

Review



# Management of Agri-Food Waste Based on Thermochemical Processes towards a Circular Bioeconomy Concept: The Case Study of the Portuguese Industry

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**Abstract:** Sustainable biomass production has a significant potential for mitigating greenhouse gas emissions, providing an alternative to produce eco-friendly biofuels, biochemicals, and carbonaceous materials for biological, energetic, and environmental applications. Biomass from agroforestry and agricultural wastes is the richest natural carbon source and a sustainable option for woody biomass from a circular economic perspective. The European Union (EU) is estimated to produce 1.3 billion tons of agri-food waste annually. Portugal has a large supply of residual biomass, as well as other byproducts and wastes from forestry, agriculture, and the food industry, and has a high availability of residual biomass. By using biomass waste to create high-value products, Portugal envisages an improvement in its economic performance, while reducing its dependence on energy imports and fossil fuel use. This review explores the potential of agri-food waste obtained from Portuguese industries through thermochemical conversion technologies as a promising sustainable substitute for wood-based biomass for the development of eco-friendly biofuels, biochemicals, and high-value carbonaceous materials, and their applications. This strategy, based on the circular bioeconomy concept, can help reduce reliance on fossil fuels, reduce greenhouse gas emissions, fulfil the needs of the growing population, and offer a sustainable waste management solution.

Keywords: agri-food waste; thermochemical conversion; Portugal; carbonaceous materials

# 1. Introduction

Current energy supplies rely on the burning of fossil fuels, which are the primary source of energy for heating, transportation, and electricity generation [1]. Fossil fuels represent approximately 81% of the world's energy, whereas renewable energy sources account for 14%, of which biomass contribution represents 70% [2]. Fossil fuel resources are mostly used to meet the rising energy demands of the expanding world population and to create a variety of synthetic polymers, cosmetics, and platform chemicals that enrich the quality of life [3]. However, fossil fuels have serious implications for climate change and global warming owing to greenhouse gas emissions. Despite these concerns, global reliance on fossil fuels continues to increase, eventually leading to fossil fuel resource depletion, energy shortages, and environmental crises [1,3]. Therefore, there is an urgent need to explore renewable, inexpensive, inexhaustible, and sustainable alternatives to fossil fuels to meet the demands of the expanding human population [1,4,5].

Organic biomass waste has been identified as a promising alternative to produce ecofriendly biofuels, biochemicals, and carbon-neutral products for biomedical, pharmaceutical, cosmetic, and other industrial uses [3,4,6]. Biomass wastes, such as plant-based matter, animal manure, sewage sludge, and industrial, forestry, and agricultural wastes [4,7], can



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). help reduce reliance on petroleum-based resources and mitigate climate change while offering a sustainable alternative for waste management [3]. Traditional methods of handling solid waste entail either disposal in landfills or open burning as undesired materials, leading to serious environmental and economic concerns, such as water and land management, energy generation, transport, and storage [7,8]. Unlike fossil fuels, biomass combustion leads to lower sulfur  $(SO_x)$  and nitrogen  $(NO_x)$  oxides and is considered carbon-neutral, as the carbon dioxide (CO<sub>2</sub>) generated in this process comes from CO<sub>2</sub> previously absorbed by plants during photosynthesis [1,4]. Therefore, given its availability in large quantities (approximately 950 million tons of biomass is produced annually in the EU [9]), low cost, rapid generation, renewable nature, and environmental benefits, biomass recycling for high-value-added products, such as biofuels, bioproducts, and carbonaceous materials, has drawn increasing attention for biomass valorisation [8]. Sustainably produced biomass has significant potential for reducing greenhouse gas emissions and seems to be the most viable economic model to complement the energy systems and products currently powered by fossil fuels [3]. The European Union (EU) has developed circular bioeconomy strategies [10] in which biomass is envisioned to play a vital part in achieving the global climate targets defined in the Paris Agreement [11]. According to the European Commission [12], circular bioeconomy strategies aim to minimise waste generation while preserving the value of goods, materials, and resources, as long as feasible [13]. For instance, the EU accounts for approximately 9% of the global biomass supply, with approximately 60% used for feed and food products, 21% for bioenergy, and 20% for biomaterials used in the wood industry [2]. An important strategy relies on the efficient utilization of resources through integrated biorefineries and the cascading use of biomass, which depends on the cooperation of local agriculture, industry, research, and regional public institutions [13]. In 2022, Portugal's total energy consumption, which includes electricity, transportation, and heat, was reported to be 258 TWh [14]. Although a significant portion of Portugal's energy still comes from fossil fuels, accounting for 76% of its primary energy supply in 2019, it is worth noting that the country is a global leader in renewable energy production. Portugal's new national energy and climate plan for 2030 aims to increase the share of renewables in electricity production to at least 80% and to further decarbonise the energy sector. Additionally, approximately 8% of Portugal's energy already comes from the use of solid biomass, which was estimated at 2.92 million metric tons of oil equivalent in 2021 [15]. However, the location, seasonal availability, dispersed nature of residue formation, and variations in local circumstances may limit the supply of biomass waste for biorefining and biomanufacturing [3]. With the COVID pandemic, the importance of securing supplies and storage, particularly food and energy, has become evident [16]. Renewable and carbon-based biomass can be used as alternatives to guarantee the EU's energy supply. Furthermore, the valorization of local biomass resources in customised biorefineries can be used for the co-production of food, feed, materials, and energy in cascaded process chains. This approach minimises long-distance transportation, promotes job creation, stimulates innovation, and boosts the economy [3,16]. Several applications of carbonaceous materials obtained from biomass are currently being sought owing to their potential cost-effectiveness, large-scale, and quality-controllable production in an environmentally responsible manner [8]. Portugal is a European country with a noteworthy potential for biomass generation, with approximately 92% of the territory occupied by agriculture, forestry, and agroforestry. However, Portugal depends heavily on imports to meet its energy demands, ranking ninth among EU countries with almost 80% of energy imports in recent years [17]. Owing to the availability of large amounts of residual biomass and the country's high productivity in the agricultural and industrial sectors, Portugal plans to decrease its reliance on energy imports and the use of fossil fuels, as there is a huge potential to raise the percentage of bioenergy while concurrently lowering the costs of managing the residues [13,18]. With regards to this point, agri-food waste constitutes a promising, but poorly explored, source of biomass but with a high potential. Despite the lack of consolidated data, the FAO estimates food waste generated in the domestic sector in Portugal above 861 tonnes/year [19]. Furthermore, alternative biomass sources to woody waste are important sources of carbon-based materials. These materials have a wide range of applications, such as environmental monitoring, energy storage, and chemical and environmental applications [5,20–23]. Therefore, it is crucial to benefit from the economic potential of biomass to increase the country's economic performance [13].

This review aims to explore the potential of agri-food waste obtained from Portuguese industries via thermochemical conversion technologies as a useful strategy for the development of eco-friendly biofuels, biochemicals, and high-value carbonaceous materials and their applications.

# 2. Plant-Based Biomass

The composition of plant-based biomass, which is abundant in biopolymers, varies depending on the type of feedstock used [4]. Based on their chemical composition, they can be categorized as lignocellulosic or non-lignocellulosic biomass. The most prevalent non-edible biomass from forestry and agricultural wastes is lignocellulosic biomass, which mostly consists of cellulose, hemicellulose, and lignin. Fruit and food waste are examples of non-lignocellulosic biomass. These wastes are rich in carbohydrates, polysaccharides, and proteins, and serve as sources of carbon and nitrogen to produce carbonaceous materials obtained from biomass [8,24]. Generally, 90% of the dry matter found during lignocellulosic biomass decomposition is related to the breakdown of naturally occurring lignin (10–25 wt%), hemicellulose (20–40 wt%), and cellulose (40–60 wt%) [3,25,26] (Figure 1). In addition to their renewable nature, these biopolymers possess other interesting properties such as biocompatibility, nontoxicity, and biodegradability. Owing to their properties, these molecules have numerous industrial applications in cosmetics, agriculture, biomedicine, and water treatment [5].



**Figure 1.** Biomass from industrial, forestry, and agricultural wastes can be used to synthesise useful carbonaceous materials obtained via thermochemical processes.

Cellulose is the most prevalent biopolymer in nature. Cellulose is a homopolysaccharide composed of repeating d-anhydroglucopyranose monomers connected by 1,4- $\beta$ -glycosidic bonds. Microfibrils composed of natural cellulose chains are bundled into fibres [4,5]. An elementary fibril is the basic unit. Cellulose fibrils contain amorphous and crystalline regions that differ in proportion between plants [4]. Nanocellulose is a crystalline substance obtained by the extraction of cellulose from plants [4,5]. Strong acids are used to hydrolyse plants and cleave glycosidic chains, leading to cellulose nanocrystals (CNCs). During hydrolysis, the amorphous regions are removed, while the crystalline regions remain intact owing to their higher resistance, forming rod-like nanocrystals whose dimensions depend on the plant source. Depending on their size, cellulose nanofibrils (CNFs) or microfibrils are obtained by applying a mechanical shear force to plants. This results in the fragmentation of the fibres into their substructural fibrils [4]. Certain bacteria can also produce cellulose, such as bacterial nanocellulose (BNC) [27]. Depending on the physiological state of the cell, bacterial fermentation through the pentose phosphate or Krebs cycle leads to BNC production. BNC have a higher chemical purity than plant cellulose and higher crystallinity because it does not contain hemicellulose or lignin [28]. BNC have other advantages, including a high degree of polymerisation, mechanical stability, water-holding capacity, biodegradability, and biocompatibility [4,29]. Remarkable features of nanocelluloses include a high and adjustable surface area, crystal structure, and exceptional mechanical strength coupled with renewability, biodegradability, and accessibility on a broad scale [5].

Lignin is one of the most abundant natural biopolymers, which serves as the glue that holds cellulose fibres together in plants. The primary sources of lignin are paper mill industrial waste and wood fibres. Lignin is a phenolic polymer with a high degree of cross-linking between the phenylpropane units. This resulted from the polymerisation of *p*coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These precursors then synthesise three main monomers of lignin: *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) [30]. Owing to its high stability at low temperatures, lignin results in a high yield of solid carbonaceous products [4]. The ratio of monomers to lignin content varies depending on the plant type. Herbaceous plants possess low amounts of lignin and are composed of all three monomers. Softwood has a higher lignin content and consists mainly of coniferyl alcohol units. Hardwood lignin contains coniferyl and sinapyl units. The properties of the final products can be affected by differences in monomer and lignin content and subsequent extraction. Based on the extraction method, lignin can be classified into kraft lignin [31], soda lignin [32], sulfite lignin [33], and organosolv lignin [34]. Kraft lignin contains more phenolic hydroxyl groups and has a more condensed carbon–carbon (C–C) structure. Soda lignin is often sulfur-free and has improved solubility. Sulfite lignin is water-soluble owing to the addition of sulfonated groups. Compared with soda lignin, organosolv lignin contains more phenolic hydroxyl groups and fewer carboxyl groups [4,34].

Hemicellulose is a heterogeneous polymer containing short, highly branched chains of sugars, namely five-carbon sugars (D-xylose and D-arabinose), six-carbon sugars (Lgalactose, D-glucose, and D-mannose), and uronic acid [1,26]. It can also contain organic acids such as glucuronic acid and acetic acid. Hemicellulose is easily hydrolysed into basic sugars. It is a linear polymer with a base composed of either repeating units of a sugar combination (heteropolymer) or the same sugar (homopolymer) [1,26]. Heteropolymers can contain several sugars, such as xylans, mannans, xyloglucans, and glucomannans, which vary in composition according to their species. This typically leads to random and amorphous hemicellulose structures [35], indicating that hemicellulose is less chemically resistant than cellulose [26]. For instance, softwood hemicellulose is mostly composed of glucomannans, whereas hardwood hemicellulose generally contains xylan [36]. Unlike cellulose, hemicellulose does not form microfibrils. However, it can also form hydrogen bonds with cellulose and lignin. Lignocellulosic biomass is a complex carbohydrate polymer mainly composed of lignin (10–25%), cellulose (35–50%), and hemicellulose (20–35%) [4], which comprise the majority of agricultural waste [26]. This type of biomass is thought to be responsible for the variation in composition, with softwood having the highest lignin content among all biomasses [37]. Lignocellulosic biomass is recalcitrant because of the crystallinity of cellulose, the high degree of aromaticity of lignin, and the encapsulation of cellulose by the hemicellulose–lignin matrix [4,38]. Furthermore, because of its interaction with cellulose and cross-linking with lignin via ester and ether bonds, hemicellulose also contributes significantly to the structural strength of biomass [35,36].

Saccharides are simple sugars produced during photosynthesis and are abundant in biomass, such as oligosaccharides and polysaccharides, including cellulose, lignin, and

starch [39]. Primary saccharides, including glucose, sucrose, and fructose, are commonly found in pollen, fruits, and plant fragments, whereas sugar alcohols such as mannitol and arabitol are typically found in fungal spores [39]. The major sources of sucrose, sugar beets and sugarcane, are widely available [40]. Thus, it is economically feasible to use saccharides to generate carbonaceous materials [4]. Upon biomass combustion, substantial amounts of monosaccharides, disaccharides, sugar alcohols, anhydrosugars, and other simple molecules are generated. Several of these compounds, including anhydro saccharides such as levoglucosan (L), mannosan (M), and galactosan (G), are produced as a result of cellulose and hemicellulose combustion, and are therefore recognised as markers of biomass burning [39,41]. The sugars found in the biomass can be transformed into usable energy through direct and indirect methods. Biomass can be burned to produce heat (direct), converted into electricity (direct), or processed into biofuels (indirect) [39,41]. Moreover, the saccharides present in biomass can serve as renewable resources for both the biochemical and biofuel industries and can be converted into a variety of biochemical, biofuel, and polymer products through biological, mechanical, or chemical methods [42].

# The Portuguese Case Study

Portugal has significant potential for producing biomass from its forests and agricultural land, with over 90% of the territory covered by forests (39%), agriculture (26.3%), bush (12.4%), agroforestry (8%), and pastures (6.5%) [43,44]. Moreover, agriculture, food processing, and forestry generate large amounts of residues and by-products [18] (Figure 2). Unfortunately, consolidated data about the amount of waste generated by these cultures are scarce and have to be indirectly estimated.



Figure 2. The main agricultural and forestry industries explored in Portugal.

A report on agricultural biomass production in the EU estimated that the average annual production of dry matter for EU-28 between 2006 and 2015 was 956 million tons [45]. A recently published article has estimated that 180 kg of food per person and per year is wasted in the EU, considering the food waste generated from all stages of the food supply chain, including production, processing, distribution, and consumption. This study highlights that EU households are the biggest contributors to food waste generation, accounting for the majority of food waste produced [46]. According to Statista portal [47], in 2021, Portugal discarded nearly 1.9 million metric tons of food, with households accounting for almost 1.3 million tons of that waste. The catering and hotel industries generated approximately 163 thousand metric tons of food waste, while retail and distribution created more than 224 thousand metric tons. Food manufacturing was responsible for the least amount of food waste, with just under 75.3 thousand metric tons. These figures provide a general idea of the scale of agricultural biomass production and the waste generated in Portugal. Recently, there has been a demand for forest-based biomass for energy production because of incentives for the construction and operation of thermoelectric plants with subsidised tariffs [48,49], alongside the recent national increase in the pellet market for heat production in domestic or industrial boilers [50]. However, if biomass continues to be increasingly used for energy production, its availability may become limited [18]. In this context, in a recent study to evaluate the potential of biomass to produce energy in Portugal, Abreu et al. [51] presented cardoon (72 kha, 1085 kt), paulownia (81 kha, 26 kt), and microalgae (29 kha, 1616 kt) as having greater viability to be exploited as biomass to energy in degraded and marginal soils. A great concern for the use of biomass to generate energy is the wildfires. Forest fires occur frequently in Portugal during summer, resulting in massive expenses for firefighting actions, considerable greenhouse gas emissions, and global warming effects [52]. Hence, there is a need to assess the possible use of other types of available biomass, namely, residual biomass from agricultural and food processing activities and other woody species [18,53]. Owing to the quality of woody biomass, these alternative by-products have different characteristics that can affect the supply and pretreatment chain, combustion processes, ash behaviour, and environmental limitations related to energy conversion processes [18,54].

The use of agroforestry and agricultural residues constitutes an alternative source of biomass to other types that already have other uses and is a sustainable option from a circular economic perspective [18]. Moreover, non-lignocellulosic biomass is rich in carbon and nitrogen, which allows for the preparation of biomass-derived carbonaceous materials [8,24]. Agricultural biomass consists of by-products from agricultural production and the agro-food industry, such as wine, horticulture, olive oil production, and cereals, and the remaining residues, solid wastes, pomace, leaves, and shells resulting from the extraction of raw products [17].

#### 3. Thermochemical Conversion of Agri-Food Waste from the Portuguese Industry

Biomass wastes often have a low bulk density, high moisture or ash content, and mechanical resistance to crushing, which hinders their exploitation in energy or material recovery. Other problems associated with biomass recovery include low density, low calorific value, and geographic dispersion. Environmental concerns include contamination with inert materials, high levels of chlorine, and high concentrations of alkali metals. Hence, an integrated characterisation of the properties of raw materials and the differentiation of different types of biomass is critical for understanding their behaviour during the burning process [13]. Moreover, the existence of updated geographic information systems (GIS) for each type of agri-food waste available in each region (Figure 2) is essential for the efficient management of this biomass. Unfortunately, such data do not seem to be available beyond the forest industry players, at least in a consolidated and freely accessible manner.

Thermochemical conversion technologies have been shown to enhance the physical and chemical properties of biomass in terms of combustibility, enable mechanical processing, increase its stability and energy density, and eliminate chlorine. Therefore, these technologies represent a potential solution for preprocessing the residual biomass [18]. Thermochemical processes use heat to break down biomass into low-molecular-weight products through a series of physicochemical reactions in a controlled environment to yield desired outputs [55]. In contrast to biochemical processes, thermochemical methods have shorter processing times, higher yields, and efficiency, and use whole biomass to produce value-added materials, providing high energy efficiency [4,5].

The thermochemical processes include pyrolysis, hydrothermal carbonisation (HTC), ionothermal carbonisation (ITC), torrefaction, and steam explosion (Figure 3). Hydrothermal processes use subcritical or supercritical water at high pressures and are more suitable for biomass with a high moisture content than other thermal processes [55]. Thermal decomposition varies with the biomass type, which eventually influences the yield and structure of the carbonisation product [4,55]. For instance, lignin content has a significant impact on the properties of carbonaceous materials [5]. In general, during carbonisation, biomass undergoes dehydration, decarboxylation, and a series of polymerisation and condensation reactions to produce a solid product. The properties of the resulting carbonaceous materials vary with the process conditions, including the type of feedstock, temperature, time, heating rate, and pressure [4,5]. Furthermore, different combinations result in diverse characteristics in terms of surface area, functional groups, porosity, and hydrophobicity. Understanding these combinations is essential for the development of carbonaceous materials for various applications [4]. Table 1 presents recent research on the thermochemical conversion of agri-food waste that can result from the main Portuguese industries.



**Figure 3.** Simplified representation of thermochemical processes: (**a**) pyrolysis, (**b**) hydrothermal carbonisation, (**c**) ionothermal carbonisation, (**d**) torrefaction, and (**e**) steam explosion.

Agri-Food Waste	<b>Experimental Parameters</b>	Conclusions	Ref.			
Pyrolysis						
Banana pseudo-stem (BPS)	5 to 10 pieces of BPS, 500 °C, 1.02 s, 200 mL/min N <sub>2</sub> flow rate	BPS bio-oil was produced at a rate of 5.35 MJ/kg, which is relatively low when compared with petroleum fuel and other biomass pyrolysis fluids	[56]			
Banana peel	1 g sample, 720 °C, 10 min, 300 mL/min $CO_2$ flow rate	Pyrolysis of the banana peel with CO <sub>2</sub> enhanced the aromaticity of biocrude, accelerating liquid pyrolysate dehydrogenation without the use of any catalysts	[57]			
Bagasse	Ba/Mg molar of 1:1, CA-to-CB ratio of 4:1, 300 °C, 20 s	BaMg-MMO demonstrated a promising catalytic performance on the synthesis of 4-vinylphenol during the rapid pyrolysis of bagasse	[58]			
Grape bagasse	100 g sample, 700 °C, a heating rate of 5 °C/ms, 60 min, 200 mL/min N <sub>2</sub> flow rate	>95% of Cu(II) was removed from aqueous media using chars produced through the thermochemical conversion of grape bagasse	[59]			
Olive oil pomace	1 mg sample, 500 °C, heating rate of 20 °C/ms, 15 s	The ashes could serve as a catalyst to create bio-oil of higher grades	[60]			
Orange peels	4.5 g sample, 9 g of metal oxide, 500 °C, 25 °C/min, 1 h	5.69 and 4.82 times more 3-furaldehyde were produced by pyrolysis with Cu <sub>2</sub> O and Fe <sub>2</sub> O <sub>3</sub> , respectively	[61]			
Peach seeds	1 g sample, 300 kPa, 15 min, 100 mL/min N <sub>2</sub> flow rate	In the range of 10–20, 37–50, and 10–20% wt. of the pyrolyzed feedstock, respectively, pyrolysis gas, oil, and char were produced	[62]			
Potato peels	30 g sample, 500 °C, 30 °C/min, 30 min, 100 mL/min of N <sub>2</sub> flow rate	The bio-oil and bio-char yield was 23.6 and 29.5%, respectively	[63]			
Sugarcane bagasse	100 μm particle size, heating rate of 50 °C/min, 15.5 min, 493 °C, 225 mL/min N <sub>2</sub> flow rate	46.7 wt% of bio-oil yield was achieved at optimal pyrolysis conditions	[64]			
Sugarcane bagasse	10% wt raw mixture, 1–3 kW, 400 °C, 25–10 kPa, 30–50 min, 500–600 mL/min N <sub>2</sub> flow rate	The microwave pyrolysis by-products suggested a CO <sub>2</sub> reduction potential of 47.9 CO <sub>2</sub> eq/kg	[65]			
Hydrothermal carbonization						
Apple bagasse	500 g sample, 3 L H <sub>2</sub> O, 180 °C, 2 h	The process provided stable carbonaceous solids that may be used as a $CO_2$ neutral fuel (30 MJ/kg) and soil enhancer, in which 80–93% of carbon was recovered	[66]			
Banana peels	5 g sample, 50 mL H <sub>2</sub> O, 300 °C, 1–2 h	The carbonized banana peel removed 99% of Cd <sup>2+</sup> , whereas the raw peel removed 75%	[67]			
Banana stalks	5 g sample, 50 mL H <sub>2</sub> O, 160–200 °C, 1–3 h	Higher heating value ranged from 18.1 to 18.9 MJ/kg, whereas the hydrochar yield ranged from 57.8 to 75.3%	[68]			
Grape pomace	250 g sample, 1250 mL H <sub>2</sub> O, 180 °C, 1 h	97.08% of hydrochar yield was attained, supporting the potential application of grape pomace for solid biofuel	[69]			
Olive pomace	1:1 sample: H <sub>2</sub> O ratio, 300 °C, 24 h	For energy purposes, the hydrochar obtained from olive pomace showed several advantages due to its lower ash content	[70]			

**Table 1.** Thermochemical conversion of agri-food waste that can result from the main Portuguese industries.

Agri-Food Waste	Experimental Parameters	Conclusions	Ref.
Orange peels	6 g sample, 1 mL H <sub>2</sub> O, 210 °C, 180 min	Upgrading of orange peels into value-added chemicals, such as 5-hydroxymethylfurfural, furfural, levulinic acid, and alkyl levulinates	[71]
Pineapple and watermelon peels	85 g sample, 4 L H <sub>2</sub> O, 180 °C, 90 min	The yields and energy content of the hydrochars generated ranged from 25 to 69% and 17 to 22 MJ/kg, respectively	[72]
Potato peels	50 g sample, 50 mL H <sub>2</sub> O, 200 °C, 25 h	Potato peel hydrochar adsorption capacity for Congo red	[73]
Sugarcane bagasse	3 g sample, 50 mL H <sub>2</sub> O, 200 °C, 18–20 h	The biochar obtained from sugarcane bagasse might be used as a sorbent to remove pollutants from water	[74]
Wine sludge	6–12 mL sample, 200 °C, 24 h	The hydrochar products' higher heating value increased from 19.5 MJ/kg for a reactor filled to 24% of its capacity to 21.36 MJ/kg for a reactor filled to 40%	[75]
Ionothermal carbo	nization (ITC)		
Coca bean shells	3 g of sample, 10.8 g [Bmim] [FeCl <sub>4</sub> ], 240 °C, 20 h	The positive effects of the ITC method on mass yield, carbon yield, and specific surface area in [Bmim] [FeCl <sub>4</sub> ] were well demonstrated	[76]
Sugarcane bagasse	1 g sample, 40.2 mmol imidazolium tetrachloroferrate, 240 °C, 20 h	High-specific surface area ionochars with tunable CO <sub>2</sub> uptake/retention, tuneable pore volume, and unique nanostructures were produced	[77]
Torrefaction			
Agri-food industry waste	50 g sample, 200–300 °C, 1 h	The hydrophobic characteristics of agri-food waste improved as the torrefaction process temperature increased	[78]
Banana leaf	260 g sample, 220–280 °C, 1 min	Torrefaction of banana leaves increased bioenergy-related qualities, showed better combustion efficiency, and decreased emissions potential	[79]
Grape pomace	60% <i>w/w</i> sample, 225–275 °C, 30 min	At 275 °C, the carbon content increased by 4.29 wt%, and the calorific value reached 25.84 MJ/kg	[80]
Grape pomace	10% <i>w/w</i> sample, 225 °C, 10 min	Using the torrefaction process, most of the phenolic compounds were not volatilized and remained in biochar	[81]
Olive pomace	16 g, 200–290 °C, 30 min	The findings showed that when the torrefaction temperature improved, the yield of mass and energy declined but the production of greater heating value rose	[82]
Orange peels	60 g sample, 200 °C, 60 min	Orange peels showed excellent odour adsorption ability	[83]
Sugarcane bagasse	DT, 5 g sample, 280 °C, 20 minWT, 5 g sample, 180 °C, 20 min	Both WT and DT processes promoted the heating value of sugarcane bagasse by around 5.0–17.9%	[84]
Steam explosion (S	5E)		
Apple pomace	500 g sample, 151.9 °C, 5 min	21.58% of soluble dietary fibre yield was achieved, and its physicochemical properties were improved	[85]
Grape pomace	100 g sample, 170 °C, 3 min	Free extracts' antioxidant activity was increased by SE whereas the activity of bound extracts was diminished	[86]
Grape seeds	100 g sample, 0–15 MPa, 30–60 s	The SE reduced the mean degree of procyanidin polymerization and made grape seeds more lose and porous	[87]

# Table 1. Cont.

Agri-Food Waste	<b>Experimental Parameters</b>	Conclusions	Ref.
Pineapple leaves	150 g sample, 204 °C, 5 min	Without the use of any chemicals, the SE treatment may raise the cellulose fraction while decreasing the partial concentrations of hemicellulose and lignin	[88]
Pineapple peel	20 g, 1.5 MPa, 30 s	SE treatment can break the bulk volume of dietary fibres and increase the surface area	[89]
Potato peel	300 g sample, 0.35 MPa, 121 s	The water-holding capacity, oil-holding capacity, and swelling capacity values for potato peel significantly increased	[90]
Olive oil bagasse	300 g, 160–200 °C, 5 min	54–76% of the bound oil and 18–32% of the bound β-sitosterol were recovered	[91]
Sugarcane bagasse	20 kg sample, 190 °C, 5 min	After pulping and bleaching, the procedure was quite effective and removed around 97% of the lignin	[92]
Sugarcane bagasse	60 g sample, 205 $^{\circ}$ C, 10 min	The cellulose nanofibers were successfully prepared by SE and could be applied in several fields (e.g., food packaging, and electronic device)	[93]

Table 1. Cont.

Abbreviations: BaMg-MMO—barium-magnesium mixed metal oxide; [Bmim] [FeCl<sub>4</sub>]—1-butyl-3-methylimidazolium tetrachloroferrate; CA-to-BA—catalyst-to-bagasse (CA-to-BA) ratios; CO<sub>2</sub>—carbon dioxide; Cu<sub>2</sub>O—cuprous oxide; DT—Dry torrefaction; Fe<sub>2</sub>O<sub>3</sub>—iron (III) oxide; N<sub>2</sub>—nitrogen; SE—steam explosion; WT—Wet torrefaction.

#### 3.1. Pyrolysis

Pyrolysis involves thermal degradation of biomass under an inert atmosphere at elevated temperatures (300–950 °C), which ensures that combustion does not occur. This method allows the formation of exceptional structures with specific surface areas and high porosity and is the most conventional method for the synthesis of biochar, the most common biomass-derived carbonaceous material [4,8,94]. However, pyrolysis requires the pre-drying of the biomass, which is costly in terms of energy. Despite this, pyrolysis is considered the most practical and economical method for converting raw biomass into carbonaceous materials for large-scale production [4,55]. Pyrolysis can be divided into primary and secondary stages (Figure 3a). During primary pyrolysis, volatile components are fragmented by dehydration, decarboxylation, and/or dehydrogenation, resulting in the formation of bio-oil upon condensation. Secondary pyrolysis is the main process by which heavyweight hydrocarbons are decomposed and converted into char or gases. The biochar produced is essentially a carbonaceous material resistant to decomposition with interesting physiochemical attributes such as high porosity and surface area [95,96]. It has been employed in various applications, such as soil amendment and adsorbents, energy generation, catalysis, carbon sequestration, and the creation of activated carbon and related materials [4,5,95,96].

The type of pyrolysis differs depending on the operating conditions, namely, temperature, residence time, and heating rate, which result in different yields of the final product [4,5]. Additionally, the heating rate and temperature influence the volatile matter, fixed carbon, porosity, surface area, and pore size distribution of the biochar produced [5].

At the domestic level, small-scale or batch pyrolysis reactors are commonly used. These reactors are often preferred for research purposes or for individuals who desire to produce biochar at a reduced scale [94,97]. Home-scale pyrolysis methods include retort kilns and converters [94,97]. Kilns are thermally insulated reactors that produce self-sufficient temperatures during biochar formation [94]. A retort kiln is one of the most efficient kilns and is normally placed in a closed chamber within the heating space. This reactor uses the heat from controlled combustion for the thermal conversion of biomass. During this process, fuel gas is recycled and combusted to generate more thermal energy for carbonisation [98]. Compared with traditional kilns, retort kiln reactors seem to reduce the environmental impact of biochar production [98]. Furthermore, the carbonisation products

obtained in this reactor have been shown to possess  $\geq$ 50% carbon content, and at high temperatures ( $\geq$ 500 °C), the products have a higher carbon content ( $\geq$ 75%) [98].

The choice of the pyrolysis method is contingent on factors such as the desired production scale, available resources, and specific application requirements.

Accordingly, at an industrial scale, pyrolysis methods often employ reactors capable of handling large quantities of biomass and providing precise control over the temperature and pressure [94]. These include converters and retorts such as fixed-bed reactors, fluidised-bed reactors, rotating cone reactors, plasma reactors, vacuum reactors, ablative reactors, microwave reactors, and auger reactors [94]. One of their main applications is the recovery of biochar, liquids, and syngas from volatile fractions [94]. Auger or screw reactors are also employed in slow pyrolysis, in which a single feedstock or a mixture of feedstocks and solid heat carriers is transported down the length of a tube by a screw [99,100]. These reactors have also gained attention because of their fast pyrolysis [99]. Fluidised beds, transported beds, rotating cones, vortices, centrifuges, entrained microwaves, and radiative reactors are a few types of units used for fast pyrolysis. Fixed- and fluidised-bed gasifiers are widely used because they provide more precise control over temperature, pressure, and ash removal, as well as high heating rates and rapid devolatilisation. Both seem to be suitable for commercial-scale operations as they improve the scale-up procedures [94].

To increase the production of bio-oil from the intermediate pyrolysis of sugarcane bagasse, Onokwai et al. [64] employed a response surface approach to optimise the pyrolysis process parameters (temperature, heating rate, reaction time, nitrogen flow rate, and particle size) over five experimental sets. In this optimisation process, it was observed that due to complete pyrolysis, the yield of bio-oil increased steadily with temperatures between 320 and 520 °C at a heating rate of 7.5–12.5 °C/min. However, it decreased at temperatures between 520 and 720 °C and heating rates of 22.5–27.5 °C/min, due to secondary cracking, such as thermal cracking, repolymerization, and recondensation, which may increase the yield of non-condensable gases and biochar. Slow pyrolysis occurs at lower temperatures  $(400 \,^{\circ}\text{C})$  with slower heating rates  $(1-10 \,^{\circ}\text{C/s})$  and long residence times (>5 min). This gives secondary reactions more time to occur, resulting in higher yields of biochar and volatiles with superior cation exchange capability and electrical conductivity. In contrast, fast or flash pyrolysis occurs at higher temperatures (>550–600 °C), characterised by rapid heating rates (10-1000 °C/s) and the short residence times of the generated vapours (<1 s). These conditions lead to lower biochar yields, as the exposure time for reactions to produce char is minimised. However, biochar is rich in aromatic carbon, microporous surface area, and alkalinity [4,5,55]. To increase the economic value of orange peels, Zhang et al. [61] performed a slow pyrolysis of this agri-food waste with various metal oxides in a tube furnace to produce high-quality bio-oil. On average, 5.69 and 4.82 times more 3-furaldehyde compounds were produced when metal oxides were used as slow pyrolysis catalysts, compared with pyrolysis without the addition of metal oxides. On the other hand, the fast pyrolysis of bagasse catalysed by mixed alkaline-earth metal oxides for the selective synthesis of 4-vinylphenol was carried out by Alcazar-Ruiz et al. [60]. It was observed that at 300 °C with a Ba/Mg molar ratio of 1:1 and a CA-to-BA ratio of 4:1, the yield of 4-vinylphenol increased to a maximum of 7.3 wt% with a matching selectivity of 44.4%, as opposed to 5.0 wt% in the non-catalytic process. The formation of carbonaceous materials is also influenced by the particle size, composition, and type of biomass. Smaller particles exhibit a larger surface area, allowing more heat to diffuse to the core and favouring more pyrolytic reactions and lower amounts of biochar that are formed. Hence, biochar yield generally increases with particle size. The biomass components do not degrade at the same rate, which influences the rate of pyrolysis. Hemicellulose is the most thermally sensitive component; thus, it first decomposes at low temperatures, followed by cellulose at slightly higher temperatures, and then lignin at high temperatures [4,26]. The pyrolysis rate is faster in biomass with a higher cellulose content, increasing the tar and gas yields while decreasing the char output. However, in biomass with high lignin content, the pyrolysis rate is slower. Furthermore, the moisture and lignin contents in biomass produce

different porosity developments, depending on the type of biomass. For instance, dry biomass with a high lignin concentration conserves energy to heat the biomass to the desired temperature, which maximises the yield of carbonaceous materials. Higher yields are attained by using a lower temperature, heating rate, and longer vapour residence time. However, carbonaceous materials show improved porosity when heated at higher temperatures and faster rates [4,55].

#### 3.2. Hydrothermal Carbonization

Hydrothermal carbonisation (HTC) is based on thermochemical decomposition, in which biomass and water react in a reactor at lower temperatures (150–350 °C), leading to the production of gases and carbonaceous materials, referred to as hydrochar [4,5]. HTC is the preferred method for biomass with high moisture content and good energy efficiency [18]. Hydrochar can be used for soil amendments,  $CO_2$  sequestration, and electrochemical applications such as batteries and capacitors [4,5]. This method allows the direct processing of wet biomass, including wet agricultural residues and municipal waste, resulting in energy savings as it eliminates the need for the feedstock to be dried [4,5,101]. Moreover, water serves as a solvent and reaction medium in which the gases generated during the carbonisation process can be dissolved, thereby minimising the impact of environmental pollution [4,5]. Therefore, HTC appears to be the most sustainable and economical method, with high efficiency and low energy consumption. However, industrial-scale HTC have not yet been achieved [4].

HTC involves hydrolysis, dehydration, decarboxylation, aromatisation, and recondensation (Figure 3b). Although the reactions occur consequently, each reaction has different kinetics and may occur simultaneously [102]. Hydrolysis has a lower activation energy than the other processes and starts biomass degradation primarily by cleaving ester and ether bonds. As a result, oligosaccharides and lignin fragments are further hydrolysed or initiate other chemical pathways and products [103,104]. After hydrolysis, the hydroxyl and carboxyl groups were removed by dehydration and decarboxylation, respectively [104]. During the initial hydrothermal treatment, 5-hydroxymethylfurfural (HMF) is formed via dehydration reactions. The majority of the intermediates lead to the production of hydrochar, whereas additional degradation produces other compounds, such as organic acids and compounds [103]. For example, formic acid, levulinic acid, and dihydroxyacetone can serve as catalysts to promote hydrolysis reactions, generating more HMF, which forms furanic compounds via a sequence of polymerisation and condensation reactions [4,104]. The hydrochar produced possesses higher dewaterability, drying performance, energy density, and porosity than the raw materials [105].

Temperature is crucial in the HTC process because it influences the properties of the hydrochar. Temperature facilitates the disintegration of bonds into fragments by providing heat. In general, the maximum production of solids occurs in a lower temperature range (150–200 °C) [106]. As the temperature increases, HTC accelerates with considerable dehydration, producing more liquid and gaseous products, which results in lower yields of hydrochar. In addition to affecting yield, higher temperatures can lead to higher surface areas [4]. The degree of aromatisation of hydrochars is also affected by the HTC temperature [4] because the hydrochars produced contain higher amounts of oxygen functional groups and lower levels of aromatisation, which enables further chemical activation [107]. HTC is a relatively slow process, as the residence time varies from a few hours to several days. Residence time has been found to affect the carbon distribution and final composition of hydrochars [4]. Moreover, the composition and biomass type affected the yield and properties of hydrochar. Owing to the complex branching which makes them less degradable, the presence of lignin improves the hydrochar yield [106]. The cellulose does not degrade at lower temperatures, indicating that the fibre structure remains intact. As the temperature increases, the fibre network begins to degrade, causing the cellulose fragments to assume a spherical shape [4]. Azaare et al. [72] evaluated the impact of the process parameters (temperature, residence time, and mixing ratio) on the hydrochar production and energy

content of the co-hydrothermal carbonization (co-HTC) of pineapple and watermelon peels. According to these findings, the hydrochar production declined with increasing temperature and residence time. On the other hand, the energy and carbon content increased as the temperature and residence duration increased.

Some common uses of biochar are restricted by the low porosity and surface area of the resultant hydrochars [4,5,108]. Post-treatments, such as activation and templating, can be employed to produce highly porous carbons, which are required for an effective mass transfer [70,108]. During physical activation, the surface area of hydrochar can be increased by thermal treatment with steam, CO<sub>2</sub>, or air at 800–900 °C [101]. During this process, small organic molecules are eliminated, resulting in the formation of microporous carbon. However, the surface area and porosity increased over time. Chemical activation involves the use of chemical activating agents such as potassium hydroxide (KOH), zinc chloride  $(ZnCl_2)$ , potassium carbonate ( $K_2CO_3$ ), and sodium carbonate ( $Na_2CO_3$ ), which dissolve cellulose under ambient or elevated temperatures. Porous carbon can be obtained by removing the ions. The hydrochars start to degrade at 200 °C because of the lower degree of aromaticity related to the cellulose content. The maximum decomposition occurs between 350 and 500 °C. During subsequent carbonisation, the mass loss increases when dissolution occurs, increasing the surface area and porosity of the hydrochars. Carbonaceous materials can also be modified by changing their functional groups or removing existing ones [109]. The use of hard templating requires a match between the carbon precursor and the surface polarity of the template for HTC-degraded compounds to successfully penetrate template pores [110]. However, it is difficult to perform infiltration procedures and template removal usually requires harsh conditions that are not environmentally friendly. In soft templating, mesoporous carbon is synthesised using a block copolymer as the soft template to form micelle-like structures [4,110,111]. Upon carbonisation, the block copolymers become thermally unstable and break down easily. Mesoporous carbon can be formed by calcination at 600 °C to remove the template. Similarly, heteroatom-doped carbons can be produced by selecting appropriate precursors [4,112].

#### 3.3. Ionothermal Carbonization

Ionothermal carbonization (ITC) uses ionic liquids (ILs) as the medium to produce porous carbon materials referred to as ionochars by analogy with hydrochars in a one-step process through dehydration, polymerisation, and condensation reactions (Figure 3c) [4]. ILs act as templates for the generation of pores without any additional use of scaffolds or additives, and as catalysts for enhancing product yields; therefore, they possess high energy efficiency [4,5,76]. The low volatility of ILs allows processes to occur at ambient pressures [113]. ITC is a relatively new approach that has not been fully explored. This process is restricted to monosaccharides and raw lignocellulosic waste [76]. Moreover, there are no data regarding the use of ITC on an industrial scale because of the high cost of ILs [5]. However, most ILs can be recovered by Soxhlet extraction and reuse [4].

The properties of the carbonaceous materials produced vary significantly with the type of ionic liquids (ILs) used. This is possible because the properties of ILs can be adjusted to meet specific requirements by selecting appropriate anions and cations [114]. Cellulose is insoluble in conventional organic solvents, but ILs bearing a halide anion also seem to be very efficient in solubilisation because of the strong chemical interaction between the anion and the hydroxyl group of cellulose as a hydrogen bond acceptor [76,113]. Different ILs can generate pores in distinct ways and with different sizes [4]. For instance, larger anions such as chloride (Cl<sup>-</sup>), tetrafluoroborate (BF<sub>4</sub><sup>-</sup>), and bistriflimide (Tf<sub>2</sub>N<sup>-</sup>) appear to yield higher pore volumes [115]. Hence, it is important to select an appropriate ionic liquid that aids in the development of a porous structure during carbonisation [113]. Different heteroatoms for doping carbon materials can be easily introduced from the anions present in the ILs. This reduces the need for additional modification steps, which benefits the use of ILs as catalysts by providing more active sites, in addition to increasing product conductivity, which is favourable for electrochemical applications [4]. Furthermore, owing

to their nitrogen-doped structure, the carbonisation of ILs provides unique physicochemical properties with attractive applications in supercapacitors and energy storage [113]. Cibien et al. [76] used a model of raw lignocellulosic agricultural waste, namely, the shells of cocoa beans, which were treated using [Bmim] IL in a Lewis acid IL. The authors observed that in lignocellulosic materials and ionochars, the coordination of  $[FeCl_4]^-$  to oxygen atoms appeared to stabilise the oxygenated carbon groups, accounting for increased mass and carbon yields, and to encourage the formation of micropores. Additionally, the sustainability of the ITC approach was demonstrated by [Bmim] [FeCl\_4] recycling, which also made this process readily transferable to other raw agri-food waste. Aldroubi et al. [77] showed that cation engineering can be used to modify the morphological and textural characteristics of ionochars, offering the possibility of controlling CO<sub>2</sub> uptake and retention.

#### 3.4. Torrefaction

Torrefaction, often referred to as mild pyrolysis or roasting, involves the removal of volatile compounds by heat application and is usually performed at temperatures ranging from 200 to 300 °C using slow heating rates to produce biochar [116]. Torrefied biomass has a modified polymeric structure, in contrast to raw biomass, with a low moisture content, high heating value, low volatile content, and resistance to biological degradation [55,116]. The thermochemical process involves four stages. The first stage consists of the drying of the biomass, in which the unbound moisture content is evaporated. The macromolecules then undergo depolymerisation and recondensation reactions. In the third stage, devolatilisation begins when the temperature reaches approximately 180 °C and progressively progresses to extensive devolatilization, and carbonisation occurs in the fourth stage at temperatures above 250 °C (Figure 3d) [55,117]. Torrefaction procedures can be classified as either dry (DT) or wet (WT) according to the reaction conditions. In DT, biomass is progressively cooked in either a low-oxygen or an oxygen-restricted atmosphere. Early in the process, dehydration and decarboxylation processes occur, and between 50 and 150 °C, the biomass moisture evaporates. As the temperature rises, lignin starts to loosen, and the bonds between hydrogen and carbon start to dissolve. Cellulose and lignin are only partially degraded, whereas hemicellulose is destroyed; the final degradation temperatures of hemicellulose, cellulose, and lignin are 220–315 °C, 315–400 °C, and 150–900 °C, respectively. DT produces three different types of products with distinct phases: (i) a liquid fraction composed primarily of volatile organic compounds, such as acetic acid, aldehydes, alcohols, and ketones; (ii) a gas product, sometimes called torr gas; and (iii) a solid product called torrefied biomass, which is used as fuel. WT, also known as hydrothermal carbonisation, occurs at lower temperatures ranging from 180 to 260 °C for approximately 2 h. WT addresses the problem of high ash and chlorine contents in waste biomass, whereas DT does not. WT is a method used in hydrothermal water, which is crucial for eliminating undesirable inorganic substances, such as potassium, sodium, sulfur, and chloride, as well as for reducing the amount of ash present [84,118,119]. Gong et al. [120] observed that WT might lower the amounts of ash, potassium, and chloride in empty fruit bunches from palm trees by up to 67.99, 98.62, and 99.27%, respectively.

Torrefaction is influenced by several biomass characteristics (source, particle size, and composition), temperature, heating rate, and the reaction atmosphere [121]. Biochar produced from torrefaction has valuable applications in soil remediation, fertiliser production, activated carbon production, and sorbents for water purification [55,121]. Dyjakon et al. [78] evaluated the hydrophobic characteristics of agri-food biomass waste according to the torrefaction temperature and exposure time to moisture adsorption conditions. It has been demonstrated that torrefaction greatly enhances the hydrophobic characteristics of biomass. Depending on the type of organic waste, the equilibrium moisture content coefficient of the non-torrefied dry material decreased by a maximum of 56.96–24.14%. Moreover, Allouzi et al. [82] verified that depending on torrefaction temperature, the mass yield for torrefied olive pomace varied from 59.2 to 82.6%. Alves et al. [79] studied the characteristics of bioenergy-related materials, combustion patterns, and probable emissions

of banana leaf waste following torrefaction. The following three temperatures were considered: 220 °C (light), 250 °C (mild), and 280 °C (severe). This investigation unequivocally demonstrated that banana leaf waste had better bioenergy-related characteristics, higher combustion performance, and reduced emission potential after torrefaction, indicating that it is a promising strategy for valorization.

## 3.5. Steam Explosion

Steam explosion is a popular hydrothermal pretreatment approach that has been used to process and modify raw dietary fibres owing to its lower energy consumption and lower use of chemicals. Other advantages include its strong applicability, short residence time, low dielectric constant of water, short-term high efficiency, lack of pollution, environmental friendliness, and industrial amplification [122–124]. Steam explosions use saturated steam at high pressure in cell walls and plant tissues by applying the thermochemical activity of high-temperature cooking combined with the physical tearing action of an instantaneous explosion. Macromolecules in fibrous raw materials undergo physicochemical changes that facilitate their separation and conversion [123].

Steam explosions include acid hydrolysis, thermal degradation, mechanical fracture, hydrogen bond destruction, and structural rearrangements. According to its functional characteristics, this process comprises two stages: (i) the high-temperature cooking-steam boiling stage and (ii) the instantaneous decompression-explosion stage (Figure 3e). In the steam boiling stage, the raw material is maintained under saturated steam pressure and high temperature (170–210 °C). The generated steam seeps into the core of the material, filling tissue pores. Subsequently, the high pressure created by the saturated steam is released within milliseconds [122]. This step allows for the hydrolytic breakdown of hemicelluloses and other parts of the raw materials to create soluble carbohydrates. The lignin in the intercellular layer becomes softer and degraded, reducing the lateral bonding strength of the fibres, while the cell pores are soaked with high-pressure water vapour, becoming soft and plastic. During the explosion stage, water in the substrate evaporates. The abrupt pressure drop leads to vapour expansion within the fibres, which disrupts the fibrous structure and cell wall rupture to form pores, resulting in an explosion. This step promotes the destruction of cellulose crystallinity, delignification, and the release of smallmolecule materials from plant cells. This also leads to the hydrolysis of hemicelluloses, making them easier to use in later processes [122,123].

Steam explosion is an appealing pretreatment method for the extraction of high-value compounds from biomass, such as phenolics and polysaccharides [123]. It has been frequently used to break the structure of lignocellulose and to prepare cellulose for enzyme conversion during the physicochemical pretreatment of lignocellulosic biomass [122–124]. Steam explosion provokes a strong alteration of lignocellulosic biomass by increasing its surface area and porosity through lignin rearrangement and modification of its structure, partial depolymerisation, solubilisation of hemicellulose, and significant improvement in the enzyme digestibility of cellulose. However, owing to the naturally resistant carbohydrate–lignin shield, the recovery of lignins and hemicelluloses for biomass valorization is energy-consuming and expensive [123,124]. Hongrattanavichit and Aht-Ong [93] employed steam explosion pretreatment at different temperatures (195–210 °C) and times (5–15 min) to extract the cellulose nanofibers from sugarcane bagasse waste. The cellulose nanofibres produced had a very small diameter between 3 and 7 nm, a high cellulose content of 92.74%, and a low density of 0.8989 g/cm<sup>3</sup>.

This process has a high potential for industrial applications and is now being explored at pilot or industrial scales for various purposes because of its economic and eco-friendly advantages for processing large quantities of food materials [125]. Steam explosions have been investigated for the extraction of oil and natural products, the hydrothermal conversion of active ingredients, and the use of raw materials. Moreover, it can deglycosylate several glycoside-active ingredients, separating the sugar group from the aglycone and promoting high activity [123]. Cui et al. [86] demonstrated that the production of bound

phenolics and flavonoids decreased whereas the yield of free phenolics and flavonoids increased as a result of the steam explosion approach in grape pomace. This method was also able to transform insoluble dietary fibre from grape pomace into soluble dietary fibre, thereby improving the oil-holding and sodium nitrite binding capacities of soluble dietary fibre.

## 4. Applications of Carbonaceous Materials

Owing to its high carbon content and renewable nature, biomass is regarded as the most sustainable and renewable source of carbonaceous materials [1,4]. Several applications of biomass-based carbon materials are being pursued, owing to their cost-effectiveness, large-scale production, and quality-controllable production in an environmentally friendly manner. Furthermore, the conversion of biomass to carbon nanomaterials, such as fullerene, carbon nanotubes, graphene, and graphene quantum dots, has revealed alluring potential for biomass valorization in contrast to the standard synthesis of biomass-derived hydrochars and biochars [8]. Carbon nanostructures and nanomaterials have received great interest for their properties and applications in the environmental, catalytic, biological, and energetic fields [4,5]. For instance, they have important applications in catalyst supports, carbon fixation, adsorbents, gas storage, electrodes, carbon fuel cells, and drug delivery [6]. Activated carbon and carbon fibres can also be prepared using additional activation and electrospinning processes, respectively [5,8]. Nonetheless, given the complex chemical components and structures of biomass, it is difficult to prepare homogeneous and controllable carbonaceous materials. Moreover, the quality, properties, and applications of carbonaceous materials differ depending on the type of biomass and conversion method used, as discussed previously [8].

## 4.1. Environmental Applications

The environmental applications of carbonaceous materials include CO<sub>2</sub> adsorbents, soil amendments, and water remediation. Increasing levels of atmospheric CO<sub>2</sub> need to be mitigated, as they influence climate change through the greenhouse effect. Biochar is an effective and economical strategy for capturing atmospheric CO<sub>2</sub> [4]. Moreover, they can remain stable in the soil for extended periods independent of mineralisation and temperature fluctuations [5]. Hydrochars derived from HTC can also act as capturing agents for  $CO_2$  given their large surface areas and tunable porosities. Additional surface functional groups can be introduced via chemical activation for further enhancement [4]. The use of pesticides and herbicides causes soil contamination through the disposal of inorganic and organic pollutants. Anthropogenic activity can also lead to the presence of unwanted metals in the soil. These highly toxic substances are harmful to human health, living organisms, and agricultural products. Therefore, it is necessary to reduce their amounts to ensure a sustainable living environment and to protect human health. The porosity of carbon materials facilitates the adsorption of contaminants in the soil and water. Biochar has received considerable attention for its potential application as a soil amendment to reduce soil contaminants and heavy metals [4]. It acts as a soil conditioner by improving the water-retaining capacity of the soil, pH optimisation, and the total uptake of phosphorus and nitrogen. Consequently, the bioavailability of required nutrients and water increases, providing a microenvironment for the growth of essential soil microorganisms, thereby improving soil fertility [4,5,126]. Frišták et al. [127] evaluated the pretreatment of sewage sludge with sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and subsequent pyrolysis at 400 °C and 500 °C for soil amendment. The authors studied the production of potential alternatives to inorganic phosphorus fertilisers and organic carbon suppliers. Peng et al. [128] produced biochar with heavy metals solidification from industrial sludge and rice straw through co-pyrolysis. This study resulted in high-quality biochar, in which the biomass composition provided energy and reduced the enrichment of heavy metals by solidification into stable forms. This approach has demonstrated potential for soil and water remediation applications. Zhu et al. [129] prepared porous carbonaceous materials from pineapple waste through

HTC followed by thermal activation using alkali metal oxalates. Pineapple waste-derived porous carbons showed an enriched  $CO_2$  adsorption performance of 1.59 mmol/g at 25 °C, indicating that these wastes are promising sorbents for capturing and separating  $CO_2$  under real conditions.

## 4.2. Catalytic Applications

Heterogeneous catalysts are essential for chemical synthesis and transformation. Carbonaceous materials have been shown to act as catalysts and catalyst supports. Hydrochars possess the desirable porosity and large surface area to speed up reactions, which have been explored in the form of carbonaceous nanofibers [4–6]. Furthermore, the combination of metallic nanoparticles results in high thermal, chemical, and mechanical stabilities [4]. The supporting materials used by heterogeneous catalysts also influence catalytic performance, which means that these materials must also have a high surface area and porosity to accelerate the reaction. HTC, followed by subsequent activation, can produce hydrochar with desirable surface area and modifiable properties for use as a catalyst or catalyst support [4]. The reusability and efficiency of these biomass-derived catalysts make them promising candidates for future industrial applications, given growing ecological concerns [4,5]. Specific catalytical applications include the use of carbon materials as supports for Pt and Pt–Ru catalysts for direct alcohol fuel cells [130], NO reduction [130], or the dehydrogenation of n-butane to olefins [131], among others.

## 4.3. Energy Conversion and Storage Applications

Carbon-based materials produced at extremely high temperatures (>1200 °C) are expected to exhibit desirable electrochemical properties. They have been considered for energy conversion and storage applications owing to their versatile dimensionality, in addition to their structure, and physicochemical properties. Examples of these properties include thermal insulation, thermal conductivity, heat resistance, hardness, softness, and insulator-semiconductor-conductor properties [132]. Carbonaceous materials are often used as electrodes because of the presence of mesopores, which allow the transport of ions and electrolytes, and have a high surface area [4,5,133]. These characteristics have led to their use in supercapacitors and energy storage devices because of their high capacitance, long life span, and fast charge/discharge rates [4]. Carbon allotropes with different structures and properties, such as  $sp^3$ ,  $sp^2$ , and sp, can be obtained from combinations of carbon atom hybridisations [132]. Carbon nanotube-based materials (sp<sup>2</sup>), for instance, possess a high surface area, thermal conductivity, electron mobility, and mechanical strength, which allow them to be used for the development of solar and fuel cells. Solar cell technologies are safe, eco-friendly, inexpensive, and can transform solar energy into electric energy. Owing to their high electrical conductivity, electrocatalytic activity, high electron mobility, good optical transparency, low cost, and high abundance, carbon nanotubes have been explored to guarantee better charge conduction and increased electrode flexibility. Moreover, the properties of carbon nanotubes can be significantly affected by the number of walls, length, diameter, defect type, concentration, and synthesis method [134]. Solid biofuels usually include renewable biological materials that can be burned to generate energy, resulting in economic and social benefits, as well as a lower environmental impact [135]. Industrial waste and sewage sludge have been transformed into clean solid biofuels via hydrothermal treatment and torrefaction [4,136]. Wang et al. [137] used HTC combined with potassium hydroxide (KOH) activation for the co-production of fermentable sugars and porous carbon with oxygen-rich groups from sugarcane bagasse to be used as supercapacitor. The authors found that the pore volume distribution and surface oxygen-containing groups played a more significant role in the electrochemical performance of the carbon materials than the specific surface areas.

## 4.4. Biological Applications

Carbonaceous nanomaterials can be used in various activation techniques and applications, owing to their long-term viability, adaptability, biocompatibility, safety, and biodegradability. They can be used as probes for in vivo imaging, diagnostics, and the profiling of molecules, as well as for drug and gene delivery [138]. Carbon quantum dots (CQDs) are small carbon nanoparticles (<10 nm) comprising amorphous or crystalline centres with a dominant *sp*<sup>2</sup> carbon. They have gained considerable attention because of their fluorescent properties, high chemical stability, good conductivity, non-blinking, and resistance to photobleaching [139–141]. Biomass can be used as a carbon source for CQD with the properties of chemical CQDs. Moreover, biomass-based CQDs are more environmentally friendly, potentially less toxic, and biocompatible, making them suitable for biomedical applications, and they can be used in medical bioimaging practices for disease detection or treatment [4,139,140]. Other applications include biosensing, biological labelling, medical diagnostics, and optoelectronic devices [138]. However, features related to safety, physicochemical properties, and pharmacokinetics must be further investigated before they can be used in medical [138].

## 5. Concluding Remarks

Our planet offers an infinite quantity of biopolymers (cellulose, hemicellulose, and lignin), in terms of nature and diversity, biosynthesized by living organisms, most of which have numerous applications in the food, pharmaceutical, and cosmetic industries, in addition to environmental (can be used for CO<sub>2</sub> capture and the adsorption of contaminants in soil and water) and energy conversion/storage field applications. In addition to their enormous potential, these abundant and renewable resources remain unexploited, even considering the high dumping fees necessary to dispose of this valuable material in landfills, which are already in short supply. Pyrolysis, HTC, ITC, torrefaction, and steam explosion have been discussed as important processes for converting biomass into carbonaceous material. Pyrolysis is currently considered the most practical and economical approach for the large-scale production of carbonaceous materials from biomass and agri-food residues. This method allows the formation of unique structures with specific surface areas and high porosity and is the most conventional method for the synthesis of biochar, the most prevalent carbonaceous material obtained from biomass. Biochar, which has interesting physicochemical attributes, demonstrates a clear ability to improve plant growth and increase soil fertility through beneficial soil microorganisms. However, their ecological interactions with microorganisms and plant roots are not yet known. HTC is considered the most sustainable and economical, as it consumes a lower amount of energy and is a more efficient process.

The advancements in several technology fields, from nanotechnology to artificial intelligence, open new avenues and sustainable alternative strategies to transform the huge numbers of tons of biomass resources generated by the agri-food based industry, into high-value products, namely carbonaceous materials, with the highest conversion and selectivity.

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