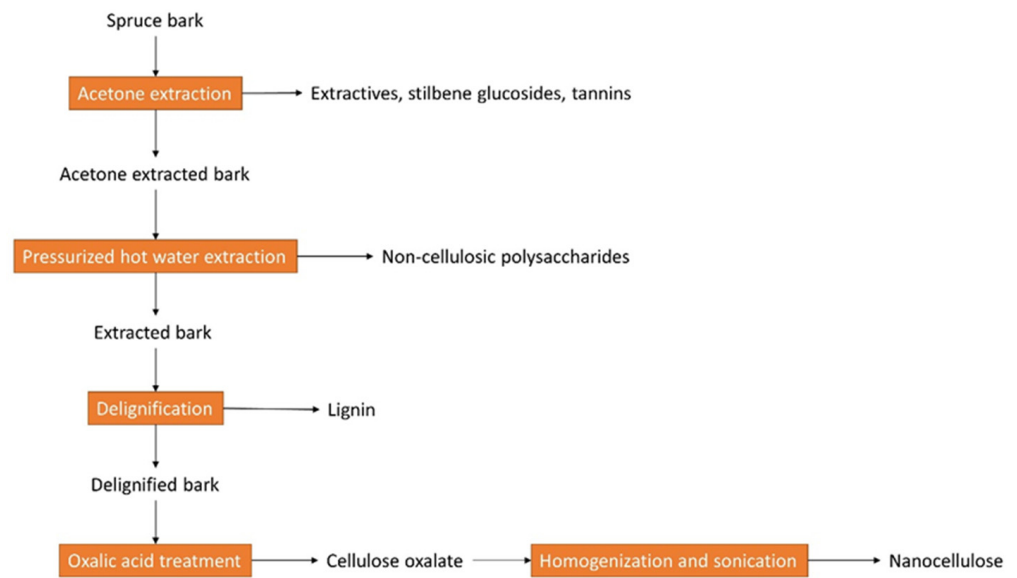


Figure 4. Spruce bark biorefineries [29].

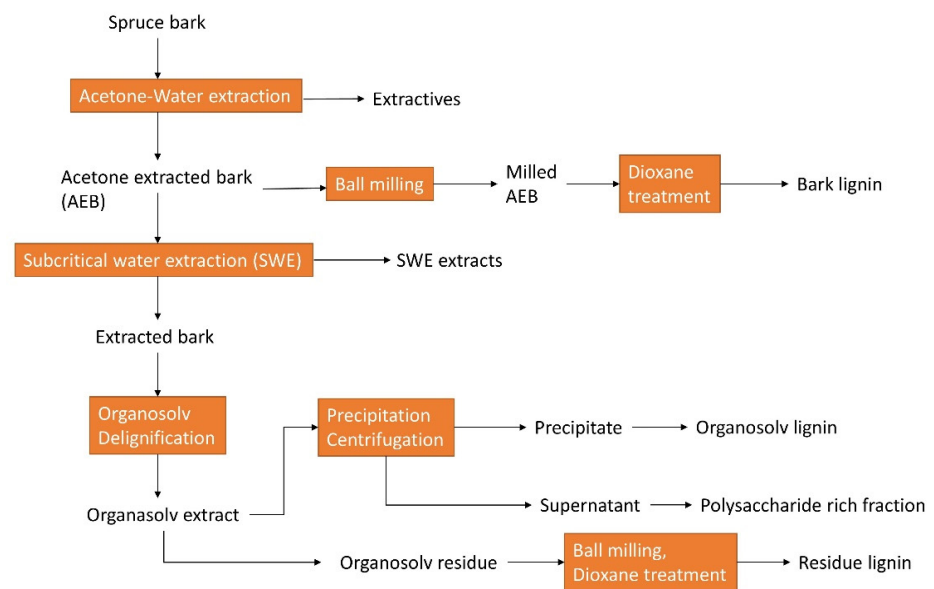


Figure 5. Spruce bark biorefineries [30].

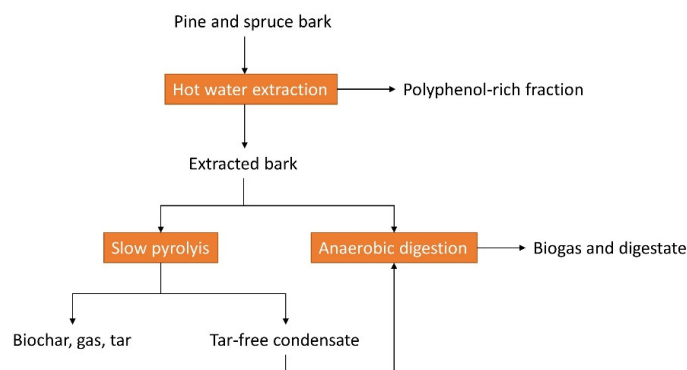


Figure 6. Pine and spruce bark biorefineries [27].

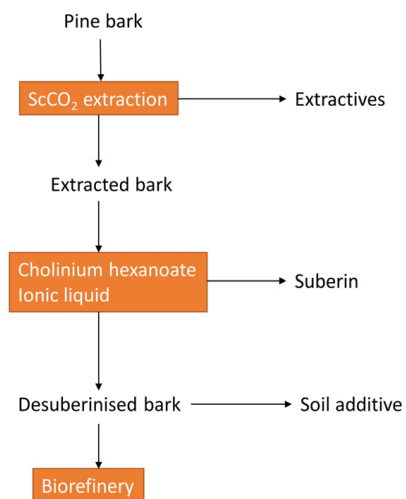


Figure 7. Pine bark biorefineries [31].

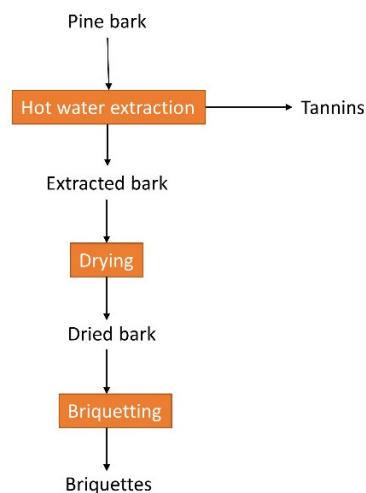


Figure 8. Pine bark biorefineries [32].

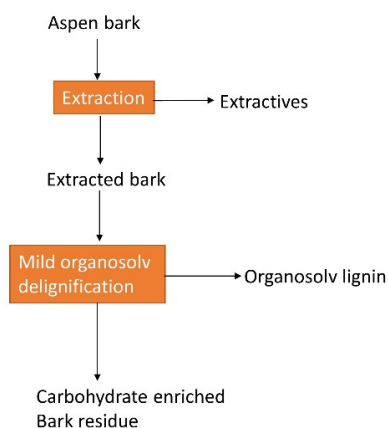


Figure 9. Aspen bark biorefineries [33].

The extraction and fractionation of bark lignin through ball milling and organosolv extraction [30] is possibly the most promising approach in bark biorefineries considering the high lignin content of barks. The bark-based lignins are alternative materials to fossil-based materials in the production of polymers and biofuels [30].

The efficiency of bark-based biorefineries may be increased by integrating different extraction, thermal conversion, and biological processes, such as extraction, slow pyrolysis,

and anaerobic digestion [27]. The extraction and slow pyrolysis methods seem to be particularly suitable for the conversion of barks in a biorefinery concept, as explained in the next chapters. Biological processes may not be efficient in a bark biorefinery process considering the recalcitrance of the biomass and low polysaccharide content. However, current information is limited and more studies are required to evaluate the performance of biological processes with bark feedstock.

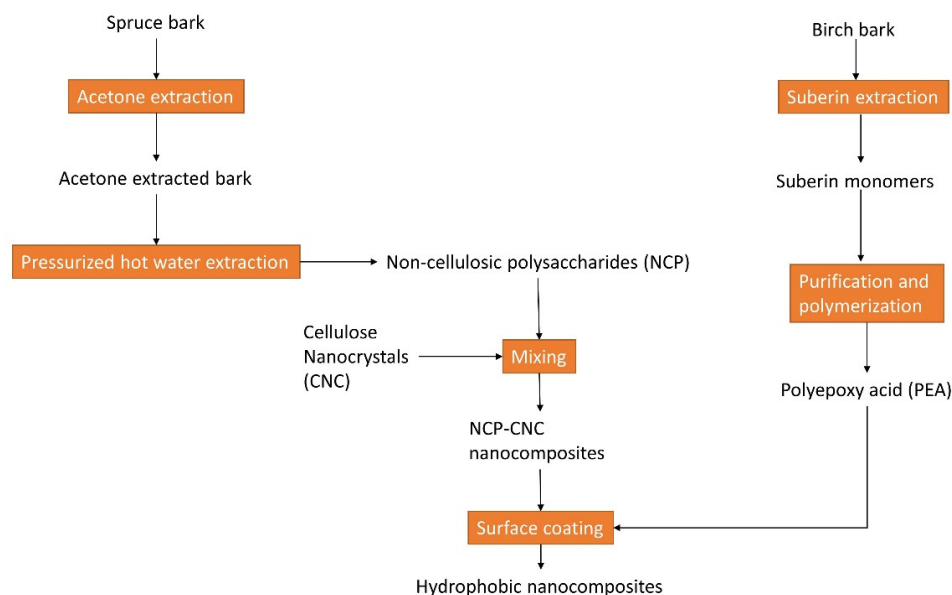


Figure 10. Spruce and birch bark biorefineries [34].

3. Pyrolysis of Bark

Pyrolysis is the thermal degradation of organic matter in the absence of oxygen. The pyrolysis process may be performed conventionally under an inert gas flow or industrially by sealing the pyrolysis chamber to prevent air oxidation [38]. The pyrolysis process may be integrated into bark-based biorefineries in a so-called thermochemical platform to produce biochars with lower moisture content, higher calorific value, and better grindability properties [39]. Different pyrolysis processes have been applied to lignocellulosic biomass, particularly to wood, which is composed mainly of cellulose and hemicellulose polysaccharides (70–75%) and contains low amounts of inorganics (less than 1%) [26]. The chemical composition of wood makes it a promising raw material for fast pyrolysis to produce bio-oils because, under high heating rates, high heat transfer coefficients, a 500 °C final pyrolysis temperature, and fast removal of the pyrolysis vapors and char, liquid yields may reach up to 80% of the wood, where 64% is bio-oil [40]. Under these conditions, the wood polysaccharides undergo an almost total conversion by devolatilization, depolymerization, and condensation (tar formation) reactions [41]. The low ash content of wood and the fast removal of pyrolysis vapors limit catalytic char formation, thereby maximizing the liquid yield in fast pyrolysis [42]. However, the fast pyrolysis bio-oils are reactive materials and require upgrading for use in industrial applications as drop-in fuels [43].

Bark is composed mainly of lignin, polysaccharides and also polyphenols and suberin, and contains a much higher amount of ash (usually over 10%) [10]. The chemical variability of barks is also much higher than that of wood, e.g., barks may be suberin-rich and the range of their extractives content is large. These chemical features of bark increase the char formation and decrease the bio-oil yield. Therefore, the fast pyrolysis of bark is usually not economically feasible due to low bio-oil yields. On the other hand, bark is a potential material for torrefaction, slow pyrolysis, and hydrothermal carbonization where the aim is to produce chars, referred to as torrefied material, biochars, and hydrochars, respectively. These processes are analyzed in this chapter.

3.1. Torrefaction

The torrefaction process is the lowest-temperature (mild) pyrolysis process, usually performed at temperatures between 200 °C and 300 °C [39,44]. This range may be extended to 180–320 °C to include the degradation range of hemicelluloses [45]. Under these conditions, the degradation of macro chemical components in biomass is small and mostly limited to hemicelluloses, and only partially to cellulose [39]. Biomass chemical composition is therefore the determining factor of mass loss in torrefaction. Hardwood hemicelluloses that are mainly composed of xylans are more degraded than softwood hemicelluloses [46] that are mainly composed of glucomannans [10] during torrefaction.

The torrefied biomass has a chemical composition similar to low-grade coals [38,47], contains less oxygen and fewer hemicelluloses, and is more hydrophobic [48]. Therefore, it is easier and less costly to grind [49,50]. The torrefied material is usually used as fuel for gasification or combustion [44]. Torrefaction may also reduce the potassium content in the lignocellulosic torrefied material, which leads to fewer ash-related problems during fuel applications [49].

The torrefaction properties of materials, such as mass loss and the resulting calorific value, depend both on the torrefaction conditions (duration and temperature) and biomass types [51]. These properties may be tuned by using torrefaction indices such as torrefaction severity index (TSI) or torrefaction severity factor (TSF), and the final material properties may be predicted [51].

The energy yield of biomass in torrefaction is calculated as a product of mass yield and the ratio of calorific values of the torrefied material and the raw biomass [49]. The energy yield indicates the amount of energy lost during torrefaction [52]. As the torrefaction temperature increases, the mass yield decreases, while the calorific ratio increases, resulting in an energy yield decrease, thereby suggesting the optimization potential of the process [49]. Possibly the most efficient method to decrease the energy yield and increase the efficiency of torrefaction is the integration of torrefaction with another process, such as co-combustion, pyrolysis, or gasification [53]. Further energy and time optimization can be achieved by using catalysts. For instance, the potassium impregnation of biomass before torrefaction was shown to increase the mass loss rate, providing a time- and energy-saving possibility [54]. Furthermore, performing torrefaction under oxygen-lean conditions, similarly to gasification, was proposed to achieve cost and energy savings [50,55].

One study using life cycle analysis (LCA) of torrefied biomass showed that torrefied biomass allows energy and greenhouse gas savings [53,56]. Under oxidative conditions, torrefaction is faster, and the operation cost is lower, but mass and energy yield are lower due to higher torrefaction temperatures [53].

3.2. Slow Pyrolysis

Slow pyrolysis (carbonization) is the main biochar production process of lignocellulosic biomass and is usually performed at moderate temperatures between 400 and 700 °C [57–59] over a few hours [59]. The produced biochars may be used as fuels [60,61], soil-amendment materials [62–64], adsorbents, or activated carbon precursors [65]. The use of biochars has been growing in recent years, and soil applications of biochars have predominated because of the following facts: biochars are recalcitrant materials in soil, they have high porosity and thus provide shelter for soil microorganisms, and they contain inorganic material that provides a source of nutrients [66]. However, they may also cause ecotoxicity [67] by leaching pyrolysis condensates, which depends on the used biomass type and applied pyrolysis temperature [38]. Biochars are also low-cost alternatives to costly activated carbons in wastewater treatment, and showed high pesticide removal efficiency from aqueous solutions [68]. Wood species may be considered as the best lignocellulosic feedstock for biochar production because wood biochars possess a higher surface area and lower ash content than other biomass types, making wood biochars more suitable for fuel, soil amendment, and adsorption applications [69]. However, wood is a versatile solid material and finds uses in many competing applications from solid wood to composites [70].

and other lignocellulosic feedstocks such as waste barks that are more available and have a lower cost than wood may become of interest. The activated carbons produced from bark biochars may be used as adsorbents or may be integrated into a biological process to enhance the caproate production [71].

Large biomass particles (5 mm to 50 mm) can be used in slow pyrolysis [59], which has a cost advantage compared with fast pyrolysis and gasification. The energy optimization in slow pyrolysis may be achieved by the utilization of pressurized pyrolysis to increase biochar and gas yields [72]. As in torrefaction, pyrolysis intensity may be tuned by using different temperatures for specific applications, e.g., lower [73] or decreasing [74] pyrolysis temperatures were shown to be beneficial in achieving energy savings while producing biochars that have similar properties to high-temperature biochars. Yet another option to decrease cost and increase energy efficiency in slow pyrolysis is to use the CO₂-containing pyrolysis gas in the pyrolysis process, rather than using expensive N₂ gas [72].

The production of biochars has positive environmental impacts, such as reduced fossil depletion, reduced water eutrophication, etc., while the transportation of biochars has a negative environmental impact on their life cycle [75].

3.3. Hydrothermal Carbonization (HTC)

Hydrothermal carbonization is defined as the combined dehydration and decarboxylation of biomass in a suspension with water under saturated pressure for several hours [76]. It is an interesting method of producing chars (referred to as hydrochars) from biomass without an energy-consuming pre-drying step [77]. Hydrothermal carbonization may be considered suitable for the conversion of materials with elevated moisture content [78–80]. The temperature applied is usually between 180 °C and 250 °C [71]. Similar to biochars, hydrochars may be used as fuels, soil amendment material, or activated carbon precursors [78,81–83]. The fuel quality of hydrochars was shown to be comparable to low-temperature biochars [84]. Hydrochars contain less ash than raw biomass and biochars, which is an advantage in fuel applications [85,86]. However, the surface areas of hydrochars are much smaller than those of biochars [78]; therefore, surface activation may be required for adsorption applications.

The process temperature and duration of the HTC process are considered to be the determining factors of its environmental performance [80,87,88] because they determine the hydrochar properties and energy yield. On the other hand, after the production of hydrochars, additional costly steps are required. Compared to dry carbonization biochars, hydrochars may contain higher moisture content, which requires a drying step, and the generated HTC effluents containing dissolved organic and inorganic compounds need to be treated before their discharge into the environment [89,90].

Table 1 summarizes important pyrolysis studies with bark, including the conditions used in the different processes and the bark species, and the obtained char yields and HHV. The bark char yields and calorific value are similar to those of other lignocellulosic biomass types. Fast-growing eucalyptus barks and abundant oak and conifer barks were the main barks analyzed.

Table 1. Conditions, char yields, and char calorific value of different barks in torrefaction, slow pyrolysis, and hydrothermal carbonization.

Process	Bark	Temperature (°C)	Time (min)	Char Yield (%)	HHV (MJ kg ⁻¹)	Reference
Torrefaction	<i>Picea abies</i>	225–300	30–60	61–90	20–24	[91]
	<i>Abies alba</i>	250	60	71	32 *	[92]
	<i>Eucalyptus saligna</i> and <i>E. grandis</i>	220–280	60–300	71–91	17–23	[93]
	<i>Eucalyptus globulus</i> and <i>E. nitens</i>	250–280	15–30	60–95	19	[94]
	<i>Quercus cerris</i>	200–300	30–60	62–90	-	[38]

Table 1. Cont.

Process	Bark	Temperature (°C)	Time (min)	Char Yield (%)	HHV (MJ kg ⁻¹)	Reference
Slow pyrolysis	<i>Leucaena leucocephala</i>	350–550	60–180	47 **	23 *	
	Pine	300–850	60	35–68	-	[95]
	<i>Maesopsis eminii</i>	500	60	32	-	[96]
	<i>Larix sibirica</i>	500–700	30–60	28–63	-	[97]
	<i>Quercus suber</i>	400–700	-	-	32	[98]
	<i>Quercus cerris</i>	325	30–60	52–73	-	[38]
	<i>Quercus petraea</i>	400–500	10	-	20	[99]
HTC	Conifer mixture (80% fir, 15% spruce, 5% pine) and <i>Robinia pseudoacacia</i>	150–185	30	71–93	20–22	[100]
	Eucalyptus	220–300	120–600	40–46	20–29	[101]
	Oak and pine	220	300	67–73	-	[102]

* Calculated using an empirical correlation based on ultimate analysis, ** optimum yield.

4. Extraction of Bark

Barks are rich sources of extractives, which are conventionally defined as low-molecular-weight compounds [10]. The amount of extractive in barks is higher than in other lignocellulosic materials and can reach 40% [26]. The bark extractives can be broadly grouped into hydrophilic and lipophilic compounds, depending on the solvent polarity used for their solubilization, and their amount and composition differ in the outer and inner bark and according to the used solvent [10]. Bark may also contain high-molecular-weight polyphenols such as condensed tannins [103] that are structurally similar to low-molecular-weight phenols but have higher molecular weights [10]. Alternatively, extractives may be defined as biomass constituents, which can be extracted by neutral solvents [104].

The most common bark extraction is of condensed tannins [105], which in different barks vary significantly between 5% and 50% [10]. Condensed tannins are used in the manufacture of leather as tanning agents or as phenol replacement in the production of phenol–formaldehyde resins for particle board and plywood [10,105]. However, barks may also contain interesting lipophilic and hydrophilic extractives that have bioactive properties.

Barks should be screened for lipophilic and hydrophilic extract yields to target specific compounds in the biorefinery [106]. There are two different approaches to obtaining extracts from biomass, the first being a conventional sequential solvent extraction, and the second being alternative extraction methods, as analyzed in the following section.

4.1. Sequential Solvent Extraction

Sequential extraction is based on the solubility difference of biomass extractives in solvents with varying polarities. First, lipophilic extractives are removed with nonpolar solvents, and later hydrophilic extractives are removed with polar solvents by increasing solvent polarity.

Interestingly, cork-rich barks contain the highest lipophilic content and the smallest hydrophilic-to-lipophilic extract ratio compared with other barks and wood, as shown in Table 2, where the extraction results were obtained with the same methodology and solvents, since extract composition and yield depend on the extraction process and solvent used. For instance, birch (*Betula pendula*) has the highest amount of lipophilic extractives followed by Turkey oak (*Quercus cerris*) and cork oak (*Quercus suber*) while eucalyptus, chestnut, oak, and some South American tree barks such as *Anadenanthera colubrina* contain a high amount of hydrophilic extracts. Barks contain in general a higher amount of hydrophilic extracts than of lipophilic extracts, as shown by the hydrophilic/lipophilic extract ratios (Table 3).

Table 2. Extraction yields of different barks with different solvents and hydrophilic/lipophilic ratios (RHL).

Bark	Extraction Yield, %				Reference
	DCM	EtOH	Hot Water	RHL	
<i>Quercus cerris</i>	10.9	3.4	2.4	0.53	[107]
<i>Quercus suber</i> —Portugal	5.8	5.9	4.5	1.79	[108]
<i>Quercus suber</i> —Bulgaria	4.4	5.4	2.7	1.84	[109]
<i>Quercus suber</i> —Turkey	7.1	3.6	1.2	0.68	[109]
<i>Quercus variabilis</i>	5.3	2.8	1.1	0.74	[110]
<i>Quercus rotundifolia</i>	1.6	6.4	9.3	9.81	[111]
<i>Quercus faginea</i>	1.9	4.9	6.4	5.95	[112]
<i>Quercus robur</i>	1.1	7.4	14.5	19.91	[113]
<i>Quercus rubra</i>	2.7	2.1	7.3	3.48	[113]
<i>Quercus rubra</i>	7.4	12.7	4.1	2.27	[114]
<i>Albiza niopoides</i>	2.7	3.9	5.2	3.37	[115]
<i>Anadenanthera peregrina</i>	3.0	21.0	4.7	8.57	[116]
<i>Anadenanthera colubrina</i>	2.8	22.5	4.1	9.50	[116]
<i>Betula pendula</i>	32.2	0.6	0.5	0.03	[117]
<i>Betula celtiberica</i>	2.7	4.1	7.5	4.30	[113]
<i>Castanea sativa</i>	2.0	9.5	20.4	14.95	[113]
<i>Copaifera langsdorffii</i>	2.1	17.4	1.8	9.14	[118]
<i>Eucalyptus sideroxylon</i>	1.7	20.1	33.9	31.76	[119]
<i>Fraxinus excelsior</i>	4.3	18.5	6.6	5.84	[113]
<i>Goupia glabra</i>	3.4	15.0	6.2	6.24	[120]
<i>Kiyelmeyera coriacea</i>	7.7	8.2	2.0	1.32	[121]
<i>Myracrodruon urundeuva</i>	4.2	9.3	13.5	5.43	[122]
<i>Plathymenia reticulata</i>	3.4	5.8	3.6	2.76	[123]
<i>Populus x canadensis</i>	3.0	13.7	5.1	6.27	[114]
<i>Robinia pseudoacacia</i>	3.6	7.2	5.5	3.53	[114]
<i>Robinia pseudoacacia</i>	3.8	3.9	5.0	2.34	[113]
<i>Salix</i>	3.3	19.9	5.9	7.82	[114]
<i>Tectona grandis</i>	2.2	2.9	7.3	4.64	[124]
<i>Pinus nigra</i> subsp. <i>laricio</i>	4.0	5.5	4.5	2.50	[114]
<i>Pinus slyvestris</i>	4.2	5.0	9.2	3.38	[125]
<i>Pinus pinea</i>	1.8	9.4	9.4	10.44	[126]
<i>Larix decidua</i>	2.8	19.1	8.2	9.75	[114]
<i>Picea abies</i>	4.8	5.3	11.2	3.44	[125]
<i>Pseudotsuga menziesii</i>	5.6	21.1	2.4	4.20	[127]
Average	4.7	9.5	7.0		
Std.	5.3	6.7	6.3		

Table 3. Comparison of average extractive yields of bark and wood by sequential solvent extraction.

Average Extractive Content (%)				
	Lipophilic	Hydrophilic	Hydrophilic/Lipophilic Ratio (RHL)	Reference
Barks	4.7	16.5	3.52	This work
Cork-rich barks	10.1	9.2	0.91	[107,108,110,117,121,123,127,128]
Hardwoods	0.7	8.6	12.29	[129,130]
Softwoods	1.5	7.9	5.27	[129,130]

4.2. Alternative Extraction Methods

The conventional sequential solvent extraction method usually uses a Soxhlet apparatus, which has some disadvantages, such as the following:

1. The extraction yield is not optimized, and it is limited because extractions are performed under atmospheric pressure and below 100 °C.
2. The usage of organic solvents renders the method not environmentally friendly.

3. It usually takes a long time, from days to weeks, to obtain the extracts.
4. It has low selectivity to target compounds.
5. The thermally sensitive extracts are lost during the hot water extraction, which may not be appropriate to produce bioactive compounds.

Alternative extraction methods such as accelerated solvent extraction, ultrasound-assisted extraction, microwave-assisted extraction, and maceration offer solutions to these problems.

Accelerated solvent extraction (ASE) is a form of pressurized liquid extraction (PLE) and is perhaps the most well-known technique to overcome the disadvantages of solvent extraction [131]. It is based on using elevated temperatures (up to 200 °C) and pressures (up to 100 bar) and the extraction time and solvent use are reduced significantly [132,133]. The disadvantages of ASE include its higher cost, usage of organic solvents, and possible loss of thermally sensitive extracts (Table 4). Ultrasound-assisted extraction (UAE) is a fast extraction method based on ultrasounds and environmentally friendly solvents such as water and ethanol [134]. As in ASE, it uses less solvent than conventional methods [135]. It is especially suitable for the extraction of hydrophilic and thermally sensitive compounds such as antioxidant compounds [134,135], while its efficiency in the extraction of lipophilic compounds may be limited [136].

Table 4. Evaluation of extraction efficiencies of bark by alternative extraction methods.

Target Extractive Efficiency			
Extraction Methods	Hydrophilic Compounds	Lipophilic Compounds	Limitations
ASE	Efficient	Efficient	High cost, use of organic solvents, and loss of thermally sensitive compounds
UAE	Efficient	Not efficient	Possible low extract yields, high energy consumption
MAE	Efficient	Efficient	Possible low extract yields, loss of thermally sensitive compounds, and high energy consumption
MAC	Least efficient	Least efficient	Longer extraction time, use of organic solvents, and low extract yields
SFE	Efficient	Most efficient	High cost

Microwave-assisted extraction (MAE) is also a fast method that applies microwaves to extract mainly hydrophilic compounds from biomass, although lipophilic compounds may also be extracted [137]. It is a selective method to extract phenolic compounds [138]. However, it may be considered a highly energy-consuming process, similar to ultrasound-assisted extraction [136]. It is likely that microwave-assisted extraction results in lower extract yields than conventional solvent extraction with bark because the extracts may undergo degradation under elevated extraction times and microwave powers [138]. However, studies with bark and MAE are scarce, and more data are needed to better understand and evaluate the potential of the MAE extraction route for bark.

Maceration (MAC) is the simplest extraction method based on the extraction of biomass with an organic solvent at low temperatures and at atmospheric pressure in a single step. Under these conditions, the extract yield is lower than with the sequential solvent extraction and the extraction time is longer. The use of organic solvents is also a disadvantage of maceration. However, maceration has certain advantages because it is more suitable for the extraction of thermally sensitive compounds and is less energy-consuming (Table 4).

Supercritical fluid extraction (SFE) removes extractives from lignocellulosic biomass with supercritical fluids, i.e., fluids that are above their critical temperature and pressure. The most commonly used supercritical fluid is CO₂, which has a critical temperature and pressure of 31.1 °C and 73.8 bar, respectively [139]. Supercritical CO₂ has interesting properties: it is an environmentally friendly solvent, it is nonpolar, and its density changes at different temperatures and pressures. Compared to water, another environmentally friendly solvent, its critical pressure and temperature are much lower.

Supercritical CO₂ is particularly suitable for selectively extracting lipophilic compounds. It is possible to increase solvent polarity by using a co-solvent such as ethanol [139], and therefore the CO₂-SFE also allows the extraction of hydrophilic compounds from lignocellulosic biomass. Another important advantage of SFE is that the extracts retain their bioactive properties [140]. The main disadvantage of this method is its relatively higher cost than other extraction methods (Table 4).

The alternative extraction methods are relatively new but have been increasingly applied to lignocellulosic biomass and barks. Triterpenoids such as friedelin, lupenone, and betulin from bark are extractives that have been obtained with SFE methods [141–150].

It is necessary to evaluate the cost-effectiveness and the environmental impact of different extraction methods on different barks, and a life cycle analysis (LCA) is also an important step in developing biorefinery routes [151,152]. LCA studies comparing different extraction methods of barks are scarce. An LCA study was performed for Norway spruce (*Picea abies*) bark to compare three different extraction methods, namely hot water extraction (HWE), ultrasound-assisted extraction (UAE), and supercritical fluid extraction (SFE), to extract polyphenols [153]. The hot water extraction (HWE) method showed the lowest environmental impact per unit of extracted phenolic compound [153].

5. Critical Evaluation of Bark-Based Biorefineries

5.1. Screening Barks for Biorefinery

Pyrolysis (slow pyrolysis, torrefaction, and hydrothermal carbonization) and extraction are considered the key conversion routes for bark, given that the technological conditions of pyrolysis processes and the high extractive content of bark favor these two routes. The development of efficient biorefineries requires the screening of barks' properties, namely moisture content, ash content, chemical composition, higher heating value, extractive yield, and composition.

Moisture content varies greatly between different barks and different positions in the tree, as well as between different seasons [3,154]. High-moisture-containing barks should be considered for the HTC process to avoid drying costs in dry pyrolysis. The ash content of barks is usually at least ten times higher than that of wood of temperate zones, which usually contains less than 1% ash [10,155]. The upper limit of ash content of bark may be considered as 20% [2]. The high ash content of bark may become problematic in thermal conversion because certain ash components such as potassium and calcium may cause slagging and fouling problems [156,157]. The high-ash-containing barks (>3%) should be pretreated with hot water to reduce the ash content if they are targeted for fuel use [158,159]. However, the ash removal from bark after hot water treatment may be insufficient [160] and in this case, the hydrothermal carbonization route should be applied to obtain higher biochar yields and to avoid ash-related problems during dry pyrolysis [161,162].

The macromolecular chemical composition of bark includes polysaccharides, lignin, and suberin. Hardwood and softwood barks may differ in their lignin and holocellulose contents as well as in their suberin content [163]. The chemical composition of different barks was reviewed in a previous article that reported 18–44% polysaccharides, 32–40% lignin, and 2–34% suberin [3]. Compared with wood, bark contains a higher amount of ash and extractives, and a lower amount of polysaccharides [10]. It also contains suberin and polyphenols which are absent in wood [3,10]. The cork-rich barks with high suberin content may be directed to obtain suberin monomers and lipophilic extracts to produce polymers and triterpenoids [141,164–168]. The lignin-rich barks should be considered for the production of biochars with higher char yields or to produce polyols and polyurethanes [169–174] or aromatics [175]. Different pretreatments such as organosolvent methods may be applied to increase the conversion efficiency of bark macromolecules such as suberin [176]. Bark polysaccharides may be considered for the production of food delivery packaging because they have a cost advantage as waste materials, they provide adequate strength, and they are biodegradable [177]. The fractionation of the

polysaccharide fraction of barks is a complicated task due to the recalcitrance of the biomass and low polysaccharide content, although catalytic fractionation may overcome these problems [27,178].

The heating value of bark is slightly higher than that of wood and ranges between 18.7 MJ/kg and 22.7 MJ/kg [10,179]. Softwood barks generally have higher heating values than hardwood barks [179]. Barks with higher calorific values are potentially better suited for fuel applications. The production of cork pellets with a calorific value of 20 MJ/kg is an example of a fuel use for bark [180]. Fuel pellets produced from softwood barks demonstrated high mechanical durability [181], which is an important parameter in handling and transportation [182].

Extractives of barks may be grouped into hydrophilic compounds, lipophilic compounds, and polyphenols such as condensed tannins. Hydrophilic compounds are the main bark extracts, as shown in the previous section, and have antioxidant and bioactive properties [183]. In the biorefinery, these compounds should be extracted in a first step under low temperatures to avoid thermal decomposition and with a suitable extraction method, considering selectivity, efficiency and environmental impact. The most important lipophilic extracts are terpenes and triterpenoids, which are likely to have therapeutic activities, including anticancer, antimicrobial, and antiviral activities [184,185]. Barks with high amounts of lipophilic extractives such as cork-rich barks should be selected for the production of triterpenoids, while barks containing high amounts of hydrophilic extractives should be selected for phenols to produce antioxidants and aromatic compounds [186,187]. Barks containing high amounts of polyphenols should be selected for the production of tannins [188–190].

5.2. Development of a Biorefinery Scheme

A biorefinery scheme for bark-based biorefineries is proposed in Figure 11, taking into account the discussed bark characteristics and screening factors. A total of three conversion loops are determined. The first loop (L1) is the extraction processes, consisting of different extraction methods to target specific extracts. The second loop (L2) is the pyrolysis processes, which consists of HTC, slow pyrolysis, and torrefaction to produce hydrochars, biochars, and fuel pellets. The third loop (L3) is the macromolecular conversion processes, consisting of the depolymerization of the bark structural components. The threshold limits for selecting conversion routes are set at 30% for moisture and at 3% for ash content. A total of nine different biorefinery products are proposed, of which six can be produced by pyrolysis and extraction methods. The transformation of the macro chemical components in bark is beyond the scope of this review and thus only briefly discussed. The proposed biorefinery products (biochars, hydrochars, fuel pellets, simple phenols, triterpenoids, and condensed tannins) suggest that waste barks can be integrated into biorefinery systems to produce chemicals and solid products. The environmental impact of different conversion routes should be analyzed before the implementation of any biorefinery scheme.

The most abundant and versatile bark biorefinery product seems to be simple phenols, which can be obtained by hydrophilic extraction, hydrothermal carbonization, or slow pyrolysis. Simple phenols are platform chemicals that may be used to produce plastics, pharmaceuticals, or other chemicals.

5.3. Current Knowledge Gaps and Future Directions

The results of this review show that bark and biorefinery studies have experienced an increasing trend in recent years, with biorefineries increasingly being directed toward waste materials including bark. However, knowledge gaps exist, and their identification and surmounting are important for developing bark-based biorefineries.

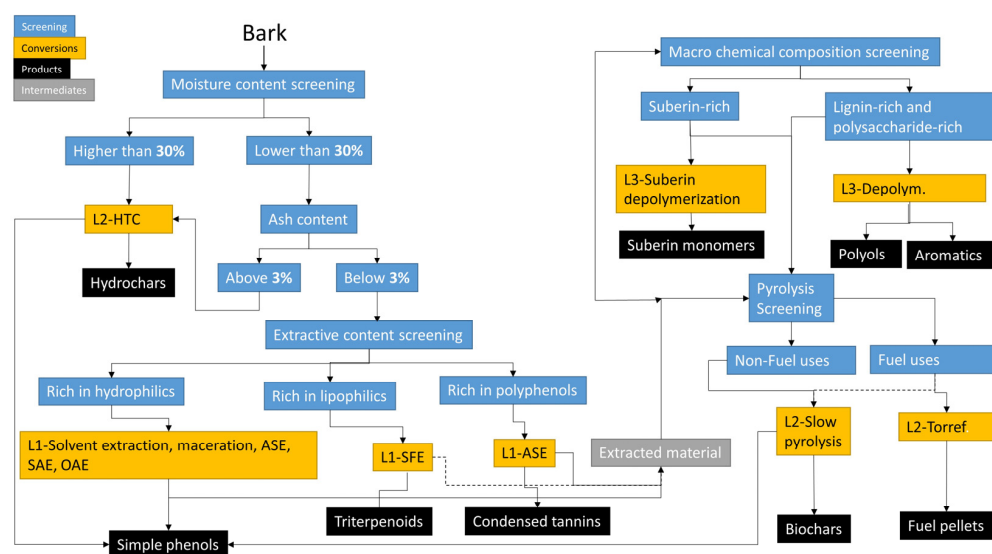


Figure 11. Proposed scheme for bark biorefineries.

The following knowledge gaps on bark conversion were identified in this work:

1. The number of bark characterization studies is insufficient: only a total of 21 articles investigated the extract composition of different barks (Table 2).
2. The applied pyrolysis conditions are non-standardized: a total of 13 articles applied different conditions (Table 1), which complicates the evaluation of the most economic processing conditions.
3. The applied extraction conditions were also variable. Since the extract composition, properties and yield depend on the applied solvent and method, we limited our discussion to cases with similar extraction procedures (Table 2).
4. Studies focused on the screening and application of different bark extracts are scarce: only Jablonsky and co-workers analyzed the potential of softwood bark extracts for the production of chemicals and nutraceuticals [185,191].
5. Energy balance is an important parameter in the evaluation of different processing paths and the scaling up of biorefinery processes. However, the pyrolysis and extraction conditions, as well as chemical properties, of different barks are highly variable which make the energy balance an unhelpful tool. More research is needed to evaluate the energy balance of different bark conversion processes.
6. There is a lack of studies on the environmental impact of bark valorization.
7. Studies combining different processing routes are insufficient: only Rasi and co-workers (2019) studied a cascade processing method consisting of hot water extraction, pyrolysis, and anaerobic digestion for pine and spruce barks [27].
8. There is a lack of studies investigating the production of bark-based platform chemicals such as simple phenols via pyrolysis or extraction.

Considering these limitations, the following recommendations can be made:

1. More research is needed on the chemical and pyrolysis properties of barks. Possibly fewer than 100 barks have been considered for valorization, which is a very small number regarding the huge potential for bark valorization given the existing number of tree species. Future bark valorization studies should apply standardized methods.
2. The bark valorization studies should consider cascade processing, combining different valorization processes instead of a single process.
3. The environmental impact of the different applied conversion processes is largely unknown, as is their economic evaluation. Energy balances should be provided in bark conversion studies.
4. Different bark extracts should be screened for antioxidant or nutraceutical potential, including pharmacokinetic profiles and drug-like properties.

5. The production of phenolic substances and simple phenols should target extractive-rich barks after chemical screening. Barks may be a source of platform chemicals such as simple phenols, as in earlier studies before their replacement with petroleum-based products. It is therefore necessary to re-consider bark for the production of platform chemicals to be used in the food, fragrance, or pharma industries. Efficient and selective production of these chemicals through extraction, pyrolysis, or depolymerization may open up new possibilities for bark valorization, namely using optimized and environmentally friendly conversion methods and improved catalysts [192].

Bark-based biorefineries require a detailed characterization of barks. In general, barks contain a high amount of extractives and inorganic compounds, a low amount of polysaccharides, and also contain suberin and polyphenols, with the cork-rich barks containing the highest amount of lipophilic extracts, e.g., triterpenoids. Therefore, pyrolysis and extraction methods are proposed for bark-based biorefineries, which should be integrated with macromolecular conversion methods.

6. Conclusions

Different pyrolysis and extraction methods were critically reviewed, considering process conditions, energy optimization, and bark as a biorefinery feedstock. The following specific conclusions are derived from this study:

1. The number of bark valorization studies has been increasing in recent years, since barks are widely available feedstocks and may be processed to produce sustainable and environmentally friendly products, including chars, antioxidants, and platform chemicals.
2. Adsorption applications and antioxidant production are predicted to be the most important topics in bark valorization in the near future.
3. More studies are required to screen different barks for their chemical composition, extractives profiles, and drug properties.
4. Bark valorization studies should be designed in the form of cascade processing and should combine different processing paths, including pyrolysis, extraction, and enzymatic digestion or chemical fractioning.

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