Review

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

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Posted Date: 20 September 2023

doi: 10.20944/preprints202309.1360.v1

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

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Abstract: Sustainable biomass production has significant potential for mitigating greenhouse gas emissions and is a promising alternative for the production of 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. Portugal has several residues and by-products of agriculture, food processing, and forestry origin, and has a high availability of residual biomass. Portugal intends to reduce its dependence on energy imports and the use of fossil fuels, thereby increasing its economic performance while using biomass waste to produce high value-added products. In this context, this review aims to explore the potential of agri-food wastes obtained from Portuguese industries via thermochemical conversion technologies as a promising sustainable alternative to woody 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 contribute to reduce the dependence on fossil fuels and minimising greenhouse gas emissions while meeting the demands of the growing population and providing a sustainable waste management solution.

Keywords: agri-food wastes; 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 fuel resources are mostly used to meet the rising energy needs of the growing world population and to create a variety of synthetic polymers, cosmetics, and platform chemicals that enrich quality of life [2]. 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 the depletion of fossil fuel resources, energy shortages, and environmental crises [1,2]. Therefore, there is an urgent need to explore renewable, inexpensive, inexhaustible, and sustainable alternatives to shift away from fossil fuels and continue to meet the demands of the growing population [1,3,4].

Organic biomass waste has been identified as a promising alternative for the production of eco-friendly biofuels, biochemicals, and carbon-neutral products for biomedical, pharmaceutical, cosmeceutical, and other industrial uses [2,3,5]. Biomass wastes, such as plant-based matter, animal manure, sewage sludge, and industrial, forestry, and agricultural wastes [3,6], can help reduce the over-dependence on petrochemical resources and mitigate climate change, while providing a sustainable alternative for waste management [2]. The traditional treatment of solid waste involves either disposal in landfills or open burning as an unwanted material, leading to serious environmental and economic concerns such as water and land management, energy production, transport, and storage [6,7]. Unlike fossil fuels, the combustion of biomass leads to lower sulfur (SO_x)

and nitrogen (NO_x) oxides and is considered carbon-neutral, as the carbon dioxide (CO_2) released in this process originates from CO_2 previously absorbed by plants during photosynthesis [1,3]. Therefore, given its availability in large quantities, 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 valorization [7].

Sustainably produced biomass has significant potential for the mitigation of greenhouse gas emissions and seems to be the most viable economic model to complement the energy systems and products currently powered by fossil fuels [2]. The European Union has developed circular bioeconomy strategies [8] in which biomass is envisioned to play a key role in meeting the global climate targets defined in the Paris Agreement [9]. According to the European Commission [10], circular bioeconomy strategies aim to minimise waste generation while maintaining the value of products, materials, and resources for as long as possible [11]. An important strategy relies on the efficient use of resources through integrated biorefineries and the cascading use of biomass, which depends on the cooperation of locals from agriculture, industry, research, and regional public institutions [11]. However, the supply of biomass waste for biorefining and biomanufacturing could be limited by geography, seasonal availability, the scattered nature of residue generation, and differences in local situations [2]. With the COVID pandemic, the importance of the security of supplies and storage, particularly food and energy, has become evident [12]. Renewable and carbon-based biomass can be used as alternatives to ensure a secure energy supply in the European Union. 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 [2,12].

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 friendly manner [7]. Portugal is a European country with noteworthy potential for biomass production, with approximately 92% of the territory occupied by agriculture, forestry, and agroforestry. However, Portugal relies to a great extent on imports to meet its energy needs, occupying the 9th position among the European Union countries with around 80% of energy imports in recent years [13]. Owing to the availability of large amounts of residual biomass and the country's high productivity in the agricultural and industrial sectors, Portugal intends to reduce its dependence 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 [11,14]. Furthermore, alternative biomass sources to woody waste are important sources of carbon-based materials. Therefore, it is crucial to leverage the economic potential of biomass to increase the country’s economic performance [11]. This review aims to explore the potential of agri-food wastes obtained from Portuguese industries via thermochemical conversion technologies as a useful strategy for the development 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 according to the type of feedstock used [3]. According to their chemical composition, they can be classified as lignocellulosic or non-lignocellulosic biomass. Lignocellulosic biomass is the most abundant non-edible biomass from forestry and agricultural wastes, and mainly consists of cellulose, hemicellulose, and lignin. Non-lignocellulosic biomass includes fruit and food wastes, which are rich in carbohydrates, polysaccharides, and proteins and provide carbon and nitrogen sources to obtain biomass-derived carbonaceous materials [7,15].

Generally, 90% of the dry matter found in lignocellulosic biomass decomposition is related to the breakdown of naturally occurring lignin (10-25 wt%), hemicellulose (20-40 wt%), and cellulose (40-60 wt%) [2,16,17] (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 [4].

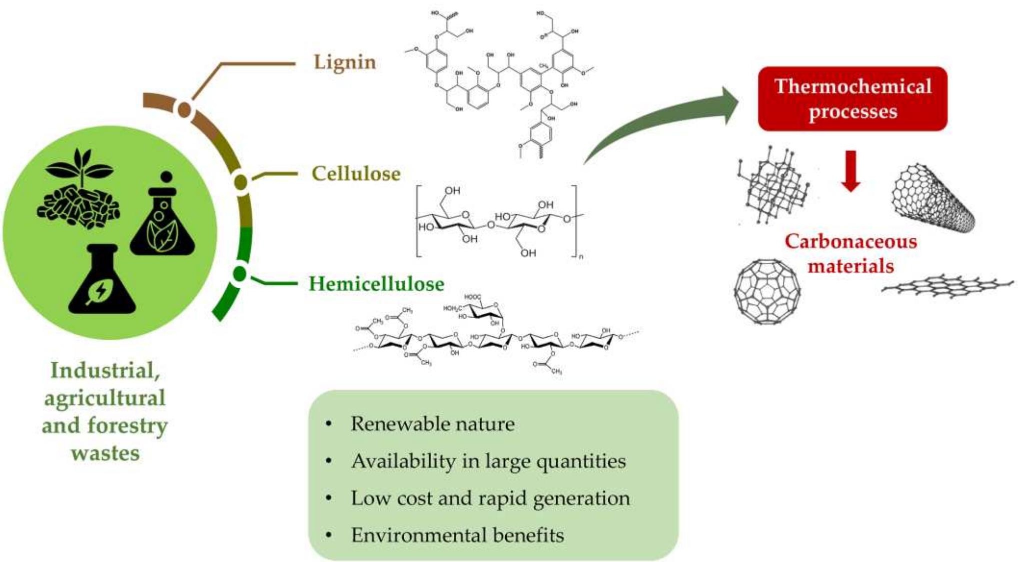

Figure 1. Biomass from industrial, forestry, and agricultural wastes is a promising starting material for the synthesis of functional carbonaceous materials that can be obtained via thermochemical processes.

Cellulose is the most abundant biopolymer in nature. Cellulose is a homopolysaccharide comprising repeating d-anhydroglucopyranose monomers connected through 1,4-β-glycosidic bonds. The native cellulosic chains form microfibrils that are bundled into fibres [3,4]. An elementary fibril is the basic unit. Fibrils of cellulose contain amorphous and crystalline regions, which vary in proportion among different plants [3]. The extraction of cellulose from plants generally yields a nanosized crystalline material referred to as nanocellulose [3,4]. The hydrolysis of plants with strong acids cleaves glycosidic chains, leading to cellulose nanocrystals (CNCs). During hydrolysis, the amorphous regions were removed while the crystalline regions remained intact due to higher resistance, forming rod-like nanocrystals, the dimensions of which 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 disintegration of the fibres into their substructural fibrils [3]. Cellulose can also be generated from certain bacteria such as bacterial nanocellulose (BNC) [18]. BNC is obtained by the fermentation of bacteria through the pentose-phosphate or Krebs cycle, which is determined by the physiological state of the cell. BNC does not contain hemicellulose or lignin, possessing a higher chemical purity than plant cellulose and, consequently, a higher crystallinity [19]. BNC provide other advantages, such as a high degree of polymerisation, mechanical stability, water-holding capacity, biodegradability, and biocompatibility [3,20]. The remarkable features of nanocelluloses include a high and controllable surface area, crystalline nature, and excellent mechanical strength, coupled with renewability, biodegradability, and accessibility on a large scale [4].

Lignin is one of the most abundant natural biopolymers and is typically found to cement cellulose fibres 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) [21]. Owing to its high stability at low temperatures, lignin results in a high yield of solid carbonaceous products [3]. The proportion of monomers and lignin content varied according to the plant species. Herbaceous plants possess lower lignin content 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 its extraction method, lignin can be classified as kraft lignin [22], soda lignin [23], sulfite lignin [24], and organosolv lignin [25]. Kraft lignin contains more phenolic hydroxyl groups and has a more condensed carbon-carbon (C–C) structure. Soda lignin has increased solubility and is generally sulfur-free. Sulfite lignin is water-soluble owing to the addition of sulfonated groups. Organosolv lignin has a higher phenolic hydroxyl content and fewer carboxyl groups than soda lignin [3,25].

Hemicellulose is a heterogeneous polymer consisting of short, highly branched chains of sugars, namely five-carbon sugars (D-xylose and D-arabinose), six-carbon sugars (L-galactose, D-glucose, and D-mannose), and uronic acid [1,17]. It can also contain organic acids such as glucuronic and acetic acids. Hemicellulose is a linear polymer with a base composed of either repeated units of a mixture of sugars (heteropolymer) or the same sugar (homopolymer), which is easily hydrolysed into basic sugars [1,17]. Heteropolymers can contain several sugars, such as xylans, mannans, xyloglucans, and glucomannans which vary in composition with different species. This results in different hemicellulose structures that are usually random and amorphous [26], indicating that hemicellulose is less chemically resistant than cellulose [17]. For instance, softwood hemicellulose is mostly composed of glucomannans, whereas hardwood hemicellulose mostly contains xylan [27]. Unlike cellulose, hemicellulose does not form micro-fibrils. 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%) [3], which comprise the majority of agricultural waste [17]. The difference in composition is attributed to the type of biomass, with softwood having the highest lignin content among all the biomasses [28]. 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 [3,29]. Furthermore, hemicellulose plays an important role in providing structural strength to biomass because of its connection with cellulose, along with cross-linking to lignin through ester and ether bonds [26,27].

Saccharides are simple sugars that are abundant in biomass as oligosaccharides and polysaccharides, including cellulose, lignin, and starch [30]. They are produced during photosynthesis, and primary saccharides, including glucose, sucrose, and fructose, are commonly found in pollen, fruit, and plant fragments, whereas sugar alcohols such as mannitol and arabitol are typically found in fungal spores [30]. The major sources of sucrose are sugar beets and sugarcane, which are widely available [31]. Hence, the use of saccharides to produce carbonaceous materials can be considered as it is economically viable [3]. 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 [30,32]. The sugars found in the biomass can be converted 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) [30,32]. 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 [33].

2.1. The Portuguese case study

Portugal has a strong potential for forest and agricultural biomass production, with over 90% of the territory occupied by forests (39%), agriculture (26.3%), forestry, bush (12.4%), agroforestry (8%), and pastures (6.5%) [34,35]. Moreover, agriculture, food processing, and forestry generate large amounts of residues and by-products [14] (Figure 2).

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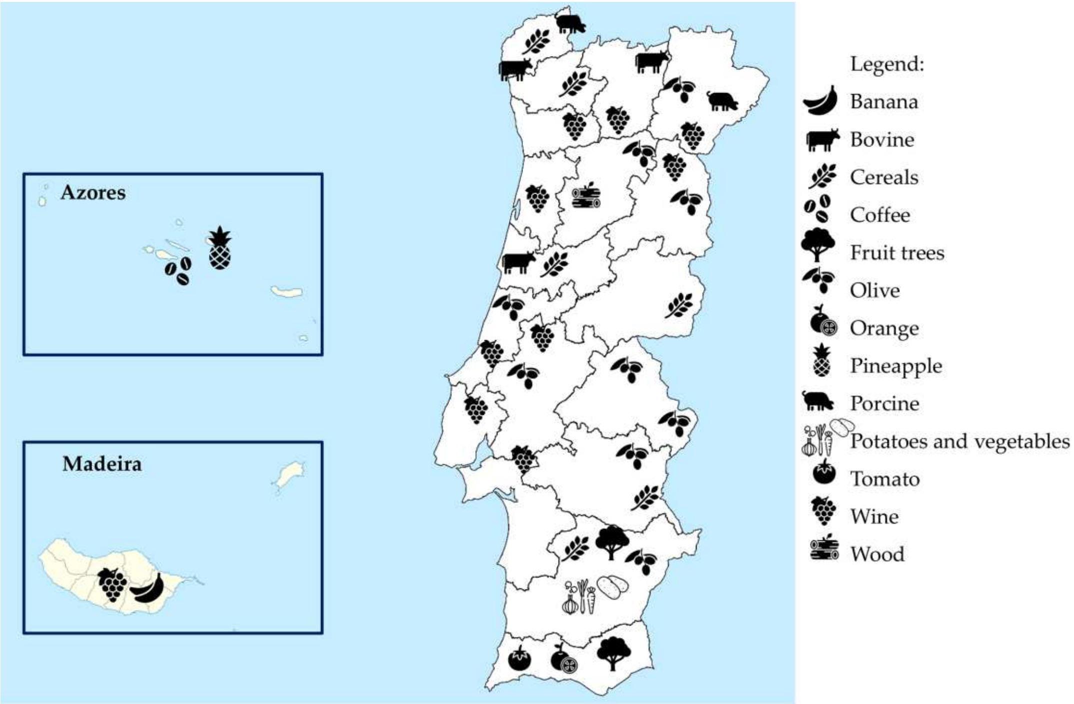

Figure 2. The main agricultural and forestry industries explored in Portugal.

According to a report on agricultural biomass production in the European Union (EU), the average annual production of dry matter for EU-28 between 2006 and 2015 was estimated at 956 million tons [36]. While this figure does not specifically refer to Portugal and the data available are not recent, it provides a general idea of the scale of agricultural biomass production in the EU. 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 [37,38], alongside the recent national growth in the pellet market for heat production in domestic or industrial boilers [39]. However, the growing use of biomass for energy production may lead to its scarcity [14]. Another concern is wildfire. Forest fires are a recurrent phenomenon in Portugal during summer, resulting in massive expenses in firefighting actions and a considerable contribution to greenhouse gas emissions and global warming effects [40]. Hence, there is a need to assess the potential use of other types of available biomass, namely residual biomass from agricultural and food processing activities and other woody species [14,41]. Owing to the quality of woody biomass, these alternative by-products have different characteristics that can influence the supply and pretreatment chain, combustion processes, ash behaviour, and environmental limitations associated with energy conversion processes [14,42].

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 economy perspective [14]. Moreover, non-lignocellulosic biomass is rich in carbon and nitrogen sources, which allows the preparation of biomass-derived carbonaceous materials [7,15]. Agricultural biomass consists of agricultural production by-products 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 [13].

3. Thermochemical conversion of agri-food wastes 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 use 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 the presence of high levels 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 [11].

Thermochemical conversion technologies have been shown to improve the physical and chemical properties of biomass in terms of combustibility, facilitating its mechanical processing, increasing its stability and energy density, and eliminating chlorine. Therefore, these technologies pose a potential solution for preprocessing residual biomass [14]. Thermochemical processes use heat to degrade biomass into low-molecular-weight products via a series of physicochemical reactions in a controlled environment to yield desired outputs [49]. 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 a high energy efficiency [3,4].

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 high moisture content, whereas other thermal processes are suitable for biomass with a comparatively low moisture content [49]. Thermal decomposition varies with the type of biomass, which eventually affects the yield and structure of the carbonisation product [3,49]. For instance, lignin content is a major factor affecting the properties of carbonaceous materials [4]. 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 depend on the process conditions, which include the type of feedstock, temperature, time, heating rate, and pressure [3,4]. Furthermore, different combinations result in diverse characteristics in terms of the surface area, functional groups, porosity, and hydrophobicity. Understanding these combinations is essential for the development of carbonaceous materials for various applications [3].

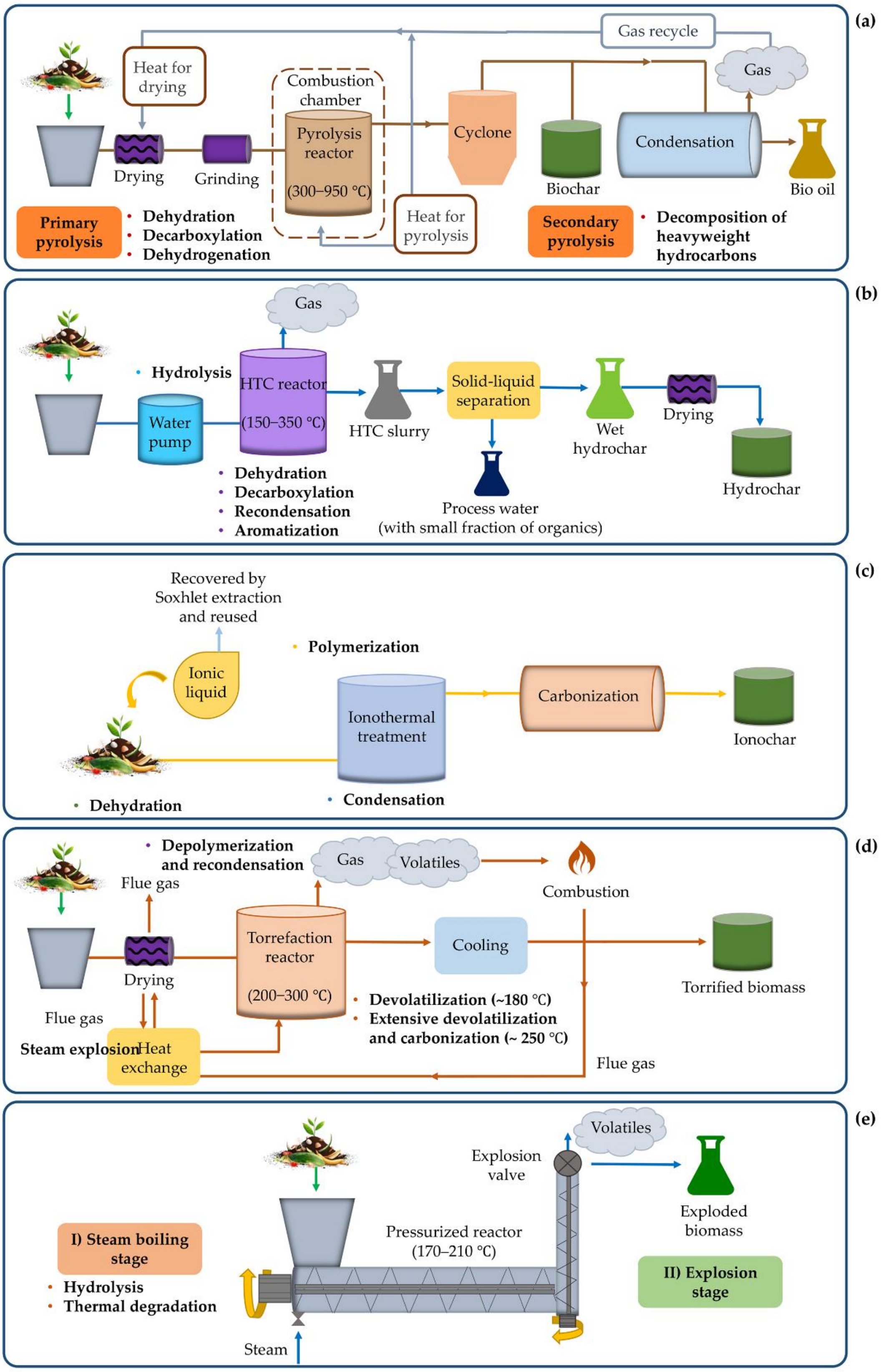

Figure 3. Simplified representation of thermochemical processes: **(a)** pyrolysis, **(b)** hydrothermal carbonisation, **(c)** ionothermal carbonisation, **(d)** torrefaction, and **(e)** steam explosion.

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

Agri-food waste	Experimental parameters	Conclusions	Ref.
	Pyrolysis		

Banana pseudo-stem (BPS)	5 to 10 pieces of BPS, 500 °C, 1.02 s, 200 mL/min N_2 flow rate	BPS bio-oil was produced at a rate of 5.35 MJ/kg, which is relatively low when compared to petroleum fuel and other biomass pyrolysis fluids	[50]
Banana peel	1 g sample, 720 °C, 10 min, 300 mL/min CO_2 flow rate	Pyrolysis of the banana peel with CO_2 enhanced the aromaticity of biocrude, accelerating liquid pyrolysate dehydrogenation without the use of any catalysts	[51]
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	[52]
Grape bagasse	100 g sample, 700 °C, a heating rate of 5 °C/ms, 60 min, 200 mL/min N_2 flow rate	> 95 % of Cu(II) was removed from aqueous media using chars produced through the thermochemical conversion of grape bagasse	[53]
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	[54]
Orange peels	4.5 g sample, 9 g of metal oxide, 500 °C, 25 °C/min, 1h	5.69 and 4.82 times more 3-furaldehyde were produced by pyrolysis with Cu_2O and Fe_2O_3, respectively	[55]
Peach seeds	1 g sample, 300 kPa, 15 min, 100 mL/min N_2 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	[56]
Potato peels	30 g sample, 500 °C, 30 °C/min, 30 min, 100 mL/min of N_2 flow rate	The bio-oil and bio-char yield was 23.6 and 29.5 %, respectively	[57]
Sugarcane bagasse	100 µm particle size, heating rate of 50 °C/min, 15.5 min, 493 °C, 225 mL/min N_2 flow rate	46.7 wt % of bio-oil yield was achieved at optimal pyrolysis conditions	[58]
Sugarcane bagasse	10 % wt raw mixture, 1-3 kW, 400 °C, 25–10 kPa, 30 – 50 min, 500-600 mL/min N_2 flow rate	The microwave pyrolysis by-products suggested a CO_2 reduction potential of 47.9 CO_2 eq/kg	[59]
Hydrothermal carbonization			
Apple bagasse	500 g sample, 3 L H_2O, 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	[60]
Banana peels	5 g sample, 50 mL H_2O, 300 °C, 1–2 h	The carbonized banana peel removed 99 % of Cd^{2+}, whereas the raw peel removed 75 %	[61]
Banana stalks	5 g sample, 50 mL H_2O, 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 %	[62]
Grape pomace	250 g sample, 1250 mL H_2O, 180 °C, 1h	97.08 % of hydrochar yield was attained, supporting the potential application of grape pomace for solid biofuel	[63]
Olive pomace	1:1 sample: H_2O ratio, 300 °C, 24 h	For energy purposes, the hydrochar obtained from olive pomace showed several advantages due to its lower ash content	[64]
Orange peels	6 g sample, 1 mL H_2O, 210 °C, 180 min	Upgrading of orange peels into value-added chemicals, such as 5-hydroxymethylfurfural, furfural, levulinic acid, and alkyl levulinates	[65]

Pineapple and watermelon peels	85 g sample, 4 L H_2O, 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	[66]
Potato peels	50 g sample, 50 mL H_2O, 200 °C, 25 h	Potato peel hydrochar adsorption capacity for Congo red	[67]
Sugarcane bagasse	3 g sample, 50 mL H_2O, 200 °C, 18-20 h	The biochar obtained from sugarcane bagasse might be used as a sorbent to remove pollutants from water	[68]
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 %	[69]
Ionothermal carbonization (ITC)			
Coca bean shells	3 g of sample, 10.8 g [Bmim][$FeCl_4$], 240 °C, 20 h	The positive effects of the ITC method on mass yield, carbon yield, and specific surface area in [Bmim][$FeCl_4$] were well demonstrated	[70]
Sugarcane bagasse	1 g sample, 40.2 mmol imidazolium tetrachloroferrate, 240 °C, 20 h	High-specific surface area ionochars with tunable CO_2 uptake/retention, tuneable pore volume, and unique nanostructures were produced	[71]
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	[72]
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	[73]
Grape pomace	60 % w/w 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	[74]
Grape pomace	10 % w/w sample, 225 °C, 10 min	Using the torrefaction process, most of the phenolic compounds were not volatilized and remained in biochar	[75]
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	[76]
Orange peels	60 g sample, 200 °C, 60 min	Orange peels showed excellent odour adsorption ability	[77]
Sugarcane bagasse	DT, 5 g sample, 280 °C, 20 min WT, 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 %	[78]
Steam explosion (SE)			
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	[79]
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	[80]
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	[81]
Pineapple leaves	150 g sample, 204 °C, 5 min	Without the use of any chemicals, the SE treatment may raise the cellulose fraction	[82]

		while decreasing the partial concentrations of hemicellulose and lignin	
Pineapple peel	20 g, 1.5 MPa, 30 s	SE treatment can break the bulk volume of dietary fibres and increase the surface area	[83]
Potatoes peels	300 g sample, 0.35 MPa, 121 s	The water-holding capacity, oil-holding capacity, and swelling capacity values for potato peels significantly increased	[84]
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	[85]
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	[86]
Sugarcane bagasse	60 g sample, 205 °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)	[87]

Abbreviations: BaMg-MMO - barium-magnesium mixed metal oxide; [Bmim][FeCl$_4$] – 1-butyl-3-methylimidazolium tetrachloroferrate; CA-to-BA - catalyst-to-bagasse (CA-to-BA) ratios; CO$_2$ – carbon dioxide; Cu$_2$O – cuprous oxide; DT – Dry torrefaction; Fe$_2$O$_3$ – iron(III) oxide; N$_2$ – nitrogen; SE – steam explosion; WT – Wet torrefaction.

3.1. Pyrolysis

Pyrolysis consists of the thermal decomposition 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 unique 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 [3]. However, pyrolysis requires the pre-drying of the biomass, which is costly in terms of energy. Despite this, pyrolysis is considered the most convenient and cost-effective method for converting raw biomass into carbonaceous materials for large-scale production [3,49].

Pyrolysis can be divided into primary and secondary stages (Figure 3a). In primary pyrolysis, the volatile components are cleaved by dehydration, decarboxylation, and/or dehydrogenation, producing bio-oil when it condenses. 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 [88,89]. It has been used for various applications, such as soil amendment and adsorbents, energy generation, catalysis, carbon sequestration, and the production of activated carbon and related materials [3,4,88,89].

The pyrolysis type differs depending on the operating conditions, namely, temperature, residence time, and heating rate, which result in different yields of the final product [3,4]. Additionally, the heating rate and temperature influence the volatile matter, fixed carbon, porosity, surface area, and pore size distribution of the produced biochar [4]. To increase the production of bio-oil from the intermediate pyrolysis of sugarcane bagasse, Onokwai et al. [58] 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 runs. In this optimisation process, it was observed that due to complete pyrolysis, the yield of bio-oil increased steadily with temperatures between 320-520 °C at a heating rate of 7.5-12.5 °C/min. However, it decreased at temperatures between 520-720 °C and heating rates of 22.5-27.5 °C/min, due to secondary cracking, such as thermal cracking, repolymerization, recondensation, which may increase the yield of non-condensable gases and biochar.

Slow pyrolysis occurs at lower temperatures (400 °C) with slower heating rates (1−10 °C/s) and long residence times (>5 min). This allows more time for secondary reactions to occur, generating biochar in higher yields and volatiles with good 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 short residence times of the generated vapours (<1 s). These conditions lead to lower biochar yields, as the exposure time for reactions to form char is minimised. However, biochar is rich in aromatic carbon, microporous surface area, and alkalinity [3,4,49]. To increase the economic value of orange peels, Zhang et al. [55] 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 to 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. [54]. 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, favouring more pyrolytic reactions, and reducing the amount of biochar formed. Hence, biochar yield generally increases with particle size. The biomass components did not degrade at the same rate, which influenced the pyrolysis rate. Hemicellulose is the most thermally sensitive component; thus, it decomposes first at low temperatures, followed by cellulose at slightly higher temperatures, and then lignin at a high-temperature range [3,17]. In biomass with a higher cellulose content, the pyrolysis rate is faster, which increases the tar and gas yields while decreasing the char yield. However, in biomass with high lignin content, the pyrolysis rate was slower. Furthermore, the type of biomass produces different porosity developments owing to their moisture and lignin content. For instance, dry biomass with a high lignin content conserves energy for heating biomass to the target temperature, which maximises the yield of carbonaceous materials. The use of a lower temperature, heating rate, and longer vapour residence time is generally preferred to obtain higher yields. However, higher temperatures and heating rates result in better porosity of carbonaceous materials [3,49].

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 [3,4]. HTC is the preferred technique for biomass with high moisture content and high energy efficiency [14]. Hydrochar can be used for soil amendments, CO_2 sequestration, and electrochemical applications such as batteries and capacitors [3,4]. 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 [3,4,90]. Moreover, water acts as a solvent and reaction medium, where the gases produced during the carbonisation process can be dissolved, thus minimising the impact of environmental pollution [3,4]. Therefore, HTC appears to be the most sustainable and economical method, with high efficiency and low energy consumption. Nonetheless, industrial-scale HTC has not yet been implemented [3].

HTC involves hydrolysis, dehydration, decarboxylation, aromatisation, and recondensation (Figure 3b). Although the reactions occur consequently, each reaction has different kinetics and may occur simultaneously [91]. Hydrolysis has a lower activation energy than the other processes and initiates the degradation of biomass by cleaving mainly the ester and ether bonds. This results in oligosaccharides and lignin fragments that can be further hydrolysed or initiate other chemical pathways and products [92,93]. After hydrolysis, the hydroxyl and carboxyl groups are removed by dehydration and decarboxylation, respectively [93]. During the initial hydrothermal treatment, 5-hydroxymethylfurfural (HMF) is formed via dehydration reactions. Most of the intermediates result in the formation of hydrochar, but further degradation results in the formation of other compounds such as organic acids and compounds [92]. For instance, formic acid, levulinic acid, and dihydroxyacetone can act as catalysts to promote hydrolysis reactions, generating more HMF, which subsequently forms furanic compounds via a series of polymerisation or condensation reactions [3,93]. The hydrochar produced possesses higher dewaterability, drying performance, energy density, and porosity than raw materials [94].

Temperature is a key factor in the HTC process, as it influences the characteristics of the hydrochar. Temperature facilitates the disintegration of bonds into fragments by providing heat. In general, a lower temperature range (150–200 °C) leads to maximum production of solids [95]. As the temperature rises, HTC accelerates with extensive dehydration, forming more liquid and gaseous products, resulting in a lower yield of hydrochar. In addition to affecting yield, higher temperatures can lead to higher surface areas [3]. The degree of aromatisation of hydrochars is also affected by the HTC temperature [3] because the hydrochars produced contain higher amounts of oxygen functional groups and lower levels of aromatisation, which facilitates further chemical activation [96]. HTC is a relatively slow process, as the residence time ranges from several hours to several days. It has been shown that residence time influences both the carbon distribution and product composition of hydrochar [3]. Moreover, the composition and biomass type affected the yield and characteristics of hydrochar. Owing to complex branching which makes them less degradable, the presence of lignin increases hydrochar yield [95]. Cellulose is resistant to degradation at lower temperatures, indicating that the fibre structure remains intact. As the temperature increases, several points of the fibre network start to degrade, resulting in cellulose fragments that take the form of a spherical shape [3]. The influence of the process parameters (temperature, residence time, and mixing ratio) on the hydrochar yield and energy content of the co-hydrothermal carbonization (co-HTC) of pineapple and watermelon peels was evaluated by Azaare et al. [66]. According to these findings, hydrochar production declined as the temperature and residence time increased. 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 [3,4,97]. Post-treatments such as activation and templating can be employed to produce highly porous carbons that are necessary for efficient mass transfer [64,97]. During physical activation, the surface area of hydrochar can be increased by thermal treatment using steam, CO_2, or air at 800–900 °C [90]. In this process, small organic molecules were removed, leading to 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 was obtained by washing off the ions. The hydrochars started to degrade at 200 °C because of the lower degree of aromaticity related to the cellulose content. The maximum decomposition occurred between 350 and 500 °C. Upon further carbonisation, the mass loss increased when more dissolution occurred, resulting in an increase in the surface area and porosity of the hydrochars. Carbonaceous materials can also be modified by changing their functional groups or removing existing groups [98]. 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 [99]. However, it is difficult to perform infiltration procedures, and template removal usually requires harsh conditions, which are not environmentally friendly. In soft templating, mesoporous carbon is synthesised using a block copolymer as a soft template to form micelle-like structures [3,99,100]. During carbonisation, the block copolymers become thermally unstable and decompose easily. The mesoporous carbon can be obtained by calcination at 600 °C to remove the template. Similarly, heteroatom-doped carbons can be obtained by selecting appropriate precursors [3,101].

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) [3]. 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 [3,4,70]. The low volatility of ILs allows the operation of processes at ambient pressures [102]. ITC is still a relatively new approach that has not yet been fully exploited. This process has mainly been restricted to monosaccharides and raw lignocellulosic waste [70]. Moreover, there is no data regarding the use of ITC on an industrial scale because of the high cost of ILs [4]. Despite this, most ILs can be recovered by Soxhlet extraction and reuse [3].

The properties of the produced carbonaceous materials depend significantly on the type of ionic liquid used, as the properties of the ILs can be tuned to meet specific requirements by the selection of the ionic liquid anion and cation [103]. Cellulose is insoluble in conventional organic solvents, but ILs bearing a halide anion also seem to be very efficient in solubilisation owing to the strong chemical interaction between the anion and the hydroxyl group of cellulose as a hydrogen bond acceptor [70,102]. Different ILs can generate pores in different ways, as well as generating various pore sizes [3]. For instance, larger anions such as chloride (Cl^-), tetrafluoroborate (BF_4^-), and bistriflimide (Tf_2N^-) appear to yield higher pore volumes [104]. Hence, it is important to choose an appropriate ionic liquid that contributes to the evolution of the porous structure during carbonisation [102]. Different heteroatoms for doping carbon materials can be easily introduced from the anions present in the ILs. This reduces the need for extra modification steps, which benefits the use of ILs as catalysts by providing more active sites, in addition to increasing the conductivity of the product, which is beneficial for electrochemical applications [3]. Furthermore, owing to their nitrogen-doped structure, carbonisation of ILs provides unique physicochemical properties with attractive applications in supercapacitors and energy storage [102]. Cibien et al. [70] 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. [71] showed that cation engineering can be used to modify the morphological and textural characteristics of ionochars, offering the possibility of controlling CO_2 uptake and retention.

3.4. Torrefaction

Torrefaction, also known as mild pyrolysis or roasting, involves the removal of volatile compounds by heat application, and is typically carried out at temperatures between 200 and 300 °C using slow heating rates to produce biochar [105]. Torrefied biomass has a modified polymeric structure compared to raw biomass, with low moisture content, high heating value, low volatile content, and resistance to biological degradation [49,105]. The thermochemical process involves four stages. The first stage is the drying of the biomass, in which the unbound moisture content is evaporated. The macromolecules then underwent depolymerisation and recondensation reactions. In the third stage, devolatilisation began when the temperature reached approximately 180 °C and gradually progressed to extensive devolatilisation and carbonisation in the fourth stage at temperatures above 250 °C (Figure 3d) [49,106]. Torrefaction techniques can be divided into dry torrefaction (DT) and wet torrefaction (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 of approximately 180-260 °C for approximately 2 h. Contrary to WT, DT does not address the issue of excess ash and chlorine content in waste biomass. 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 lowering the amount of ash present [78,107,108]. Gong et al. [109] 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 [110]. Biochar produced from torrefaction has valuable applications in soil remediation, fertiliser production, activated carbon production, and sorbents for water purification [49,110]. Dyjakon et al. [72] evaluated the hydrophobic characteristics of biomass from agri-food 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

doi:10.20944/preprints202309.1360.v1

decreased by a maximum of 56.96-24.14%. Moreover, Allouzi et al. [76] verified that depending on torrefaction temperature, the mass yield for torrefied olive pomace varied from 59.2 to 82.6%. On the other hand, Alves et al. [73] studied the characteristics of bioenergy-related materials, combustion patterns, and probable emissions of banana leaf waste after torrefaction. 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 widely used hydrothermal pretreatment method that has been applied to the processing and modification of dietary fibre raw materials owing to its lower energy consumption and lower chemical usage. 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 [111-113]. Steam explosions use saturated steam at high pressure into cell walls and plant tissues by applying the thermochemical action of high-temperature cooking coupled with the physical tearing action of an instantaneous explosion. The physicochemical properties of macromolecules in fibrous raw materials change, promoting subsequent separation and conversion [112].

Steam explosions include acid hydrolysis, thermal degradation, mechanical fracture, hydrogen bond destruction, and structural rearrangements. According to its functional characteristics, this process is mainly divided into 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 permeates into the interior of the materials, filling the tissue pores. Subsequently, the high pressure created by the saturated steam is released within milliseconds [111]. This step allows hydrolytic breakdown of hemicelluloses and other parts of the raw materials to form soluble carbohydrates. The lignin in the intercellular layer is softened and partially degraded, which reduces the lateral bonding strength of the fibres, while the cell pores are filled with high-pressure water vapour, becoming soft and plastic. During the explosion stage, the water in the substrate evaporated. The sudden pressure drop leads to vapour expansion inside the fibres, which disrupts the fibrous structure and cell wall rupture to form pores, resulting in an explosion. This step promotes the destruction of the reduction in cellulose crystallinity, delignification, and the release of small molecular material from the plant cells. It also causes hydrolysis of hemicelluloses, making them easier to use in subsequent processes [111,112].

Steam explosion is an appealing pretreatment method for the isolation of high-value compounds, such as phenolics and polysaccharides, from biomass [112]. It has been widely used in the physicochemical pretreatment of lignocellulosic biomass to open up the structure of lignocellulose and to make cellulose amenable to enzyme conversion [111-113]. Steam explosion provokes a strong alteration of lignocellulosic biomass by increasing its surface area and porosity through lignin relocation and modification of its structure, partial depolymerisation and solubilisation of hemicellulose, and a strong increase in cellulose enzymatic digestibility. However, owing to the naturally resistant carbohydrate-lignin shield, the recovery of lignins and hemicelluloses for biomass valorization is energy consuming and expensive [112,113]. Hongrattanavichit and Aht-Ong [87] used steam explosion pretreatment at various temperatures (195-210 °C) and times (5-15 min) to isolate 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^3.

This process shows high potential for industrial applications and is currently being developed at pilot or industrial scales for different applications because of its economical and eco-friendly advantages for processing large quantities of food materials [114]. Steam explosions have been investigated for the wall-breaking extraction of natural products, oil extraction, hydrothermal conversion of active ingredients, and the use of raw materials. Moreover, it has a deglycosylation effect on some glycoside-active ingredients, separating the sugar group from the aglycone and promoting a high activity [112]. Cui et al. [80] demonstrated that the yield 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, increasing the oil-holding capacity and sodium nitrite binding capacity of soluble dietary fibre.

4. Applications of carbonaceous materials

Biomass is considered the most sustainable and renewable source for the synthesis of carbonaceous materials because of its high carbon content and renewable nature [1,3]. Several applications of biomass-based carbon materials are currently being sought owing to their potential cost-effectiveness, large-scale, 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 comparison to the standard synthesis of biomass-derived hydrochars and biochars [7]. Carbon nanostructures and nanomaterials have received great attention because of their properties and applications in the environmental, catalytic, biological, and energetic fields [3,4]. For instance, they have shown important applications in catalyst supports, carbon fixation, adsorbents, gas storage, electrodes, carbon fuel cells, and drug delivery [5]. Activated carbon and carbon fibres can also be prepared using additional activation and electrospinning processes, respectively [4,7]. 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 depend on the type of biomass and conversion methods used, as previously discussed [7].

4.1. Environmental applications

The environmental applications of carbonaceous materials include CO_2 adsorbents, soil amendments, and water remediation. Increasing levels of atmospheric CO_2 need to be mitigated, as they influence climate change through the greenhouse effect. Biochar is an effective and economical strategy for capturing atmospheric CO_2 [3]. Moreover, they can reside stably in the soil for extended periods, independent of mineralisation and temperature fluctuations [4]. 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 through chemical activation for further enhancement [3]. The use of pesticides and herbicides causes soil contamination through disposal of inorganic and organic pollutants. Anthropogenic activity can also lead to the presence of unwanted metals in the soil. These contaminants are highly toxic, can be harmful to living organisms, and pose a threat to health and agricultural products. Hence, it is essential to reduce their quantities 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 [3]. It serves as a soil conditioner by enhancing the water-retaining capacity of the soil, pH optimisation, and the total uptake of phosphorus and nitrogen. The bioavailability of the required nutrients and water is thus increased, providing a microenvironment for the growth of essential soil microorganisms, thereby improving soil fertility [3,4,115].

4.2. Catalytic applications

Heterogeneous catalysts play a fundamental role in chemical synthesis and transformation. Carbonaceous materials have been shown to act as catalysts and catalyst supports. Hydrochars possess the desired porosity and high surface area for accelerating reactions, which have been explored in the form of carbonaceous nanofibers [3-5]. Furthermore, the combination of metallic nanoparticles results in high thermal, chemical, and mechanical stabilities [3]. 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 areas and modifiable properties for use as a catalyst or catalyst support [3]. The high reusability and efficiency of these biomass-derived catalysts make them promising candidates for future industrial applications, given the growing ecological concerns [3,4].

4.3. Energy conversion and storage applications

Carbon-based materials produced at elevated temperatures (>1200 °C) are likely to exhibit desirable electrochemical properties. They have been considered in energy conversion and storage applications owing to their versatile dimensionality, in addition to their structures and physicochemical properties. Examples of these properties include thermal insulation, thermal conductivity, heat resistance, hardness, softness, and insulator-semiconductor-conductor properties [116]. 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 [3,4,117]. These characteristics have also led to their use as supercapacitors and energy storage devices known for their high capacitance, extended life span, and quick charge/discharge capabilities [3]. Carbon allotropes with different structures and properties, such as sp3, sp2, and sp, can be obtained from combinations of carbon atom hybridisations [116]. Carbon nanotube-based materials (sp^2), 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 convert 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 ensure better charge conduction and improved electrode flexibility. Moreover, the properties of carbon nanotubes can be significantly affected by the number of walls, length, diameter, type of defects, concentration, and synthesis method [118]. Solid biofuels typically include any renewable biological material that can undergo combustion to generate energy, with economic and social benefits as well as a lower environmental impact [119]. Hydrothermal treatment and torrefaction have been used to convert industrial wastes and sewage sludge into clean solid biofuels [3,120].

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 profiling of molecules as well as for drug and gene delivery [121]. Carbon quantum dots (CQDs) are small carbon nanoparticles (<10 nm) comprising amorphous or crystalline centres with dominant sp^2 carbon that have gained much attention because of their fluorescent properties, high chemical stability, good conductivity, non-blinking, and resistance to photobleaching [122-124]. 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 can be employed in medical bioimaging practices to detect or cure diseases [3,122,123]. Other applications include biosensing, biological labelling, medical diagnostics, and optoelectronic devices [121]. However, features related to safety, physicochemical properties, and pharmacokinetics must be further investigated before they can be used in medicine [121].

5. Concluding remarks

Our Planet offers us an infinite quantity of biopolymers (namely cellulose, hemicellulose, and lignin), in terms of nature and diversity, biosynthesized by living organisms, most of them with numerous applications namely in food, pharmaceutical and cosmetic industries, in addition to environmental (can be used for CO2 capture and adsorption of contaminants in soil and water), and energy conversion/storage fields applications. Besides its enormous potential, these abundant and renewable resources remain unexploited, even considering the high dumping fees that are necessary to dispose of this valuable material in landfills, which are already in short supply. Pyrolysis, HTC, ITC, torrefaction and Steam explosion were discussed as important processes to convert of biomass to carbonaceous materials. So far, pyrolysis is considered the most convenient, and cost-effective method to convert biomass and agri-food residues into carbonaceous materials with large-scale production. 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 common biomass-derived carbonaceous material. Biochar endowed with interesting physicochemical attributes, demonstrates a clear ability to improve plant growth and increase soil fertility through beneficial soil microorganisms. However, its 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 has a more efficient process.

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

Supplementary Materials: Not applicable.

Author Contributions: J.S.C. and C.V.B. planned and managed the manuscript; C.V.B. and J.A.M.P. collaborated on Section 1 and Section 2; C.V.B and R.P. collaborated on Section 3; C.V.B. and J.S.C. collaborated on Section 4; J.S.C. was responsible for Section 5; C.V.B. prepared the Figures; J.S.C. and J.A.M.P. edited the manuscript; J.S.C. made its submission. All the authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by FCT-Fundação para a Ciência e a Tecnologia through the CQM Base Fund, UIDB/00674/2020, and Programmatic Fund, UIDP/00674/2020, by Interreg MAC 2014–2020 Cooperacion territorial through AD4MAC project (MAC2/1.1b/350), and by ARDITI-Agência Regional para o Desenvolvimento da Investigação Tecnologia e Inovação through the project M1420-01-0145-FEDER-000005-Centro de Química da Madeira-CQM+ (Madeira 14-20 Program). The FEDER (AD4MAC project) is also acknowledged for the invited researcher contract granted to J.A.M.P.. The authors also acknowledge financial support from the FCT and Madeira 14-2020 program to the Portuguese Mass Spectrometry Network through the PROEQUIPRAM program, M14-20 M1420-01-0145-FEDER-000008.

Data Availability Statement: Not applicable.

Institutional Review Board Statement: Not Applicable.

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

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