Review

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Recovery of Added-Value Products from Biowaste by Subcritical and Supercritical Water Technologies—A Review

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Abstract

The introduction of sustainable practices into waste management can have favorable environment impact, increase resource value, and economic gains. Hydrothermal technologies have strong potential for the production of up-cycled ingredients from biowaste (amino acids, sugars, phenols, pharmacologically-active compounds, etc.), enabling additionally high energy recovery (50-80%) from biowaste with net-negative carbon emission. This review discusses the use of subcritical and supercritical water technologies for sustainable valorization of biowaste and conversion of biomass into high-value chemicals and biofuels. The potential for the extraction/generation of bioactive compounds from plant and animal waste is presented, emphasizing the efficiency, compound stability, and bioactivity of fractions obtained. The possibilities of simultaneous extraction of added-value compounds and hydrolysis of feedstock biopolymers by said technologies are elaborated. The review further addresses the production of biofuels through hydrothermal carbonization for solid fuels, hydrothermal waste liquefaction for liquid fuels, and supercritical water gasification for gaseous fuels. The paper highlights the environmental and economic advantages of technologies based on sub- and supercritical water, over conventional chemical and fermentative routes, emphasizing their contribution to circular bioeconomy by converting biowaste into value-added products and sustainable energy sources.

Keywords: biowaste valorization; subcritical and supercritical water processes; extraction; sugars; organic acids; amino acids; bioactive compounds; biofuels

1. Introduction

Sound biomass management represents a key part in circular bioeconomy concept, especially taking into consideration growing production of biowaste by different sectors and increasing environmental burden. Strategic handling of biowaste, from production and collection to processing, conversion, and final use, ensures efficient, sustainable, and minimal environmental impact.

Biodegradable waste is generated by different industries and, according to its origin, can be categorized to agricultural waste (high in cellulose and lignin: crop, fruit and vegetable residues), forestry and wood processing waste (high in lignin: bark, sawdust, off-cuts), animal waste (high in nitrogen: abattoir waste, bedding waste, manure), municipal waste (high moisture, fast decomposition: eggshells, food waste, paper), food processing waste (nutrient-rich: spent brewers grain, whey, fruit pulp, skin, seeds, meat and fish by-products) (Figure 1) [1,2].

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Figure 1. Categories of biodegradable waste by origin. (Figure generated using DALL-E 3 AI software.).

The amount of biodegradable and waste, in general, has been steadily increasing due to ever-growing world population, change in lifestyle and consumption habits, urbanization, economic growth and industrialization [3]. It is estimated that 88 million tons of food waste is generated annually in the European Union alone (173 kilograms per capita) [4]. Biowaste digestion poses environmental threat through the production of methane, accounting for around 4.6% of total greenhouse gas emissions in 2021 [5] and contributing to global warming and climate change. The carbon footprint associated with food waste is also significant, equivalent to annual accumulation of 3.3 billion tons of biogenic CO_2 [6]. The increasing amount of biodegradable waste also affects soil health and biodiversity, crop productivity, groundwater safety and human health [3].

Valorization of biomass implies conversion of raw biological material into higher-value products, energy, or chemicals. Instead of treating biomass as waste, valorization aims to increase its value in sustainable, and economically profitable way. Reducing waste and fossil fuel use represent key points in circular bioeconomy concept. Conventional biowaste management technologies driven by linear economy, such as open dumping, landfilling and incineration, increase greenhouse gasses emissions: carbon dioxide, methane, carbon monoxide and nitrogen oxides. A fundamental alternative to this linear economic model is the circular economy model, whose main objective is to produce and utilize products in the most efficient way by managing waste in an economically and environmentally appropriate manner [4].

In recent years, global attention has focused on utilization of biowaste in food, cosmetics and pharmaceutical industries, as animal feed, renewable energy source and for the production of platform chemicals. The management of biowaste is different in each region relying on respective legislation, facilities, experience and technical advances [7].

Most common valorization pathways of biomass encompass thermochemical, bio-chemical and biorefinery technologies. Thermochemical processes, such as pyrolysis, simple combustion, gasification and torrefaction (production of solid coal-like fuels), require previous biomass drying, consuming additional energy. Biochemical processes, such as fermentation, anaerobic digestion, enzymatic hydrolysis of simple composting, is mostly suited for wet biomass. Biorefinery approach adds the highest value to the waste, converting it to biofuels (bioethanol, biodiesel, biogas, syngas, bio-oil), bioplastics (polylactic acid, polyhydroxyalkanoates), biochemicals (furfural, levulinic, lactic, succinic, acetic acids) or high-value molecules, such as fibers, proteins, pigments, nutraceuticals, antioxidants or amino acids.

In recent years high-pressure technologies relying on utilization of subcritical (SW) and supercritical water (SCW), established themselves as very versatile and promising for valorization of different types of biowaste. By altering operational parameters, water can acquire different solvating

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and reactive properties. High reactivity of hot compressed water under high operating temperature can decompose virtually any organic material and can be used to depolymerize matrix biopolymers and produce chemicals, added-value products and biofuel [8]. The basic concept of this technology is the use of water at high temperatures and pressures as an extraction or reaction medium. Temperatures of compressed water up to subcritical (between 100 °C and 374 °C) or beyond the critical (>374 °C) radically alter physicochemical properties of this fluid [8–10]. The temperature-pressure phase diagram of water is shown in Figure 2. Under these conditions water falls into an intermediate state between the states of liquid and gas, making easy to manipulate it`s reactivity only by altering operational parameters [9,11]. The density of water changes becoming between that of water in the liquid state (1 g/cm^3) and that in the gaseous state (0.001 g/cm^3) [11]. As a cheap, green and safe solvent, water in its subcritical state can be conveniently used for the extraction of wide array of different polarity compounds. Changes in water properties and hydrogen bonds as a function of temperature and pressure lead to changes in the dielectric constant [9]. Due to reduced number of hydrogen bonds in heated water, the dielectric constant decreases from 80 for water at room temperature and atmospheric pressure to values corresponding to conventional organic solvents, depending on a temperature. Moderately polar and unpolar organic compounds, thus, can easily be solvated by water in near-critical range to complete solvatation [12]. Compared to traditional extraction methods (solvent extraction, Soxhlet extraction, hydrodistillation), extraction with subcritical water usually provides higher yields, faster processing times, and higher purity of desired compounds [13–15].

The properties and reactivity of water in subcritical and critical state change dramatically. The concentration of H^+ and OH^- ions in water at 300 °C and 220 bars (subcritical conditions) is around 3 x 10^{-6} mol/dm^3, while at 400 °C and 220 bars (supercritical conditions) it is 3 x 10^{-10} mol/dm^{-3} [16]. Subcritical water has much higher concentration of H^+ and OH^- ions and its high reactivity is prevalently associated with ionic mechanisms, while supercritical water reactivity is the consequence of radical-mediated reactions [17]. Owing to their exceptional solvating and reactive properties, subcritical and supercritical water technologies are used in various areas, including waste treatment and environmental applications/remediation, production of renewable energy, production of pharmaceuticals and platform molecules, biomedical and agricultural applications [9,18,19].

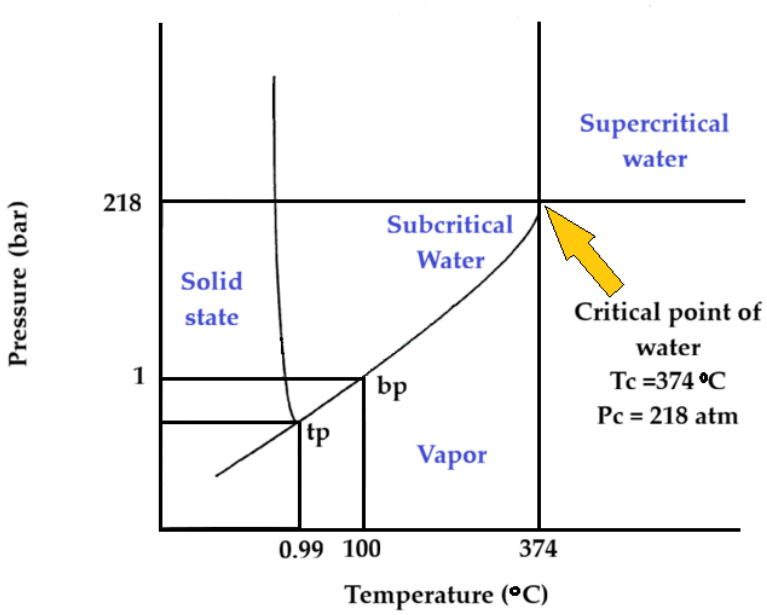

Figure 2. Phase diagram illustrating the different states of water.

Subcritical and supercritical water processes can be carried out in batch, semi-batch, and continuous reactors. In a batch process, the raw material and reaction solvent are placed in a closed

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reactor. In semi-batch processes, the raw material is subjected to continuous flow of the solvent; the raw material remains static while the solvent flows through it, while in a continuous process, both the raw material feed and the solvent continuously enter and exit the reactor [20]. Continuous systems offer advantages such as high reaction rates achievable at high temperatures, but technical challenges related to pumping the biomass slurry must be addressed. Careful engineering experiments and design are necessary to optimize subcritical and supercritical water processes, reduce capital and operating costs, and maximize yields of the desired products.

1.1. Significance and Novelty of the Study

To our knowledge, this is the first review to address the use of subcritical and supercritical water technologies in the two main directions of sustainable valorization of biowaste and biomass: the production of high-value chemicals with potential application in various industries (food, pharmaceutical, and cosmetic), such as carbohydrates, organic acids, proteins and peptides, and bioactive compounds on one hand, and biofuel production on the other. A detailed literature review revealed that existing articles focus either on the use of subcritical water for obtaining high-value compounds important for various industries, or on the use of high-pressure hydrothermal technologies for producing different biofuels. This review provides a comprehensive overview of the broad application of these high-pressure technologies in biowaste valorization, their environmental impact, advantages, and technical and economic challenges.

The aim of this review was to cover the most recent research related to different applications of subcritical and supercritical water in biowaste valorization, including agricultural residues, industrial waste, and other waste streams, with particular emphasis on target products. The manuscript is structured according to final fraction, a product, or compound, that can be produced by these technologies, starting from different biowaste sources.

1.2. Methodology

This paper presents an extensive literature search and analysis of research papers on the use of subcritical and supercritical water technologies for valorization of biowaste from various sources. Relevant literature was identified, assessed, and synthesized to interpret the results. Articles were collected from Web of Science, Scopus, and PubMed. The combined keywords were: biowaste valorization, subcritical water, supercritical water technology, bioactive compounds, carbohydrates, organic acids, proteins, and biofuels. Generally, recent articles published from 2020 to 2026 were included in the review. If recent literature was unavailable, older, but relevant sources, were also reviewed. Some references appear in different sections, as various products were recovered from the same starting raw material.

2. Recovery of Carbohydrates

Alongside proteins, lipids and polynucleotides, polysaccharides are the main components of all living organisms. Polysaccharides, the most prevalent type of carbohydrates in nature, are macromolecules that are structurally composed of homo- or heteromonosaccharides combined with uronic acids and linked by glycosidic bonds [21–24]. These biomolecules are widely applied in food industry in their natural or modified state. Some of their extensive roles in food industry include emulsification, suspension, stabilization, encapsulation, flocculation, film formation, binding and coating. Polysaccharides also play an important role in controlling the texture of foods as well as their taste, appearance and color [25]. In addition to their enormous and irreplaceable role in food industry, this extremely heterogeneous group of functional compounds has also found use in the pharmaceutical industry due to their exceptional properties as antioxidant, antimicrobial and antitumor agents [26–28]. In addition, their versatility supports applications in cosmetics, medical, petrochemical and paper industries [22,29,30].

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Depending on the source, natural polysaccharides can be categorized into plant polysaccharides, animal polysaccharides, algal polysaccharides and microbial polysaccharides. The most commonly extracted polysaccharides from different sources are pectin, cellulose and hemicellulose, starch, galactomannans, arabinoxylans and inulin from plant waste, β-glucans from bacteria, fungi and cereals, alginates, carrageenan, agar and fucoidans from algae, while chitin and chitosan are extracted from crustacean shells [19,31].

Waste rich in carbohydrates usually comprises unconsumed parts of vegetables, fruits, other plants, as well as by-products of harvests that are discarded [32]. Cellulosic biomass is considered a promising biomaterial due to its wide availability and great quantities generated [33].

Subcritical water is increasingly used for the extraction of natural polysaccharides [32], while hydrolysis is the basic step for the conversion of polysaccharides into more applicable compounds [33]. Extraction with subcritical water (SWE) not only leads to a higher recovery of polysaccharides, but also to extraction of polysaccharides with better functional properties [34]. Compared to the polysaccharides extracted with hot water from *Auricularia cornea* var. Li., a white-fleshed edible mushroom, the polysaccharides obtained by SWE formed hydrogels with a denser network structure, improved rheological and textural properties and had a stronger ability to stabilize emulsion gels [35].

Different polysaccharides have different solubilities in subcritical water under different conditions, allowing selective extraction of specific polysaccharides and minimization of co-extraction of impurities. Subcritical water increases the yield of polysaccharides via two main pathways: (1) promoting dissolution of soluble polysaccharides and (2) promoting the conversion of insoluble polysaccharides into soluble ones through hydrolysis induced by high temperature and the acidic environment created by heating water above its boiling point under pressure [34].

Some examples of soluble polysaccharides are chitosan [36], polysaccharides excreted from mycelium of higher fungi [37], high-methoxy pectin [38], macromolecular carbohydrates from baobab fruit pulp [39]. Soluble polysaccharides containing numerous polar groups, such as hydroxyl groups, show strong polar interactions with water at room temperature. However, as the temperature of subcritical water increases, the polarity of water decreases significantly. Nevertheless, hydrogen bonds within the polysaccharides and between the polysaccharides and the surrounding water molecules, weaken, facilitating their dissolution in water [40]. In addition, the increase in temperature leads to a higher diffusion coefficient and lower viscosity, which allows the water molecules to penetrate the biomass faster and reduce the mass transfer resistance, so that the dissolved polysaccharides can diffuse well into the surrounding solvent [34].

Efficient extraction of polysaccharides with subcritical water can be attributed to rupture the plant cell walls and the microbial cell membranes in this medium, exposing the polysaccharides to direct contact with the solvent [34]. For insoluble polysaccharides such as cellulose, hemicellulose and protopectin, higher temperatures of subcritical water are required. Extraction of polysaccharides from complex matrices with subcritical water, is often accompanied with the production of by-products such as organic acids, especially acetic, formic, citric, malic and levulic acids, due to high water reactivity. Formed organic acids can further promote degradation of polysaccharides and conversion of insoluble polysaccharides into soluble oligosaccharides [41]. Subcritical water has also been shown to be effective in the extraction of waterinextractable arabinoxylans [42,43], hemicellulose [44], cellulose [45] and pectin from cocoa pod husk [46] and apple pomace [47]. **Table 1** presents studies in which various polysaccharides, oligosaccharides, and monosaccharides were extracted from biowaste using subcritical water, or in which the hydrolytic effect of SW was used to hydrolyze polysaccharides into oligosaccharides.

Table 1. Subcritical water extraction of carbohydrates from different biowaste sources.

Biowaste source	Final product	Conditions	Reference
Posidonia oceanica leaves (aquatic plant)	Cellulose (24-25 g/100 g sample)	170 °C; 30 min;	[45]

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		9.5 bars	
Rice straw	Cellulose (46.2 g/100 g sample)	180 °C; 30 min; 11 bars; S/L[1] = 1/10	[48]
Wood waste sawdust	Microcrystalline cellulose (56.8 g/100 g sample)	0.5 M NaOH; 100 °C; 60 min; S/L = 1/20	[49]
Phragmites karka wetland reed grass	Cellulose (35.1 g/100 g sample); Total reducing sugars (15.5 g/100 g sample)	170 °C; 30 min; 35 bars; S/L = 1/50	[50]
Castor steams	Xylo-oligosaccharides (63.6 g/100 g sample); Lignin (57.3 g/100 g sample)	180 °C; 30 min; S/L =1/15 SW-HDES[2]: 140° C; 3h	[51]
Sesam seed husks	Crude cellulose (70.7 g/100 g sample); Purified cellulose (11.6 g/100 g sample)	180 °C; 30 min; S/L = 1/15	[52]
Corn strover	Cellulose (74.06 g/100 g sample); Fermentable sugars (19.28 g/100 g sample)	[3]SE: 200 °C; 10 min; [4]SWH: 230° C; 30 min; S/L = 1/40	[53]
Durian (*Durio zibethinus*) rind	Pectin (5.43 g/100 g sample)	120° C; 18.5 min; S/L = 1/15	[54]
Cocoa pod husk	Pectin (6.58 g/100 g sample)	120 °C; 10 min; S/L = 1/15	[46]
Apple pomace	Pectin (20–40 g/100 g freeze-dried sample)	120 °C; 140° C; 5, 10, 15 min; pH 3.0-7.0	[47]
Apple pomace	Pectin (2.69–14.89 g/100 g oven-dried sample)	100–180 °C; 5–15 min; S/L = 1/20	[55]
Passion fruit (*Passiflora edulis*) rinds Residual biomass (after UAPLE[6] of phenolic compounds)	Pectin (19.1 g/100 g sample) Pectin (27.6 g/100 g sample)	PNaDES[5] (Citric acid, glucose, water): 120 °C; 30 min; S/L =1/30	[56]
Pistachio industry waste (leaves, stems, twigs, and shells)	Pectin (15.5 g/100 g sample)	MASWE[6]: 120 °C; 30 bars; microwave power 700-800 W; irradiation time: 4 min	[57]
Shrimp shells	Chitin (26.39 g/100 g sample)	260 °C; 40 min; 40 bars	[58]
Shrimp cephalothorax wastes	Hydroxyapatite—α-chitin (82.2 g/100 g sample)	260 °C; 30 min; S/L = 0.17	[36]
Portunus trituberculatus (swimming crab) shells	Chitosan	170 °C; 60 min; S/L = 1/15	[59]

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	(12.2–13.2 g/100 g wet sample)		
Pleurotus ostreatus mushroom by-products	Chitosan (11.4 g/100 g sample)	120 °C; 10% malic acid; 30 min; S/L = 1/4	[60]
Saccharina japonica (brown algae)	Fucoidan (13.56 g/100 g freeze-dried sample)	127.01 °C; 11.98 min; S/L = 0.04; 80 bars	[61]
Nizamuddinia zanardinii (brown algae)	Fucoidan (25.98 g/100 g sample)	150 °C; 29 min; S/L = 21	[62]
Ascophyllum nodosum (beach-cast brown seaweed)	Fucoidan (38.48 g fucoidan/100 g sample)	138 °C; 46 min heating time; 12 min hold time; S/L = 1/30	[63]
Undaria pinnatifida (New Zealand Wakame brown seaweed)	Fucoidan (4.6 g/100 g sample)	120 °C; 5 min; S/L = 1/50	[64]
Rice husk	Fermentable sugars (40.68 g/100 g sample)	180° C; 5 min (steam explosion pretreatment in 3 cycles); 230° C; 20 min; S/L = 1/80 (Hydrolysis)	[65]
Defatted rice bran	Fermentable sugars (7.16 g/100 g sample)	PLE[7]: 140 °C; 240 ml methyl acetate/g sample; SWH: 200 °C; 30 min; S/L = 1/66	[66]
Olive pomace	Fermentable sugars (7.06 g/100 g sample)	PLE: 130 °C; 120 g ethanol/g sample; SWH: 250 °C; 45 min; S/L = 1/90	[67]
Pereskia aculeata Miller (Barbados gooseberry)	Fermentable sugars (14.25 g/100 g sample)	220 °C; 60 min; 150 bars	[68]
Cashew nut shells	Fermentable sugars (61.41 g/100 g sample)	180 °C; 45 min; 15 bars; S/L = 1:20	[69]
Cashew apple bagasse	Fermentable sugars (31.14 g/100 g sample)	220 °C; 30 min; 200 bars; 5 ml/min; pH = 2; S/L = 1:20	[70]
Oat hulls	Fermentable sugars (14.56 g/100 g sample)	SE: 200 °C; 4 min; SWH: 260 °C; 20 min; S/L = 1/90	[71]

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Sorghum bagasse	Fermentable sugars (72.59 g/100 g sample)	SE: 200° C; 5 min; SWH: 260 °C; 30 min; S/L = 1/32	[72]
Orange peel (pre-treated in Soxhlet system)	Fermentable sugars (5.31 g/100 g sample)	180 °C; 60 min; 150 bars	[73]
Orange bagasse (pre-treated in Soxhlet system)	Fermentable sugars (4.26 g/100 g sample)	200 °C; 60 min; 200 bars	

[1]S/L—Solid to liquid ratio; [2]HDES—hydrated deep eutectic solvents treatment; [3]SE—steam explosion pretreatment; [4]SWH—Subcritical water hydrolysis; PNaDES[5]—Pressurized natural deep eutectic solvents; MASWE[6]—Microwave assisted subcritical water extraction; PLE[7]—Pressurized liquid extraction. Contents are expressed on a dry sample basis; if otherwise, it is indicated.

2.1. Subcritical Water Extraction of Cellulose, Hemicellulose and Lignin

Cellulose is the most abundant polymer in nature and consists of glucose monomers linked together in the *β*-(1-4) position. It is a biodegradable and inexpensive polymer that is obtained from renewable resources: wood and plant cell walls, some bacteria and even from tunicates—the only known cellulosic animals. Corn, rice and wheat are the three most important crops in the world for human and animal consumption and their residues can be considered as cellulose-rich biomass [32]. Cellulose particles have a wide range of applications, such as for cellulose films and aerogels, reinforcing agents for composite materials, electronic and acoustic devices or biomedical (tissue engineered products for wound care and organ regeneration), and pharmaceutical applications (drug delivery systems or binders) [45].

Hemicellulose is a heteropolysaccharide consisting of hexoses and pentoses, such as glucose, mannose, xylose and arabinose. Hemicelluloses and the monomeric sugars of which they are composed of, have a variety of applications in chemical, pharmaceutical and food industries [44]. Lignin is a biopolymer that binds cellulose and hemicellulose fibers and gives stiffness to plants. It is a three-dimensional amorphous aromatic polymer of phenolic nature whose composition varies depending on the plant species [31]. Lignin, a biopolymer co [74–76mposed of phenyl isoprenoid units, is the most difficult to be depolymerized by conventional technologies, however technologies relying on sub- and supercritical water are able to confront the challenges related to its resistant chemical structure [74–76].

Subcritical water extraction was primarily used to promote the separation of non-cellulosic compounds—hemicellulose and lignin—from stone pine, holm oak, and Norway spruce [44]; *Posidonia oceanica* waste [45]; rice straw [48]; sawdust from wood waste under hydrothermal alkaline treatment [49]; reed grass (*Phragmites karka*) from wetlands [50]; and sesame husks [52]. The typical treatment of the remaining solid fraction after extraction involved bleaching with hydrogen peroxide to obtain high-purity cellulose (~90%) [45] or pulping with NaOH [50]. Evidence shows that integrating hydrated deep eutectic solvents with subcritical water hydrolysis is highly effective for xylan removal (76.2%) and delignification efficiency (60.5%) [51]. The extraction conditions and the yields of cellulose products obtained by subcritical water technology from various sources are listed in **Table 1**.

2.2. Subcritical Water Hydrolysis of Lignocellulosic Biomass to Fermentable Sugars

Lignocellulosic biomass is a renewable resource with significant potential for producing bioproducts within the biorefinery concept, offering a promising alternative to mitigate environmental impacts. These polysaccharides can be broken down into fermentable sugars, which

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can then be converted into biofuels (such as ethanol, biohydrogen, or biomethane) through microbial fermentation.

Subcritical water hydrolysis (SWH) can simultaneously hydrolyze hemicellulose and cellulose from biomass in a short period (a few minutes), compared to enzymatic hydrolysis, which can take several hours or days [71]. This technique has been used to break down *Pereskia aculeata* Miller biomass to produce fermentable sugars and platform chemicals [68]. The biomass used was residual material obtained after extracting bioactive compounds by pressurized liquid extraction. Cellobiose was the predominant sugar in the hydrolysate, with a content of 11.8 g/100 g biomass [68]. Subcritical water was also used to extract fermentable sugars (xylose, glucose, arabinose) from cashew nut biowaste [69] and cashew apple bagasse [70].

The structural recalcitrance of many lignocellulosic biomasses, resulting from lignin and cellulose crystallinity, hinders direct biological, chemical, or thermochemical conversion. Efficient pretreatment methods are necessary to break down this barrier and enhance polysaccharide accessibility. Steam explosion combines high temperature (160-240 °C) and pressure (7-48 bars) with rapid decompression, ensuring selective hydrolysis. This pretreatment method generally increases the cellulose content of biomass while reducing hemicellulose content. Lignin may undergo depolymerization and form pseudolignin through condensation reactions. During the instantaneous pressure drop in steam explosion, the objective is to overcome the recalcitrance of the lignocellulosic structure. The rapid expansion of liquid into vapor phase within the biomass can lead to breakdown and depolymerization of cellulose and lignin. Furthermore, conditions of SWH favor sugar conversion reactions to platform chemicals or partially hydrolyze polysaccharides into oligosaccharides. Therefore, monosaccharide yields are often low. Introducing steam expansion pretreatment can optimize these processes for desired products [71]. To maximize the production of fermentable sugars while minimizing the formation of undesirable inhibitory molecules, Draszewski et al. [65] proposed an integrated steam explosion and subcritical water hydrolysis process for the valorization of rice husk biomass. The biomass underwent successive explosion cycles (3 cycles, 180° C, 5 minutes each), followed by subcritical water extraction at 230° C. The yield of fermentable sugars (glucose, cellobiose, arabinose, and xylose) was 40.68 g per 100 g rice husk, which was 12 times higher than that of untreated biomass. The formation of inhibitors (HMF and furfural) was less than 0.6 g per 100 g rice husk, and organic acids were less than 5.83 g per 100 g rice husk under these conditions. The maximum sugar production rate was 5.4 g fermentable sugars per 100 g rice husk per minute. SWH with integrated steam explosion was also used to produce fermentable sugars from oat hulls, increasing production by 122% and yielding 14.56 g per 100 g sample [71]. To increase fermentable sugar yield from corn stover, Vezaro et al. [53] also used steam explosion and semi-continuous subcritical water, achieving a cellulose content of 74.06% and a fermentable sugar yield of 19.28 g per 100 g biomass. The benefit of steam explosion pretreatment with sequential SWH was also confirmed by Ten Caten et al. [72]. The authors obtained a yield of fermentable sugars of 72.59 g per 100 g sorghum bagasse, a value approximately 30% higher than that obtained without the pre-treatment step (48.27 g per 100 g sorghum bagasse). Some authors highlight the importance of removing lipids from the matrix to improve hydrolysis efficiency, using the classic Soxhlet method, supercritical CO_2 extraction [73], and pressurized liquid extraction with methyl acetate [66] and ethanol [67] before SWH. This pre-treatment step prevents the formation of emulsions and the possible degradation of oily material into free fatty acids, acetones, aldehydes, polar compounds, and oxidation products that can affect sugar purity and process efficiency.

Spohr et al. [77] investigated the influence of pressure and temperature in SWH of sweet sorghum. According to this study, at 200 °C, an induced pressure of 100 bars significantly accelerated biomass conversion, whereas pressurization above saturation at elevated temperatures (240 °C and 280 °C) did not affect biomass conversion.

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2.3. Subcritical Water Extraction of Pectin

In the extraction of pectin with subcritical water, three main phases can be recognized [78,79]. The first phase of extraction begins with the conversion of insoluble protopectin into pectin by hydrolysis, followed by the diffusion of dissolved pectin from biomass to bulk solvent. The diffusion of pectin through the pores of solid biomass to the surface limits extraction time. Once the pectin has reached the surface, it is solvated by subcritical water. The final concentration of pectin in subcritical water depends on the equilibrium between the solvent and the solid phase. Traditional acid extraction of pectin is still popular because it is easy to control, cost-effective and energy-efficient, although it has the disadvantages typical of traditional extractions, such as long extraction times and excessive decomposition of delicate and complex pectin structure. Subcritical water has strong hydrolytic properties that make it suitable for the hydrolysis of pectin to produce pectic oligosaccharides—potential prebiotics and functional food ingredients with beneficial effects on gut health and other physiological functions [78].

As shown in **Table 1**, the extractions of pectin from different sources were carried out at three different temperatures: low (100—120 °C), medium (140 °C) and high (160–180 °C). A study reported by Zhang et al. [55] summarizes the importance of the temperature regime used. Subcritical water at lower temperatures resulted in extracts with high molecular weight pectin, a high degree of esterification and high content of galacturonic acid. Medium extraction temperatures provided an optimal balance between extraction and degradation, resulting in high extraction yield and therefore the best option for efficient pectin extraction. At high temperatures, degradation processes in pectin were more pronounced, leading to lower viscosity, higher flowability and increased antioxidant activity of these obtained fractions, making them suitable for functional food applications. Different properties of pectin extracted with SWE at different temperatures make it applicable for various purposes. The pectin extracted at low temperatures by SW has excellent antioxidant and gelling properties making it useful as a thickener. A medium temperature is best suited when extraction yield is the main goal, and SWE of pectin at higher temperature is best suited to obtain pectin for functional food applications. This study stresses, once again, the importance of the right temperature selection in SWE and presents SWE as an efficient, flexible technique that could be used for pectin production on an industrial scale [55].

2.4. Subcritical Water Extraction of Chitin and Chitosan

Another interesting application of subcritical water is the extraction of chitin, the most abundant polysaccharide biopolymer after cellulose, and chitosan, its natural derivative, i.e. the deacetylated form of chitin. Chitin is a long-chain polymer of *N*-acetyl-D-glucosamine. Due to their biocompatibility, biodegradability and non-toxicity, both biopolymers have numerous applications in various industries as fillers, adsorbents, biomaterials, etc. Their use is also widespread in food industry, agriculture, pharmaceutical industry, paper industry, biomedical industry and many others [80]. Chitin and chitosan exhibit anti-tumor, hemostatic, wound-healing, antimicrobial and antioxidant activities [81].

The presence of chitin-binding proteins poses a major challenge in isolating high-purity, high-quality chitin. Traditional chemical processes for isolating this macropolysaccharide typically generate large amounts of chemical waste and degrade chitin quality [81]. The yield of chitin depends mostly on the source (e.g., shrimp, crab, mushrooms) and the sequential order of demineralization, deproteinization, and deacetylation [82]. Some of the recent studies have shown high deproteinization efficiency in starting biomass by subcritical water while maintaining the structural integrity of chitin during extraction, and modifying its mineral composition [36,59]. In one study conducted on shrimp cephalothorax waste, the effects of temperature, reaction time and waste-water ratio were investigated [36]. The treatment of shrimp cephalothorax at 260 °C for 30 minutes resulted in the highest α-chitin content (82.2 wt%). Obtained chitin was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray fluorescence analysis (XRF), X-ray diffraction analysis (XRD), and scanning electron microscopy with X-ray energy dispersion system (SEM-EDS). The study confirmed

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that optimization of the extraction parameters reduced unwanted degradation of chitin and improved its crystallinity. An important observation of this study was that SWE increased the crystalline domain size of the α-chitin fibers, which improved their mechanical and physicochemical properties. This treatment promoted the crystallization of both minerals as microcrystals of calcite and nanocrystals of hydroxyapatite with needle and flake shapes, as well as intermediate morphologies. Subsequent spectrometric analyses of chitin separated by SWE confirmed that the biomolecule preserved characteristic amide I and II bands, while degree of deacetylation (DD) was increased. These results are consistent with other studies indicating that SWE improves the structural properties of chitin and thus facilitates its transformation and further processing to chitosan [58,60].

An interesting study was performed on insects [81]. Chitin was isolated from black soldier fly (*Hermetia illucens*) larvae using a subcritical methanol-water mixture (7:1, *w*/*w*) at 250 °C for 250 minutes. The purity of chitin obtained under these conditions was 74.7%, calculated as the mass fraction of *N*-acetyl-D-glucosamine per 100 g of the solid fibrous fraction obtained after SWE.

The industrial utilization of SWE for chitin production could significantly reduce the environmental footprint of biopolymer production while improving the functionality of the target product. The study by Hao et al. [59] has also shown that SWE not only facilitates chitin extraction, but also preserves the structural integrity of the biopolymer while avoiding the use of harsh chemicals.

2.5. Subcritical Water Extraction of Fucoidans

Fucoidan, which consists mainly of fucose with high proportion of sulphate groups (6-40%) [83,84], is a polysaccharide present in brown algae, constituting about 25-30% of the dry weight. Fucoidans are of low toxicity and have medically beneficial properties. They are regarded as promising anticoagulant [85], antitumor [86,87], and anti-inflammatory agents [88–90]. Recently, fucoidans have acquired special importance as potential components of antiviral drugs [91], activators of hematopoiesis [92] and reagents for use in nanomedicine as imaging agents and drug carriers [93].

Fucoidan is a molecule with various structural forms that depend on the brown seaweed species, age, geographical origin, harvest season, and extraction technique. The structure can influence fucoidan's thermal stability [64]. Several studies have reported the use of SWE to isolate fucoidans from different brown algae, aiming to maximize yield while maintaining bioactivity. Temperature, the main factor in SWE, ranged from 120 to 160 °C for fucoidan extraction from several algae species: *Saccharina japonica* [61], *Nizamuddinia zanardinii* [62], *Himanthalia elongata* [94], and *Laminaria ochroleuca* [95]. The extraction conditions and yields of cellulose products obtained by subcritical water technology from various sources are listed in **Table 1**.

Despite the high yield of fucoidan that can be achieved by subcritical water extraction, this technique has some drawbacks. According to the review of Du et al. [96], the fucoidan extracts obtained by subcritical water contained higher levels of impurities than those obtained by traditional extraction methods. This is reasonable, considering the broad selectivity and reactivity of the solvent used. Fucoidan is a polyanionic molecule, meaning it has negative charges at different sites within its structure, which allows ion exclusion chromatography to be effective for separating the molecule. Gan and Baroutian [64] used an HPLC method with an ion exclusion column to separate fucoidan from subcritical water extracts of New Zealand Wakame seaweed. The authors obtained a fucoidan yield of only 4.6 g per 100 g sample, compared to the yields of crude fucoidan from the commonly used ethanol precipitation method (**Table 1**), which usually contains impurities.

3. Organic Acids

Organic acids have variety of applications in food and chemical industries. Due to their good solubility, hygroscopicity, biodegradability, biocompatibility, buffering and chelating properties, they are used as additives, pharmaceutical intermediates and plastic monomers. These compounds can be classified as short-chain (1-6 carbon atoms), medium-chain (7-10 carbon atoms) and long-chain

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organic acids (more than 11 carbon atoms). Short-chain organic acids, particularly fumaric, citric, itaconic, adipic and muconic acids, are used in various branches of industry, including pharmaceutical, chemical, cosmetic and food industries [97].

Organic acids are conventionally produced by catalytical chemical processes using petrochemicals as raw materials, or by fermentation with genetically modified microorganisms. The chemical route for the production of organic acids is associated with considerable environmental impact [98]; however fermentative production has much lower productivity.

The hydrothermal decomposition of low-cost, renewable lignocellulosic biomass to produce high-value chemicals such as organic acids has recently attracted much attention. Subcritical and supercritical water treatments have mainly been used in combination with homogeneous or heterogeneous catalysts and oxidizing agents. In the study by Mangi et al. [98], acetic acid was produced from corn cobs by subcritical water via hydrolysis coupled with oxidation, without using any toxic reagents. Corn cobs are an abundant agricultural residue with high contents of cellulose and hemicellulose, convenient for acetic acid production. CO_2 was used for pressurization and as a catalyst in the first step to hydrolyze the lignocellulosic biomass into reactive intermediates: furans, lactic and levulinic acids. After depressurization, these intermediates were oxidized to acetic acid (16.7 g per 100 g of sample) in the second step using O_2.

Marine algal biomass, consisting of microalgae and macroalgae, is emerging as a promising energy resource due to its rapid growth rate, ease of cultivation, excellent CO_2 consumption, and absence of lignin. Alginate, a long-chain polysaccharide made of mannuronic and guluronic acid units, is a major component of algae cell walls [99]. The physical and chemical properties of alginate change with its molecular weight and mannuronic acid/guluronic acid ratio, which vary according to its origin. Aida et al. [100] studied the depolymerization of sodium alginate to its monomers, mannuronic acid and guluronic acid, using hydrothermal treatment at 180-250° C, with reaction times ranging from 6 to 30 minutes. In a different study [101], the same authors further converted these monomers to organic acids using subcritical/supercritical water. The formation of organic acids suggests that the carboxyl group structure of the alginate was preserved during hydrothermal decomposition. The formation of dicarboxylic acids (succinic and malic acids) is evidence that oxidation occurs during hydrothermal treatment, introducing carboxyl groups into the decomposition products. The produced organic acids were analyzed by GC-MS, confirming the presence of formic, lactic, glycolic, 2-hydroxybutyric, succinic, malic, mannuronic, and guluronic acids, with a total yield of 46%. Lactic acid is fairly stable under supercritical water conditions, and, together with 2-hydroxybutyric acid and glycolic acid, may be the final target products of the hydrothermal process. On oppose, dicarboxylic acids, such as formic, malic and succinic acids, are readily degraded in sub- and supercritical water due to decarboxylation and decarbonylation reactions [101].

Jeon et al. [99] applied catalytic hydrothermal conversion of macroalgae-derived alginate to produce valuable organic acids. The hydrothermal decomposition of sodium alginate was carried out in subcritical water at reaction temperatures between 150° C and 250° C, with a reaction time of less than 1 hour. A base-catalyzed reaction at pH 13 promoted the decomposition of alginate, resulting in the production of lactic acid and dicarboxylic acids, such as fumaric and malic acids, as major products. At pH 1, acid-catalyzed hydrothermal decomposition of alginate monomers (mannuronic acid and guluronic acid), produced mostly furfural, and glycolic acid. In addition to catalysts, as expected, the reaction temperature significantly influenced the reaction pathways in hydrothermal conversion of alginate into organic compounds. At 250 °C furfural was decomposed at pH 1, while malic and fumaric acids degraded at pH 13, yielding acetic acid and succinic acid. Lactic acid was stable under all pH conditions at 250 °C without a decrease in yield [99].

Yüksel Özşen [102] used subcritical water treatment to convert cellulose from hazelnut shell waste into levulinic acid. Levulinic acid is considered one of the most promising platform molecules, with potential applications in food, pharmaceutical and cosmetic industries, and agriculture. Levulinic acid derivatives, particularly esters, are attractive renewable fuel additives, plasticizers,

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solvents, and compounds used in organic synthesis [103]. In Yüksel Özşen's study [102], increasing the reaction temperature up to 280 °C led to a considerable increase in the yield of levulinic acid. Sulphuric acid was used as the reaction medium. In the same study, a green hybrid process combining hydrolysis and electrolysis in subcritical water—a hydrothermal electrolysis of cellulose—was proposed. Electrolysis in subcritical water could reduce the thermal energy required to hydrolyze the β(1-4) glycosidic linkage. By applying a constant current of 1 A and a constant voltage of 8.0 V, the temperature required for maximum cellulose conversion decreased to 200 °C. High yields of levulinic acid (41 g per 100 g of dry sample) and acetic acid (34 g per 100 g of dry sample) were obtained in the study by Passos et al. [68] using subcritical water hydrolysis of cactus (*Pereskia aculeata* Miller), native to South America. The hydrolysis of cactus produced three times more levulinic acid than hazelnut shells in the previous study. The process was carried out at 220 °C and 150 bar for 60 minutes. These high yields of organic acids from *Pereskia aculeata* Miller can be attributed to the relatively low lignin content in cactus leaves [104], which allows greater carbohydrate accessibility for effective subcritical hydrolysis of the cellulose present.

Subcritical water treatment has recently been used for the chemical decomposition of bio-based polymers such as polylactic acid (PLA), which, despite its origin, is not readily biodegradable and requires industrial composting [105,106]. Temperature and solid to liquid ratio were identified as the main parameters influencing PLA hydrolysis.

4. Proteins and Peptides

Among all natural biopolymers proteins have been most frequently hydrolyzed by subcritical water. Hot compressed water has high hydrolytical potential breaking down proteins into valuable peptides and free amino acids [107–109], which can be easily recovered using techniques such as membrane extraction, ultrafiltration or spray drying [110,111]. Proteins are essential for structural and physiological functions and contribute to overall health [112,113]. Recently, interest in bioactive peptides produced from different protein sources has increased [113–115]. Bioactive peptides (BAP) are protein fragments, typically consisting of 2 to 20 amino acids with a molecular weight less than 3 kDa, with beneficial effects on body functions [115]. Biological activity of peptides depends on factors such as protein source, amino acid sequence and molecular weight [114,116,117]. Studies have shown that BAP exhibit antioxidant, anticarcinogenic, anti-inflammatory [115,118], and antimicrobial properties [119,120]. They also have antihypertensive, antithrombotic, and antidiabetic activities [121,122]. Some studies have highlighted the mineral-binding, opioid, and immunomodulatory properties in both in vitro and in vivo models [123–128].

In human body, amino acids are metabolized to form protein chains, but there is always a pool of free amino acids [129]. Free amino acids in foods play a key role in acceptability of foods as they influence flavor and taste. Many free amino acids serve as functional markers for food quality control [130]. In living organisms, they serve as precursors of biogenic amines, neurotransmitters, enzymes, and components of receptors and muscle tissue [131]. Increase in concentration of free amino acids in food can indicate proteolytic and hydrolytic activities during food processing [132]. In addition, free amino acids contribute to the development of color, aroma and flavor compounds through the Maillard reactions (non-enzymatic browning) when they react with reducing sugars at high temperatures [133,134].

From an environmental perspective, the extraction of peptides and amino acids from biowaste promotes more sustainable and environmentally-friendly practices by increasing waste value. In addition, the recovery of proteins maximizes the value of raw materials [135].

In recent years subcritical water hydrolysis has proven to be an efficient and sustainable technique for recovering peptides and amino acids from various protein sources [107–109,136,137]. Subcritical water produces hydronium ions (H_3O^+) and hydroxide ions (OH^-), which act as acid and base catalysts for protein hydrolysis [119,138]. As the temperature increases, the concentration of these ions increases as well [138,139] promoting the production of low-molecular peptides

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[119,140,141]. In addition, hydrolysis with subcritical water can complete the process in just 60 minutes and is therefore faster than enzymatic hydrolysis [139].

In hot compressed water the proteins lose their structural conformation. The qua-ternary structure (if present) is the first to break, as it is the most sensitive to temperature and pressure [142]. This is followed by unfolding of the tertiary structure, which depends on both pressure and temperature. For longer reaction times, the peptides are further degraded into amino acids, which can eventually break down into organic acids [137].

Before hydrolysis, it is crucial to characterize and prepare the material correctly in order to obtain the desired hydrolysates. The efficiency of hydrolysis depends on the characteristics of the sample, including matrix composition, porosity, surface area to volume ratio and particle size. Therefore, pretreatment methods such as grinding, sieving or mixing with an inert carrier are often required prior to treatment with sub-critical water [143]. Materials with high fat content (>10%) are often degreased prior to treatment. This can be achieved by supercritical CO_2 extraction [119,138,144] to reduce potential negative effects on the hydrolysis process [145].

The optimum temperature and reaction time to achieve the desired degree of hydrolysis varies considerably in different studies. In general, the hydrolysis of animal proteins [146–149] requires higher temperatures or longer processing times compared to plant [150,151] and algal proteins [136,152,153]. As a rule, an inverse relationship is observed between processing time and temperature—higher temperatures accelerate hydrolysis and shorten the reaction time. However, optimizing these conditions is crucial if bioactive peptides are to be obtained. Although higher temperatures accelerate the process, they can also lead to break down of heat-sensitive peptides and amino acids [138]. In addition, excessive heating can promote Maillard reaction products (browning) [146] and generate degradation by-products such as organic acids [154]. The processing parameters should match the targeted end product. Some studies focus on the production of amino acids from organic waste [149,155], while others optimize the conditions for peptide production [135,151,156–158]. Extraction of amino acids or peptides from the same source typically requires different operating settings [159,160].

Other factors, such as the reaction volume and protein concentration in the starting material, must also be considered when developing a hydrolysis process with subcritical water.

For biowaste to be considered as a valuable source of proteins, it must fulfil three key criteria: it should have high protein content, with a balanced composition of essential amino acids, and must be free of toxic or allergenic substances [161]. Protein sources from food waste can be broadly categorized into plant and animal sources based on their origin, availability and nutritional value.

4.1. Plant Biowaste

Several plant by-products are considered as valuable protein sources due to their high nutritional value, particularly their essential amino acid profiles. Notable examples include oat and rice waste, and wheat bran proteins [162–164]. Wheat bran, containing 13% to 18% of proteins, is a promising source, with particularly high levels of lysine and arginine [163]. It also contains significant amounts of tryptophan, tyrosine, and cysteine [165]. Additionally, oilseed cakes, which remain after oil extraction, are rich in protein (15% to 50%) and are recognized as a valuable source of extractable proteins [107,108,166]. Other high-protein plant-based waste sources include mushrooms waste and sugar beet flakes, which contain about 40% of essential amino acids, making them a potential source of proteins for animal feed [167].

Subcritical water hydrolysis has been widely used to process waste material from various plant sources (**Table 2**). These studies highlight the potential of plant-based food waste materials as valuable sources of proteins and peptides, which can be effectively extracted using subcritical water hydrolysis under specific conditions.

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4.2. Animal Biowaste

Processing conditions in subcritical water technology vary depending on objectives and starting raw material. For most of the protein-rich matrixes temperatures in the range 170 °C to 250 °C, with reaction times from minutes to hours, are applicable [137]. Animal protein hydrolysates generally require higher temperatures and longer processing times to obtain bioactive peptides.

Slaughterhouse byproducts, often considered as waste, can be revalorized for the production of peptides and amino acids. Rogalinski et al. [168] studied the hydrolysis of bovine serum albumin (BSA) hydrolysis by subcritical water. Álvarez et al. [157] hydrolyzed porcine hemoglobin at 180 °C for 360 minutes, producing peptides with improved antioxidant properties. Furthermore, Álvarez et al. [169] improved previously defined hydrolysis protocol by adding oxygen. Treatment at 180 °C and 4 bars for 240 minutes transformed 83% of the hemoglobin into decolored low-molecular-weight peptides (2.1 kDa) with enhanced antioxidant activity, solubility, and emulsifying properties compared to native hemoglobin or enzymatic hydrolysates.

Fibrous protein-rich matrices, such as hair, silk, and feathers, are difficult to process due to their low solubility but have a great potential due to high protein content and specific composition. Esteban et al. [147] hydrolyzed hog hair, recovering side-chain amino acids as the most abundant products. Lamoolphak et al. [159] studied silk waste hydrolysis, extracting fibroin and sericin proteins, as well as amino acids.

In hydrothermal hydrolysis, the process can be improved by using additives or modifying the atmosphere. Espinoza and Morawicki [170] found that the addition of sodium bicarbonate (0.83 mol/l) in subcritical water during the treatment of whey protein isolate at 264 °C for 29 minutes increased amino acid recovery fourfold compared to treatment with water alone. Marcet et al. [135] studied the hydrolysis of insoluble egg yolk granular protein at 180 °C in nitrogen and oxygen atmospheres at 40 bars. Compared to enzymatic hydrolysis, subcritical treatments in both gas environments resulted in higher recovery of soluble peptides, obtained in 4 hours for nitrogen and 2 hours for oxygen. Subcritical water oxidation promoted hydrolysis but also caused transformation of amino acids. Zhu et al. [148] hydrolyzed poultry intestines at 263 °C for 28 minutes, with 0.02% sulfuric acid as a catalyst. Addition of sulphuric acid improved amino acid recovery; however higher concentrations were not recommended since they promoted also degradation of amino acids.

The giant African snail (*Achatina fulica*), a crop-threatening pest, has a high protein content (62.89%). Cho et al. [171] examined the hydrolysis of snail proteins under subcritical water (100 °C–300 °C for 10 minutes), detecting different bioactivities of obtained peptides, depending on processing conditions. Antioxidant activity peaked at 250 °C, angiotensin I-converting enzyme (ACE) inhibition at 200 °C, and acetylcholinesterase (AChE) inhibition at 300 °C. The best overall balance was achieved at 250 °C, 25 bars and 10 minutes treatment time. Cai et al. [172] used subcritical water to hydrolyze eggshell membrane, a unique protective layer composed of a three-dimensional protein fiber network. Due to its high keratin content and abundant disulfide bonds, which cause poor solubility, its wider application is limited. The highest content of chondroitin sulfate (11.68 mg/g dry weight) was obtained in hydrolysates produced at 180 °C and the highest content of hyaluronic acid (8.19 mg/g dry weight) in hydrolysates obtained at 210 °C.

4.3. Marine Biowaste

The marine industry is under increasing pressure to implement sustainable practices to reduce waste and minimize environmental impact. It is estimated that 35% of harvested fish is lost during postharvest processing, and 70% of processed fish generates significant amounts of by-products [173]. These by-products, primarily composed of proteins and lipids, pose economic and ecological challenges due to their high organic load. However, extensive research over recent decades has shown that marine waste is a valuable source of bioactive molecules, including peptides, amino acids, omega-3 fatty acids, enzymes, and vitamins, which have applications in nutraceutical, pharmaceutical, and cosmetic industries [40,116,138,174,175]. Compared to bovine or porcine protein sources, marine-derived proteins are nutritionally superior and face fewer ethical and health-related

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constraints. Various extraction and hydrolysis methods can be applied to obtain marine protein hydrolysates with improved physicochemical and biological properties, among which subcritical water hydrolysis has gained significant attention as an environmentally friendly and efficient technique for converting marine biomass into valuable compounds [176].

Several studies have demonstrated the effectiveness of subcritical water hydrolysis in processing marine by-products. Tavakoli and Yoshida [149] investigated the hydrolysis of scallop viscera and found glycine to be the predominant amino acid. Ahmed and Chun [119] treated Bigeye tuna skin using subcritical water. The optimal conditions for bioactive peptide extraction were processing at 280 °C for 5 minutes, while the highest degree of hydrolysis occurred at 250 °C. The resulting hydrolysates exhibited antioxidant and antimicrobial activities, proving effective against the foodborne pathogens *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Bacillus cereus*, highlighting their potential for food preservation applications. Similar results were obtained by Haq et al. [146], who subjected Bigeye tuna skin collagen to catalyst-assisted subcritical water hydrolysis. Sodium bicarbonate was the catalyst that led to the highest antioxidant and antimicrobial activity in the obtained extracts [146]. Salmon heads and cape hake by-products were also subjected to subcritical water hydrolysis, demonstrating that this technique performed at 250 °C is a viable alternative to time-consuming and high-cost enzymatic methods for producing fish protein hydrolysates [177]. The resulting hydrolysates contained bioactive peptides and amino acids with high antioxidant and chelating properties. Salmon head hydrolysates had higher levels of glycine and proline, while cape hake hydrolysates contained higher concentrations of glutamic acid, leucine, threonine, and phenylalanine.

Squid by-products have also been studied extensively. Uddin et al. [178] investigated the hydrolysis of squid viscera, showing that proteins from de-oiled samples were more efficiently recovered at higher temperatures, while raw squid waste produced the highest amino acid yield. Asaduzzaman and Chun [179] examined squid muscle hydrolysates, determining that peptide yield was the highest at 160 °C, while free amino acid recovery peaked at 250 °C. Essential amino acids were most abundant in hydrolysates obtained at 220 °C, indicating degradation at higher temperatures.

Similarly, shrimp processing waste has been targeted for the recovery of added-value compounds. Quitain et al. [158] hydrolyzed shrimp shells at 250 °C and found glycine and alanine to be dominant amino acids in the hydrolysate. Cho et al. [180] demonstrated that shrimp hydrolysates processed at 200 °C exhibited strong antioxidant activity, suggesting their potential use in functional foods and supplements.

Shellfish by-products, such as *Atrina pectinata* viscera, have also been investigated. Kim et al. [181] optimized SWH for bioactive peptide recovery, finding that the treatment at 170–230 °C produced hydrolysates with enhanced antioxidant and antihypertensive properties.

Melgosa et al. [138] studied the sequential extraction of bioactive compounds from sardine (*Sardina pilchardus*) viscera, demonstrating that hydrolysates obtained at 250 °C exhibited strong radical scavenging and antiproliferative effects against HT-29 adenocarcinoma cells. The increased bioactivity at higher temperatures was attributed to the presence of Maillard reaction by-products and neo-formed lipid-derived compounds, suggesting potential applications in pharmaceuticals and cosmetics. Rodrigues et al. [182] investigated the hydrolysis of *Cancer pagurus* (brown crab) shells, assessing various operational parameters to maximize protein recovery. They also found that higher temperatures enhanced hydrolysis and improved antioxidant activity due to the formation of smaller peptides and Maillard reaction products.

The versatility of subcritical water hydrolysis extends to other seafood by-products, including fish-derived waste from white croaker and bonito [183] and mackerel [184]. As an efficient and sustainable technique, subcritical water hydrolysis enables the valorization of marine industry waste into high-value compounds, supporting a circular economy approach while reducing environmental pollution. The continued investigation of optimal conditions for hydrolysis across various marine

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species highlights its potential for large-scale applications in food and pharmaceutical industries, and biotechnology.

4.4. Biowaste of Other Origin

Other raw materials have also been used as substrates for protein extraction using subcritical water. Lamoolphak et al. [160] investigated the subcritical water hydrolysis of Baker's yeast cells to obtain peptides and amino acids. They found that the highest protein yield (0.16 mg/mg dry yeast) was observed in extracts obtained at 250 °C after 20 minutes of extraction, while the lowest yield of amino acids (0.063 mg/mg dry yeast) was obtained at 100 °C for 15 minutes treatment time. The authors also confirmed that high temperatures can cause amino acids to break down rapidly into organic acids during longer reaction times.

The valorization of alternative protein sources, such as algae, by subcritical water hydrolysis, for production of peptides useful for improving food functionality, has also been studied. An innovative approach combining ultrasound with subcritical water hydrolysis has recently been developed. Fan's team [185] designed a system integrating ultrasound into the reactor to improve the extraction of bioactive peptides from *Spirulina platensis*, a high-protein algae (50-70%). The results demonstrated that this combined method was more efficient than standard subcritical water hydrolysis in terms of time, yield, and molecular distribution. Using response surface methodology, the optimal conditions for peptide release were determined to be 153 °C, 221 W, 64 minutes, and 100 bars. The coupled ultrasound-assisted process primarily produced small molecular peptides (<1000 Da), while enzyme treatments (papain, pepsin, trypsin, Alcalase, and Protamex) generated larger peptides (1–5 kDa), high-lighting the advantage of the ultrasound-assisted method in releasing lower molecular weight peptides without the need for enzymes or high temperatures.

Additionally, Park's team [153] used subcritical water treatment on *Pyropia yezoensis*, a type of seaweed, to obtain hydrolysates with antioxidant activities, aiming to enhance its functionality as a food ingredient. The study involved varying temperatures between 120 °C and 230 °C, at 30 bars for 30 minutes with constant stirring. The antioxidant activities of the hydrolysates were evaluated using DPPH and ABTS tests, revealing higher radical-scavenging activities compared to control treatments. The optimal conditions were found to be 210 °C, with reported radical-scavenging activity of 16.63 mg TE/g for DPPH and 19.45 mg TE/g for ABTS, demonstrating the potential of *Pyropia yezoensis* as a valuable source of anti-radical compounds.

Enteshari and Martínez-Monteagudo [186] investigated subcritical water hydrolysis of proteins from ice cream wastewater to obtain bioactive peptides and add value to this by-product. They studied water temperatures from 130 °C to 230 °C and pressures between 20 and 60 bars, using a continuous stirred-tank reactor. The highest degree of hydrolysis, 41%, was achieved at 230 °C for 240 minutes treatment. Their results showed that the hydrolysates exhibited significant bioactivity, demonstrating both antioxidant and ACE-inhibitory activity, with maximum ACE inhibition reaching 98.0% in hydrolysates obtained at 230 °C.

The protein/peptide yields and amino acid yields from different biowaste sources obtained by subcritical water are shown in **Table 2**.

Table 2. Protein/peptide and amino acid yields in extracts/hydrolysates obtained by subcritical water from different biowaste sources.

Biowaste source	Conditions	Protein/Peptide yield	Amino acid yield	Reference
Plant sources				
Deoiled rice bran	200 °C; 30 min; S/L[1] = 1/5	21.9 g/100 g sample	0.8 g/100 g sample	[187]
Raw rice bran Deoiled rice bran Soybean meal	200-220 °C; 10-30 min; S/L = 1/5	10.6 g/100 g sample	0.75 g/100 g sample	[151]

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Deoiled soybean meal		13.0 g/100 g sample 16.57 g/100 g sample 20.50 g/100 g sample	0.96 g/100 g sample 1.86 g/100 g sample 2.06 g/100 g sample	
Soybean protein isolate	250 °C; 14 min; S/L = 1/10	Not determined*	63 g/100 g sample	[188]
Rapeseed cake	205 °C; 51 min; S/L = 1/10	Not determined	13.59 g/100 g sample	[189]
Barley husk (*Hordeum vulgare* L.)	NDES[2]: Lactic acid/Choline chloride (1:2); 180 °C; 20 min; 40 bars; S/L = 1/10	22.81 g/100 g sample	0.16 g/100 g sample	[150]
Laver red algae (*Pyropia yezoensis*)	120-180 °C; 30 min; S/L = 1/20	20.21 g/100g sample	6.27 g/100 g sample	[153]
Animal sources				
Sericin (silk waste)	120-160 °C; 10-60 min; S/L = 1/20 – 1/100	46.6 g/100 g raw silk waste	20.3 g/100 g raw silk waste	[159]
Fibroin (silk waste)	220 °C; 10-60 min; S/L = 1/50 – 1/100	45.5 g/100 g silk fibroin	75.5 g/100 g silk fibroin	[159]
Porcine haemoglobin	180 °C; 360 min; S/L = 1/20; ~40 bar N_2	80 g/100 g sample	Not determined	[157]
Porcine haemoglobin	180 °C; 240 min; S/L = 1/20; ~40 bar O_2	83 g/100 g sample	Not determined	[169]
Granules from egg yolk protein	180 °C; 240 min; S/L = 1/20; 40 bars N_2 180 °C; 120 min; S/L = 1/20; 40 bars O_2	80 g/100 g sample 95 g/100 g sample	Not determined	[135]
Eggshell membrane	180-240 °C; S/L = 1/15; 220 bars	Protein yield: 4.06 g/100 g sample (180° C); Peptide yield: 2.04 g/100 g sample (210° C)	23.10 g/100 g sample (240° C)	[172]
Hog hair	250 °C; 60 min; S/L = 1/100	Not determined	30.62 g/100 g sample	[147]
Poultry wastes	260 °C; 28 min; 0.02% H_2SO_4 (wt)	Not determined	11.5 g/100 g sample	[148]
Giant African snail (*Achatina fulica*)	200 °C; 10 min; S/L = 1/50	20 g/100 g sample	Not calculated	[171]
Marine sources				
Fish entrails	250 °C; 60 min; S/L = 1/20	Not determined	13.7 g/100 g sample	[155]
Scallop viscera	280 °C; 50 min	Not determined	15.0 g/100 g sample	[149]
Shrimp shells	250 °C; 60 min; S/L = 1/25	Not determined	7.0 g/100 g sample	[158]

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Defatted sardine (*Sardina pilchardus*) waste	190 °C; water flow rate: 10 ml/min	16.19 g/100 g sample	15.14 g/100 g sample	[138]
Abalone viscera	170 °C; 60 min; S/L = 1/15	28.0 g/100 g raw sample	19.27 g/100 g raw sample	[190]
Oyster (*Crassostrea gigas*)	225 °C 175 °C 5 min; S/L = 1/30	22.48 g/100 g sample	1.35 g/100 g sample	[191]
Blue mussel (*Mytilus edulis*)	180 °C 120 °C 30 min; S/L = 1/20	15.38 g/100 g sample	0.023 g/100 g sample	[144]

[1]S/L—Solid to liquid ratio; [2]NDES—Natural deep eutectic solvents. * Yield not determined indicates that the primary objective of the process was to produce peptides or amino acids. Contents are expressed on a dry sample basis; if otherwise, it is indicated.

5. Bioactive Compounds

Bioactive compounds are important ingredients of different final products. Naturally, plants are considered to be the richest sources of these compounds, which include various chemical classes such as polyphenols, alkaloids, terpenoids, etc. [14]. Agricultural and food processing waste, such as seeds, peels, leaves, rinds and pomace, is often unexploited source of valuable bioactive compounds such as carotenoids, polyphenolics, vitamins, enzymes and essential oils [192]. These compounds are associated with important biological activities such as antioxidant, antimicrobial, antidiabetic, and anticarcinogenic activities. They also have immuno-boosting, anti-allergic, anti-ageing, cardioprotective and neuroprotective properties [193–195]. Recovery technologies of these valuable compounds are constantly improving, and subcritical water extraction (SWE) is becoming increasingly popular due to its safety, efficiency and environmental friendliness. Hot compressed water has been used to extract a variety of natural bioactive compounds including, but not limited to polyphenolics, flavonoids, organic acids, alkaloids, essential oils, lignans, quinones, steroids and terpenoids from various fruit and vegetable wastes, marine wastes and algae [196]. These valuable compounds could be incorporated into functional foods, turning waste into food and drug ingredients.

5.1. Polyphenolic Compounds

The most common polyphenolic classes found in a wide range of biowaste include phenolic acids and flavonoids. Polyphenolics are generally considered to be heat-sensitive compounds, as they are usually degraded at temperatures above 80 °C in conventional extraction methods [197]. However, studies on subcritical water extraction of polyphenolics from various plant sources show a high yield of these compounds even at temperatures above 100 °C. Possible explanations could be the degradation of the lignin-phenolic acid bonds in the biomass and degradation of lignin itself, releasing more polyphenolics [198]. According to most studies, the optimal temperature for subcritical water extraction of polyphenolic compounds is between 110 °C and 160 °C. Different polyphenolic compounds require different extraction temperatures. Even in the same class of polyphenolic compounds, variations in thermosensitivity and solubility can be observed. For example, in the study by Krivošija et al. [199], the optimum extraction temperature for the extraction of naringin from orange peel dust was 120° C and the naringin content obtained was 62.37 mg/l, while hesperidin was most efficiently extracted at 160 °C with the content of 662 mg/l. In the study of Silva et al. [200], the extract of kiwiberry leaves prepared at 160 °C had the highest concentration of phenolic acids (18.42 mg/g DW), while the extract obtained at 110 °C yielded in the lowest content (11.29 mg/g DW). In the same study, gallic acid was the major phenolic acid in the extracts obtained

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at 148 °C and 160 °C (6.88 mg/g DW and 9.69 mg/g DW, respectively). The major phenolic acid in extracts obtained at lower temperatures (110-135° C) was protocatechuic acid, which was probably formed by thermal degradation of catechin. According to this study, flavanols and flavonols were favorably extracted at lower temperatures (123 °C). Benito-Román et al. [201] performed a SWE of onion peel waste and concluded that the extraction of flavonoids is temperature-sensitive and that the optimal temperature for flavonoid extraction is 145 °C. Under this extraction temperature the total flavonoid content reaches the maximum value of 27.4 mg/g sample, of which quercetin and quercetin-4'-glucoside account for about 90% of the total flavonoids identified. Akter et al. [202] investigated the extraction of bioactive compounds from spent mushroom substrates of shiitake and oyster mushrooms. For both spent mushroom substrates, higher temperatures and time resulted in higher concentration of total phenolics, of which phenolic acids were the most abundant, especially vanillic acid (4 mg/l extract and 20.4 mg/l extract for shiitake and oyster mushroom substrates, respectively). The same authors applied pressurized ethanol extraction (PEE) with 40% ethanol (v/v) to the same samples under the same experimental conditions and found the same trend as with SWE, namely an increase in total phenolic compounds with temperature and longer extraction times. The concentration of total phenolic compounds in shiitaki and oyster mushroom substrates was higher in PEE than in SWE (**Table 3**). Yuan et al. [203] used a subcritical ethanol solution (50%) for the extraction of bioactive compounds from buckwheat waste. The authors concluded that the treatment with subcritical ethanol could depolymerize buckwheat waste and extract total phenolics (20.1 mg GAE/g) and other bioactive compounds better than hydrothermal treatment (14.5 mg GAE/g) or low-temperature ethanol treatment. Some studies report modification of SWE with natural deep eutectic solvents (NADES). Loarce et al. [204] used NADES in the SW extraction of polyphenolic compounds from grape pomace. They used a mixture of choline chloride and urea (1:2) in water (30%). The results showed that the use of NADES in combination with SWE improved the extraction of catechins, tannins, hydroxycinnamic acids and flavonoids, resulting in extracts with high antioxidant capacity. For example, the content of catechins obtained by SWE alone was 16.80 mg/g DW, while the combined SWE-NADES method produced 118.77mg/g DW. Roy et al. [150] obtained the highest total phenols content (TPC) and total flavonoids content (TFC) in barley husk extracts by subcritical water modified with lactic acid—choline chloride (1:2) and glycerol—choline chloride (1:2) as NADES, showing that SWE modified with NADES can be a promising method to obtain high quality bioactive compounds. The most abundant phenolic compounds recovered from spent grains were gallic acid, protocatechuic acid, catechin, 4-hydroxybenzoic acid, naringin and ferulic acid. In the study by Ferreira et al. [205], the polyphenolic content and antioxidant activity of microalgae *Tetradesmus obliquus* extracts increased approximately fourfold by increasing the temperature from 120 to 220 °C, suggesting that compounds that contribute most to antioxidant activity are non-polar compounds requiring higher temperatures of extraction. Freitas et al. [206] investigated antioxidant and antimicrobial properties of extracts obtained from grape stalks using subcritical water and their potential use in the development of biodegradable active food packaging. The main polyphenolic compounds in grape stalks extracts were hydroxycinnamic acids: 8,8'-diferulic acid (31-32%), p-coumaric acid (25-26%), ferulic acid (~20%), caffeic acid (~15%) and cinnamic acid (~7%). The obtained extracts were incorporated into compostable poly (lactic acid) films. In the study by Capaldi et al. [207], subcritical water was combined with microwave extraction. The extracts obtained from the hazelnut skin contained approximately twice the amount of phenolic acids than extracts obtained by conventional extraction with ethanol and up to 3.5 times as many flavan-3-ols.

Table 3 shows the SWE conditions for the extraction of polyphenolic compounds from different biowaste sources.

Table 3. Total phenolic and flavonoid content in subcritical water extracts obtained from different biowaste sources.

Biowaste source	Conditions	Polyphenolics content	Reference

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Brown alga (*Ecklonia stolonifera*)	198.5 °C; 36.21 min; 30 bars; S/L[1] = 12.23 g/ml	TPC[2]: 50.01 mg phloroglucinol/ g sample; TFC[3]: 43.58 mg QE[4]/g sample	[208]
Hazelnut (*Corylus avellana* L.) skin	MASWE[5]: 150 °C; 1500 W; 30 min; 5 bars; S/L = 1/30	TPC: 103.7–199.0 mg GAE[6]/g sample	[207]
Orange (*Citrus sinensis* L.) peel dust	180 °C; 15 min; 20 bars; S/L = 1/20; PEE[7]: 50% ethanol (*v*/*v*); 220 °C; 15 min; 20 bars; S/L = 1/20	TPC: 36.52 mg GAE/g sample TPC: 70.56 mg GAE/g sample	[199]
Orange (*Citrus sinensis*) peel	120 °C; 5 min; 15 bars; S/L = 1/20	TPC: 45.45 mg GAE/g sample; TFC: 9.29 mg RE[8]/g sample	[194]
Onion agricultural waste Garlic agricultural waste	180 °C; 15 min; 20 bars; S/L=1/20; 200 °C;	TPC: 199.36 mg GAE/g sample; TPC: 50.96 mg GAE/g sample	[209]
Brevery spent barley (*Hordeum vulgare* L.) husks	NDES-SW[9]: 180 °C; 20 min; 40 bars; S/L = 1/10	TPC: 8.00 mg GAE/g sample; TFC: 22.87 mg RE/g sample	[150]
Mango (*Mangifera indica* L) seed kern	116 °C; 45 min; 35 bars; S/L = 0.048	TPC: 9.95 mg GAE/g sample	[210]
Cocoa (*Theobroma cacao*) hull	150 °C; 30 min; 30 bars; S/L = 1/30	TPC: 15.3 mg GAE/g sample; TFC: 7.42 mg RE/g sample	[211]
Buckwheat waste	Subcritical ethanol solution (50%); 120 °C; 45 min; 5 bars; S/L = 1/20	TPC: 20.1 mg GAE/g sample; TFC: 10.6 mg RE/g sample	[203]
Kiwifruit (*Actinidia deliciosa*) peel	160 °C; 20 min; 30 bars; S/L = 1/50	TPC: 51.2 mg GAE/g sample; TFC: 22.5 mg CE[10]/g sample	[212]
Acerola (*Malpighia emarinata* DC.) seeds and pomace	130 °C; 15 min; 100 bars; 4 ml/min	TPC: 362 mg GAE/g fresh sample	[192]
Distillery sillage	140 °C; 200 °C; 30 min; 41.4 bars; S/L = 1/15	TPC: 4.88 mg GAE/g sample; TFC: 1.24 mg QE/g sample	[196]
Coffee silverskin	240 °C; 10 min; S/L = 1/25	TPC: 51.86 mg GAE/g sample	[213]

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Waste cotton (*Gossypium hirsutum* L.) flowers	180 °C; 60 min; 65% ethanol; S/L = 1/65	TPC: 92.51 mg GAE/g sample; TFC: 10.02 mg GAE/g sample	[214]
Onion (*Allium cepa* cv. Horcal) skin	145 °C; <30 min; 50 bars; 2.5 ml/min	TFC: 27.4 mg/g sample	[201]

[1]S/L—Solid to liquid ratio; [2]TPC—Total phenolic content; [3]TFC—Total flavonoid content; [4]QE—Quercetin equivalent; [5]MASWE—Microwave-assisted subcritical water extraction; [6]GAE—Gallic acid equivalent; [7]PEE—Pressurized ethanol extraction; [8]RE—Rutin equivalent; [9] NDES-SW—Natural deep eutectic solvent-induced subcritical water; [10]CE—Catechin equivalent. Contents are expressed on a dry sample basis; if otherwise, it is indicated.

5.2. Caffeine

Caffeine is a natural alkaloid, typically with a bitter taste and some biological activity [215]. This alkaloid stimulates respiration and the central nervous system [216]. Being one of the world's most important crops, coffee processing generates different biowaste, such as skin, pulp, mucilage, parchment, silverskin from coffee cherries, and spent coffee grounds discarded after brew preparation. Caffeine extraction by subcritical water from coffee biowaste was rarely reported in scientific literature. In contrast, supercritical extraction with CO_2 is commonly used for decaffeination of coffee beans [217].

Strieder et al. [218] proposed an integrated and automated procedure to extract, separate, and quantify caffeine and 5-caffeoylquinic acid (5-CQA) from the mixture of arabica husk and defective beans. The two-dimensional system consisted of a pressurized liquid extraction (PLE), which is often used for the extraction with water, as a replacement of SWE, coupled in-line with solid phase extraction (SPE) and on-line with HPLC-PDA (PLE-SPE × HPLC-PDA). PLE was performed off-line, in static mode, using subcritical water at 125° C for 15 minutes, which resulted in the highest extraction yields of caffeine (9951 μg/g DW) and 5-CQA (7064 μg/g DW). Extracted caffeine was retained on an SPE polymer-based reversed-phase sorbent and eluted with a hydroethanolic mixture. The eluate was analyzed by HPLC-PDA. In the study by Shang et al. [219], spent coffee grounds from ten different coffee cultivars were compared for their antioxidant activity after pressurized liquid extraction with water and ethanol. Optimized conditions included extraction at 195 °C with ethanol/water mixture of 70/30 (*v*/*v*) for 10 minutes, at 100 bars. The caffeine and 5-CQA content in the resulting extracts ranged from 3-9 and 51-201 mg/g dry sample, respectively. These extracts also showed high TPC, namely 19-26 mg GAE/g dry sample, with DPPH activity of 16-38 mg AAE/g dry sample and ABTS activity of 10-28 mg AAE/g dry sample. Shalmashi et al. [220] extracted caffeine from tea waste from Northern Iran using continuous mode subcritical water extraction with hot compressed water at a flow rate of 4 g/min. The optimum operating conditions were 175 °C and 120 minutes extraction time. Subcritical water recovered 0.77% (*w*/*w*) of the caffeine present in the tea waste.

5.3. Bioactive Compounds from Ashwagandha

Although ashwagandha (*Withania somnifera* L.) is not a biowaste, its impressive therapeutic effects and thousands of years of tradition in Ayurvedic and Chinese medicine make this medicinal herb very interesting for the extraction of pharmacologically active compounds. The main chemical constituents of ashwagandha are withanolides, which have shown neuroprotective, hepatoprotective, anticancer, hypoglycaemic, and antiarthritic effects [221–223]. To our knowledge, there is only one study on subcritical water extraction of bioactive compounds from ashwagandha, conducted by Nile et al. [224]. The research team extracted withanosides and withanolides from ashwagandha root and leaves and studied their biological activities. The extract obtained at 160 °C for 20 minutes at 100 bars showed the highest total phenolic content (82.5 mg GAE/g dry extract) and the highest antioxidant activity (DPPH 80.3%; FRAP 60.5%; ABTS 78.9%). The in vitro enzyme

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inhibition assay showed that the ashwagandha extract had potent inhibitory effects on xanthine oxidase, acetylcholinesterase, butyrylcholinesterase, α-amylase, α-glucosidase, and tyrosinase. It was also found that ashwagandha extracts were effective against HeLa cancer cells (IC50 = 10 mg/ml), without cytotoxic effects on healthy cells except at high concentrations (70.8 mg/ml). The pure compound withaferin A showed a cytotoxic effect with an IC50 of 8.5 μmol/l. The potent anticancer activity of ashwagandha is believed to be due to withaferin A, which is widely distributed in the leaves, bark, stems, and roots of ashwagandha [225].

6. Biofuels

Increased biofuels production emerged due to the environmental and energy challenges associated with the use of fossil fuels. As conversion technologies improved, biofuels emerged as a scientifically viable and scalable option for sustainable energy production [226]. Despite their finite nature and negative environmental impact, fossil fuels still account for 82% of the global energy supply, with oil representing 35%, coal 29%, and natural gas 24% [227–229]. The largest energy consumer is certainly industrial sector, using approximately 37% of total produced energy, followed by the transportation sector (28%), household consumption (22%) and the commercial sector (13%). Although renewable energy has the potential to meet global energy demands, it currently accounts for less than 13% of the total energy supply. Well-established supply chains and existing infrastructure for fossil fuels hinder transitioning to renewable biofuels that would require significant technological innovation. In addition, production of biofuels confronts economic challenges; for example, producing a barrel of algal-based fuel costs between 7.5 and 32.5 times more than petroleum-based fuel [230].

To date, biofuels have been classified into four generations based on their feedstock origins. First-generation (G1) biofuels are produced from food crops and edible oils such as corn, sugarcane, rapeseed, sunflower, soybean, palm, mustard, coconut, wheat germ, animal fats (including beef tallow and lard), and nut oils (such as almond, walnut, and pistachio), using established processes such as anaerobic fermentation, transesterification, and pyrolysis. These fuels include biodiesel and bio-alcohols and are widely used worldwide. However, concerns about G1 biofuels include the "food vs. fuel"debate, which raises issues regarding land use, water consumption, and competition with food production [231,232].

Second-generation (G2) biofuels are produced from non-food biomass sources, such as agricultural waste (corn stalks, wheat stalks, rice husks, sugarcane bagasse), forestry residues, inedible and waste oils (used cooking oil), inedible oil crops (Jatropha, neem, jojoba, mahua, rubber seed, babassu tree), and animal wastes (manure, animal processing waste). G2 biofuels minimize the impact on food production while addressing environmental concerns by reducing waste and promoting a circular economy. These fuels can be produced through fermentation, gasification, and hydrothermal liquefaction, and include syngas, bioethanol, butanol, and biohydrogen [231].

Third-generation (G3) biofuels are primarily sourced from microalgae (Chlorella, Spirulina, Chlamydomonas), macroalgae, also known as seaweed (Saccharina, Sargassum, Laminaria, Gracilaria, Ulva), and other aquatic biomass (water hyacinth, duckweed, insects). As this biomass is rich in lipids and carbohydrates, it is particularly suitable for biofuel production. Third generation biofuels are produced by biochemical, thermochemical, and chemical methods. Algae-based biofuels include syngas, biohydrogen, and bio-oil. In addition to their high biogas yields, algae absorb CO_2 during growth, reducing greenhouse gas emissions. They are fast-growing organisms that do not compete with food crops for agricultural land [231,233]. Second- and third-generation biofuels are still under development and research, and are therefore collectively regarded as advanced biofuels [233].

Fourth-generation biofuels (G4) are produced using advanced technologies such as genetically modified organisms, most often algae, which are engineered to improve photosynthetic efficiency and increase light penetration, as well as photobiological solar fuels and electro-fuels. G4 biofuels are

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not yet commercially available, as they are still in development and face ethical and regulatory concerns, but they have the potential for higher yields and lower costs than G2 and G3 biofuels [231].

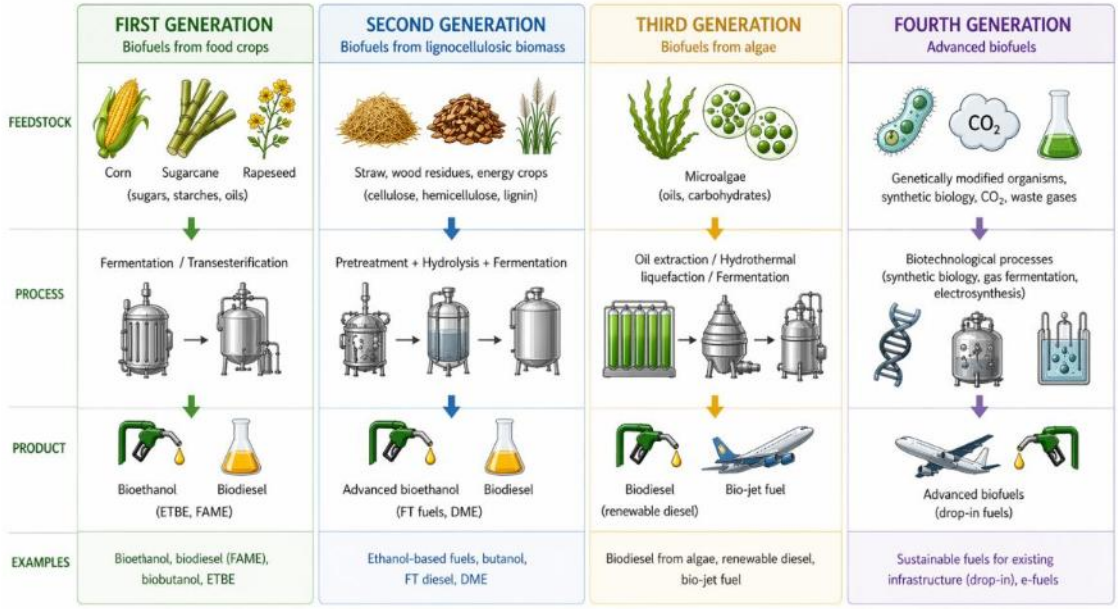

Figure 3. Classification of biofuels into four generations based on their feedstock origin. (Figure generated using DALL-E 3 AI software.).

As biofuels are primarily derived from agricultural plant-derived by-products, their combustion for energy production does not have a net negative CO_2 footprint, since plants absorb CO_2 during photosynthesis, almost same amount that is produced during combustion. In addition to traditional lignocellulosic biowaste, scientists have recently focused on valorizing biowaste such as sludge and microalgae [234]. Biofuels refer to either one of the solid (charcoal, biochar), liquid (biodiesel, bioethanol), or gas (biogas, biohydrogen) fuels. Technologies for converting biomass into biofuels with high caloric value are categorized into two main groups: biochemical conversion technologies and thermochemical conversion technologies [235].

Biochemical conversion technologies use enzymes or microorganisms to decompose biomass to different products, depending on the biochemical pathway. Degradation of biomass through these processes occurs naturally and includes both aerobic and anaerobic digestion, as well as fermentation. In anaerobic digestion, bacteria utilize oxygen from the biomass, resulting in the production of biogas (CH_4, CO_2) and solid by-products [235]. This process mimics the natural formation of underground natural gas over millions of years and involves several stages: hydrolysis of organic molecules into smaller units, acidogenesis to volatile fatty acids, acetogenesis, and finally methanogenesis. The final product is a mixture of methane (55-90%) and carbon dioxide, with minor impurities such as hydrogen sulphide and mercaptans. Thus, produced biogas represents a sustainable energy source with substantial heating capacity when methane exceeds 50% [231].

Aerobic digestion involves microorganisms that oxidize biomass with air oxygen and generate CO_2, heat, and solid residues. Fermentation is a process in which yeasts convert biomass into sugars, followed by further conversion to bioethanol and other chemicals, mainly liquid products [235]. Bioethanol is produced from crops high in polysaccharides, such as sugarcane, sweet sorghum, sugar beet, corn. Sustainable feedstock alternatives include algae, straw, forestry waste, and other lignocellulose biowaste [231].

Thermochemical conversion technologies apply heat to achieve degradation and include combustion, pyrolysis, gasification and hydrothermal processes (hydrothermal carbonization and hydrothermal liquefaction). Combustion is the oldest thermochemical method, in which the biomass reacts with oxygen, releasing thermal energy [235]. Pyrolysis is an endothermic process involving the

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thermal decomposition of biomass in an oxygen-free or low-oxygen environment, causing the biomass to break down into a mixture of gases, liquids (bio-oil), and solids (biochar). Pyrolysis is a crucial preliminary stage for combustion and gasification processes [236]. Bio-oil is a promising liquid biofuel with high caloric value and high content of added-value compounds, such as aromatic compounds. In addition to bio-oil, volatile products such as synthesis gas (syngas) and a solid carbonized waste (biochar) are produced in pyrolysis processes [237].

Direct liquefaction converts biomass into liquid fuel using high temperatures and pressures. Produced liquid fuel usually requires further refining. The technology usually requires the addition of solvents, such as water or alcohols, and the use of catalysts [235].

In gasification a biomass is converted into gaseous fuel or syngas, which contains varying fractions of H_2, CO, CO_2, and CH_4. This process requires a gasification agent, which is usually a steam, air, CO_2, O_2, or their mixtures; however, oxygen is the most commonly used. In gasification, produced energy is stored in the chemical bonds of the resulting gases, whereas combustion releases energy directly by breaking these chemical bonds. In most gasification technologies, prior biomass treatment, the oxygen is removed from the raw material through decarboxylation or dehydration, resulting in a gas product with a high hydrogen-to-carbon (H/C) ratio [235].

Biological hydrogen (biohydrogen) is a clean and renewable fuel that produces water as a by-product upon combustion. It is being developed as a sustainable alternative to conventionally produced hydrogen from steam methane reforming, water electrolysis, and coal gasification, as these methods pose serious environmental challenges and/or high production costs. Biohydrogen can be produced from various biomass or organic waste sources via biochemical processes: direct or indirect biophotolysis, photo-fermentation, or dark fermentation (anaerobic digestion), carried out by bacteria, algae, and archaea [238]. Hydrogen production through combustion increases yields from fossil fuels (heavy oil or bitumen) or biomass by integrating processes such as in-situ combustion with steam or CO_2 injection. Catalysts or sorbents, such as CaO or nanoparticles, are typically used to capture CO_2 and shift reactions towards greater H_2 production. Biomass gasification can be improved with inert porous media for better heat management, significantly increasing H_2 output compared to basic combustion or reforming methods, resulting in cleaner energy and enhanced oil recovery [239–241].

In biofuel production, hydrothermal technologies exploiting high reactivity and hydrolytical potential of subcritical and supercritical water, are primarily used to recover sugars from biomass feedstocks. These methods offer cost-effective alternatives to enzymatic processes and address the limitations of chemical methods such as acid and alkaline treatments. They are also used in supercritical water gasification processes, where they improve efficiency [20]. Carbonaceous char is often generated as a co-product generated in hydrolysis and gasification processes. This co-product has been recognized as an economically valuable material (in power generation as a “renewable coal”, in water purification, electrochemistry, and catalysis). Procedures known as “hydrothermal carbonization “(HTC) have been developed to maximize the yield of solid carbon products. Unlike pyrolysis, HTC is suitable for both wet and dry feedstock, which can result in a superior energy balance.

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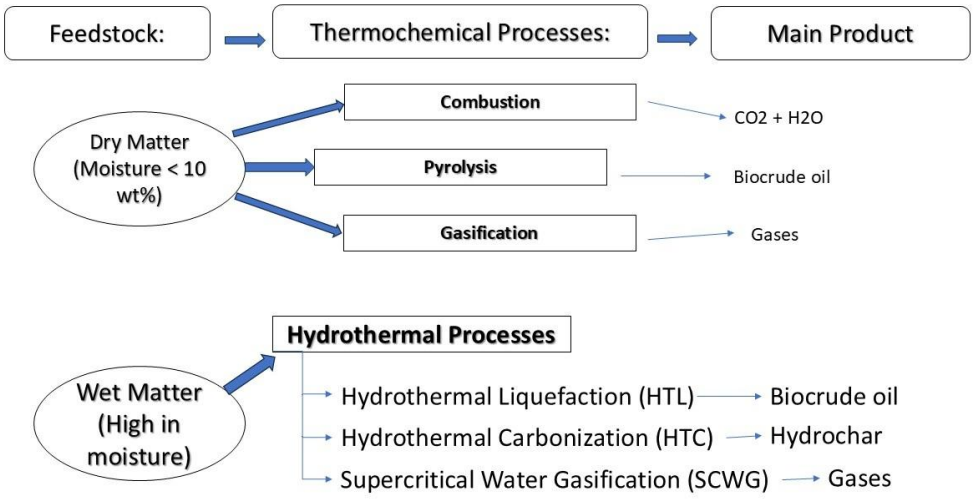

Figure 4. Classification of thermochemical processes and their main products.

6.1. Supercritical Water Gasification (SCWG)

Supercritical water gasification (SCWG) technology is used to produce gas fuel and is particularly advantageous for processing wet biomass, such as lignite, sludge and algae. It is also suitable for converting high-moisture biomass from kitchen waste [242]. The technology itself does not require energy-consuming drying, gasifying biomass into a mixture of gases, most prominent being hydrogen (H_2), carbon monoxide (CO), methane (CH_4), and carbon dioxide (CO_2) [243]. The target product of biomass gasification is hydrogen, which is considered a completely clean fuel, since its combustion produces only water. Hydrogen, together with carbon monoxide, forms a synthesis gas or syngas [235]. The produced fuel gas comprises 70-80% of the original energy of the feedstock [244].

Being an endothermic process, supercritical water gasification is typically carried out at temperatures above 680 °C [235]. SCWG yields a higher hydrogen content at high temperatures (>700 °C) and a higher methane content at lower temperatures (<600 °C) [244]. At lower temperatures, cellulose and hemicellulose are primarily responsible for gas production, while at higher temperatures, lignin conversion becomes predominant [75]. High temperatures promote endothermic steam reforming reactions, producing large quantities of H_2 [245]. During SCWG, supercritical water acts both as an efficient solvent and a reactant. In this environment, biomass undergoes rapid thermochemical decomposition, involving key interphase reactions such as hydrolysis and pyrolysis, followed by subsequent homogeneous gas-phase reactions, including methanation and water-gas shift reactions [246]. In first stages of the process, the organic components of biomass, including carbohydrates (hemicellulose, cellulose, lignin), proteins, and lipids, are hydrolyzed by supercritical water into intermediate products. These intermediates are subsequently converted into H_2-rich syngas [235]. Although high temperatures in SCWG usually improve gasification efficiency, under certain conditions they may also accelerate the reverse re-polymerization pathways—dehydration and condensation processes—leading to formation of carbonaceous solid deposits such as tars and coke [75]. Tar is an inevitable by-product of biomass pyrolysis and gasification and can reduce syngas yield and deactivate catalysts during refinement processes [236]. Tar is primarily composed of aromatic compounds, including hazardous substances such as toluene, benzene, naphthalene, phenol, styrene, and polycyclic aromatic hydrocarbons. Condensation of these compounds can cause mechanical failures throughout the system. The key challenge for this technology is to addresses tar removal and its conversion into syngas [236,247]. Currently, the efficiency of SCWG of biomass can reach 100%, with hydrogen comprising over 50%

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of the gas produced. This technology enables the gasification of biomass with more than 50% moisture content, eliminating the need for energy-intensive pre-drying required in conventional biohydrogen production technologies. In addition, under supercritical conditions, sulphur, nitrogen, and other elements are converted to their gaseous forms, which are easier to capture and manage, thereby reducing pollutant emissions [235].

To optimize the hydrogen production ratio, that is, to increase the volume fraction of hydrogen in the gas product to over 50%, reaction conditions can be adjusted. The most relevant operational variables influencing SCWG performance include reaction temperature, reaction time, feedstock-to-water ratio, and operating pressure. Reaction temperature has the most significant influence: higher temperatures notably improve carbon gasification efficiency and hydrogen yield [248].

Catalysts can mitigate thermal and mass transfer limitations and reduce the activation energy of reactions [236]. Introducing catalysts in SCWG processes can significantly lower the required reaction temperatures and times, contributing to higher gasification efficiency of biomass under milder conditions, and simultaneously reducing tar formation [20,235]. Even without catalysts superheated water undergoes partial homolytic splitting, producing $OH^{\bullet}$ and $H^{\bullet}$ radicals, due to high thermal energy. Due to drop in water density, formed free radicals are recombined slowly [249]. In the presence of oxygen, secondary radicals, such as $HO_2^{\bullet}$ and $O^{\bullet}$, are also formed [250].

Catalysts (especially metals like Ni, Pt, Ru, or metal oxides) lower the energy required for homolytic splitting and promote surface-mediated radical formation. Noble metals (Pt, Ru) often enhance hydrogen radical production and hydrogen generation, whereas transition metal oxides (e.g., Fe_2O_3, MnO_2) tend to favor hydroxyl radical formation and oxidation pathways. The catalysts act like surface-catalyzed bond activators, increasing the number of formed radicals and affecting the type of the dominant species. Catalyst-assisted free radicals are often concentrated near catalyst surface, on oppose to radicals' distribution in water, which is uniform, and require lower activation energy [251,252].

Catalysts used in SCWG processes can be homogeneous (metal ions or alkali metal compounds) or heterogeneous (noble or transition metals). Homogeneous catalysts such as KOH, NaOH, $NaHCO_3$, K_2CO_3, and Na_2CO_3, can significantly increase gas yield and play an important role in reducing tar production. However, the use of homogeneous catalysts in SCWG presents some challenges: equipment corrosion and blockage, as well as the recovery of these catalysts at the end of the SCWG process, which is both difficult and costly. In addition, the use of alkaline catalysts in SCWG raises environmental and safety concerns. These drawbacks limit their future industrial applications [235].

Heterogeneous catalysts offer advantages such as non-corrosiveness, high catalytic activity, thermal stability, and excellent recyclability. They can effectively promote gasification of biomass under milder temperature conditions, making them particularly suitable for large-scale applications in SCWG. Heterogeneous catalysts facilitate the cleavage of carbon-carbon and carbon-oxygen bonds in gasification, while also stimulating the water-gas shift reaction [235], which consumes CO and H_2O and generates H_2 and CO_2 [253]. Additionally, they reduce coke formation and increase the yield of favored products (H_2 and CH_4) [244]. Heterogeneous catalysts used in SCWG can be categorized into two types: transition metal catalysts (including their oxides) and activated carbon catalysts. In addition, activated carbon adsorbs efficiently total tar due to its highly porous surface, making it convenient for subsequent cracking. Despite its relatively high price, it is widely used as a support material for metal-based catalysts. Examples of heterogeneous catalysts include Ru, Pb, Rh, Ni, and Zr [225,237], Ni-Cu/Al_2O_3 [242], $NiFe_2O_4$ [244].

In addition to catalysts, gasification performance can be enhanced by the addition of reactive co-solvents, which serve as radical initiators under SCWG conditions. Cui et al. [254] tested nine different co-solvents for lignocellulosic feedstock (corn stalk) gasification. N-methyl-2-pyrrolidone and tetrahydrofuran co-solvents released polar aliphatic heteroatom-containing radicals, which induced cleavage, oxidation, and amination of the carbon skeleton and increased the hydrogen yield.

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Supercritical water gasification of biomass is a promising, highly efficient technology, but its net energy balance depends greatly on system integration and feedstock properties. Although it is not yet a fully mature industrial technology, it is widely considered a sustainable method for producing renewable biohydrogen due to its unique ability to directly process wet organic waste without energy-intensive pre-drying [255]. It is more energetically efficient than conventional gasification processes, which require dry feedstock. Reported energetic efficiencies vary, but when optimized, they range from 40% to more than 80%. The energy content of the generated H_2 (approximately 120-142 MJ/kg) often exceeds the net electrical and thermal energy required to operate at temperatures as high as 700 °C and pressures up to 250 bars [256].

Table 4. Supercritical water gasification (SCWG) of different biowaste, final products and yields.

Biowaste	Catalyst	Final product and yield	SCWG conditions	Reference
Food waste (model compounds)	None	H_2 (6.19 mol/kg); CH_4 (8.83 mol/kg)	650 °C; 30 min; 250 bars; S/L[1] = 1/50	[245]
Food waste (model compounds)	5% NaOH	Total syngas: 14.26 mol/kg; H_2 (12.73 mol/kg)	450 °C; 60 min; 250 bars; S/L = 1/20; 200 rpm	[257]
Food waste (+30% algae booster)	3% Ru/Al_2O_3	H_2 (72.3 mol/kg, 74.3% molar fraction); CH_4 (4.5 mol/kg, 4.7%); CO_2 (3.1 mol/kg, 13.4%); CO (1.8 mol/kg, 5.9%)	700 °C; 60 min; 250 bars; S/L = 1/5	[258]
Ethanol, glycerol model solution (C_{eth}:C_{gly} = 25:75)	0.01% Na_2CO_3	H_2 (63.75 mol/kg)	700 °C; 1.75 min; 25 g Carbon/l	[259]
Cedar tree trunk	None	Carbon gasification efficiency: 61.88%; Total syngas: 24.64 mol/kg; H_2 (3.53 mol/kg)	700 °C; 3 min; S/L = 1/40; 750 °C; 5 min; S/L = 1/20	[246]
Bamboo biowaste	K_2CO_3 C/F[2] = 0.05/1 (*w*/*w*)	80 mol/kg CO, 1.2 mol/kg H_2	900 °C; Gasification agent: Ar, CO_2	[236]
White-poplar wood chips	Ru-impregnated activated carbon (10%)	H_2 (20.1 mol/kg C in poplar); CH_4 (12.7 mol/kg C in poplar)	600 °C; 1h; N_2; S/L = 1/12.5	[260]
Pinewood Cornstalk	5% K_2CO_3	H_2 (2.00 mol/kg); H_2 (1.75 mol/kg)	550 °C; 10 min; S/L = 1/10	[261]
Canola straw Canola hull Canola meal	None	H_2 (7.1 mol/kg) H_2 (6.2 mol/kg) H_2 (5.5 mol/kg)	500 °C; 40 min; S/L = 1/6	[262]
Wheat straw	None	H_2 (12.88 mol/kg)	700 °C; 30 min; 23 MPa	[263]
Sugar beet vinasse	None	Total syngas: 27.48 mol/kg; H_2 (7.5 mol/kg); CH_4 (8.86 mol/kg);	600 °C; 245 bars; S/L = 1/6.7	[264]

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	Raney nickel C/F = 0.98	CO_2 (8.79 mol/kg) Total syngas: 28.25 mol/kg; H_2 (8.02 mol/kg); CH_4 (11.02 mol/kg); CO_2 (8.81 mol/kg)	450 °C; 260 bars; S/L =1/6.7	
Sugarcane bagasse	KOH C/F = 1/2	H_2 (6.64 mol/kg); CH_4 (5.5.mol/kg); CO_2 (0.45 mol/kg) H_2 (75.6 mol/kg)	400 °C; 75 min; 250 bars; S/L = 9/100 800 °C; 15 min	[265]
Swine manure	None	Total syngas: 27.53 mol/kg (40.16% H_2)	660 °C; 45 min; S/L = 1/9	[266]
Real municipal wastewater-derived sewage sludge	1% Na_2CO_3	H_2 (21 mol/kg—48% molar fraction); CO_2 (12.5 mol/kg); CH_4 (5 mol/kg); CO (1 mol/kg)	450 °C; 30 min; 300 bars;	[267]
Sewage sludge	6% KOH	H_2 1.6 mol/kg biomass (37% of the total syngas)	400 °C; 60 min; 221 bars N_2; 80 rpm; S/L = 1/10	[268]
Liquid effluents from the torrefaction of oat hull and canola hull	10% KOH	Total syngas: 25.9 mmol/g (12.8 mmol/g H_2)	525 °C; 45 min; 50-100 bars N_2; S/L = 1/10	[269]
Oily wastewater	None	H_2 (58.25 mol/kg) CH_4 (31.94 mol/kg)	700 °C; 250 bars; Water/oil ratio= 9/1	[270]
Coking wastewater (from coke plants and coal gasification plants)	15% KOH	Total syngas: 21 mol/kg (47% H_2, 44% CO_2, 4.5% CH_4, 2% CO)	540 °C; 20 min; 250 bars	[253]
Soda black liquor	Co_2O_3 C/F = 1/1 ZnO	H_2 (21.67 mol/kg); H_2 (21.03 mol/kg)	600 °C; 30 min; 240-260 bars	[271]
Kraft black liquor	None	Total syngas: 18.31 mol/kg; H_2 (7.87 mol/kg); CO_2 (5.84 mol/kg); CH_4 (1.96 mol/kg)	500 °C; 250 bars; S/L = 1/23.51	[272]

[1]S/L—Solid to liquid ratio; [2]C/F—Catalyst to feed ratio.

6.2. Hydrothermal Carbonization (HTC)

Hydrothermal carbonization (HTC) is technology for converting organic compounds into structured carbon, usually applying temperatures 180-250 °C and reaction times 1-24 hours, with saturated steam produced at pressures of 10-50 bars [273]. Hydrothermal carbonization typically yields gaseous, liquid and solid products, including bio-oil fraction [274]. The reaction conditions are relatively mild compared to pyrolysis or SCWG, using both bound and free water as a reaction

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medium [275]. For recovering biofuel by pyrolysis, the high moisture content of biomass is the main drawback. On oppose, in HTC high moisture content is advantage giving this technology a potential to replace traditional pyrolysis pathways. Additionally, HTC technologies are flexible in regulation, have higher efficiency and shorter biomass pretreatment times. Nevertheless, solid-liquid separation is required for the hydrochar and the liquid phase, which hinders further industrial application of HTC. In HTC of biowaste, the feedstock undergoes hydrolysis, dehydration, and decarboxylation reactions, after which intermediate products such as 5-hydroxymethylfurfural (HMF) undergo further dehydration or isomerization. Polymerization of these products forms a typical hydrochar with a core-shell structure. These processes are generally regarded as mimicking natural coalification.

In HTC hydrothermal parameters and feedstock type are the dominant factors. In most studies, the quality of produced hydrochar was close to that of lignite. The calorific value of the obtained biofuel typically ranges from 15 to 35 MJ/kg [234,276]. With increasing temperature, the atomic ratios of O/C and H/C decrease, increasing the calorific value of produced hydrochar accordingly, making it comparable to that of lignite and high heating value coals such as bituminous and even anthracite coal [277]. Reaction time is also an important factor that influences hydrochar quality. Short reaction times lead to low-yield products with high oxygen content, due to insufficient polymerization of hydrolyzed intermediates [278]. On the other hand, long residence times require high energy consumption. Therefore, reasonable control of temperature and residence time are key factors for the industrial application of HTC technology.

The composition of feedstock is another factor influencing the quality of hydrothermal coals, as it affects the elemental composition and calorific value of the final product. A high organic content in biowaste is preferred over a high ash content [234]. The nitrogen content in biowaste is also important, as it affects the degree of carbonization. Nitrogen participates in Maillard reactions, resulting in higher ratio of nitrogen incorporated into hydrochar. Nitrogen-containing hydrochar has different physical and chemical properties from lignocellulosic hydrochar; it has increased mechanical strength and improved combustion characteristics, making it more suitable as a solid biofuel [275]. Varying elemental content, along with high energy consumption in hydrothermal carbonization processes, are bottlenecks for further industrial application of HTC in solid biofuel production [234].

Hydrochar has been applied in many fields, such as catalysis [279], production of activated carbon materials [280], soil remediation [274,281,282], energy recycling [283,284], and others. Production of fuel pellets is one of the most important application scenarios for hydrochar. Temperature, pressure, moisture, particle size, and the addition of binders have been shown to be critical factors in increasing the energy density, mechanical strength, and stacking density of pellets [275]. The pelletization process is generally conducted from room temperature up to 140 °C. Cross-linked structures, “solid bridge” structures, and enhanced attractive forces such as hydrogen bonding and van der Waals forces have been identified as the main pelletization mechanisms in lignocellulosic hydrochar pellets [285]. Solid bridges result from crystallization of certain components, chemical bonding, hardening of binders (such as starch, molasses, tar, or calcium oxide), solidification of molten components, or linkages between particles [285,286]. Binders can soften at their glass transition temperatures or melt at their melting points, providing a liquid binder between particles and mediating covalent bonds [287]. Since moisture acts as a binder and lubricant during pelletization, water is added in 5-15% mass ratio to the process. In addition, degradation products formed during hydrothermal treatment usually improve binding.

6.3. Hydrothermal Liquefaction (HTL)

Hydrothermal liquefaction (HTL) is a promising technology that enables the conversion of organic substrates into bio-oil (biocrude) through reactions in liquid water at moderate temperatures (250-400 °C), high pressures (40-250 bars), residence times of 30-120 minutes, with or without catalysts, and dry solid loadings of 5-30% [288]. Under these conditions, significantly altered water properties promote the solubilization of organic matter and facilitate the breakdown of complex

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molecules in the feedstock. This process allows a portion of the carbon in the organic matter to be converted into biocrude, a precursor for producing liquid fuels such as aviation fuel or other drop-in transportation fuels. In addition to biocrude oil, carbon-rich materials, such as biochar, as well as gas products and a nutrient-rich aqueous phase, are produced. The final products and biocrude composition mainly depend on the specified experimental parameters, but especially on the feedstock properties. Biomass rich in carbohydrates is effectively converted to biocrude in the presence of alkali catalysts, whereas biomass rich in lipids and proteins is best processed without any added catalysts [289]. A wide range of feedstocks has been researched with HTL: municipal primary sludge [290], swine manure with rice stalk and camphor tree [291], chicken carcass and wheat straw [292], Canadian spruce and poplar wood [293], mustard meal and canola meal [294]. In these studies, bio-oil yields ranged from 11.5 wt% to 51.25 wt%.

HTL offers an energetic advantage over pyrolysis because it does not require prior drying of the biomass feedstock. HTL can be integrated with biological processes (e.g., anaerobic digestion) to enhance the recovery of carbon and energy and lower environmental impacts. It is particularly suitable for wet biowaste conversion, such as the digestate of municipal solid waste obtained after anaerobic digestion. The wet digestate, a by-product of anaerobic digestion, can be used as feedstock for HTL, while the process water—the by-product of HTL—can be utilized as the organic carbon source for anaerobic digestion [289]. Tito et al. [288] subjected this challenging byproduct to HTL processes at different operational temperatures (300-360 °C). Higher temperatures increased the production of energy-dense biocrude (~31 MJ/kg) up to 32 wt% and altered its composition, increasing aromatics content and reducing sterols content.

Predictive models can address challenges in simultaneously estimating the yields and characteristics of products from the HTL of biomass. Umeda et al. [295] developed an efficient elemental-based kinetic model to predict the yields, higher heating values, and fuel characteristics (H/C and O/C ratios) of heavy bio-oil and solid residue, showing high consistency with experimental results. The model was based on temperature (250-350 °C), residence time (5-60 min), solid loading (5-15 g per 100 ml water), and the elemental composition of corn stover.

6.4. Subcritical and Supercritical Water Technologies for Biodiesel Production

Biodiesel, a mixture of fatty acid methyl esters, is one of the most widely used biofuels. It is typically produced from readily available vegetable oils through catalytic transesterification of fatty acids with methanol [296]. The alkaline catalytic conversion with ethanol is not suitable for biodiesel production, since ethanol, nowadays mostly produced from renewable sources, induces saponification between bases and oils [297].

The supercritical ethanolysis of the second- and third-generation lipid resources to produce ethyl biodiesel is a simple and efficient route that satisfies sustainability criteria [298]. In this technology, lipid feedstock is transesterified with ethanol under supercritical conditions. This conversion technology enables biodiesel production from a wide variety of lipid sources, including vegetable oils, waste oils, animal fats, and algae [296]. As reactivity of bioethanol increases in supercritical states, esterification and transesterification reactions occur without the need for catalysts, reducing the number of chemicals used, the amount of wastewater and by-product generation [297]. The glycerol, produced during transesterification, can decompose under supercritical conditions, integrating into the final product and enhancing overall system efficiency [296]. Supercritical ethanolysis exhibits lower sensitivity to the presence of free fatty acids and moisture in the raw material [299], compared to conventional catalytic transesterification, in which free fatty acids slow down the reaction and moisture induces saponification. Supercritical ethanolysis is generally performed in the temperature range 300-480 °C and at pressures from 100 to 180 bars, which are the most influential operational parameters on the products obtained [297].

Subcritical water has also been used in the conversion of natural triglycerides and free fatty acids to biodiesel and other liquid biofuels. Choi et al. [300] converted soybean oil to gasoline, jet fuel and diesel-fraction hydrocarbons with low oxygen content under optimized reaction conditions of 420

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°C, 45 bars, oil to water ratio of 6:1, and a reaction time of 10 minutes. Spent coffee grounds were used to produce biodiesel through ethanolic extraction of lipids and subsequent transesterification at 325 °C, with a reaction time of 29.4 minutes and a pressure of 150 bars. The molar ratio of ethanol to oil content was 30:1. The highest ester content in the biodiesel was 88.37% [297].

Aghilinategh et al. [301] used supercritical methanol for biodiesel production from *Chlorella vulgaris* microalgae in the presence of a heterogeneous nano-photocatalyst, CaO/TiO_2, and subcritical water (methanol-to-water ratio was 12:1, *v*/*v*). The reaction was conducted with a solid-to-liquid ratio of 1:40 and a catalyst-to-feed ratio of 0.67, at a temperature of 260° C and a pressure of 90 to 100 bars for 1 hour. The components of the produced biodiesel were analyzed by gas chromatography-mass spectrometry, and the results indicated that the major compounds in the biodiesel were hydrocarbons, esters, and oxygenates. The addition of catalyst and water to supercritical methanol increased the total product yield 51.6%, with the fatty acid methyl esters yield reaching to 28.1% [301].

A two-step subcritical/supercritical water and ethanol process for non-catalytic biodiesel production was proposed by Hassan et al. [302]. The first step involved hydrolysis of triglycerides from waste cooking oil under subcritical water conditions to generate and increase free fatty acid content, for subsequent ethyl ester production in the second step. Esterification with ethanol was carried out under subcritical conditions, without any catalysts. The optimal temperature was 300 °C, reaction pressure 100 bars, and reaction time 20 minutes. The esterification process was completed in 5 minutes and the conversion rate was greater than 98%.

6.5. Bioethanol Production

Plant-derived biomass rich in lignocellulose represents the largest available biomass resource. Fractionation of lignocellulose into its constituent biopolymers—cellulose, hemicellulose, and lignin, and their subsequent depolymerization to simple monomers, is a critical step in the biorefinery concept for producing various valuable molecules from this biomass [303]. In bioethanol production, subcritical water technologies are mainly used as clean and efficient biomass pretreatment techniques. During the conversion of biomass to bioethanol, pretreatment is considered the key step that can significantly improve the accessibility of cellulose and hemicellulose for enzymes or microorganisms, and further enhance conversion efficiency [304]. Fermentable sugars obtained by depolymerization of biopolymers by subcritical water are then used as feedstock in biochemical conversion technologies for bioethanol production. One of the main obstacles to using plant biomass hydrolysates in fermentation processes is the presence of fermentative inhibitors (organic acids, furanic aldehydes, and phenolic compounds) [70]. Organic acids and furanic aldehydes are produced as degradation products of pentoses and hexoses during biomass thermal or acid hydrolysis. Even at low concentrations, these inhibitors can be highly toxic to bacteria and yeasts, compromising the efficiency of the fermentation process. Barroso et al. [70] coupled an in-line prepurification process with an optimized subcritical water hydrolysis method to remove fermentative inhibitors. They integrated an activated carbon adsorption column and achieved a 36% reduction in TPC and a 23% reduction in organic acids, with minimal sugar loss of 5.72%. Methods using subcritical water for the treatment of various types of biomasses rich in cellulose and hemicellulose for the recovery of fermentable sugars are described in Chapter 2.2. of this review.

7. Challenges and Limitations of Subcritical and Supercritical Water Technologies

Despite significant advantages of subcritical and supercritical water technologies, several challenges remain to be confronted. Because these technologies operate at high temperatures and pressures, they require specialized equipment, resulting in high initial investments. Hydrothermal water technologies are generally energy-intensive processes, but consumption can be minimized by using well-insulated reactors, efficient heat exchangers and optimized operational parameters [305]. Operational costs are particularly high in technologies aiming supercritical state, such as supercritical

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water gasification, which maintains the system at up to 800 °C and above 220 bars, or supercritical ethanolysis, which operates at temperatures up to 480 °C [235,298,306]. At such high temperatures, regenerative heating minimizes the need for external energy input [307], imposing additional technical and engineering requirements. Additional drawbacks that hinder industrial adoption of hydrothermal technologies include severe corrosion and equipment scaling due to harsh operation conditions associated with formation of acidic by-products, as well as plugging from salt precipitation [306]. In animal biowaste processing sulfur or chlorides are usually released more abundantly [308,309], aggravating plugging issues. Continuous flow systems are particularly affected by these obstacles [310]. Most sub- and supercritical water applications described in the literature remain at the laboratory or pilot scale, not addressing scale-up challenges, reaction kinetics, life cycle, and economic analyses. Large-scale industrial applications require transition to continuous systems, bringing numerous technological and economic risks and unpredictability.

7.1. Future Research

Current research on supercritical water technologies focuses on the development of corrosion-resistant reactor materials, management of salt precipitation through self-cleaning design systems, and focusing on novel catalytic processes to lower the required operational temperature [306]. Sound approach for future research should include Techno-Economic Analysis (TEA) and Life Cycle Assessment (LCA) of the proposed technologies. Despite integrated process modeling, enhancement of energy regeneration processes, and material innovation, a scalability remains a challenging task. Future work should continue to focus on adaptation of subcritical and supercritical water technologies for biowaste treatment on industrial-scale.

8. Conclusions

A sustainable and transformative framework for valorizing diverse biowaste and biomass streams, such as agricultural residues, food waste, and marine by-products, can be achieved through subcritical and supercritical water technologies. This approach directly supports the transition to a circular bioeconomy by converting residues into high-value compounds. Carbohydrates, organic acids, proteins, peptides, amino acids, bioactive compounds, and biofuels, can be produced with these technologies at high yields, over-coming many limitations of conventional chemical and enzymatic methods. Hydrothermal processes allow precise control of reaction pathways, yields, and product selectivity, influenced by temperature, pressurizing fluid, pressure, pH, catalysts, and reaction time. Organic acids such as acetic, lactic, and levulinic acids can be obtained from lignocellulosic residues, marine algae, and biopolymers, while bioactive compounds can be efficiently recovered by extraction, or generated during biowaste treatment. Furthermore, hydrothermal carbonization produces hydrochar, a solid biofuel with properties comparable to lignite, while subcritical and supercritical water processes enable the production of biodiesel, bioethanol, and hydrogen-rich syngas from diverse feedstocks. Overall, technologies that utilize the unique properties of hot compressed water provide environmentally friendly, cost-effective, and scalable solutions for biowaste valorization, supporting the transition toward a circular bioeconomy and sustainable energy systems.

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Abbreviations

The following abbreviations are used in this manuscript:

SW	Subcritical Water
SWE	Subcritical Water Extraction
SWH	Subcritical Water Hydrolysis
SCW	Supercritical Water
SCWG	Supercritical Water Gasification
MASWE	Microwave-Assisted Subcritical Water Extraction
BAP	Bioactive Peptides
PLA	Polylactic Acid
PLE	Pressurized Liquid Extraction
PPE	Pressurized Ethanol Extraction
ACE	Angiotensin-Converting Enzyme
PEE	Pressurized Ethanol Extraction
HTC	Hydrothermal Carbonization
HTL	Hydrothermal Liquefaction
HMF	5-Hydroxymethylfurfural
HDES	Hydrated Deep Eutectic Solvents
NDES	Natural Deep Eutectic Solvents
TPC	Total Phenolic Content
TFC	Total Flavonoid Content
GAE	Gallic Acid Equivalent
RE	Rutin Equivalent
QE	Quercetin Equivalent
CE	Catechin Equivalent
S/L	Solid to Liquid Ratio
C/F	Catalyst to Feed Ratio
DW	Dry Weight

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