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Review Article

Aqueous byproducts from biomass wet thermochemical processing: Valorization into fuels, chemicals, fertilizers, and biomaterials

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ABSTRACT

Thermochemical pretreatments are employed prior to energy, chemicals, and fuels production from biomass. Wet thermochemical processes (WTCP) are treatments used to modify biomass properties in water as the primary solvent, with or without added reactants/catalysts. WTCP includes hot water extraction, steam explosion, hydrothermal liquefaction, hydrothermal carbonization (HTC), and supercritical water gasification. WTCP also includes processes that add chemicals to reduce reaction time and improve efficiency, i.e., organosolv, alkali, and low acid pretreatment. Operational parameters in WTCP are usually selected to optimize the yields of sugars after enzymatic hydrolysis of the resulting solids and biogas from the pretreated solids, or to ensure that hydrochar (e.g., from HTC) performs adequately in environmental applications. However, a key byproduct from WTCPs is an aqueous fraction (rich in nutrients, hemicellulose-derived sugars, and chemicals) often disposed of as waste. The necessity of resource conservation and proper management and the need to make WTCP-based biorefineries economically and environmentally sound require using all the byproducts of biomass processing. Options for downstream conversion of the WTCPs' aqueous byproducts are dispersed in the literature. Thus, this paper aims to put together works that report the parameters of WTCPs that allowed removing hemicellulose-derived fractions and nutrients from biomass (either partially or almost entirely), the yields and properties of this aqueous byproduct, methods of characterization, current and expected uses, and the challenges for scaling up WTCPs and using the aqueous stream. The paper focuses on expected and existing methods that allow the valorization of the aqueous fraction and reduce wastes within a circular bioeconomy framework.

1. Introduction

According to the United Nations [1] the world population is expected to surpass 11 billion inhabitants by the year 2100. One of the consequences of a growing population is the need for more materials and energy to satisfy the increasing requirements of food, housing, transportation, fertilizers, clothing, and several vital services. While electricity can be produced from different renewable energy sources (e.g., solar, wind, hydropower, and geothermal), biofuels, chemicals, and other renewable materials (e.g., fibers for wood composites, fuel pellets, firewood, fertilizers, and charcoal) can only be obtained from biomass. Therefore, a renewed global interest in biomass processing and use has been witnessed in the last two decades. However, the use of biomass is far from reaching its full potential, and the terms "waste" and "residues" are frequently employed to refer to poorly utilized biomass, including

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Nomenclature

ACE	Autocatalyzed ethanol
AD	Anaerobic digestion
AI	Artificial intelligence
ASP	Acetone soluble products
Bio-PE	Bio-polyethylene
BOD	Biological oxygen demand
COD	Carbon-rich compounds
DOC	Dissolved organic carbon
DOE	Design of experiments
DSS	Dewatered sewage sludge
EFB	Empty fruit bunch (from oil palm)
FID	Flame ionization detection
GC–MS	Gas chromatography mass spectrometry
GC-TOF-MS	Gas chromatography coupled with time-of-flight mass spectrometry
GGM	Galactoglucomannan
HMF	5-Hydroxymethyl-furfural
HPAEC	High-performance anion exchange chromatography
HPAEC-PAD	High-performance anion-exchange chromatography with pulsed amperometric detection
HPLC	High-performance liquid chromatography
HRT	Hydraulic retention time
HTC	Hydrothermal carbonization
HTL	Hydrothermal liquefaction
HWE	Hot water extraction
IC	Ion chromatography
LCA	Life Cycle Assessment
MALDI-TOF-MS	Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
NMR	Nuclear Magnetic Resonance
OLR	Organic load rate
P, N, K, Ca, Mg, Fe, Cl	Phosphorus, Nitrogen, Potassium, etc.
PBR	Packed bed reactor
PLA	Polylactic acid
RP	Reactive phosphorous
SACE	Sulfuric acid catalyzed ethanol
SCB	Sugarcane bagasse
SCWG	Supercritical water gasification
SG	Switchgrass
SS	Sewage sludge
TOC	Total organic carbon
TKN	Total Kjeldahl Nitrogen
TP	Total phosphorous
TS	Total solids
TEA	Technoeconomic assessment
UASB	Upflow anaerobic sludge blanket reactor
UHPLC-IM-Q-TOF-MS	Ultra-high-performance liquid chromatographyion mobility quadrupole time-of-flight mass spectrometry
VFAs	Volatile fatty acids
VS	Volatile solids
W:B	Water to biomass relationship (ratio)
WO	Water oxidation
WS	Wheat straw
WSP	Water soluble products
WTCP	Wet thermochemical process

food-crop residues, wood processing byproducts, municipal waste, urban wood waste, animal waste (i.e., manure), and terrestrial and aquatic plants [2–5]. If not used, these materials are lost or disposed of under conditions frequently resulting in uncontrolled degradation. A strategy to make better use of biomass is through biorefineries, using processes that allow adding value to all biomass constituents for producing energy, fuels, and several valuable chemical drop-in materials as substitutes for petroleum-based products [6,7]. Using all biomass constituents, i.e., with the zero-waste generation, is a fundamental part of the circular bioeconomy framework to prevent an "unfettered extraction of biological resources" [8]. Biorefineries can serve as model systems for adopting the circular bioeconomy [9].The economic viability of biorefineries hinges on obtaining commercially competitive products from the products and byproducts of biomass processing [10–13]. However, biomass cannot be used as received, and different pretreatment operations are required [14]. The main constituents of lignocellulosic biomass are cellulose (40 to 50 % dry mass), hemicellulose (25–30 % in softwood and 25–35 % dry basis in hardwood species), and lignin (18 to 35 % dry basis) [15]. One of the challenges of biomass processing is the difficulty of simultaneously separating and fractioning each constituent. Thus, pretreatment operations intend to break down hemicelluloses and remove the resulting isolated products but leave cellulose and lignin partially, if not entirely, intact. The extracted products of the hemicellulose fractionation are contained mainly in an aqueous byproduct and can serve to produce, for example, specialty chemicals [16–22], while the remaining cellulose-rich product (i.e., a solid fraction) can be utilized for biofuels production after a hydrolysis step. Processes such as hot water extraction (HWE) or autohydrolysis (in the presence of water only) are possible pathways toward this goal [14]. Combination of alkali or dilute acids in water with heat can also be used. These processes are part of the so-called wet thermochemical processes (WTCP).

WTCP refers to treatments used to modify biomass properties in the presence of water as a solvent, reactant, and catalyst or catalyst precursor (at specific temperatures), with or without additional reactants and catalysts. Fig. 1 depicts the types of WTCPs and the main products of each process. It is seen that WTCP includes steam explosion, HWE, hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), supercritical water gasification (SCWG), supercritical water oxidation (SCWO), organosolv, and dilute acid and alkaline hydrolysis.

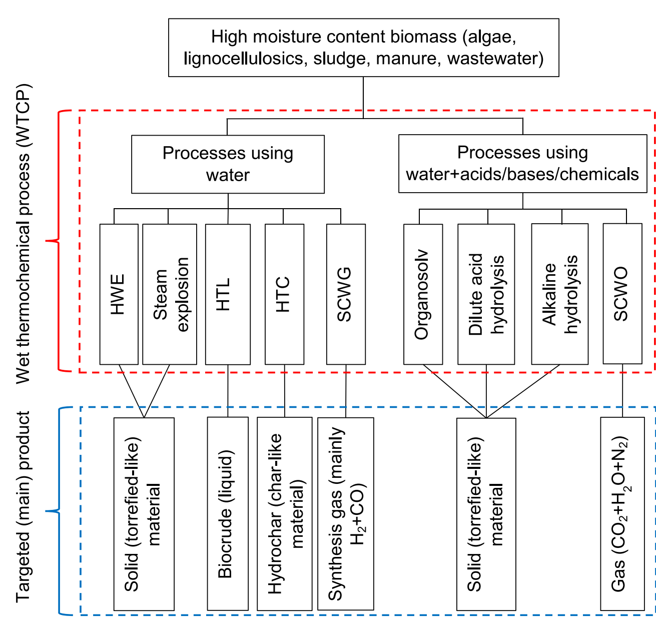

Fig. 1. Wet thermochemical processes (WTCP) used for biomass treatment and their corresponding main products (HWE – Hot water extraction, HTL – Hydrothermal liquefaction, HTC – Hydrothermal carbonization, SCWG/O – Supercritical water gasification/oxidation).

HWE, steam explosion, organosolv, dilute acid and alkaline hydrolysis, HTC, and HTL are conducted in water subcritical conditions, and SCWG and SCWO are conducted in supercritical conditions. As seen in the figure, organosolv, SCWO, and acid/alkaline hydrolysis use chemicals and acids/bases for the process and are frequently included in the "chemical processes" category. However, the operational conditions (i.e., temperature and pressure) and properties of the aqueous byproducts of these processes are similar to those of the processes that do not use chemicals but only water. In fact, thermochemical processes are seen as improvements of chemical processes that intend to reduce reaction time and improve efficiency [23]. WTCPs are usually carried out separately, but integration of processes is an option for specific applications [2425]. For example, the aqueous byproduct from HTL can be processed using SCWG. Combining these processes allows hydrogen production (via SCWG) from the HTL aqueous phase to upgrade the biocrude (i.e., HTL bio-oil) [25].

One of the main advantages of WTCPs is that they allow processing biomass with high moisture content [26 27], including agricultural (lignocellulosic) residues (e.g., residues from harvesting and processing vine, date palm, sugarcane bagasse, corncob, coconut shell and fiber, rice husk, palm oil empty fruits, and flax), forest residues, algae, sewage sludge, manure (chicken, swine, and cow manure), among others. Therefore, WTCPs avoid expensive pre-drying steps, as required in alternative dry thermochemical processes (i.e., torrefaction, pyrolysis, gasification, and combustion). Alternative methods such as anaerobic digestion (AD) can process high-moisture content biomass, but AD requires long processing times, possesses relatively low efficiency, and does not properly remove organic matter, especially with materials such as municipal sludge [28]. WTCPs also show opportunities for reclaiming nutrients (i.e., P) from sewage sludge [29,30], manure produced in animal farms [31,32], and other biomass sources with promising results [33]. Up to 90 % of the P in the manure can be recovered in the solid products after thermal treatment [34,35], in addition to N and organic carbon [30]. Similarly, the aqueous effluent from microwave torrefaction of biomass can be treated using WTCPs [36]. The carbon conversion efficiency of high moisture municipal sludge is higher in WTCPs such as SCWG than in its comparable thermal gasification [37].

WTCPs are typically employed as pretreatment operations to reduce the biomass's natural recalcitrance to enzyme attack for sugars and chemicals production [13,38–42]. Thus, WTCP parameters are usually selected to optimize the yields of sugars (after the enzymatic hydrolysis step) of the resulting solid, and biogas production (also using the pretreated solid), or to ensure that hydrochar (in HTC) performs adequately in environmental applications. In WTCPs, the aqueous byproduct (or aqueous stream), rich in nutrients and hemicellulose-derived products, sugars, and other chemicals, is often disposed of as waste. Handling this aqueous byproduct must be considered when designing WTCPs [43,44]. Table 1 presents a list of review papers related to WTCPs and the main topics covered, suggesting that no review has been entirely devoted to the aqueous byproduct resulting from WTCPs. Still, there is an increasing amount of publications showing that these aqueous streams possess some common characteristics (e.g., chemical composition), offering the potential for several products such as biofuels [45,46], polymer blend films [7], and chemicals that can be transformed into biofuels and other bioproducts [47–49]. However, proper valorization of the aqueous byproduct of WTCPs still deserves attention [43 50,51].

In Table 1 it is seen that the processing and use of hemicelluloses for chemicals, fuels, and other bioproducts has received strong interest, especially in the last decade. However, the strategies for the valorization of the WTCPs' aqueous byproducts deserve more attention [62]. Therefore, there is a necessity for an updated and expanded discussion on the following aspects: 1) WTCP operational conditions and leading products and byproducts, with emphasis on the aqueous stream yields, 2) methods for the characterization of the aqueous fraction derived from WTCPs, 3) technological routes to add value to these fractions, 4) expected products and uses; and, 5) potential challenges associated with

Table 1
Some review papers on biomass WTCPs: Synthesis of topics covered, processes, and products.

Topic covered	Main points discussed in the review paper(s)	Reference (s)
Municipal sludge treatment via thermochemical processes	Dry and wet thermochemical processes for sludge treatment; focus on sludge only; the work covers: a) mechanisms and kinetics of the processes, b) limitations, c) factors affecting the process, d) challenges and prospects, and d) value of some products. No details are presented on uses of aqueous byproduct.	[37]
Potential of xylan for chemicals	Key points: The paper focuses on methods for hemicelluloses extraction and hemicelluloses purification, as well as production of bioproducts from xylose. Only xylose is studied for chemicals.	[21]
Xylose for xylitol production	Xylitol from xylose using enzyme technology as an alternative to both chemical and microbial processes; biological conversion of xylose and uses of xylitol; catalytic routes for xylose conversion to value-added chemicals; challenges to produce bioproducts based on xylose.	[16,18,44]
Furfural and HMF using water-based pretreatment process	Possibilities of producing furfural and HMF from biomass using water-based pretreatments (steam explosion and hot water extraction). Hemicellulose degradation chemistry in water; process parameters for furfural and HMF.	[52]
Bibliometric study on hemicellulose valorization	Bibliometric study on the trend (from 2000 to 2016) of works related to the valorization of hemicellulose	[53]
HWE vs dry torrefaction comparison	Comparison of HWE (wet torrefaction) with dry torrefaction; differences on product's properties; challenges of managing the aqueous byproduct.	[43]
Catalytic HTC	Role of catalysts in HTC process and solid product (hydrochar) for fuel applications; effect of W:B ratio; types of catalysts.	[54]
Hemicellulose-based biorefineries	Biomass pretreatment operations	[55]
Cellulose and hemicellulose valorization	Challenges and strategies for technical implementation of platform molecule production from cellulose and hemicellulose; selective synthesis of such molecules, further transformation into targeted products, separation of products, and catalyst stability are key challenges.	[56]
Hemicelluloses removal for wood composites	HWE removes hemicelluloses from wood, with positive effect on wood composites; water affinity of the composites is reduced and dimensional stability is increased.	[11].
Chemical pretreatment for fuels and chemicals	Biomass chemical pretreatment routes, with emphasis on acid and alkaline hydrolysis, to produce fuels and chemicals; effect of working process on hemicellulose degradation.	[57]
Integration of HTC with AD	The aqueous stream after HTC can be processed using AD; such integration is important to improve energy recovery from biomass.	[58].
Uses of hemicelluloses	Different types of chemicals produced from hemicelluloses; direct modification or degradation are the paths for hemicelluloses utilization.	[59]

(continued on next page)

Table 1 (*continued*)

Topic covered	Main points discussed in the review paper(s)	Reference (s)
Technoeconomic analysis and sustainability	Technoeconomic analysis of products using selected WTCPs; capital and operational costs for large-scale processes; profitability indicators for biorefineries. Need of more studies to confirm the sustainability of biorefineries.	[60]
Hemicelluloses recovery	Hydrothermal treatment as fractionation technique and recovering hemicelluloses.	[61]

the adoption and scaling up of WTCPs and the valorization strategies of the aqueous streams. This review aims to cover these necessities and compile works that have studied pathways for using the aqueous byproducts from WTCP operations for chemicals, biofuels, fertilizers, and other materials. The review results from the necessity to understand better the potential of these liquid fractions to advance the circular bioeconomy in biorefineries. Recovering and using the aqueous byproduct from WTCPs is important because a) adding value to this aqueous stream will reduce wastes in biorefineries, b) neutralization steps (due to aqueous byproduct's low pH) will be avoided before final disposal, c) large volumes of the aqueous stream due to the expected increase of WTCP plants globally [63] will require adequate processing strategies, d) revenues of refineries will increase if all byproducts of WTCPs are employed, and e) better use of products and byproducts of WTCPs will help to advance the circular bioeconomy.

2. Wet thermochemical processes for biomass pretreatment

In WTCP, biomass is treated in the presence of water that can be combined or not with other types of fluids (e.g., solvents) in an extended range of temperatures, from relatively low (e.g., close to 100 °C) to high temperatures (e.g., >700 °C). The conditions for each process (i.e., temperature, pressure, and residence time) differ depending on the targeted products and the type of material employed. Fig. 2 summarizes common values of temperatures and pressures reported in the literature for WTCP, showing a broad range of the working conditions for each process. It is seen that some processes' operational conditions overlap with others', making it difficult to distinguish one process from another. Besides, as previously recognized, a process could be referred to by different names in the literature [11]. For example, Nakason et al. [64] used the term HTC to refer to a process using water only at temperatures from 140 to 200 °C for 1 to 4 h. However, as seen in Section 2.1, and these processes' conditions fit better in the HWE category (also called thermal hydrolysis or autohydrolysis). Therefore, a key difference among WTCPs is the targeted product, which dictates the conditions of the process. HWE aims to produce a torrefied-like material (i.e., not char, as defined elsewhere [65], HTC intends to produce high yields of a char-like solid (called hydrochar), HTL is used to produce a bio-oil as the main product, and SCWG is used to produce high yields of syngas. A discussion about the conditions of each process and the yields and characteristics of the hemicellulose-derived byproducts is presented in the following subsections.

2.1. Hot water extraction

The use of hot water to modify wood properties has been practiced since ancient times, as evidenced, for example, by the early fabrication of canoes and ships [82]. The preparation of wood to remove fibers using water started in the 19th century when Behrend, in 1869, showed that if the wood is exposed to hot water (at temperatures in the 160–180 °C range), it is softened enough to make the separation of the fibers easier [83]. Boiling or steaming processes have become a common practice since then [83]. Although the fermentation of hemicellulose into organic acids and alcohols using bacteria was reported as early as the beginning of the 20th century [84], the interest in using hot water to remove lignocellulosic constituents intentionally is more recent. Bobleter et al. [85] reported a work (therein called hydrothermal process) using water as the "extraction medium" to degrade hemicellulose and cellulose into sugars to produce furfural. The authors, nevertheless, mentioned that, previously, the Scholler process, using dilute acids (at temperatures from 160 to 180 °C), was practiced in Germany until WWII. The process in which only water is employed is called hot water extraction (HWE), but other names such as autohydrolysis, hydrothermal treatment, liquid hot water treatment, hydrothermolysis, hot compressed water treatment, water hydrolysis, wet torrefaction, aqueous fractionation, aqueous extraction, solvolysis, aquasolv, hot water pretreatment, and cooking refer to the same process [11,48]. Because of the lack of agreement on the term, we use "hot water extraction" herein. HWE offers advantages over other treatments, despite the further necessity of downstream hydrolysis to convert oligosaccharides into monosaccharides [48], as it uses only water. HWE is a mature technology that has reached pilot and demonstration scale, and at least one industrial plant has been reported in China [86].

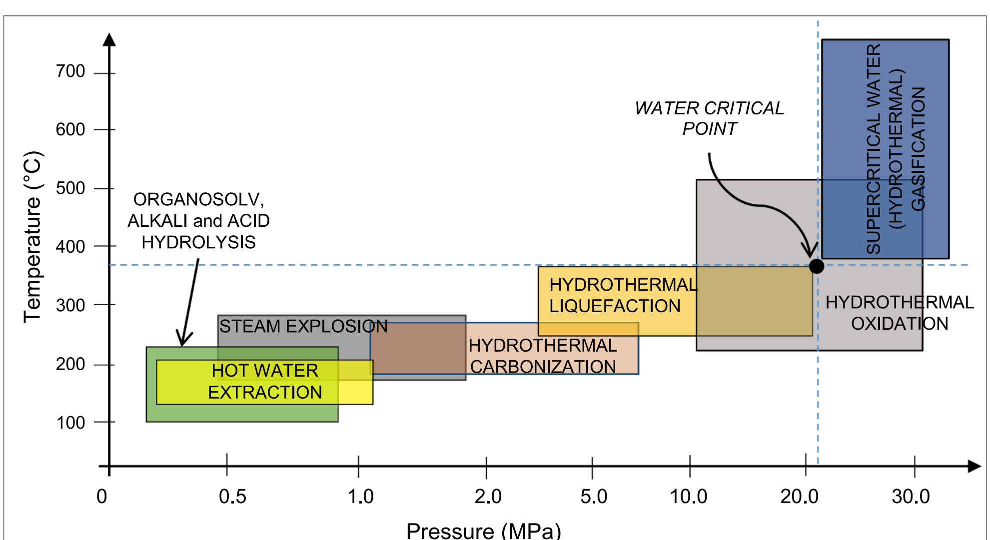

Fig. 2. Ranges of temperatures and pressures used for biomass WTCP operations (Fig. not to scale). Based on data reported by [11,14,31,33,35,36,66–81].

In HWE, relatively small particles of biomass (e.g., wood chips, shavings, splinters) and sawdust/powder are heated at temperatures up to ~ 200 °C under water saturation conditions. A possible risk of higher temperatures is that carbonization of the particles inside the container can occur unless sufficient water is added [87]. Although there is no agreement on how much water should be used for the process, water-to-biomass (W:B) relationships of 4 [49,87] to 9 [35] and 10 [45] have been reported for wood chips treatment. Lower ratios could limit the extraction of hemicelluloses, as shown by [88], who used a W:B = 3. Higher W:B relationships appear necessary as the process's temperature increases and the sample's particle size decreases. For example, Ståhl et al. [77] used a W:B = 40 for their HWE process (therein called hydrothermolysis) conducted at temperatures from 200 to 240 °C using pine wood, and Zhang et al. [89] used a 33.3 relationship (for macroalgae). Continuous reactors appear to work better with higher W:B [48], and some laboratory studies report even higher ratios. For example, Grenman et al. used a W:B = 180 and Rissanen et al. reported a W:B = 160 [90,91]. High W:B relationships are expected to help minimize possible limitations on the solubility of extracted components [90–92]. A potential drawback of high W:B could be the necessity of expensive downstream operations to "concentrate" the hemicellulose-derived compounds (e.g., via distillation). However, as in other WTCPs (e.g., HTC), these compounds in the liquid can be too diluted, making it necessary to use liquid–liquid extraction methods instead [26,46].

After the HWE process, the reactor is cooled down (preferably close to room temperature) before the separation of the products. From our own experience, the opening of the reactor should be conducted under a fume hood due to the release of fumes/steam and their potential impacts on human health. The resulting liquor is acidic, with pH values varying from 3 to ~ 4.5 for wood treatment liquor [87,93]. The pH of the liquor obtained in WTCP of manure and microalgae varies from 5 at low processing temperatures to neutral and basic at higher temperatures (e.g., in HTL and HTC) [35]. Adding buffers to control the pH of the liquor has been reported [94]. The longer the treatment times, the lower the pH when processing wood [49,91]. Thus, neutralizing the treated solid materials (e.g., via washing) can be necessary [87,91,92,95].

HWE is effective in modifying the properties of wood [96] and sugarcane bagasse [97] for biofuels production, composting [98], or manufacturing wood plastic composites and particleboard with reduced water uptake and thickness swelling, with improved or not negatively affected mechanical properties and reduced springback (attributed mostly to hemicelluloses removal) [11,99]. The water-based biomass biorefinery shows potential routes towards the use of HWE as a pre-treatment method to modify biomass properties intending the production of fuels, chemicals, fuel pellets, energy, and other byproducts (e.g., wood composites) [49,100,101]. Hydrothermal processing conditions (i.e., temperature and residence time) play an essential role in the impact of HWE on each biomass constituent [7]. Fig. 3 shows an example of the composition of the "extract" derived from a hardwood species (sugar maple) processed at 160 °C for 90 min. It is seen that around 23 % of the initial biomass is removed from the raw wood in the form of extracts (constituted by glucan, xylan, mannan, galactan, arabinan, rhamnan, acetyl, degraded lignin, and other unidentified compounds). These oligomers can be converted into sugars during the HWE process by increasing the residence time or via a downstream enzymatic digestion process [49].

A criterion commonly employed to evaluate the intensity of the process is the "severity factor" (R_0) [102], which is based on the process isothermal temperature and a reference temperature (usually 100 °C). In processes where the heating-up step is relatively long compared to the duration of the isothermal step, the degradation of wood constituents happens before reaching the target temperature [92]. The corresponding effect can be accounted for by converting the heating-up time into an equivalent isothermal reaction time, as suggested by Borrega et al. [92]. The degradation rate required for the corresponding computation can be determined as the ratio of the fraction of mass degradation (loss) during the HWE process at a specific temperature to the isothermal HWE time. The required activation energy (E_a) can be computed, for example, as per ASTM D1641. The E_a does not change significantly in the ranges of temperatures commonly used for HWE of softwood species. The E_a of, for example, raw ponderosa pine wood is ~ 175 kJ/mol, and the E_a of HWE-treated pine wood at 160 °C is ~ 160 kJ/mol [87]. Lower values of E_a have been reported for spruce (120 kJ/mol) [91]. Depending on the target isothermal temperature, the converted time can increase the equivalent isothermal conditions time by up to 5 % (e.g., for temperatures above 200 °C), with only a slight effect of E_a on the results [87]. Thus, in most HWE conditions, such an effect can be disregarded. If the heating step is relatively long, a similar approach can be used for other WTCP, such as steam explosion. A strategy to avoid long heating-up steps is to use hot baths (e.g., molten salt baths) in which the HWE reactor is immersed for fast heating, as reported by Kim et al. [45].

Table 2 summarizes works on HWE for modifying biomass

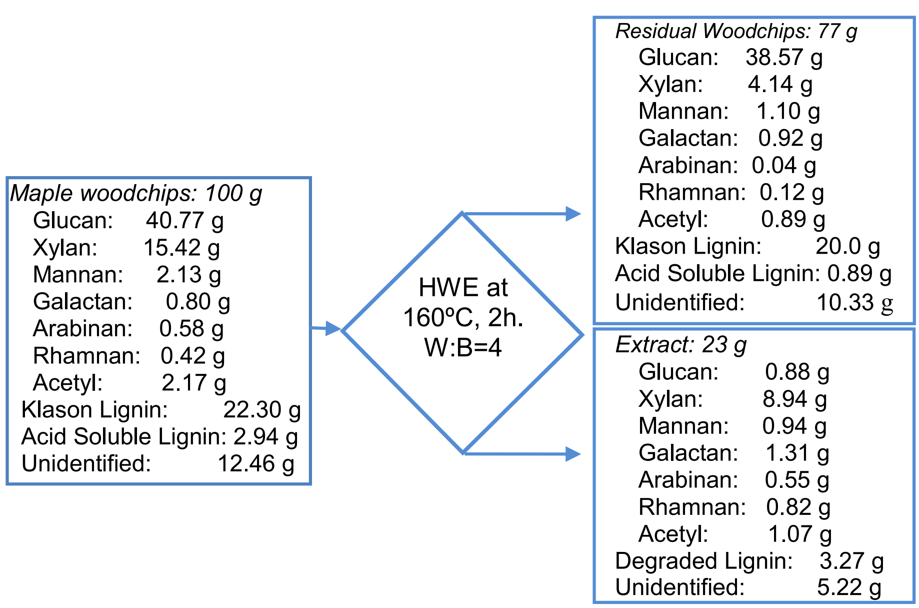

Fig. 3. Composition of sugar maple chips, distribution of solid fraction after HWE, and composition of the extract after processing the wood at 160 °C for 90 min [49], with permission.

Table 2
Summary of works involving HWE for biomass pretreatment and the corresponding byproducts yields and composition.

Raw material	HWE conditions	Main findings, product yields, composition	References
Works using softwood species			
Spruce	Chips and small particles. Batch cascade reactor. HWE at 120 to 170 °C, for 5 to 240 min (longer times for lower temperatures). W:B = 180.	Higher temperatures result in higher extraction yields. Smaller particles showed higher conversion than larger ones, regardless of temperature and processing time.	[91]
Spruce wood	HWE of ground wood and chips, at temperatures from 100 to 180 °C, for 5 to 100 min.	Extraction at 170–180 °C for 60 min showed better results. Longer times did not increase extraction. ~ 70 % of the total extracts comprised carbohydrates derived from hemicelluloses. ~ 75 % of the extracted carbohydrates were from galactoglucomannan.	[106]
Spruce wood	Ground spruce wood (<2 mm particle size). HWE at 170 °C, different pH levels (3.8, 4.0, 4.2 and 4.4, using phthalate buffers), for 20, 60, and 100 min.	Extracted non-cellulosic carbohydrates were constituted mainly by galactoglucomannans. Controlling pH positively impacts the extraction of hemicelluloses with high molar mass.	[94]
Spruce	A cascade reactor setup (Parr reactors in series) was used. Process: 150–170 °C with a particle size of 1.25–2 mm, W:B = 160.	Extracts contained up to ~ 170 mg/g wood of hemicellulose products in the process at 170 °C for 60 min. At lower temperatures the extraction was ~ 140 mg/g. Mannose constituted about 70 % of the hemicellulose extracts. A kinetic model predicted the products' yields.	[90]
Norway spruce	120–240 °C using a flow-through system. Particles < 2 mm.	Only small amounts of hemicelluloses were removed at or below 160 °C. All hemicelluloses and 15 % of lignin were released at 220 °C. Cellulose degradation occurs only at higher temperatures (i.e., 240 °C).	[107]
Pine (*Pinus pinaster*)	Two-step extraction: 1) remove extractives (130 °C), and 2) remove hemicelluloses (130 to 240 °C, different times). W:B = 8.	Max.yields of removed compounds (derived chiefly from hemicelluloses) occurred at around 210 °C. Liquor at this temperature was primarily constituted by mannose (~12 g/L), followed by xylose (~5 g/L), and galactose (~3 g/L).	[108]
Pine chips	HWE (hydrothermolysis) at 200, 220, and 240 °C for 60 to 120 min, W:B = 40, particles passed through a 1 mm screen.	Complete conversion of hemicelluloses in all treatments. Liquor also contained cellulose-degraded fractions. At 200 °C, 10 min, the maximum of mono-, oligo- and polysaccharides found in the hydrolysates was 226 mg/g.	[77]
Loblolly pine	Wet torrefaction (equivalent to HWE at work's lower conditions) at: 200, 230,and 260 °C for 5 min, W:B = 5.	In treatment at 200 °C, the composition of the aqueous fraction was ~ 1.2 % xylose, ~1.1 % arabinose, ~0.7 % mannose, ~0.5 % glucose, and 0.5 % galactose. These compounds were not found at higher temperatures but glucose and 5-HMF were found instead.	[109]
Loblolly pine	Chips treated at 160, 170, and 180 °C, different times. W:B = 45.	Up to ~ 12 % of the wood mass was extracted as sugars at ~ 170 °C for 90 min. The sum of all monomeric and polymeric sugars reached ~ 12 %. Extraction yield depends on the pH of the extracts. Maximum yield was obtained at a pH = 3.5.	[110]
Pine (*Pinus pinaster*) chips	HWE at 175 °C for 26 min, W:B = 8, after water-soluble extractives removal (at 130 °C).	Liquor contained glucose, xylose, galactose, arabinose, mannose, and acetic acid, among others. Aqueous phase was used for levulinic production.	[111]
Works involving hardwood species			
Sugar maple	HWE at 160 °C for 90 min, using relatively large equipment (1.84 m^3).	~23 % of the raw biomass is removed from the raw wood in the form of extracts (constituted by glucan, xylan, mannan, galactan, arabinan, rhamnan, acetyl, degraded lignin, and other unidentified compounds).	[49]
Eucalyptus sawdust (mix of three eucalyptus species)	Particles with size in the range 0.5–6.5 mm, W:B = 8. Temperatures of 170 and 180 °C, different times.	Aqueous phase contained monomeric and oligomeric glucose and xylose, acetyl groups, formic acid, furfural, and HMF. Yields of oligomeric and monomeric xylose were higher in the 170 °C treatment (up to ~ 8.5 g/L). Yields of acids, furfural, formic acid, and HMF were close in all treatments.	[95]
Eucalyptus nitens (from a pulp mill)	Particle size < 10 mm. W:B = 8. Temperatures: 170–220 °C. Solid was subjected to organosolv delignification (to remove lignin).	The aqueous phase contained 2.88 % xylose, 10.07 % xylooligosaccharides, and 0.06 % furfural. Maximum yields of hemicellulose-derived compounds at 195 °C.	[112]
Birch wood	Temperatures: 180, 200, 220, and 240 °C for up to 180 min. W:B = 3.	Batch reactor: maximum amount of xylose in the hydrolysates was ~ 65 % for meal but only 25 % for chips, corresponding to wood yields of ~ 60 % and 80 %, respectively, due to a low W:B ratio.	[88]
Eucalyptus globulus	Particles passed through an 8-mm screen. W:B = 6–10. Temperature from 145 to 190 °C for 1 h (for the 175 °C treatment).	Mechanism of deacetylation during the treatment was proposed.	[113]
Birch wood	Temperatures 180 to 240 °C, for 30, 60, and 180 min (lower times for higher temperatures). W:B = 40.	Kinetics of xylan degradation was proposed. Max. *xylo*-oligomers extracted was ~ 15 % of the dry wood mass, i.e., 70 % of the initial xylan in birch. Increasing extraction temperature shifted the maximum towards shorter extraction times.	[92]
Hardwood chips	Not specified (objective was to use the extracts for producing carboxylic acids).	Carboxylic acids (i.e., C_1-C_7) were produced using mesophilic and thermophilic microbes growing on hot water extracts.	[114]
Hardwood and softwood residues (three materials)	Batch-mode, high-pressure reactor, temperature from 170 to 220 °C, 15–180 min, W:B = 15.	Recovery of hemicellulose products reached a maximum of 60 % at ~ 70–85 % hemicellulose removal (based on initial	[103]

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Table 2 (*continued*)

Raw material	HWE conditions	Main findings, product yields, composition	References
		hemicellulose content) in the treatments at lower temperatures. Solids used for sugars production.	
Hybrid poplar	Particles < 1 mm, HWE from 160 to 210 °C for 10 to 30 min (different combinations), W:B = 5)	Neutral reducing sugars (glucose, xylose, galactose, arabinose, and mannose) and acetic acid, furfural and 5-HMF were identified in the aqueous phase.	[93]
Poplar branches (which were compared with grapevine residues and pine sawdust)	Batch reactor HWE at 170–220 °C, for 15–180 min, W:B = 15. Heating rate: 7 °C/min.	Max. xylan removal in all materials in the 170 °C treatment (and longer times), reaching up to 80 % from the initial content. Galactomannan removal reached up to 90 %.	[103]
Eucalyptus globulus (which was compared with wheat straw and miscanthus)	Temperatures: 190 and 210 °C, reached at 60 and 72 min after starting the heating process, respectively. W:B = 7.	Eucalyptus sample showed the highest yield of xyloses, while more arabinose was identified in the wheat straw and miscanthus samples.	[104]
Mix of hardwood chips (black gum, oak, maple, poplar & sycamore, and southern magnolia	150 °C for different times. W:B=~3.7.	150 °C is sufficient for the degradation of hemicelluloses. Xylan dissolves as oligosaccharides in the autohydrolysis process and then depolymerizes slowly into xylose at longer treatment times. Xylo-oligosaccharides are the most abundant components. Generation of furfural was very low.	[115]
Mix of hardwood chips	160 °C, W:B = 4.	Process used either water alone or 2 % total titratable alkali (TTA) of green liquor (containing 0.88 g/l NaOH, 2.57 g/l Na_2S, and 8.16 g/l Na_2CO_3). The aqueous byproduct was used for lactic acid production.	[116]
Works using other types of materials			
Wheat straw	Treatment at 200–275 °C, 22 to 45 min.	“at lower temperatures, the hemicellulose … was converted to xylose and arabinose; and then at higher temperatures, the cellulose was converted to glucose and cellobiose”.	[85]
Sugarcane bagasse	170–230 °C, for 1 to 46 min, using a 25 L batch reactor. Particle size > 14 mesh. Solids concentration below 8 %.	Xylan recovery in HWE was compared with xylan recovery in steam explosion. In general, higher in HWE (up to 70 %).	[117]
Sugarcane bagasse	170 °C for 60 min. W:B = 6, using a 23 L batch digester with a rotary stainless-steel vessel (4 rpm).	The HWE removed 68.8 % of xylan of the raw material.	[118]
Sugarcane bagasse	150, 170, and 190 °C for different times	Liquid fraction was primarily constituted by xylose, besides glucose and galactose. Treatment at 170 °C for 2 h offered the highest yields of xylose.	[119]
Mix of primary and secondary sludge from a sewage treatment plant	Sludge (10 % solids) was treated at 120, 170, and 190 °C for 10 to 60 min, using a hot bath. The treated sludge was centrifuged and the supernatant was used for AD.	1.0 g VS of supernatant treated at 170 °C produces 369.3 mL of biogas containing 256.7 mL of CH_4 (~82 % higher than from raw sludge). Heating 1.0 kg sludge needs 0.34 MJ of energy. High soluble COD and TOC concentration and high content of P and N in the liquid.	[120]
Dewatered sewage sludge (DSS)	SS with ~ 94 % MC at 170, 200, 230C, 260, 290, and 320 °C for 30 min; heating rate 10 °C/min under agitation (at 500 rpm). Process is called hydrothermal treatment.	Aqueous fraction contained carbohydrates and proteins. High content of proteins in process at 170 °C (5005 mgCOD/L). This fraction was subjected to fermentation to determine VFA. The highest yield of VFAs was 0.59 $gCOD_{VFA}$/gCOD. Higher temperatures produced recalcitrant organic compounds.	[121]
DSS	DSS with ~ 94 % MC was processed at 170, 200, 230, 260, 290, and 320 °C, residence time 0.5–6 h.	The aqueous fraction was used for AD. Methane yields were higher (286 mL CH_4/g COD) when the sludge was treated at lower temperatures and shorter residence times.	[122]
Primary sewage sludge	Process at 140, 160, 180, and 200 °C for 15 to 240 min.	Aqueous fraction contained acetic acid, benzene acetic acid, butanoic acid, pentanoic acid, and propanoic acid, plus alkenes, phenolic and aromatic compounds, regardless of treatment conditions. Extract was used for AD.	[123]
Sewage sludge	140 to 220 °C for 30 to 120 min. Tests at bench and pilot scales. W:B = 5.	Liquid byproduct was used for AD.	[124]
Palm oil empty fruit bunches (EFB)	100, 150, 180 and 220 °C for 30 min, W:B = 10.	HWE removes up to 55 % of ash in EFB, lowering the K and Cl contents to 0.84 % and 0.18 %, respectively. Maximum of 37 % N, 65 % K, and < 10 % P in EFB were dissolved into the liquid product. HWE helps nutrient recovery from EFB.	[125]
Palm oil empty fruit bunches (EFB)	100, 150, 180 and 220 °C for 30 min, W:B = 10.	Increasing HWE temperature impacted N, P, and K solubilizations (max. solubilization ratios of 37.2, 9.8, and 64.8 %, respectively). Phototoxicity tests were performed, and the liquid was used as a fertilizer.	[126]
Date palm (trunk chips)	HWE at 160, 180, 200 and 220 °C for 30 min, under agitation (200 rpm).	Extracts contained ~ 72 % and ~ 68 % xylose in the aqueous fraction of the 160 °C and 180 °C treatments, respectively. Decrease in liquids in treatments ≥ 200 °C. Only small amounts of cellulose-degraded compounds (up to 3 %) in the liquid from the treatment at 180 °C.	[98]
Vine pruning	Two-stage HWE: 180 °C for 60 min with W:B = 6, and 180–200 °C for 30–40 min.	Two aqueous fractions (one from each treatment) were obtained. Both fractions contained oligosaccharides and phenolic compounds.	[127]
Vine shoots	Treatment at 180–215 °C, W:B = 8.	Oligosaccharides, monosaccharides, and other minor compounds constituted the aqueous fraction.	[128]
Macroalgae Enteromorpha prolifera	Process at 140 and 240 °C, without a catalyst, and at 160 °C with formic acid as catalyst.	Hemicelluloses conversion reached 70.8 % and 92.9 % in process at 140 and 240 °C, respectively. The highest yields of rhamnose were at 160 °C with catalyst (i.e., 41.7 % of products contained rhamnose in the liquid product).	[89]

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Table 2 (*continued*)

Raw material	HWE conditions	Main findings, product yields, composition	References
Flax shives	Temperatures 130, 150, and 190 °C at a constant flow rate of 1.0 mL/min, for 30 min.	84 % hemicellulose and 32 % lignin were removed at 190 °C, flow rate of 1.5 mL/min, for 30 min. Extract was constituted by 15.8 % xylan, 0.9 % glucan, and 4.8 % lignin.	[129]
Wheat straw	Ground wheat straw was subjected to HWE at 160, 180, and 200 °C from 10 to 50 min.	Liquid fraction to reinforce κ-carrageenan/locust bean gum (κ-car/LBG) polymeric blend films, with positive effects on the films.	[7]
Wheat straw	Particles 1–6 cm, HWE at a combination of 175, 185, and 195 °C and 6, 9, and 12 min, using a pilot scale continuous reactor (100 L/h).	Hemicelluloses recovery in the liquid fraction was higher as the intensity of the process increased. Close to 40 % of the hemicelluloses were recovered when the severity factor (R_0) reached 3.95.	[130]
Wheat straw	HWE followed by organosolv. For HWE, temperature was 160 °C for 90 min.	Washing HWE solids removes sugars. Sugar in HWE extracts: between 12 and 18 g/L of total hemicellulosic sugars. Degradation products: ~1 g/L of acetic acid and between 0.5 and 1 g/L of furfural.	[131]
Triticale straw (*cv. AC Ultima*),	Ground straw (passing a 2 mm holes screen) heated to 130, 150, or 170 °C, for 1 h, before flowing through a continuous reactor. W:B = 60.	Best results in treatment at 170 °C. Total yield of xylose oligomers and monomers was 72 % at 170 °C and fell to 60 % at 150 °C. Models were developed and validated to predict the yields and composition of products.	[132]
Corncob	150 to 190 °C, from 1.5 to 330 min, W:B = 8.	Max. yield ~ 50 % xylan at 150 °C for 200 min. Higher temperatures slightly increase the yield of *xylo*-oligomers. Longer times (constant temperature) produced *xylo*-oligomers with higher contents of xylose and lower content of arabinose/acetyl groups.	[133]
Corncob	Continuous flow reactor, 200 °C for 10 min.	In treatment at 200 °C, 32.8–34.9 wt% of corncob was solubilized by the hydrothermal reaction. Contents of xylan and arabinan were 29.9 wt% and 3.4 wt%, respectively.	[134]
Rapeseed straw	HWE at temperatures from 170 to 210 °C for 10 to 50 min, using particles < 10 mm.	The extracts were constituted by sugars (xylose, glucose, arabinose, mannose, and galactose) and acetic acid, formic acid, furfural, and HMF. Solids for sugars (for ethanol).	[135]
Sugarcane straw	HWE at temperatures from 170 to 220 °C for 5 to 15 min, using particles < 2 mm.	The treatment at 195 °C for 10 min resulted in 85.5 % removal of hemicelluloses (with xylose and glucose as the most abundant compounds and arabinose in smaller amounts) and cellulose solubilization reached 9.8 %.	[136]
Rye straw	Particles 3–4 cm, HWE at 200 °C for 10 min, W:B = 10.	The extract recovered 98.7 ± 6.1 % xylose, 80.3 ± 5.5 % arabinose, and 5.3 ± 0.4 % glucose (from the original constituents in the raw material).	[137]
Barley straw	HWE 200–230 °C.	Aqueous phase contained up to 168 g of hemicellulose-derived compounds per kg of raw material.	[138]
Microalgae, digestate, swine, and chicken manure	HWE at 170 °C for 1 h. W:B = 9. Comparison of results with HTC, HTL, and SCWG. Objective was to compare the behavior of the materials under different conditions.	N in the aqueous phase as organic-N and NH_3–N. The proportion of organic-N is higher at lower temperatures. Extraction of P is linked to the presence of inorganics (Ca, Mg, and Fe) in the feedstock. Microalgae and chicken manure release P more easily than other feedstocks.	[35]
Swine manure	HWE at 110, 150, 180, or 200 °C for 10, 30, or 60 min, with agitation (60 rpm).	The treatment at 200 °C for 60 min converted up to 98 % of N in manure into soluble form.	[27]
Coconut husk and Rice husk	HWE from 140 to 200 °C for 1 to 4 h.	Content of furfural, furfuryl alcohol, HMF, lactic acid, formic acid, acetic acid, and levulinic acid in the aqueous phase increased as the treatment temperature increased.	[64]

W:B refers to water to biomass relationship.

properties, the main findings, and the composition/characteristics of the aqueous byproduct. The findings presented in Table 2 are expanded upon in the subsequent sections (from 2.1.1 to 2.1.3). Table 2 has been divided into three categories: works involving softwood species, works using hardwood species, and works using other materials. One of the reasons for separating the materials into these three categories (apart from better organization) is that, as shown by Mok and Antal [101], Nitsos et al. [103], and Vilcocq et al. [104], the yields of hemicellulose degradation products (i.e., the extract composition) differ (at least slightly) in the HWE process of these three biomass categories. Research commonly uses batch reactors, but some studies can employ small continuous reactors (e.g., [105]). Both batch and flow-through systems can be equally efficient in removing carbohydrates from biomass (e.g., wood) [88]. The effect of the particle size on the process has been studied by Rissanen et al. [91], who showed that HWE of small particles results in a higher conversion of hemicelluloses than larger particles, no matter the processing temperature, which has been attributed to internal diffusion restrictions in large biomass particles. These results agree with those of Song et al. [106]. Detailed mass balances of the HWE using hardwood species can be found, for example, in [18,92].

2.1.1. Works involving softwood species

Rissanen et al. conducted HWE of spruce using small and relatively large particles (i.e., wood chips and 10x10x10 mm wood blocks), temperatures from 120 to 170 °C, for different times, and a very high W:B (i.e., 180) [91]. As expected, higher temperatures resulted in higher extraction yields. Fig. 4 shows a comparison of the effect of the particle size on the conversion of hemicelluloses during HWE for small and larger particles, suggesting that smaller particles perform better. Small particles of spruce have also been used by Leppanen et al. [107] (See Table 1). Other works using spruce agree with the results of Rissanen et al. [91]. Song et al. [106] showed that the highest extraction yields using small particles of the same material (i.e., spruce groundwood) occur at 170–180 °C for 60 min [106]. Around 70 % of the total extracts were carbohydrates derived from hemicelluloses and ~ 75 % of the extracted carbohydrates were from galactoglucomannan (GGM). Similar findings were reported by Grenman et al. [90] (See Table 1). Other extracts included xylans, arabinogalactans, lignin, and acetic acid. Up to 80–90 % of the GGM in the wood was extracted at 170–180 °C for 1 h. Longer treatment times do not increase extraction. Song et al. [94] showed that controlling the pH during the treatment (for example using phthalate buffers) positively impacts the extraction of hemicelluloses

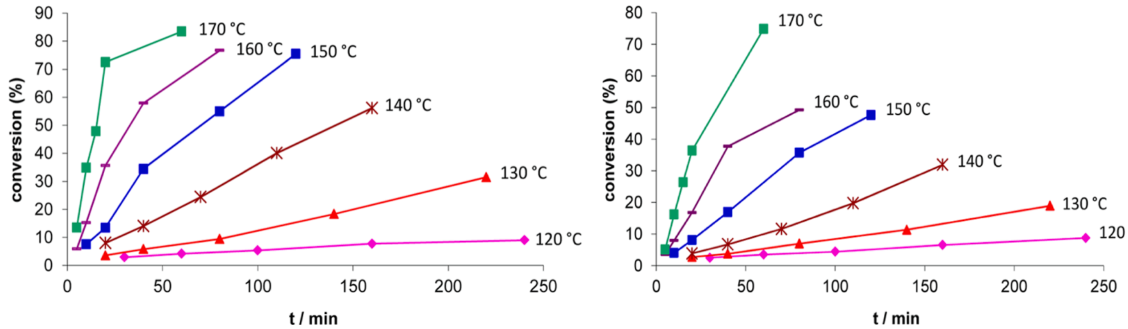

Fig. 4. Comparison of the effect of particle size (for similar temperature and residence time) on the conversion of the overall hemicellulose extraction: chips (left) vs wood cubes (right). Reproduced from [91], with permission.

with high molecular mass.

Stahl et al. [77] used pine particles (<1 mm) that were subjected to HWE (in the work called hydrothermolysis) at temperatures from 200 to 240 °C and times up to 120 min. High W:B (i.e., W:B = 40) intended to minimize limitations in solubility of wood components. Results showed that hemicelluloses are completely degraded even at the process lowest temperatures. The maximum yields of the total of mono-, oligo- and polysaccharides in the hydrolysates was 226 mg/g (dry basis) or 32 % of the total carbohydrates in pine wood in the treatment at 200 °C for 10 min. 75–85 % of all oligosaccharides in the hydrolysates can be attributed to the C_6-derived sugars, with the mannan-derived oligosaccharides as a major component. Autohydrolysis at 200 °C for 12 min removed 20 % of the original lignin in the wood (soluble + insoluble lignin). Higher temperatures promoted significant acceleration of carbohydrates degradations since only traces of oligosaccharides were found in the hydrolysate at 240 °C for 10 min. These results on the yields of hemicellulose derived products are in agreement with the results of Yan et al[109 115], who used loblolly pine that was subjected to "wet torrefaction" at temperatures 200, 230, and 260 °C for 5 min, using a W:B of 5. The lower treatment conditions of "wet torrefaction" correspond to those of HWE. The composition of the aqueous byproduct of the material treated at 200 °C was, approximately, 1.2 % xylose, 1.1 % arabinose, 0.7 % mannose, 0.5 % glucose, and 0.5 % galactose. These compounds were not found at higher temperatures but glucose and 5-HMF were found instead.

Other works using pine include those of González-Muñoz et al., Yoon et al., and Rivas et al. [108,110,111]. González-Muñoz et al. [108] conducted a two-step process to remove extractives (using water only, at 130 °C) and hemicelluloses at higher temperatures (up to 240 °C) from *Pinus pinaster*. The duration of the process varied, which was accounted for using the severity factor. The resulting liquor at 240 °C was primarily constituted by mannose (~12 g/L), followed by xylose (~5 g/L), and galactose (~3 g/L). These materials reached the maximum yield at this temperature. Rivas et al. subjected extractives-free pine chips to HWE at 175 °C for 26 min and found that the aqueous fraction contained several oligomers (e.g., glucose, xylose, galactose, arabinose, mannose, acetic acid, among others) that served to produce levulinic acid [111].

Yoon et al. described the HWE results of loblolly pine at temperatures of 160, 170, 180, and 190 °C for various times (accounted by an H-factor), using chips ranging from 5 to 10 mm and a W:B of 45. For an H-factor of 1500 h (equivalent to ~ 170 °C for 90 min), the extraction (as sugars) reached a maximum of 12 % of the wood [110]. The results showed that the extraction is highly dependent on the pH of the liquor. Maximum yield resulted when the pH was ~ 3.5, but the yields decreased at lower pH values. Nitsos et al. [103] compared the behavior of softwood and hardwood species using similar processing conditions and the same equipment and showed that the maximum recovery of hemicellulose products is approximately identical for both materials, which occurs at comparable treatment conditions.

2.1.2. Works involving hardwood species

HWE of eucalyptus (*eucalyptus nitens*) showed that the liquid product contained 2.88 % xylose, 10.07 % xylooligosaccharides, and 0.06 % furfural. Maximum yields of hemicellulose-derived compounds occurred when the autohydrolysis was conducted at 195 °C and a severity factor of 3.62 [112]. In the work, the material was ground to obtain particle size below 10 mm prior to the HWE process. The W:B was 8 and the processing temperatures ranged from 170 to 220 °C. The remaining solid was subjected to organosolv delignification. In another work, HWE of sugar maple was reported by Amidon and Liu [49].

Cebreiros et al. [95] conducted a study on the use of HWE (therein called autohydrolysis) to pretreat another type of hardwood species (eucalyptus) aiming to produce ethanol. A mix of three eucalyptus species (with 92 % of the particles between 0.5 mm and 3 mm), with a W:B of 8, was subjected to HWE at 170 and 180 °C and different times (from 15 to 120 min). A hot bath was employed to heat the reactor to the desired temperature, after preheating to 100 °C. The liquid fraction was separated from the solid one via filtration and washed to reach neutral pH. The liquid was constituted by monomeric and oligomeric glucose and xylose, acetyl groups, formic acid, furfural, and HMF. Yields of oligomeric and monomeric xylose were higher in the 170 °C treatment (up to ~ 8.5 g/L). Yields of acids, furfural, formic acid and HMF were approximately similar in all treatments. The process was accompanied by an organosolv treatment (see Section 2.3) for comparison of results. Tunc and van Heiningen have also reported results on HWE (at 150 °C and time from 15 to 500 min) of a mix of hardwood species; i.e., chips of black gum (35 %), oak (35 %), maple (15 %), poplar and sycamore (12 %), and southern magnolia (3 %) [115]. This temperature is relatively lower than those reported in other works. However, it was sufficient to degrade hemicelluloses. Xylan dissolved as oligosaccharides in the autohydrolysis process and then it depolymerizes slowly into xylose at longer treatment times. Xylo-oligosaccharides are the most abundant components in the liquor. Generation of furfural was very low. A mix of chips of hardwood species was also used by Walton et al., who processed the chips either under water only or under a 2 % total titratable alkali of green liquor [116]. The aqueous byproduct was used for lactic acid production.

Kim et al. conducted colloid milling followed by hot-water pretreatment of oak prior to enzymatic hydrolysis. The study showed that the aqueous byproduct from the process contains 12.7 mass% of xylan, 1.5 mass% of glucan, and 3.4 mass% of lignin. If the colloid milling process is not conducted the xylan content slightly decreases to 11.3 mass%, glucan increases to 3.5 mass%, and lignin remains approximately similar (3.9 mass%) [45]. Thus, the solid fraction after the treatment favors the digestibility and composition of the solid treated material for increased fermentable sugar (i.e., the mass% of glucose was 38.3, compared to 8.3 of the material that were not colloid milled).

Birch wood was subjected to HWE using a W:B of 40, at temperatures from 180 to 240 °C for 30 to 180 min (the longest treatments for lower temperatures). Maximum *xylo*-oligomers extracted was ~ 15 % of the dry wood mass, i.e., 70 % of the initial xylan in birch. Increasing the extraction temperature shifted the maximum towards shorter extraction times [92]. The study also proposed a model for the kinetics of xylan degradation during the process. In another work, Dai and McDonald [93] conducted HWE of hybrid poplar as a pretreatment step prior to producing sugars for chemicals (specifically for polyhydroxybutyrate-PHB). Small particles of poplar (<1 mm) were treated at temperatures from 160 to 210 °C for 10 to 30 min (different combinations, W:B up to 5). Again, neutral reducing sugars (glucose, xylose, galactose, arabinose, and mannose) and acetic acid, furfural and 5-HMF were identified in the liquid extract.

An interesting comparison of results on the use of a hardwood species, a softwood species, and a type of agricultural residue (grapevine pruning), using HWE under the same conditions, has been reported by Nitsos et al. [103]. The authors employed a batch reactor with a W:B of 15 and working temperatures from 170 to 220 °C for 15 to 180 min. The maximum xylan removal in the three types of materials was approximately similar and verified at the 170 °C treatment (and long treatment times), reaching up to 80 % of the initial content. Galactomannan removal reached up to 90 %. Another work comparing autohydrolysis (HWE) of different materials (i.e., eucalyptus residues, wheat straw, and miscanthus) was conducted by Vilcocq et al. [104], using a two-step process consisting of HWE followed by hydrolysis with a solid acid catalyst. For HWE, a W:B of 7 was used. The temperatures were 190 and 210 °C, which were reached 60 and 72 min after starting the heating process, respectively. The reactor was turned off and cooled down immediately after reaching the target temperature. The HWE liquor of the eucalyptus sample showed the highest yield of xyloses, while more arabinose was identified in the wheat straw and miscanthus samples, resulting from the high arabinoxylan content of herbaceous materials. Other works on HWE using hardwood species have been reported by Kilpeläinen et al. and Testova et al. [139,140].

2.1.3. Works using other types of materials

Qiao et al. [120] used sludge (composed of 15 % solid, 73 % organic content, with organic components, i.e., fibers, lipids, and proteins of 21 %, 14 %, and 20 %, respectively) from a sewage treatment plant to test the potential of producing biogas after hydrothermal processing. Water was added to the sludge to reach 10 % total solids and was treated using a hot bath at three temperatures (120, 170, and 190 °C) for 10, 15, 20, 30, 45, and 60 min. The treated sludge was centrifuged and the supernatant (after thermal treatment, with pH: 6.47; Mean COD: 25,000 mg/L; TOC: 17,000 mg/L; VFA: 8300 mg/L; TN: 2700 mg/L; NH^{4+}-N: 1000 mg/L; TP: 710 mg/L; PO_4^{3-} -P: 510 mg/L) was subjected to anaerobic digestion using an up flow anaerobic sludge blanket (UASB, 8.6 L) reactor.

Other works on the use of HWE (therein called hydrothermal treatment) of sewage sludge have been conducted by [121,122], where the sludge contained ~ 94 % moisture content. The temperature of the process varied from 170 to 320 °C for 30 min to 6 h, under agitation in the former work, and for 30 min in the second. The liquid fraction was subjected to a) anaerobic fermentation to determine fatty acids content and b) anaerobic digestion [121]. In additional work, Danso-Boateng et al. used primary sewage sludge and processed it at 140, 160, 180, and 200 °C for 15 to 240 min. Although the authors refer to the process as HTC, the corresponding parameters used for the treatment fit in the HWE category. Since the aqueous phase was used for AD, emphasis was put on characterizing the liquid to identify properties of interest for this process. TOC values in the liquid ranged from 4.87 g/L (in the treatment at 140 °C), to 7.67–13.68 g/L (in the treatment at 200 °C), compared with 2.08 g/L found in the filtrates of the untreated feedstock. Only a marginal increase of COD and BOD was detected as the temperature of the treatment process increased. The BOD varied from 8.18 g/L in the treatment at 140 °C to 9.92 g/L at the highest temperature (i.e., 200 °C), compared with 4.66 g/L for the untreated material [123]. The study also identified that the liquid contains Maillard products such as aldehydes, furans, pyrazines, pyrroles, and pyridines in the liquor obtained from the treatments at 180 and 200 °C. Furthermore, the use of HWE for sewage sludge treatment at bench and pilot scale has also been reported prior to biogas production [124] (See Section 4.1.3). Adding alkali (See Section 2.7) improved the dewatering of sewage sludge and reduced energy consumption [141].

Novianti et al. [126] studied HWE (in their work called thermal hydrotreatment) of palm oil empty fruit bunches (EFB) intending to: a) evaluate the energy content of the HWE solid fraction, and b) study the suitability of the aqueous fraction as a fertilizer (See details in Section 4.3). In this work, the W:B was 10 and the process was conducted at four different conditions: 100, 150, 180 and 220 °C for 30 min, using a 500 mL batch reactor. Filtration was used for separating the solid from the liquid fraction. The hypothesis on the potential of the liquid fraction as a fertilizer was based on the solvent role of water, which could remove high loads of organic and inorganic compounds, and that, expectedly, P from biomass is removed by the liquid fraction. Results showed that increase of the HWE conditions (i.e., higher temperatures) impacted N, P, and K solubilizations, with maximum solubilization ratios of 37.2, 9.8, and 64.8 %, respectively. A related work of Nurdiawati et al. [125] showed that HWE of EFB removes up to 55 % of ash, reduces the P and Cl contents down to 0.84 % and 0.18 %, respectively, and a maximum of 37 % N, 65 % K, and < 10 % P in EFB were dissolved into the liquid product. Therefore, HWE shows potential for nutrient recovery from EFB.

Wheat straw has been subjected to HWE at temperatures of 160, 180, and 200 °C for 10, 30, and 50 min [142]. The extracted liquid fraction of the material treated at 180 °C for 30 min was constituted mostly by xylan (82.2 mol%) and arabinan and glucan in less amounts. The extracted hemicellulose was used for reinforcing κ-carrageenan/locust bean gum (κ-car/LBG) polymeric blend films (See Section 4.2). These results have been confirmed Serna-Loayza et al. [131], who found that, for the same material (i.e., wheat straw), three treatment combinations (160 °C for 90 min, 180 °C for 30 min, and 180 °C for 60 min) showed approximately comparable total sugar concentrations (~12 g/L). Also, the treatment conducted at 160 °C for 90 min resulted in the lowest concentration of degradation products (0.2, 0.01, and 1.4 g/L for furfural, HMF, and acetic acid, respectively) and lignin hydrolysis (2.2 g/L). HWE of wheat straw at higher temperatures (above 200 °C) produces sugars derived from both hemicellulose and cellulose, with higher amounts of glucose as the temperature further increases [85].

Petersen et al. [130] also used wheat straw for HWE, using a continuous flow reactor with 100 L/h processing capacity. Fig. 5 presents the hemicelluloses recovery in both the solid and the liquid fractions as a function of the treatment conditions, measured by the severity

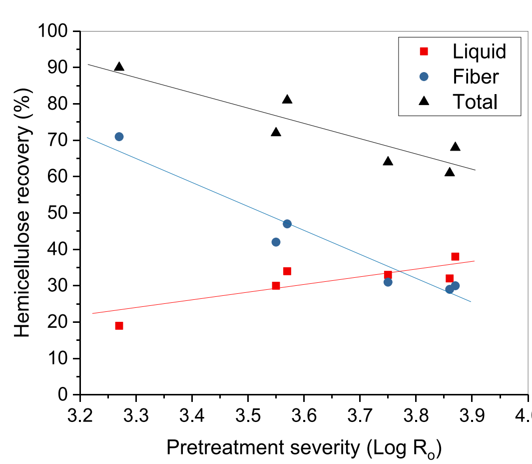

Fig. 5. Recovery of hemicellulose in fiber fraction (○), liquid fraction (□), and total recovery (▲) in pretreatment experiments at different severities [130], with permission (Redrawn).

factor (R_0). It is seen that close to 40 % of the hemicelluloses were recovered at high R_0 conditions. In another work using triticale straw (a wheat straw-related material) the material was treated at temperatures of 130, 150, and 170 °C for 1 h prior to flowing through a continuous reactor, using a W:B of 60 [132]. The treatment at 170 °C resulted in aqueous byproduct with the highest concentration of hemicellulose (17.0 mg/mL), constituted by 72 % of xylose oligomers and monomers. According to the authors, in continuous flow rate, the effect of temperature is more important than flow rate. Developed hydrolysis models allowed the authors to predict yields of the products with good accuracy. Related works involving wheat straw HWE can be found in Serna-Loayza et al. [131] and Ruiz et al. [142,143]. Serna-Loayza et al. [131] used HWE in conjunction with organosolv pretreatment for fractionating wheat straw. The authors found that washing solids after HWE removes sugars that otherwise would remain in the solid. The sugars concentration in HWE extracts was 12–18 g/L of total hemicellulosic sugars. The yields of degradation products were ~ 1 g/L for acetic acid and between 0.5 and 1 g/L for furfural.

Other types of straw, such as rapeseed straw, barley straw, sugarcane straw, and rye straw, have also been pretreated using HWE before biofuels production [135–138]. Diaz et al. [135] processed rapeseed straw at temperatures from 170 to 210 °C for 10 to 50 min, using particles with particle size < 10 mm. Although it was of interest to evaluate the ethanol production of the pretreated solids, the extracts were also characterized, showing that, as in other types of lignocellulosic materials, the extracts contain hemicellulose-derived products (xylose, glucose, arabinose, mannose, and galactose), in addition to inhibitors (acetic acid, formic acid, furfural, and HMF). In the work of Vargas et al. [138], HWE of barley straw (at 200–230 °C) resulted in an aqueous byproduct containing up to 168 g/kg of hemicellulose-derived compounds. Furthermore, sugarcane straw was ground to obtain particles < 2 mm and subjected to HWE from 170 to 220 °C for 5 to 15 min, with the treatment at 195 °C for 10 min showing the best results [136]. At these conditions, hemicelluloses removal reached 85.5 % (with xylose and glucose as the most abundant compounds and arabinose in smaller amounts), and cellulose solubilization reached 9.8 %. Ingram et al. [137] showed that rye straw, processed at 200 °C for 10 min, resulted in extract that recovers 98.7 ± 6.1 % xylose, 80.3 ± 5.5 % arabinose, and 5.3 ± 0.4 % glucose of the original corresponding constituents in the raw material.

The perspectives of processing macroalgae for rhamnose production (which is of interest in the cosmetic industry) via HWE have been assessed by [89]. The HWE process (called hydrothermal conversion by the authors) was conducted from 140 to 240 °C for 60 min, with and without formic acid (as a catalyst), employing a W:B of 100. Conversion of hemicellulose was high, even at low temperatures (i.e., 70.8 % conversion at 140 °C), reaching up to 92.9 % in the process at 240 °C. The catalyst increased the conversion of both hemicellulose and cellulose. High conversion rates of hemicellulose might result in large part from the formation of H^+ in water due to the presence of the acid. The highest yield of rhamnose was 41.7 %, at 160 °C with the catalyst, which is eight times higher than without the catalyst.

Dewatered sewage sludge has been subjected to HWE at different temperatures (from 170 to 320 °C) for 30 min [121]. The process in the work is called hydrothermal conversion. The treatment at higher severity could more appropriately fit in the HTC category. However, this work is included in this section because the best results on the aqueous byproduct were verified at the lower processing conditions. The authors found that the aqueous phase was constituted by proteins and carbohydrates, with higher yields at the lowest processing temperature. The liquid fraction was then subjected to anaerobic fermentation to assess the VFAs content. As shown in Fig. 6, higher yields of VFAs are also produced in the treatment at 170 °C (0.59 $gCOD_{VFA}$/gCOD. Reduction of VFAs as the temperature increases results from the higher thermal degradation of carbohydrates, proteins, and other compounds at high temperatures [121]. In a related study [122], longer residence times were employed for the thermal treatment of the same material, aiming to assess the CH_4 yields of the liquid products.

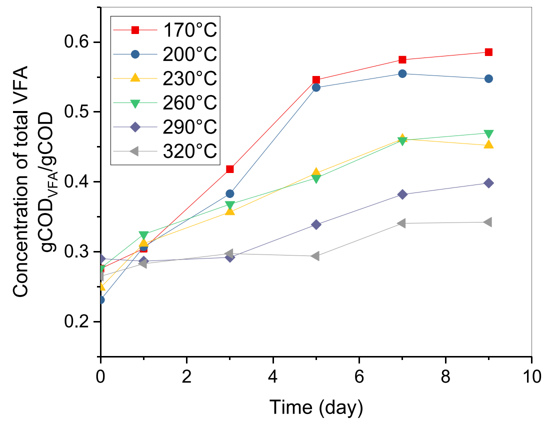

Fig. 6. Cumulative production of VFAs in the liquid fraction after HWE of sewage sludge at different temperatures [121], with permission (Redrawn). Only mean values are shown.

Other agricultural residues used for HWE include vine residues, date palm residues, corncob residues, coconut husk, and rice husk. Jesus et al. and Davila et al. showed that HWE of vine residues (in the range of temperatures from 180 to 200 °C) results in an aqueous byproduct constituted by oligosaccharides, monosaccharides, and phenolic compounds [127,128]. Nakhshiniev et al. [98] conducted HWE of date palm lignocellulosic residues (trunk chips, constituted by 43.4 % C, 0.38 % Total N, 0.1P, and 0.9 K, in dry basis) at 160, 180, 200 and 220 °C (at an average heating rate of 7.2 °C/min), under agitation (200 rpm), for 30 min. The solids were subjected to aerobic digestion for fertilizer production, and the extracts were separated and analyzed. The extracts were constituted by approximately 72 % and 68 % xylose in the liquid products of the 160 °C and 180 °C treatments, respectively. The yields of xylose abruptly decreased in the liquids corresponding to the treatments at and above 200 °C, which can be explained by the volatilization of hemicelluloses into volatile organic compounds that, in part, escaped (in the form of steam) during the decompression process. The aqueous phase contained furfural, 5-HMF, acetic acid, formic acid, and lactic acid. The portion of lignin in the residues from the 200 and the 220 °C treatments were 31.7 and 39.4 %. Small amounts of cellulose-degraded compounds (up to 3 %) were identified in the liquid resulting from the treatment at 180 °C.

HWE of corncob conducted by Nabarlatz et al. and Makishima et al. [133,134] showed that the higher yields of hemicellulose-products in the liquid fraction after the HWE process occurs in the 190–200 °C range of temperatures. The extracts, as in other materials, are constituted mainly by xylan. This result confirms findings reported by other authors using sugarcane, flax shives, and oak wood [45,117–119,129,144]. Furthermore, Nakason et al. [64] subjected coconut husk and rice husk to HWE (therein referred to HTC, but the process's temperature justifies including this work in the HWE category) at temperatures from 140 to 200 °C for 1 to 4 h. The work intended to produce a solid material with improved fuel properties (i.e., increased high heating value). The liquid extracts from both rice husk and coconut husk contained furfural, furfuryl alcohol, HMF, lactic acid, formic acid, acetic acid, levulinic acid, and propionic acid. The concentration of these compounds typically increased as the treatment conditions were more severe.

An interesting work comparing the behavior of different types of materials (microalgae, digestate, swine, and chicken manure) under HWE at 170 °C for 1 h, using a batch reactor, has been reported by Ekpo et al. [35]. The work focused on removing inorganics using HWE and compared the results with HTC, HTL, and SCWG. Nitrogen is present in the aqueous phase as organic-N and NH_3–N. The proportion of organic-N is higher HWE than in other WTCPs at higher temperatures (Table 3). As expected, the pH increases as the severity of the treatment increases (i.

Table 3
Comparison of pH, total organic carbon (TOC), N, P, and K in the extracted aqueous fraction of four types of WTCP. "Hyd" stands for "hydrothermal" treatment (i.e., HWE). Typical pH values ± 0.1. Reproduced from [35], with permission.

Material and Conditions	Concentration (mg/kg)				
	pH	TOC	Total N	Total P	Total K
C. vulgaris					
Hyd 170 °C	5.0	196,870	47.960	8,510	4,850
HTC 250 °C	7.1	179,120	60,390	8,370	3,820
HTL 350 °C	8.3	94,640	62,040	6,450	2,850
SCWG 500 °C	8.8	83,370	55,690	3,070	5,240
Digestate					
Hyd 170 °C	5.1	65,740	19,560	1,360	2,330
HTC 250 °C	7.7	62,350	18,610	840	2,340
HTL 350 °C	8.2	46,980	17,110	560	2,040
SCWG 500 °C	8.7	34,170	13,780	600	1,440
Swine manure					
Hyd 170 °C	4.9	118,870	10,640	2,060	8,120
HTC 250 °C	5.9	108,840	12,790	650	7,890
HTL 350 °C	6.7	80,780	15,820	800	7,790
SCWG 500 °C	8.2	44,510	19,970	710	6,050
Chicken manure					
Hyd 170 °C	5.0	184,180	33,430	5,250	19,030
HTC 250 °C	7.2	141,120	32,770	1,470	19,080
HTL 350 °C	8.0	102,800	31,700	820	18,520
SCWG 500 °C	8.5	48,670	34,300	1,060	12,600

e., from HWE to more severe processes such as HTC and HTL). Extraction of P is linked to the presence of inorganics such as Ca, Mg, and Fe in the feedstock. Microalgae and chicken manure release P more easily than other feedstocks. Yuan et al. [27] have also used HWE (therein called hydrothermal treatment – HTT) to assess the solubilization of nutrients (P, N, and organics) from swine manure (See details on manure characteristics in the referred paper). The process was conducted from 110 to 200 °C for 10 to 60 min. The aqueous byproduct from the process was then tested for phytotoxicity in seed germination (See Section 4.3).

2.1.4. The role of water in hemicelluloses degradation and removal

In WTCPs, water plays an active role as a reactant, solvent, processing medium, and catalyst or catalyst precursor [145 146,147]. Water properties change as the temperature is increased. Thus, depending on water's thermodynamic state, water can exert different actions on lignocellulosic reactants [145]. Water at high temperatures has a lower dielectric constant, fewer and weaker hydrogen bonds, and higher isothermal conductivity than at ambient temperature [146]. For example, the water dielectric constant decreases from 80 at 25 °C to < 2 at 450 °C and the ion product increases from 10^{-14} at 25 °C to 10^{-11} at temperatures close to 350 °C and decreases by five orders of magnitude (or higher) above 500 °C [38]. Thus, water behaves differently as the temperature of the WTCP is raised, directly impacting the process intensity and the resulting products.

The key role of water in WTCPs has been demonstrated through studies on organosolv processing of biomass. Parchami et al. [148] showed that the pH of the organosolv medium is higher (i.e., less acidic) than in HWE processes. This finding could result from the lower dissociation of acetic acid in ethanol (used in the organosolv process) than in water. Higher water content during WTCPs could lead to more hydronium ions than in the presence of ethanol, promoting higher hemicellulose hydrolysis. The behavior and structural changes of hemicelluloses occurring during WTCPs and the mechanism and kinetics of the formation of hemicellulose-derived products have been reported in previous studies [91,92,100,113,149]. Yu et al. showed how lignin level influences the release of hemicellulose-derived sugars in HWE [150]. Sun et al. [86] reviewed these topics and discussed the fate of hemicelluloses and lignin during WTCPs.

Biomass constituents (cellulose, hemicellulose, and lignin) are bonded primarily by intramolecular and intermolecular ester and ether bonds that are susceptible to breakage by ionic hydrolysis. During hydrothermal operations such as HWE, the ester bonds tend to be hydrolyzed (wholly or partially) into hydroxyl and carboxyl groups. Meanwhile, ether bonds are broken to form two free hydroxyl groups, depending on the process conditions [86]. In the presence of water, degradation of biomass (e.g., wood) constituents proceeds via hydronium-catalyzed reactions. Changes in water ionization as the temperatures increase results in hydronium ions generation. Hydronium ions cleave the acetyl groups bound to hemicelluloses and form acetic acid and other acidic compounds [77,91,92,113]. Acetic acid acts as ab acidic catalyst and lowers the pH of the medium, accelerating further the hydrolysis degree of the bonds [45]. Controlling hemicelluloses degradation is possible via: a) selecting a relatively high temperature (below 200 °C) and short times, or b) working with lower temperatures and extending the treatment process. Cellulose is less prone to degradation at temperatures below 200 °C because of its strong hydrogen bond interactions. Above this temperature, the water ionic constant increases abruptly, and cellulose breakdown into cello-oligosaccharides, glucose, and 5-HMF (among other compounds) occurs [86].

2.2. Steam explosion

The first records of the use of steam explosion for wood pretreatment appeared almost a century ago. Mason, in 1926, used steam to modify wood properties for pulp and wood board manufacture, and Babcock (in 1932) patented a method to produce "fermentable sugars and alcohols from wood" after steam treatment [151,152]. The combined possibility of manufacturing wood composites from steam-treated wood and recovering hemicellulose-derived fractions is also seen in the works of Boehm in the 1930 s [153,154]. The working principle of steam explosion has not changed substantially over time. Wood chips, small logs, or small biomass particles are fed into a chamber where water is added and heated to reach high pressure and temperature (e.g., up to 240 °C and 3.5 MPa) [155,156]. Alternatively, high-temperature steam (up to around 230 °C) can be directly fed to the digester's chamber [117,157]. After relatively short times at these conditions (in the order of seconds to a few minutes), the material is discharged through an outlet valve and explodes at atmospheric pressure. A further separation process (e.g., via filtration) is used to isolate the solid from the liquid products. This separation step is commonly accompanied by a washing step to remove hemicellulose-derived products [158].

A related process, steam pretreatment, has also been employed with a similar purpose to steam explosion [155,159]. The difference between steam explosion and steam pretreatment processes is that in steam explosion there is a rapid depressurization (i.e., explosion) and cooling down of the treated material at the end of the process, but a slow cooling process occurs in steam pretreatment [155]. As in HWE, steam explosion is a process where autohydrolysis of biomass is achieved using water only. Therefore, the mechanism of hemicelluloses degradation discussed in Section 2.1.1 applies to steam explosion. In some works, steam explosion can add a catalyzer (e.g., SO_2) to modify the process and improve the desired product yields [160]. The so-called "wet explosion" is a variant of the steam explosion process, in which oxygen is added as a catalyst when the materials reach the target conditions [161,162].

Steam explosion has been used to pretreat biomass prior to a) sugars production [159], b) anaerobic digestion of biomass [163–166], c) wood composites manufacture [11], d) pulping [167], e) fuel pellets [168], or as a pretreatment process before fast pyrolysis to improve bio-oil yields [169]. Biomass pretreatment using steam explosion makes biomass available to enzymes attack for sugars production. In the case of fuel pellets, despite their better quality after steam explosion, the production costs are still higher than using untreated biomass [170]. Table 4 shows a list of works on biomass steam explosion and findings on the aqueous byproduct.

Ewanick and Bura [160] subjected switchgrass (SG) and sugarcane bagasse (SCB) to steam explosion after soaking in water (for 48 h) and an

Table 4
Works involving steam explosion/steam pretreatment of biomass.

Raw material	Steam explosion conditions	Main findings, product yields, composition	References
Switchgrass (SG) Sugarcane bagasse (SCB)	Material with 80 % MC, SO_2 impregnated; SG: 195 °C for 7.5 min; SCB: 205 °C for 10 min.	The majority of the hemicellulosic sugars solubilized into the aqueous fraction. The aqueous fraction contained glucose, xylose, furfural, and HMF.	[160]
Pine chips	197°C, 10 min for steam explosion, followed by hot water extraction (90°C, 120 min, W:B = 39) to extract carbohydrates.	Aqueous fraction contained 0.5 g arabinose, 2.1 g xylose, 7.9 g mannose, 2.3 g galactose, and 3.7 g glucose per 100 g of raw pine.	[171]
Poplar woodchips	Chips were heated at 170 °C for 3 min before steam explosion using pilot-scale equipment.	Aqueous fraction was used for bioxylitol after a concentration step (to reach 31.6 g/L).	[172]
Corn stover (from Italy and the US)	Steam pretreatment (no explosion), 170 °C for 9 min, with and without SO_2.	Up to 5.7 g/L of glucose and 21.7 g/L of xylose in the aqueous phase from CS.	[159]
Douglas fir	Wet explosion (steam explosion with 7.2 % O_2) at 170–190 °C for 10 to 30 min	Glucose, xylose, galactose, arabinose, mannose and soluble lignin were identified in the aqueous fraction.	[161]
80 % birch (*Betula pendula*) + 20 % European beech (*Fagus sylvatica*) wood chips	Steam explosion (210 °C for 5 min) followed by hydrotropic extraction	~73 % of xylose and 3 % of glucose were recovered by adding a washing of the pretreated solids step	[158]

impregnation process with 3 % SO_2 to improve the treatment. The materials were kept in a 1.5 L batch steam gun at 195 °C for 7.5 min and 205 °C for 10 min, respectively, before steam explosion. The aqueous phase derived from SG was constituted by 7.8 g of glucose, 36.2 g of xylose, 1.42 g of furfural, and 0.21 g of HMF per 100 g of raw material. In the case of SCB, the aqueous fraction contained up to 7.1 g of glucose, 16.0 g of xylose, 0.72 g of furfural, and 2.52 g of HMF per 100 g of raw SCB. The work showed that soaking materials and including an impregnation process (using SO_2, which works as a catalyst) before the steam explosion operation can help improve biomass treatment [160]. Depending on the raw materials, the yields of hemicellulose-derived products in the aqueous byproduct can differ, even using similar steam explosion conditions. Jung et al. reported that the composition of the aqueous fraction from pine wood, after steam explosion at 197 °C and 10 min, contains 0.5 g of arabinose, 2.1 g of xylose, 7.9 g of mannose, 2.3 g of galactose, and 3.7 g of glucose per 100 g of raw pine [171].

Vithanage et al. [172] used poplar woodchips for steam explosion treatment. Before the process, the chips were soaked in water at 100 °C for 1 h and heated to 170 °C for 3 h. During this time, purges containing hemicellulose-derived products were collected. After the steam explosion, the treated fibers were pressed, and the resulting liquid was mixed with the purges. The mix was then concentrated by rotary evaporation to reach 31.6 g/L of xylose, used for xylitol production (See Section 4.1.1). The solid fraction, conversely, was used for ethanol production. The effectiveness of microwave irradiation and steam explosion on the biodigestibility of wheat straw (WS) in anaerobic digestion was assessed by Sapci et al. [163]. In the work, the straw was milled to obtain ~ 80 % of the material with particle size ranging from 5.66 to 0.20 mm. The microwave treatment consisted of heating the material at 200 and 300 °C for 15 min. The steam explosion was carried out immediately after heating the material at 210 °C for 10 min. The authors found that the biogas yields from steam-exploded WS increased by ~ 20 %, compared to the untreated materials, and that the microwave-treated material poorly performed in the AD process, suggesting that the wet treatment (steam explosion) is more promising to improve the AD of WS than dry treatment (microwave treatment). An additional work conducted by Olsson et al. [158] reported a mass balance of steam exploded wood chips (at 210 °C for 5 min), including the effect of washing the steam exploded materials on the recovery of hemicellulose-derived products.

Öhgren et al. conducted steam pretreatment (i.e., without explosion) of two types of corn stover (CS) (from the US and Italy) at 170 °C for 9 min with 3 % SO_2, and at 190 °C for 5 min with and without a catalyzer (3 % SO_2), aiming to study the effect of the steam pretreatment of the potential of CS for sugars production [159]. The aqueous fractions resulting from the most severe treatment were constituted by 5.7 g/L of glucose and 21.7 g/L of xylose for the corn stover from the US and 4.6 g/L of glucose and 18.7 g/L of xylose for the material from Italy. A positive effect of adding SO_2 to the treatment was found.

2.3. Organosolv

Organosolv is a biomass pretreatment process that uses water with different types of organic solvents with low-boiling points, such as short-chain aliphatic alcohols (e.g., methanol and ethanol), or polyhydric alcohols (e.g., glycerol, ethylene glycol, and triethylene glycol) and other types of solvents [50,75,173]. The diversity of solvents employed and the conditions of the process has led to the use of specific names to identify the processes, which is the case of Formiline, Acetoline, sulfuric acid-catalyzed ethanol (SACE), and auto-catalyzed ethanol (ACE) [174]. A catalyst (normally H_2SO_4 or formic acid) can be added to the process (see, e.g., [78,148,174,175]). The role of acid catalysts is to increase the lignin removal rate and decrease the required pretreatment temperature. Cleavage of aryl-ether bonds for lignin fragmentation and increased hemicellulose hydrolysis rate are also promoted by the acids [176]. Temperatures for the organosolv process range from around 107 to 250 °C (See Fig. 2). Excessive increase in the process severity (i.e., at higher temperatures) can adversely affect the process since enzyme and fermentation inhibitors (furfural, HMF, levulinic acid, and formic acid) are formed [75]. Solvents recovery is necessary to make the process economically and environmentally attractive [50,174].

Organosolv has been seen as a feasible operation for selective fractionation of lignocellulosic biomass, i.e., to obtain cellulose-, hemicellulose-, and lignin-rich streams with relatively high purity [50], or as a pretreatment operation before the production of sugars, especially for biofuels from the pretreated solids [75,78,177,178]. Fig. 7 shows a flowchart of a typical organosolv process and the streams resulting from the treatment. Advantages of organosolv over other thermal pretreatment methods include obtaining relatively pure lignin, low toxicity, and the ability to retain most of the cellulose fraction in the substrate. However, using chemicals can increase the cost of the process and the process-associated risks [75,78,179,180]. Removal of solvents is necessary before the production of biofuels as they could inhibit enzymatic hydrolysis. Publications of interest reviewing the organosolv process as a pretreatment process for sugars in biorefinery concepts can be found, for example, in [50,75].

Different materials (generally with high moisture content) have been pretreated using organosolv, including hardwood and softwood materials [71,75,176,181], brewer's spent grain [148], sweet sorghum stalks [182], water hyacinth [183], sugarcane bagasse [184], sugarcane trash [185], corn stover [186], rice straw [187], and wheat straw [174] Table 5 summarizes works that employ the organosolv process for biomass pretreatment and the main products' yields and characteristics. A brief description of these works is presented following.

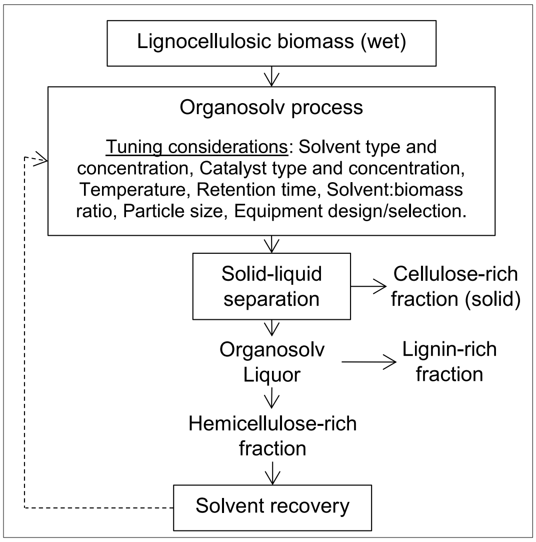

Fig. 7. Flowchart showing the organosolv process and the cellulose, hemicellulose, and lignin streams resulting from the treatment. Adapted from [50] (with permission).

Romani et al. [71] subjected *eucalyptus globulus* to organosolv pretreatment with a 56:44 glycerol:water solvent at 200 °C for 69 min. The treated solid retained up to 99 % of the original cellulose. Lignin precipitation of the extracted liquor (with 0.3 M HCl) and further centrifugation allowed to recover up to 65 % of the lignin and 94.2 % of the hemicelluloses, constituted by arabynoologosaccharides (0.09 g/L), xylooligosaccharides (11.08 g/L), glucooligosaccharides (0.96 g/L), acetyl groups (4.91 g/L), and furfural (0.75 g/L) (referred to g of monomer equivalent). Cebreiros et al. [95] conducted a comparative study on organosolv and HWE treatments using a mix of eucalyptus sawdust (See Table 1 for details on the corresponding HWE treatment). As expected, organosolv is more effective for lignin removal. Delignification was up to 60 % more intense in organosolv than in HWE in the treatment at 180 °C. However, organosolv resulted in lower xylan removals (25–69 % for the 170 and 180 °C treatments, respectively) than in HWE (75 and 87 %, respectively), with xylan being solubilized mostly in oligomeric form (95 %). This result may be ascribed to the weaker auto-catalyzed reactions in the organosolv process, compared to HWE. Higher xylan-derived sugars were recovered in the liquid corresponding to the treatment with 50 % ethanol than in the process using 75 % ethanol. Acetic acid followed the same trend, which explains in part the results on xylan removal at the higher temperature (i.e., reduction of the catalytic effect of acetic acid occurs due to the presence of lower amounts of acetic acid), as confirmed by another study [148]. Comparison of results on the composition and yields of hemicellulose-degradation products between HWE and organosolv, using different raw materials, has also been reported by Serna-Loayza et al. [131] and Ingram et al. [137]. Serna-Loayza et al. [131] also showed that HWE degrades hemicelluloses more intensely than organosolv. An additional work on the use of eucalyptus wood (*Eucalyptus pellita*) has been published by Choi et al. [176], intending to produce furfural from the aqueous fraction (See Section 4.1.1.1).

Fig. 8 shows an example of the mass balance of the organosolv pretreatment of yellow poplar with and without a SCBLF (slurry composting and biofiltration liquid fertilizer) treatment, as reported by [181]. The work was conducted at 133.2 to 166.8 °C, with a catalyst (0.2–1.8 % of H_2SO_4) for 1.6 to 18.4 min. Solvent was 50 vol% in water. The highest overall glucose yield (44.0 %) was achieved from pretreatment at 140 °C with 1.5 % acid concentration for 5 min. The liquid fraction contained glucose (0.5 % in mass), xylose (7.4 %), and acetic acid (1.8 % from the original mass) for both materials (See Fig. 9). Another interesting work comparing results from different organosolv pretreatments (namely

Table 5
Works that used the organosolv process for biomass pretreatment and yields and composition of products.

Raw material	Organosolv conditions	Main findings, product yields, composition	References
Eucalyptus globulus wood	Process at 200 °C for 69 min using 56 % of glycerol (in water) as solvent. Solvent to wood ratio of 10.	Products: 1) Solid with up to 99 % of the original cellulose, 2) High purity lignin (up to 65 % of that in the raw wood), 3) Black liquor (aqueous fraction) containing hemicellulose-derived products.	[71]
Eucalyptus wood (mix of three types of eucalyptus sawdust)	Ethanol concentration of 50 % and 75 %. Process at 170 and 180 °C, for 15, 30, 45, and 90 min. Solvent: wood = 8.	Lower xylan removals (25–69 % for the 170 and 180 °C treatments, respectively) achieved in organosolv compared to HWE (75–87 %), with xylan being solubilized mostly in oligomeric form (95 %). Delignification was up to 60 % more intense than in HWE in the treatment at 180 °C (See Table 1, same authors).	[95]
Sitka spruce sawdust (0.3–1.0 mm range of particle size)	Ethanol:water mixtures with dilute H_2SO_4 (0.75 w% to 1.25 w%); solvent: biomass = 10. Organosolv at 150–180 °C (heating rate of 25 °C/min) for 25 to 85 min.	Organosolv promoted biomass degradation from 46 to 54 %, with lignin up to 18–24 % and 20–24 % of monosaccharides (quantified as their anhydrides) and products derived from these, including furfurals and ethylglycosides.	[78]
Yellow poplar (after slurry composting and biofiltration liquid fertilizer-SCBLF treatment)	Reaction temperature: 133.2 °C to 166.8 °C; acid concentration (H_2SO_4): 0.2 % to 1.8 %; reaction time: 1.6 to 18.4 min. Solvent was 50:50 ethanol:water (vol%).	Aqueous fraction contained glucose (0.5 %), xylose (7.4 %), and acetic acid (1.8 % from the original mass) (Fig. 8).	[181]
Wheat straw	Four types of organosolv pretreatments: Formiline, Acetoline, sulfuric acid-catalyzed ethanol (SACE) and auto-catalyzed ethanol (ACE).	Results depend on the process. Objective was not to optimize hemicellulose-derived products, but these products were identified in the aqueous stream from the pretreatment (Fig. 8).	[174]
Brewer's spent grain	120, 140, and 180 °C for 10 to 120 min, and 0 % v/v and 50 % v/v ethanol as solvent. pH was set to 3.5 using H_2SO_4. Reactor stirring at 100 rpm.	Temperature, retention time, ethanol concentration, and their 2-way and 3-way interactions significantly affected the hemicellulose removal. Hemicellulose removal increased from 22 % to 91 % when the	[148]

(continued on next page)

Table 5 (*continued*)

Raw material	Organosolv conditions	Main findings, product yields, composition	References
		temperature increased from 120 °C to 180 °C.	
Sweet sorghum stalks	Isopropanol, ethanol, or their mixture as solvents, with or without H_2SO_4. Solvent to biomass ratio of 5. Treatment at 120, 140, or 160 °C for 30, 45, or 60 min.	Aqueous fraction contained sucrose (6.8–0.7 mass% at the less severe and most severe conditions, respectively), fructose, glucose, and xylose (which increased with treatment severity). The aqueous fraction was used for AD.	[182]
Eucalyptus (*Eucalyptus pellita*)	Ethanol with 1 % H_2SO_4. 140–170 °C, solvent to wood ratio of 8.	Organosolv lignin was precipitated from the liquid byproduct. Aqueous fraction contained glucose, xylose, mannose, furfural, and lignin. This fraction was used for furfural production.	[176]

Formiline, Acetoline, SACE, and ACE) has been reported by Chen et al. [174]. Formiline was conducted at 107 °C for 1 h, using 78 % formic acid, followed by deformylation with 2 w/w% $Ca(OH)_2$ at 120 °C for 1 h. Acetoline employed 90 % acetic acid with the addition of 0.3 % H_2SO_4 at 110 °C for 2 h, followed by deformylation with 2 w/w% $Ca(OH)_2$ at 120 °C for 1 h. SACE used a 60 % (w/w) ethanol–water solution containing 30 mM H_2SO_4 and was conducted at 190 °C for 1 h. ACE was performed at 220 °C for 20 min using a 65 % (v/v) ethanol–water solution. Fig. 9 shows the mass balances of each process. The “liquid” stream resulting from the pretreatment shows the composition of the extract byproduct in each case. Although the compounds identified in each case are similar, the presence (percentage) of each compound is notably different. For example, the Formiline process of 100 g of wheat straw yields, in the liquid byproduct, 22.0 g of xylose and formaldehyde derivatives, 1.58 g of arabinose, and 0.65 g of glucose. Conversely, the SACE process yields 3.57 g of xylose, 1.51 g of arabinose, 0.75 g of glucose, and 2.31 g of furfural.

Bouxin et al. [78] used a softwood species (Sitka spruce) sample for organosolv pretreatment with ethanol from 50 to 70 vol% and catalyst from 0.75 to 1.25 H_2SO_4. The authors found that organosolv promoted biomass loss from 46 to 54 mass%. Among the degraded products, Klason lignin accounted for 18–24 mass%, and monosaccharides (quantified as their anhydrides) and products derived from these, including furfurals and ethylglycosides, by up to 20–24 mass%. Efficient organosolv pretreatment resulted in subsequent saccharification yields up to 86 %. These conditions also reduced the conversion of pentoses to furfural, the ethyl glycosides were more stable to dehydration than the parent pentoses.

Organosolv process of Brewer’s spent grain (BSG) has been carried out at 120, 140, and 180 °C for 10, 30, 60, and 120 min, and 50 %vol ethanol as solvent, pH of 3.5 (adjusted by adding H_2SO_4 solution) and stirring the reactor (a Parr reactor) at 100 rpm [148]. After the process, the pretreatment slurry was emptied into a sieve (200 µm pore size) and the liquid byproduct was centrifuged (4500 x g for 5 min) to separate suspended solids (separated solids were collected as first phase lignin). The filtered liquid was diluted with water prior to a second centrifugation (also 4500 x g for 5 min) to precipitate the lignin (second phase lignin). Statistical data analysis showed that all three parameters (temperature, retention time, and ethanol concentration) and their 2-way and 3-way interactions significantly affected hemicellulose removal. Hemicellulose removal increased from 22.2 % to 91.1 % by augmenting the temperature from 120 °C to 180 °C. In addition, increasing retention time from 30 min to 120 min resulted in hemicellulose removal growth from 39.2 % to 57.2 %.

Nozari et al. [182] carried out organosolv treatment of sweet sorghum stalks using two types of solvents (isopropanol, ethanol, and their mixtures), with and without H_2SO_4, and a solvent-to-biomass ratio of 5. The process was conducted at 120, 140, and 160 °C for 30, 45, or 60 min. As expected for this type of material (due to its composition), the primary free sugars in the liquid fraction were sucrose, fructose, glucose, and xylose. In the treatment at the lower severity conditions (i.e., 120 °C, 30 min, without the catalyst), the liquids contained up to 57 % of the sucrose in the raw material (in mass%), 19 % of the fructose, 22.5 % of the glucose, and no xylose was detected. At the higher severity conditions (i.e., 160 °C, for 60 min, with the catalyst), the yields were 0.1 %, 47.5 %, 50.8 %, and 10.8 % for sucrose, fructose, glucose, and xylose, respectively. The liquid was subjected to anaerobic digestion for biogas production (see Section 4.1.3).

2.4. Hydrothermal carbonization (HTC)

Hydrothermal carbonization (HTC) was conceived at the beginning of the 20th century when Bergius (in 1913) found that it is possible to artificially produce a coal-like material derived from carbonaceous materials [26]. Some works showing the historical evolution of the process, starting with the work of Bergius, are described by Funke and Ziegler [188]. HTC is a WTCP employed for treating carbonaceous materials, especially biomass with high to very high moisture content, to produce char as the main product, and liquid and gaseous byproducts [65,66,189]. Other names for HTC are wet pyrolysis, hydrous pyrolysis [68], wet carbonization [190], and hydrothermal pretreatment [120]. The solid product is also called hydrochar, bio-coal, or hydrothermal carbon [26]. The liquid byproduct is also called “process water” [58,191–193], “HTC process water” [194], or “spent liquor” [195]. This aqueous byproduct can contain up to 15–20 % of the initial carbon, mainly in the form of sugars, acetic acid, nutrients, and other compounds [196]. The gas byproduct yield is only marginal (1–5 % of the

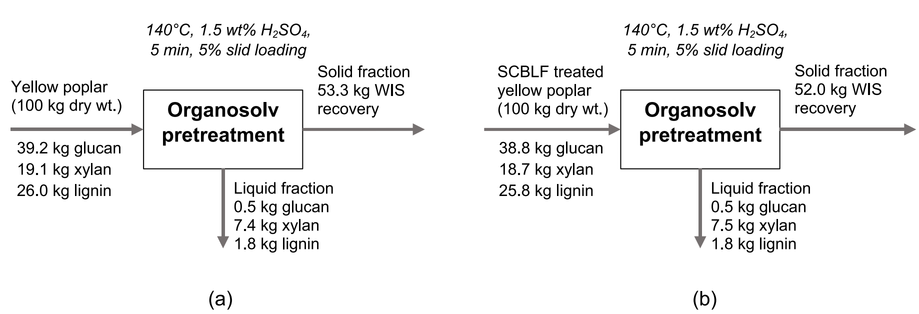

Fig. 8. Mass balance for organosolv pretreatment of yellow poplar (a) without and (b) with an SCBLF (slurry composting and biofiltration liquid fertilizer) treatment [181] (WIS – Water insoluble solids).

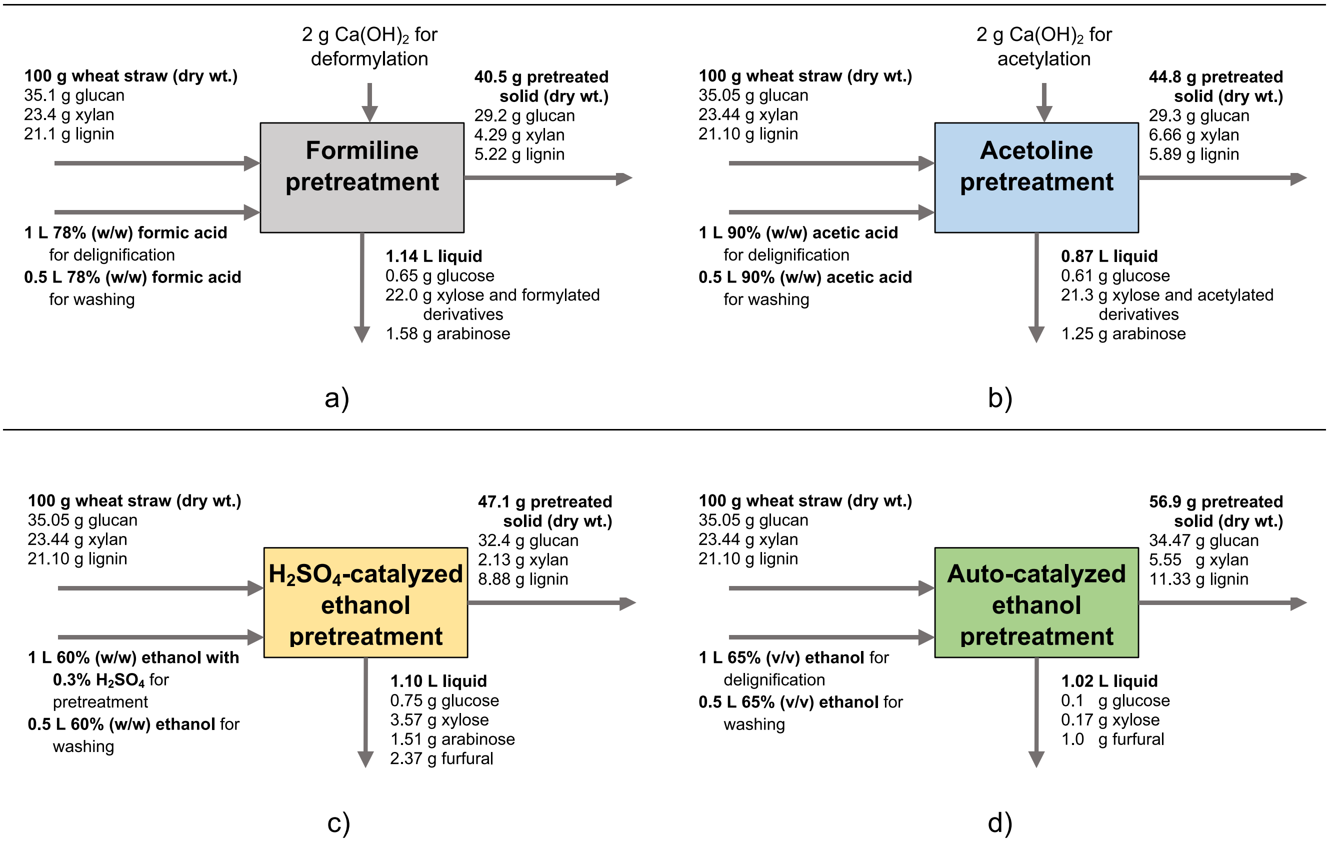

Fig. 9. Mass balances of different organosolv pretreatments for sugar or ethanol production (a: Formiline; b: Acetoline; c: SACE; d: ACE). Adapted from Chen et al. [174].

original raw material) and is constituted mainly by CO_2, CO, CH_4, H_2, and organic volatile compounds (e.g., alcohols and alkylated naphthalenes) in smaller proportions [58].

There is no agreement on the conditions of the HTC process, but the temperatures can vary in the 200–300 °C range, and pressures up to around 20 MPa (i.e., under water subcritical conditions) [79,197]. Temperatures as low as 140 °C [123] and as high as 300 °C [66] have been reported for HTC processes (See Table 2). However, it is important to note that processes below 200 °C fit better in the HWE category. The W:B ratio also varies among works, but Aragon-Briceno et al. showed that higher W:B ratios increase hydrochar mass yields [30]. Jiang et al. [37] present a discussion on the effect of this ratio on the HTC reaction mechanism and product yields. The duration of the process is generally in the order of a few hours (See Table 6). Very informative reviews on the HTC process and the resulting products and the corresponding characteristics can be found, for example, in [68,79,81,198].Table 7..

Works on HTC have typically focused on optimizing the process conditions for obtaining high solid yields (i.e., hydrochar). However, HTC has also been used as a pretreatment step before pyrolysis of, for example, brewer's spent grains, which helped to increase the porosity and relative C content of the obtained biochar and to reduce its ash content [199], or for fuel pellets with improved properties [200]. As in the case of biochar produced via fast or slow pyrolysis, hydrochar has several potential or proven applications for environmental remediation, soil amendment, carbon sequestration, and energy storage [26,201]. The yields of the aqueous byproduct in HTC depend of the raw materials and the process conditions [68]. The aqueous byproduct of HTC of materials such as wastewater can have high chemical oxygen demands (CODs) and high total organic carbon (TOC) content, besides phenols, sugars, and polycyclic aromatic hydrocarbons [196,202,203]. Thus, this liquid can constitute an environmental pollutant [203]. The viability of HTC is expected to improve if this fraction is adequately used [58,189], with biogas production as a leading option (Section 4.1.3). Different types of materials have been processed via HTC as shown in Table 6. A detailed discussion on the integration of HTC with AD of the liquid byproduct, including LCA (life cycle assessment) and economic analyses, has been reported by Ipiales et al. [58]. Following, we discuss some findings reported on biomass HTC and the aqueous byproduct.

As seen in Table 6, sewage sludge is a material commonly used for HTC. The interest on using wet thermochemical processes for treating sewage sludge arises from the necessity of processing such high-moisture content material and the presence of pollutants (e.g., pathogens, heavy metals, and persistent organic pollutants), besides its unpleasant smell. As in the case of other WTCPs such as HWE, there is no common criterion for the conditions of the process (i.e., temperature or the water to biomass ratio). Villamil et al. and Rubia et al. conducted HTC of dewatered sewage sludge at 208 °C for 1 h (using a pressure vessel reactor), using a 4.44 water to biomass ratio (mass), with a heating rate of 3 °C/min [196,212]. The liquid byproduct's properties were as follows: pH: 5.1 ± 0.1, COD: 95.5 ± 0.4 g O2/L, BOD_5: 25.6 ± 1.1 g/L, TS: 55.7 ± 0.5 g/L, VS: 46.2 ± 0.5 g/L, TOC: 42.6 ± 0.9 g/L, and TKN: 8.7 ± 0.1 g/L. This material was subjected to AD for methane production. The concentrations of formic, acetic, *iso*-butyric, and butyric acids were 1420 ± 20 mg/L, 2269 ± 33 mg/L, 930 ± 11 mg/L and 94 ± 4 mg/L, respectively.

He et al. [204] carried out a study that helped to identify how HTC conditions remove metals from dewatered sewage sludge. The authors conducted HTC at temperatures varying from 200 to 380 °C for 20 min in each case. It was found that Cu and Pb concentrations in the liquid fraction remain constant. However, the concentrations of Cr, Zn, Ni, Ca, Al, Fe, and P decrease as the treatment temperature increases. Ni was not detected in the liquid resulting from the treatments above 260 °C

Table 6
Some works on biomass HTC and main findings about liquid byproduct properties.

Raw material	HTC conditions	Products: Main findings, yields, and properties	References
Dewatered sewage sludge (DSS) (85 % moisture content)	HTC of DSS at 208 °C for 1 h (heating rate of 3 °C/min).	Liquid fraction characteristics: pH: 5.1, soluble COD: 95.5 g O_2/L, TS: 51.9 g/L, VS: 46.2 g/L, BOD: 25.6 g/L, TOC: 42.6 g/L, TKN: 8.7 g N/L. This liquid fraction was used for AD.	[58,196]
Dewatered AD sewage sludge	320 and 380 °C for 20 min. W:B=~4.7. CaO as CO_2 were added to the process.	CaO improves dehydration reactions. Decarboxylation and hydrolysis reactions dominate the process.	[204]
Sewage sludge	170 to 320 °C, 0.5 to 6.0 h.	The liquid fraction was separated via centrifugation and used for AD.	[122]
Sewage sludge	170 to 320 °C, for 30 min, agitation at 500 rpm.	The liquid fraction was separated via centrifugation at 10,000 prior to AD.	[121]
Sewage digestate	250 °C for 30 min. HTC solids concentrations: 2.5, 5.0, 10.0, 15.0, 17.5, 20.0, 25.0, and 30.0 % w/w.	pH of the process above 7.7 for all treatments. P content (total and reactive) increased as the solid loading increased, but HTC removed only a fraction of the total P in the feedstock. Liquid was used for AD.	[193]
Sewage Sludge (mix of primary and secondary sludge)	190 °C for 1 and 3 h. Recycling of process water and hydrochar.	Treatment time does not affect concentrations of, e.g., NH_4^+-N and TCOD. Liquid was used for AD.	[205]
Swine manure	190 °C for 1 h.	Solid was used for AD and liquid was used as a fertilizer.	[206]
Wood mix	HTC at 215–295 °C for 5 to 60 min.	Higher sugars content in the liquid fraction were obtained in the material processes at low temperature; acetic acid increased as the processing temperature increased.	[66]
Poplar wood chips	HTC at 220 °C for 4 h. W:B = 5. Process water recirculation (4 cycles for water characterization. 19 cycles to reach equilibrium).	~15 % of the C in biomass was dissolved in the liquid fraction. pH ~ 3.5. Up to 50 % of TOC originated from organic acids.	[207]
Corn silage (processed in a technical scale plant)	Treatment at 220 °C for 6 h.	Main compounds identified: acetic acid (which accounted for 13 % of the overall TOC content), propionic acid, and phenols.	[208]
Orange pomace	Temperatures from 175 to 260 °C for 30, 60, 90, and 120 min. W:B = 8.	pH of liquid: 3.6 to 4.9. Main compounds detected: sacarose, fructose, formic acid glycose, lactic acid, acetic acid, and HMF and furfural, depending on the process's conditions.	[195]
Algae (*Laminaria*)	220 °C for 120 min, using a W:B = 20. Process water was recirculated 12 rounds.	Water recirculation increased hydrochar yield. VFAs accumulated in the process water by up to 19.5-fold. COD of the process water increased 7.9-fold, TN content increased 9.4-fold, and TP increased from 27.1 to 207.9 mg/L after water recirculation.	[191]
Microalgae	150 °C for 30 min*, using a 1.5 L reactor	Aqueous phase contained 56.5 g/L SCOD, 18.5 g/L TOC, and 1.65 g/L of reducing sugars. The sum of acidic components (formic + lactic + acetic + succinic + propionic + butyric acids) was 62. 86 g/L. This material was treated via AD	[209]
Poultry litter	200 and 250 °C for 1 h. W:B = 3. Pilot scale reactor to produce large amounts of liquids. Process water was recirculated for 5 cycles.	DOC concentrations increased after the recirculation of process water. A similar trend was found for dissolved N and TAN, but the opposite was verified for TP.	[189]
Wheat straw and other woody materials	190, 230, 250, or 270 °C for 6 h.	TOC was not affected by process severity (i. e., temperature) or feedstock type. Both temperature and raw material, however, C_2-C_6 affected fatty acids content.	[210]
Agricultural digestate	200 °C for 270 min at isothermal conditions.	Liquid phase contained: acetic acid, 3-pyridinol, 1-hydroxyacetone, and 1,3-propanediol.	[211]

Nomenclature: TS - total solids, VS- volatile solids, BOD - biochemical oxygen demand, TOC – total organic carbon, TKN - total Kjeldahl nitrogen, AD - anaerobic digestion, SCOD – Soluble chemical oxygen demand. *Despite the low temperature of the process, the authors refer to it as HTC.

(suggesting that this temperature shows the best metals immobilization performance). Higher temperature treatment had positive effects on Cr precipitation (from 1.12 mg/L at 200 °C to 0.78 mg/L at 380 °C). The authors mentioned that metals were transformed into dissolved ions under hydrothermal conditions and metal sulfonation took place after cooling down [204]. Another work using sewage sludge was conducted by Chen et al., who characterized the liquid byproduct of HTC at temperatures ranging from 170 to 320 °C and from 0.5 to 6.0 h [122]. Additionally, Chen et al. [121] also used similar temperatures for HTC of the same material, but at shorter times. In both works, the wastewater was then used for AD (See Section 4.1.3).

Aragón-Briceño et al. processed sewage sludge at 250 °C for 30 min, varying solids concentrations from 2.5 to 30.0 % w/w. pH of the process

Table 7
Ph and group parameters (toc, cod, bod, uv) of process water at the beginning of the htc and after recirculation[207], with permission.

Sample	pH	TOC (g/L)	COD (g/L)	BOD_{10}[a] (g/L)	UV_{254} (1/m)	COD/TOC (mgO_2/mgC)	UV_{254}/TOC
HTC-Ref	3.4	17.4	50	24	23.1	2.8	1.3
HTC-Recirc1	3.3	25.1	72	nd	24.5	2.8	1.0
HTC-Recirc2	3.3	33.0	82	nd	28.7	2.4	0.9
HTC-Recirc3	3.4	33.7	91	nd	31.2	2.7	0.9
HTC-Recirc4	3.4	39.2	101	55	27.2	2.5	0.7

nd – Not determined.
[a] – Dilution 1:1000.

was above 7.7 for all treatments [193]. The sum of total and reactive P increased as the solids load increased, but saturation was reached at 15 % solids load. Nevertheless, the P removed was only a fraction of that in the feedstock. HTC reduced between 24 and 37 % of the feedstock mass. TS concentration in process waters increased from 2.4 g/L initially present in the digestate liquor to 39 g/L in the process water at 30 % solids loading. Fig. 10 shows the behavior of COD, VFAs, TOC, TKN, TP, RP, TS, and VS in the liquid as the solubilization changes. Another work on HTC processing of sewage sludge shows that recirculation of the liquid fraction and part of the hydrochar is a promising path for improving biogas yields [205]. In a related work, Ferrentino et al. showed options for using the liquid as fertilizer [206].

Hoekman et al. [66] conducted HTC of a mix of wood materials at temperatures from 215 to 295 °C, and times from 5 to 60 min. Higher temperatures reduced the yield of chars and increased the yield of gaseous and liquid products. The char's energy content was highest when the process was conducted at 255 °C for 30 min (i.e., 39 % higher energy density than the raw material). As expected, the aqueous byproduct obtained at lower processing conditions (215–235 °C) showed higher levels of sugars than in the process at higher temperatures, while acetic acid yields increased. Thus, the yields of solids or liquid products can be controlled by controlling the process conditions. The aqueous byproduct is considered biodegradable [81].

Other materials processed via HTC are orange pomace, corn silage, wheat straw, ad agricultural digestate. Erdogan et al. used HTC to treat orange pomace at temperatures from 175 to 260 °C for 30, 60, 90, and 120 min [195]. The pH of liquid varied from 3.6 to 4.9. The main compounds found in the liquid were: saccharose, fructose, and formic acid (at lower treatment conditions), glycose (at high treatment conditions), lactic acid, acetic acid (which increased as the severity of the treatment increased), and HMF and furfural that decreased as the temperature of the treatment increased. The aqueous byproduct was used

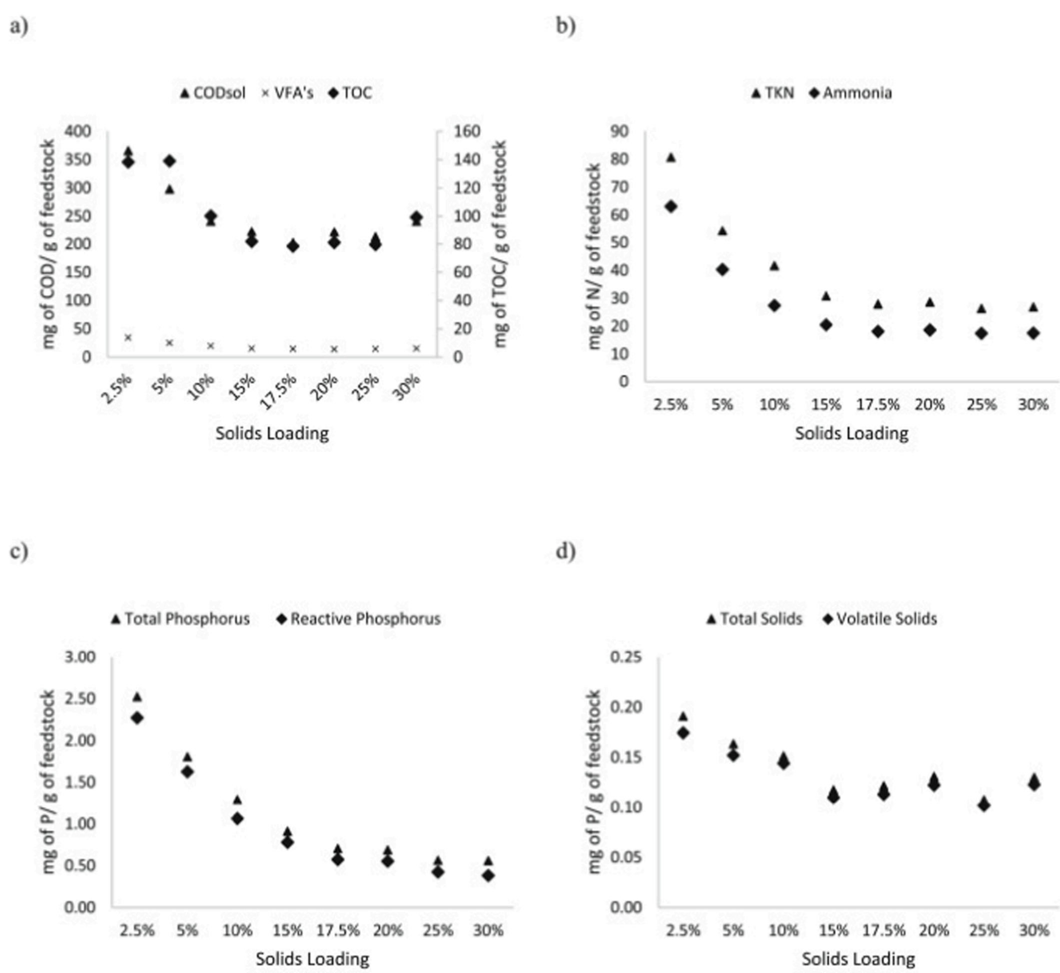

Fig. 10. Solubilization of (a) carbon-rich compounds (COD), VFAs, TOC); (b) nitrogen-rich compounds (TKN and Ammonium; (c) phosphorus-rich compounds (TP and RP); and (d) solids (TS and VS) [193].

for AD. Wirth and Mumme [208] used the aqueous fraction from HTC of corn silage for AD. This appears to be one of the few works that employ a technical scale plant for HTC of biomass. The material was treated at 220 °C for 6 h. The properties of the liquid were as follows: pH: 3.88, TS: 2.80 w%, VS: 79.06 w%, TOC: 15.66 g/L, COD: 41.35 g/L, acetic acid: 5.26 g/L, propionic acid: 0.34 g/L, phenols: 0.29 g/L, S: 90.80 mg/L, P: 197.40 mg/L, ammonia nitrogen: 229.50 mg/L, and TKN: 685.50 mg/L. As in the work of Erdogan et al. [195], the aqueous byproduct was also used for AD. Results of the AD of the aqueous phase showed that COD degraded up to 75 % and TOC up to 54 %. A work using wheat straw and other woody materials carried out by Becker et al. concluded that the severity of the HTC process and the type of material do not affect the TOC of the liquid byproduct [210]. However, these two process parameters did affect C_2-C_6 fatty acids abundance. An additional work used agricultural digestate for HTC treatment and found that the aqueous byproduct was constituted mainly by acetic acid, 3-pyridinol, 1,3-propaneidiol, 1-hydroxyacetone, and acetone, as well as formic acid, methanol, propionic acid, and 2-methoxyphenol in smaller amounts [211]. A subsequent ultrafiltration process (10 kDa membrane) allowed the reduction of COD by up to 30 %, BOD by up to 10 %, and DOC by up to 21 % in the liquid.

Table 6 shows that anaerobic digestion (AD) is a standard treatment for the aqueous byproduct obtained from HTC. Aerobic degradation has recently been tested as another potential method for this purpose, but the corresponding treated liquid can still be too polluted to be discharged in wastewater treatment plants [194]. Recycling process water is a feasible strategy to make the liquid byproduct less toxic and more suitable for AD. This also helps in conserving water resources [189,191,207,213,214]. Stemann et al. subjected poplar wood chips to HTC at 220 °C for 4 h. The process water was recirculated four cycles to characterize the water properties and 19 cycles to assess equilibrium behavior [207]. The liquid contained up to 50 % of TOC (total organic carbon) (Tabe 7), mainly from organic acids. Fig. 11 shows the main compounds identified, along with their respective concentrations.

Wang et al. [191] explored the impact of process water recirculation on the properties of HTC products using algae. The HTC process was carried out at 220 °C for 120 min with a W:B ratio of 20. The researchers recirculated the process water 12 times and found that this approach increased the hydrochar yield and helped to reduce water process toxicity. Additionally, VFAs accumulated in the liquid during the water recirculation, which appeared to benefit methane production in AD. VFAs concentration of the process water increased 19.5 times from step 0 to step 8 (i.e., from 3.4 to 85.2 g COD/L). The VFAs corresponded to 13.8 % of the total COD in step 0, and increased to 57.7 % in step 8. The COD of the process water increased 7.9-fold (i.e., from 23 to 185 g/L) and the TN (total nitrogen) content increased 9.4-fold (i.e., from 315.5 to 2973.7 mg/L) from step 0 to step 12, which is attributed to proteins degradation. After water recirculation, TP (total phosphorous) increased from 27.1 to 207.9 mg/L. Other characteristics of the water process that changed due to recirculation were conductivity and salinity. Algae has also been processed via HTC by Yang et al. [209]. The aqueous byproduct was constituted by 56.5 g/L SCOD, 18.5 g/L TOC, 1.65 g/L of reducing sugars, 22.18 g/L of soluble protein, and 11.35 g/L of soluble total carbohydrate, in addition to 62. 86 g/L of acidic components (formic + lactic + acetic + succinic + propionic + butyric acids) and small amounts of furfural and HMF. This liquid fraction was treated via AD.

In a work of Mau et al. [189], poultry litter was processed at 200 and 250 °C for 1 h, using a W:B = 3, intending to concentrate nutrients before using it as a fertilizer. The process water was recirculated for five cycles. Then, large amounts of the aqueous phase were obtained using a pilot-scale plant (30 L HTC reactor, at 200 °C for 1 h) to test as a fertilizer. As in the work of Wang et al. [191], DOC concentrations increased after recirculating the process water (from 24 to 49 g/L), but such increase was verified until HTC cycle 3 only. A similar trend was found for dissolved N and TAN. However, dissolved P and PO_4^{3-}-P showed a decreasing tendency. Salinity also increased and the concentration of organic acids reduced pH. The work shows that combining aqueous-phase recirculation and using it as a fertilizer could be a strategy for increasing HTC efficiency and economic feasibility.

2.5. Hydrothermal liquefaction (HTL)

Both HTC and HTL are conducted under water subcritical conditions, but HTL is carried out at higher temperatures than HTC (in the 250–370 °C range; i.e., below the critical point of water) and intends to produce predominantly a liquid product called "biocrude" [33,79]. Regarding the main target product, biomass HTL can be comparable to biomass pyrolysis, but in HTL water acts as a catalyst that can help reduce O content in bio-oil [215]. Processes at the pilot and demonstration scales have been reported [79], including, for example, Genifuel Corporation (licensing a technology from the Pacific Northwest National Laboratory – PNNL) (https://www.merrick.com/project/hydrothermal-processing-pilot-system/) [37]. A few companies are reaching or have reached commercial scale to process biomass and for plastics recycling. These companies include MURA and its HydroPRS™

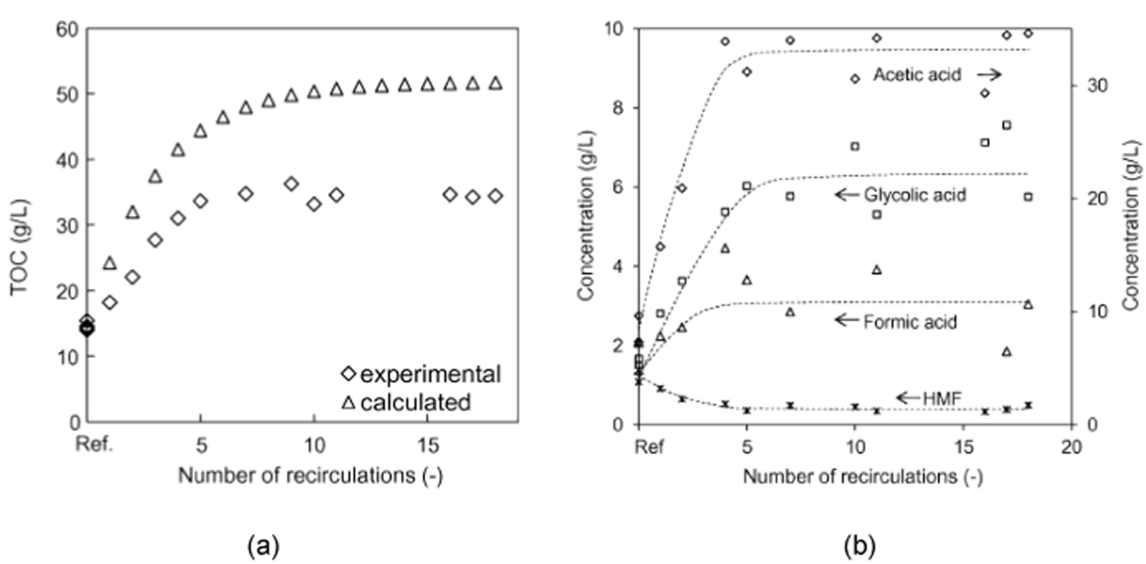

Fig. 11. (a) TOC and (b) concentration of identified compounds in process water as a function of recirculation cycles in HTC of poplar chips [207], with permission.

technology (https://muratechnology.com/news/), Licella and its Cat-HTR™ technology (https://www.licella.com/technology/cat-htr/), HyFlexFuel (https://www.hyflexfuel.eu/technologies/), and Circlia Nordic (https://circlianordic.com/), showing that HTL is one of the most advanced WTCPs for biomass processing to fuels. HTL is employed for processing wet biomass sources (e.g., microalgae, macroalgae, sewage sludge, and various types of lignocellulosic biomass and organic wastes) to produce crude bio-oil. In addition to the biocrude, other products of HTL are char, an aqueous byproduct (sometimes called HTL wastewater), and gases in relatively smaller amounts [216]. The gas byproduct from wet distillers' grains HTL can be composed of up to 95 % CO_2, 1.6 % H_2, and small amounts of N_2, CO, CH_4 and traces of short-chain alkanes and alkenes [217]. Alkaline catalysts can help suppress char formation and improve bio-oil yield and quality [79].

Depending on the conditions of the liquefaction process, the aqueous byproduct from HTL can contain between 27 and 50 % of the biogenic carbon [218]. This byproduct has until recently been seen as a waste stream that could hinder the possibilities of scaling up the HTL technology. Thus, proper valorization of it is necessary. The separation of the aqueous fraction from the crude bio-oil can be carried out, for example, via extraction with organic solvents such as hexane [219] and dichloromethane [220]. The aqueous fraction contains N-heterocyclic structures (mostly pyrazine derivatives) and other organic compounds [221,222]. A review describing the HTL process, the products' characteristics and yields, and the possibilities of separating and adding value to the aqueous byproduct from this process has been carried out by Watson et al. [223], and the mechanism that governs the HTL process can be seen, for example, in Jiang et al. [37]. Therefore, this section presents only a synthesis and a quick update about works reporting yields and composition of the HTL aqueous byproduct. Table 8 shows works on biomass processing via HTL and relevant findings on the aqueous phase.

An important parameter to expectedly help the valorization of the HTL aqueous phase is its chemical composition, which depends on the raw material and the thermal processing conditions. Lopez Barreiro et al. [220] subjected algae (both marine and freshwater algae) to HTL at 300 °C for 15 min. The yields of the aqueous phase ranged from 18 to 32 %. This phase was constituted by acids (glycolic, formic, acetic), which were more abundant in the freshwater algae byproduct. In the liquid, TC varied from ~ 1200–16400 mg/L, TOC from ~ 10100–14100 mg/L, TN from ~ 4000–5400 mg/L, and NH_4^+ from ~ 2700 to 4400 mg/L. In another study with algae, Maddi et al. [224] subjected to HTL at 350 °C. The composition of the HTL aqueous phase included organic acids (acetic, propanoic, and butanoic acids), N-containing compounds (e.g., pyridine, pyrazine, acetamides, 2-piperidinone, 2-pyrrolidinone, succinimide, and their alkyl derivatives), and oxygenates (e.g., cyclopenatanone, 2-butanone, 2-pentanone, and dianhydromannitol). An additional study with algae (*Chlorella pyrenoidosa*) conducted by Gai et al. [225] (with HTL at 260–300 °C for 30–90 min) showed that the byproduct contained high C (COD up to ~ 62740 ± 2950 to 104000 ± 45700 mg/L), N (TN: ~11000 ± 306 to 31700 ± 1350 mg/L), and P (TP: ~5440 ± 255 to 18900 ± 915 mg/L), which resulted from the algae lipids and nutrients content.

Zhou et al. [226] reported the effect of Na_2CO_3 (as a catalyst) in the HTL in the range of temperatures from 220 to 320 °C using marine macroalgae. The yields of water-soluble products (aqueous fraction) were 34.3–45.2 wt% [226]. The process without the catalyst showed a pH in the range of 6.5–7.0, but adding the catalyst increased the pH (to 7.5–8.0). The main compound identified in the aqueous fraction in the process without a catalyst of HTL at 300 °C was acetic acid (~34.7 % of the total), which increased to ~ 57 % when the catalyst was added.

A method to reduce the yields of aqueous byproducts (thus making the HTL process more sustainable) is recirculating the aqueous phase [213,220 217,232]. However, the biocrude can become richer in N as the aqueous phase recirculates, thus limiting the number of recirculation cycles [213]. In a different work, using spiruline, Egerland et al. [222]

Table 8
Works involving HTL of biomass and main findings on the yields and composition of the aqueous byproduct.

Raw material	HTL conditions	Main findings	References
Marine and freshwater algae	HTL at 350 °C for 15 min, in microautoclaves.	Yield of aqueous phase ranges from 18 to 31 % and biocrude from 52 to 60 % and contains glycolic acid, formic acid, and acetic acid. pH > 8.	[220]
Algae (both marine and freshwater algae)	350 °C (20.7 MPa) using a continuous-flow, bench-scale system.	The aqueous phase contained organic acids, N-containing compounds, and oxygenates.	[224]
Algae (*Chlorella pyrenoidosa*)	260–300 °C, 30–90 min.	pH around 8, High C, N, and P content.	[225]
Macroalgae *Enteromorpha prolifera*	Batch reactor, temperatures 220–320 °C, with Na_2CO_3 as catalyst.	HTL at 300 °C with 5 wt% Na_2CO_3 for 30 min led to the highest bio-oil yield of 23 wt%. The aqueous byproduct was constituted mainly by acetic acid.	[226]
Swine manure	270 ± 10 °C and with a solids content of 13 %, for 1 h.	COD and BOD_5 concentration of the aqueous phase was ~ 39,825 mg/L, and ~ 12,200 mg/L, respectively. Aqueous phase was used for AD.	[227]
Terrestrial biomass	Unknown	Carboxylic acids were used for H_2 production (via AD) using different catalysts.	[218]
Spirulina	260 °C for 60 min. Solids concentration of 20 wt%.	Characteristics of aqueous phase: COD: 162.1 g/L, pH: 8.42, TN: 16.1 g/L, NH_4^+-N: 8.9, TP: 0.76 g/L, TS: 38.3, TVS: 33.6 g/L. Byproduct was used for AD.	[222]
Cornstalk	260 °C; reactor was stopped immediately after reaching the target temperature.	Aqueous byproduct was constituted of formic acid, lactic acid, acetic acid, propionic acid, butyric acid, 5-HMF, and furfural	[228]
Human waste	280 °C for 60 min.	COD concentration of 52606 mg/L, TN: 1160 mg/L, ammonia: 592 mg/L.	[229]

(*continued on next page*)

Table 8 (*continued*)

Raw material	HTL conditions	Main findings	References
Sewage sludge	325 °C for 30 min.	Aqueous phase characteristics: TS: 16.53 ± 0.94 g/L, VS 15.18 ± 0.73 g/L, COD: 19.30 ± 0.90 g/L, TOC: 4.44 ± 0.44 g/L, TN: 3.04 ± 2.52 g/L. The byproduct was used for AD.	[230]
Sewage sludge	220 °C for 3 h.	Filtrate's final concentration and mass of TAN increased with the increasing hydrothermal temperature and duration.	[231]
Sewage sludge	170–320 °C, 0.5–6.0 h using a buffer ($NaHCO_3$).	Temperature and time impact NH_3-N, proteins, and carbohydrates content in the aqueous phase. Byproduct was used for AD.	[122]
Sludge	347 °C, externally heated reactor	Water with soluble organics (acidic acid, acetone, methanol), ammonia, and metal salts	[232]
Wet distillers grains	CatLiq® process, 350 °C for 6 h.	In addition to acids (acetic, propionic, butanoic), aqueous fraction contained methanol, ethanol, 1-propanol, and butanol in small amounts.	[217]

showed that the characteristics of the aqueous phase from HTL of spirulina were: COD: 162.1 ± 2.98 g/L, pH: 8.42, TN: 16.1 g/L, NH_4^+-N: 8.9 ± 0.73, TP: 0.76 ± 0.06 g/L, TS: 38.3 ± 0.14, TVS: 33.6 ± 0.26 g/L. In another publication, the aqueous fraction of corn stalk HTL (at 260 °C) contained reducing sugars: 11.34 ± 3.01 mg/L, TOC: 28.60 ± 1.34 mg/L, TN: 1.05 ± 0.09 mg/L, COD: 76.19 ± 1.56 mg/L, formic acid: 8.51 ± 1.54 mg/L, lactic acid: 9.76 ± 1.39 mg/L, acetic acid: 22.34 ± 2.48 mg/L, propionic acid: 2.73 ± 0.86 mg/L, butyric acid: 9.07 ± 2.14 mg/L, 5-HMF: 1.35 ± 0.30 mg/L, and furfural: 0.14 ± 0.02 mg/L [228]. The type of raw material, combined with recirculation of the aqueous fraction, can also result in the presence of small amounts of alcohols (e.g., methanol, ethanol, 1-propanol, and butanol), as reported by Toor et al. [217], who subjected wet distillers' grains to HTL at 350 °C for 6 h, and Snowden-Swan et al. [232], who worked with sludge (at 347 °C). In these works, however, it is not mentioned how recirculation impacts the formation of the alcohols in the aqueous byproduct.

A study that used swine manure showed that the characteristics of the HTL aqueous phase were: COD and BOD_5 concentrations of 39825 ± 884 mg/L and 12200 ± 346 mg/L, respectively; acids detected included lactic acid (7597 ± 873 mg/L), acetic acid (2415 ± 170 mg/L), propionic acid (2176 ± 31 mg/L), i-butyric acid (456 ± 76 mg/L), n-butyric acid (2464 ± 86 mg/L) and valeric acid (489 ± 10 mg/L). The TN was 1685 ± 53 mg/L and the NH_4^+-N was 555 ± 7 mg/L [233].

HTL of sewage sludge (at 325 °C for 30 min) resulted in an aqueous phase constituted by: TS: 16.53 ± 0.94 g/L, VS: 15.18 ± 0.73 g/L, COD: 19.30 ± 0.90 g/L, TOC:4.44 ± 0.44 g/L, TN: 3.04 ± 2.52 g/L, phenolic compounds 2654.11 ± 98.71 mg/L, acetate 1531.86 ± 66.37 mg/L, propionate 748.03 ± 36.38 mg/L, butyrate 125.39 ± 8.07 mg/L, Na: 59.23 ± 1.62 mg/L, ammonium 1993.71 ± 26.36 mg/L, K: 179.64 ± 9.43 mg/L, Mg: 29.15 ± 1.01 mg/L, Ca: 1.97 ± 0.12 mg/L, chloride 197.98 21.11 mg/L, phosphate 36.31 ± 1.15 mg/L, and sulfate 497.08 ± 27.44 mg/L [230]. In another study using the same material, the COD of the aqueous fraction from HTL at 220 °C for 3 h was 72800 ± 300 mg/L [231]. Longer treatment times resulted in increased TAN. Moreover, Chen et al. showed that the temperature and time of the HTL process of sewage sludge decrease protein and carbohydrates content in the aqueous fraction [122]. Also, the HTL of human waste processed at 280 °C for 60 min was constituted by COD concentration of 52606 ± 1577 mg/L, TN: 1160 ± 28 mg/L, and ammonia concentration of 592 ± 88 mg/L [229].

2.6. Supercritical water gasification

WTCPs for biomass conversion under supercritical water conditions include supercritical water oxidation (SCWO) and supercritical water gasification (SCWG) [37,74,234]. To the best of our knowledge, the literature does not report works that have included separating and characterizing the aqueous byproduct after biomass SCWO. At commercial scale, SCWO is used for industrial wastewater treatment. An example of a company offering this technology is Aquadern Technologies (https://aquarden.com/the-scwo-method/) and its SuperOx® process. A related process called hydrothermal oxidation (which is conducted under subcritical water conditions) is a technology also used for municipal and wastewater treatment. Examples of this technology are a) the Athos™ process, owned by Veolia Water Technologies (https://www.veoliawatertechnologies.com/en/solutions/technologies/athos), and b) the Aquacitrox® process (owned by the H + E Group) (https://www.he-water.group/en/technologies/aquacritox.html), designed to operate under supercritical conditions but nowadays operating at subcritical conditions. Therefore, this section focuses on SCWG. SCWG, or hydrothermal gasification, is a thermochemical process for obtaining synthesis gas (constituted by H_2, CO, CH_4, and CO_2, in different proportions) from biomass, using water as the medium and main reactant [235]. Hydrogen is frequently the targeted product in biomass SCWG [80]. Water acts as a solvent with high solubility for organic compounds and gases under supercritical conditions [76]. Thus, the role of water is twofold: to work as a reactant and medium by generating H^+ and OH^- ions that promote an environment for hydrolysis and pyrolysis reactions [236]. SCWG is conducted at temperatures up to ∼ 800 °C and pressures up to 36 MPa, using different types of raw materials: from biomass constituents (e.g., cellulose and lignin) to sawdust, bagasse, leather residues, sewage sludge, black liquor from pulp mills, or animal manure, in either batch or continuous reactors [80]. Examples of companies offering SCWG for wastewater treatment include Gasunie (https://www.gasunie.nl/en/projects/supercritical-water-gasification), TreaTech (https://trea-tech.com/technology/), and Cade Engineered Technologies (https://cadeengineering.com/scwg/).

Because the targeted product in SCWG is syngas, authors only sporadically report the composition of the aqueous product after SCWG of, for example, dairy manure, a common material that has been processed using these WTCPs [237]. The composition of the aqueous byproduct from SCWG can be very complex, depending on the raw materials and the treatment conditions [238]. In addition to hydrogen, targeted products from SCWG include liquid fuels, such as diesel (e.g., via gas-to-liquid technologies), and chemicals [72,80]. Integration of SCWG with HTL processes is an option for better use of biomass constituents [239,240]. The process governing parameters are temperature, pressure, feedstock concentration, and residence time [241]. Heating the water to reach the processing parameters can be expensive due to high energy requirements. Table 9 shows some works on biomass SCWG, the conditions of the processes, and the aqueous product yields and composition.

Nanda et al. processed pinecone under different thermal conditions (including subcritical water treatment) [243]. For SCWG, the material was processed at 550 °C (and 23 MPa) for 15, 30, 45, and 60 min using a batch (tube) reactor. The yield of the aqueous fraction varied from 77.7 to 64.7 wt% as the treatment time increased and was constituted by acetic acid (67.3 mM concentration), acetone (33.1 mM), glycolic acid (1.4 mM), methanol (140 mM), phenol (6.2–9.1 mM), and propionic acid (7.2 mM). In another work, woody materials (sawdust) subjected to SCWG (at 500–600 °C) resulted in aqueous fraction constituted by carboxylic acids (acetic acid, formic acid, and hydroxyacetic acid) and furfural, phenols, and aldehydes. As expected, the yield of the liquid byproduct decreased as the temperature increased [244].

SCWG is a preferred route to produce hydrogen from some types of biomass, such as chicken manure with high moisture content [72,245]. The hydrogen yield using SCWG is higher than in other biomass thermochemical processing routes [80]. Cao et al. studied the effect of adding activated carbon in the SCWG of chicken manure (after a preliminary cleaning process) at temperatures from 500 to 620 °C. Both liquid and gas products were characterized [72]. The hydrogen yield was highest at 600 °C (25.2 mol/kg of manure). The aqueous byproduct was constituted by a long list of C_4-C_{14} compounds, with visible abundance of phenols (e.g., phenol, 4-methyl phenol, and 4-ethyl phenol, regardless of the processing temperature), N-heterocyclics, benzene and substituted benzenes, aromatics (e.g., indole and 4-methyl-1H-indole), and carbocyclics. The presence of these compounds decreased as the temperature of the process increased. Such abundance and diversity of compounds could result from the complex chemical composition of chicken manure (e.g., fats, protein, and other inorganic materials, in addition to lignocellulosic components) [246]. Some compounds such as indole, pyrimidine, and aniline in the aqueous fraction can serve as platform chemicals [247].

Table 9
Works on SCWG of some types of biomass sources: conditions and products.

Raw material	SCWG conditions	Product yields and composition	References
Chicken manure	SCWG in fluidized-bed reactor at 500–620 °C, with and without catalyst (activated carbon-AC).	Max. H_2 yield 25.2 mol/kg, at 600 °C, with 6 wt% AC. Aqueous byproduct contained phenol and substituted phenols, N-heterocyclics, benzene and substituted benzenes, carbocyclics. Organic compounds decreased as temperature increased.	[72]
Sunflower stalk, corncob, leather waste	Batch reactor at 500 °C (heating rate 3 °C/min), for 1 h at isothermal conditions, using four types of catalysts.	The aqueous byproduct contained phenols, furfural, formic acid, and acetic acid, among other compounds.	[242]
Pinecone	Tubular batch reactor, 550 °C for 15–60 min, with and without catalysts.	Aqueous fraction decreased as treatment time increased. Identified compounds: Acetic acid, acetone, glycolic acid, methanol, phenol, propionic acid.	[243]
Woody wastes (from pine and fir)	500–600 °C (20.0——42.5 MPa) with or without catalyzer (10 wt% K_2CO_3).	Aqueous byproduct contained carboxylic acids, furfurals, phenols, aldehydes, and ketones.	[244]

Yanik et al. used three types of biomass sources (sunflower stalk, corncob, and leather waste) for SCWG, using a batch reactor and four types of catalysts (K_2CO_3, Trona ($NaHCO_3.Na_2CO_3{\cdot}2H_2O$), red mud (Fe-oxide containing residue from Al-production), and Raney-Ni) [242]. The reactor was slowly heated (at a heating rate of 3 °C/min). Hydrogen production was around 2.5 times higher when catalysts were employed. Phenols, furfural, formic acid, and acetic acid, among other compounds constituted the aqueous byproduct. Table 10 shows the products' composition of the liquid after SCWG of the three raw materials. The increase of TOC seems to result from the increase in phenol concentration of the aqueous phase.

2.7. Alkali and low acid pretreatment processes

2.7.1. Alkali pretreatment

Alkaline and diluted acid hydrolysis are the two preferred chemical processes for lignocellulosic biomass pretreatment to obtain sugars in high yields and relatively low costs [57,248]. These processes can be used alone or combined with other treatments. Alkaline pretreatment is one of the oldest WTCPs employed for the modification of biomass properties. It has its roots in the work of Watt, who patented the well-known soda-pulping process in 1854 [249]. Alkaline pretreatment processes include ammonia recycle percolation (ARP), ammonia fiber explosion/expansion (AFEX), soaking in aqueous ammonia (SAA), low-liquid ammonia (LLA), low-moisture anhydrous ammonia (LMAA), and other alkaline technologies using NaOH and $Ca(OH)_2$. The process is carried out at temperatures relatively lower than or close to those used in other thermal pretreatments such as HWE, steam explosion, and HTC (i.e., at up to ~ 120 °C [250]. However, some processes can work at temperatures as high as 180 °C for several minutes, with hemicelluloses degradation up to 50 % [248], and even higher temperatures (e.g., up to 220 °C) [124]. Processes conducted at temperatures above 200 °C could fit in the HTC category (Section 2.4), but they are included in this section due to the use of alkali or acids. Table 11 synthesizes published works on alkali and low acid treatments and the main findings related to the aqueous byproduct.

In alkaline pretreatment, the digestibility of cellulose is improved, and the degradation of hemicelluloses is less intensive than in acid treatment; alkaline reagents are more efficient for lignin removal [248]. One of the drawbacks of the alkali treatment process could be the high cost of alkalis [251]. However, the alkali WTCP has shown advantages compared to thermal treatment without alkali (at the same temperatures), as shown, for example, by Li et al. [124], who subjected sewage sludge to alkaline hydrothermal pretreatment using $Ca(OH)_2$ to adjust the pH to 9.0–11.0. The treatments were conducted in the 140–220 °C range for 30 and 60 min. The process results were compared with those of a thermal treatment under similar temperatures but without adding $Ca(OH)_2$. Adding $Ca(OH)_2$ performed better in the mechanical dewatering of the pretreated sludge. The higher the pH, the better the dewaterability of the pretreated sludge. Puitel et al. [250] conducted alkali thermal treatment of corn stover and wheat straw at temperatures from 80 to 120 °C for 60 to 120 min, with 2-10 wt% NaOH. Higher temperatures and longer treatments resulted in yields of hemicelluloses (in the aqueous byproduct) up to 62 % and ~ 51 % for wheat straw and corn stover, respectively, with xylose as the main constituent. In another work, cotton stalk was processed to obtain xylan that, with lignin, was used for producing composite films (See Section 4.2) [252].

Yang et al. [253] conducted hydrothermal treatment of husks of nuts from *Carya cathayensis* Sarg. in the range of temperatures of 180 to 260 °C with pH varying from 4 to 10 (pH was adjusted with HCl or NaOH). Water soluble and acetone soluble products (WSP and ASP, respectively) were quantified to determine the total soluble products resulting from the treatment. The yield of WSP slightly decreased as the processing temperature increased, while the ASP increased when the treatment temperature increased. However, the total of WSP and ASP remained almost unchanged as the temperature increased from 180 to

Table 10
Yields of constituents in the aqueous fraction after SCWG of sunflower stalk, corncob, and leather processes at 500 °C for 1 h, using different 4 types of catalysts [242] (with permission).

Constituent	Sunflower stalk					Corncob					Leather				
	No AC*	K_2CO_3	Trona	Red mud	Ra-Ni	No AC	K_2CO_3	Trona	Red mud	Ra-Ni	No AC	K_2CO_3	Trona	Red mud	Ra-Ni
TOC	17.09	14.11	19.03	12.90	13.68	20.01	25.17	23.10	29.79	34.59	19.47	10.89	18.19	10.05	–
Phenols	7.52	4.85	6.32	4.57	5.38	0.60	8.45	8.11	11.36	11.51	0.68	3.90	4.54	None	–
Furfurals	0.48	0.03	0.05	0.01	0.03	0.09	0.01	0.03	0.02	0.04	0.01	0.14	0.03	0.03	–
Formic acid	1.19	2.02	2.57	1.22	0.89	0.75	1.24	1.27	0.89	0.31	0.83	1.45	1.07	0.44	–
Acetic acid	0.79	0.59	1.45	1.24	0.74	3.90	1.13	0.92	2.93	9.42	1.68	0.45	0.54	0.67	–
Dioxan	0.25	0.13	0.20	0.19	0.17	0.04	0.05	0.02	0.10	0.05	0.16	0.13	0.17	0.16	–
Hydroxy acetic acid	0.07	0.08	0.13	0.20	0.06	0.03	0.08	1.12	0.08	0.09	None	None	0.06	0.09	–

* AC – Activated Carbon.

Table 11
Works that used alkali and low-acid thermal processes for biomass pretreatment and main findings related to the aqueous byproduct.

Raw material	Process conditions	Main findings	References
Alkali treatments			
Corn stover and wheat straw	80–120 °C with 2-10 wt% NaOH.	Xylan extraction yields of 62 % and ~ 51 % for wheat straw and corn stover, respectively.	[250]
Cotton stalk	Alkali extraction (solution containing KOH + $NaBH_4$).	Xylan without complete removal of lignin (used for composite film production).	[252]
Low-acid treatments			
Grape stalks	Low-acid treatment (121 °C for 90 min, 2 % H_2SO_4).	Main hemicellulose-derived products: Furfural, 5-HMF, and gallic acid.	[254]
Corn stover	165–195 °C for 3–12 min, with 0.5–1.4 % H_2SO_4.	Aqueous phase contained 34 g/L xylose, 8 g/L glucose, 8 g/L acetic acid, 0.73 g/L furfural, and 1 g/L HMF.	[255]
Husks of nuts from *Carya cathayensis* Sarg	180 to 260 °C for 10 min, varying pH (from 4 to 7).	Water-soluble products and acetone-soluble products were separated. The optimal treatment was 180 °C.	[253]
Wheat straw	200–260 °C for 6 h, solvent: biomass = 20.	pH of liquid was ~ 4 in all treatments. Most abundant compounds: furfural, HMF, formic acid, lactic acid, and glucose in the treatment at 200 °C. Lactic acid and glucose in the treatment at 260 °C.	[256]
Pine wood	Low-acid thermal treatment, 140–190 °C.	Liquid was used for furfural and acetic acid production.	[46].

260 °C, suggesting that the lower treatment temperature was adequate for processing these materials.

2.7.2. Low-acid pretreatment

Low-acid hydrothermal (LAH) treatment is usually conducted at temperatures higher than in alkali pretreatment processes. While dilute acid favors hemicellulose hydrolysis, alkaline hydrolysis targets the lignin fraction [57]. The acids frequently used for LAH treatment are sulfuric acid [46] and formic acid [257]. The severity of the process can be evaluated using the severity factor, the combined severity factor, or an extended severity factor [257]. As in previously discussed hydrothermal operations such as HWE and steam explosion, the yields of hemicellulose-derived products (e.g., xylose) increases as the severity of the process becomes more intense. The kinetics of LAH treatment depends on acid load, temperature, residence time, and liquid-to-biomass ratio [258].

Jung and Oh [46] investigated a process to optimize the yields of hemicellulose-derived sugars from pine wood via a low-acid catalyzed hydrothermal process (Table 11). LAH was conducted at 140–190 °C for 5–30 min, with 0.25 and 0.50 % H_2SO_4. The maximum yield of hemicellulose-derived sugars was 82.5 wt% when the wood was treated at 190 °C with 0.5 wt% H_2SO_4 for 10 min. This fraction was then used for furfural production (See Section 4.1.1). Grape stalks processed under low-acid conditions (at 121 °C for 90 min) resulted in a liquid byproduct containing mostly furfural, 5-HMF, and gallic acid [254].

Another type of material subjected to hydrothermal modification using both acid and alkali conditions is wheat straw, which was treated at temperatures from 200 to 260 °C for 6 h using a solvent to biomass ratio of 20 [256]. The liquid from the HTC at 200 °C contained furfural, HMF, formic acid, lactic acid, fructose, sucrose, and glucose, whereas the aqueous f product from the treatment at 260 °C was rich in lactic acid and glucose. Additionally, Agbogbo and Wenger [255] subjected corn stover to acid hydrolysis at 165–195 °C for 3–12 min, with H_2SO_4 (0.5–1.4 %). The aqueous byproduct contained up to 33.54 g/L xylose, 8.19 g/L glucose, 7.93 g/L acetic acid, 0.73 g/L furfural, and 1.00 g/L HMF. This fraction was used for ethanol production.

3. Characterization of hemicellulose-derived products

The potential applications of hemicellulose-derived products depend chiefly on their properties. Thus, a necessary step before deciding about such applications is the characterization of the aqueous fractions. No matter the WTCP employed to obtain hemicellulose-rich aqueous fractions, the set of techniques used for the characterization is similar. Characterization techniques allow us to 1) identify and quantify chemical compounds in the aqueous fraction and 2) identify the paths for the formation of hemicellulose-derived compounds during WTCP. Appropriate analytical techniques also help us to understand the reaction mechanism(s) that result in specific compounds or intermediate products [259]. The analytical methods employed to characterize hemicellulose-derived compounds include: a) high-performance liquid chromatography (HPLC), b) ultra-high-performance liquid chromatography – ion mobility – quadrupole time-of-flight – mass spectrometry (UHPLC-IM-Q-TOF-MS), c) High-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD), d) gas chromatography- mass spectrometry (GC–MS), e) Gas Chromatography Flame Ionization Detection (GC-FID), f) Nuclear Magnetic Resonance (NMR), g) Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), and h) ion chromatography (IC).

Sugars, byproducts, and degradation products can be analyzed by HPLC following the National Renewable Energy Laboratory method

(NREL/TP-510-42623) [260] or via IC [4]. HPLC with refractive index detection can directly quantify monomeric sugars, byproducts, and degradation products. Oligomeric sugars can be converted into monomers via acid hydrolysis and then quantified by HPLC with refractive index detection [148,260]. Furanic and phenolic compounds can be identified by using HPLC [261]. Likewise, the presence of sugars can be detected using IC [4]. UHPLC-IM-Q-TOF-MS has also been used to characterize degradation products with high molecular weight that may be generated during the thermal process [259]. HPAEC-PAD is an analytical technique for carbohydrates determination [262]. Monteiro et al. employed hydrothermal treatment to depolymerize hemicellulose in mango seed shell to produce xylooligosaccharides, and HPAE–PAD was used to quantify xylose and xylooligosaccharides generated during the process [263]. Sun et al. used integrated pretreatment to degrade poplar structure, and HPAEC was employed using an integral amperometric detector to measure monosaccharides and xylooligosaccharides content [264] Similarly, Chen et al. [265] applied HPAEC to determine monosaccharides and xylooligosaccharides in an aqueous solution, Sun et al. [266] also studied an integrated method coupling ultrasonic and hydrothermal pretreatments with sequential alkali post-extractions to isolate and characterize hemicelluloses from perennial ryegrass and enhance the enzymatic hydrolysis. In this study, the sugars and uronic acids were determined by HPAEC.

Identification of the volatile compounds generated from hemicellulose-derived compounds in the aqueous phase can be determined by GC–MS or GC-FID [261,267]. Organic acids, fatty acids, aromatic compounds, and modified sugars are some examples of compounds that GC–MS can identify. The composition of the liquid fraction after supercritical water gasification has been characterized using GC–MS. Cao et al. [72] conducted supercritical water gasification (SCWG) of chicken manure to produce hydrogen, and GC–MS was used to investigate the organic compounds in the liquid effluent. The results showed that the main compositions of liquid products include phenol and substituted phenols, N-heterocyclics, benzene, and substituted benzenes and carbocyclics. GC–MS detected some products such as indole, pyrimidine, and aniline. Organosolv pretreatments using ethanol and water mixtures with dilute sulfuric acid were employed on Sitka spruce sawdust to obtain improved saccharification yield and valuable co-products [78]. A high amount of hemicellulose sugar in this pretreatment process was converted into ethyl glycosides as detected by GC–MS [78]. GC–MS has also been used to identify monosaccharide composition, including glucose, galactose, mannitol, gluconic acid, xylose, and ribose generated in HWE of *Deverra tortuosa* waste [268]. However, GC–MS has some limitations in detecting high molecular weight and complex compounds [259]. Degradation compounds formed during WTCP can be detected and quantified by NMR. Fuso et al. [259] used ^{1}H NMR to detect and quantify organic acids, modified sugars, and aromatic compounds generated during the hydrothermal treatment of hemicellulose. The acetyl groups attached to the xylan backbone were evaluated by H NMR analysis. Gas chromatography coupled with time-of-flight mass spectrometry (GC –TOF–MS) is a more advanced analytical technique that provides more information about the chemical composition of the WTCP's aqueous phase [62].

MALDI-TOF-MS is another effective tool to analyze oligo- and polysaccharides derived from hemicellulose [269]. Nakahara et al. [270] used MALDI-TOF/MS analysis, which can identify structural characteristics without denaturation of the molecular structure, to study the behavior of beech xylan as treated by semi-flow hot-compressed water. In addition, Chemical Oxygen Demand (COD) is a testing method to determine the amount of organic pollution found in wastewater that has been used to evaluate the effect of WTCP [271]. Other methods to assess COD before and after WTCP are, for example, the Open Reflux Method, Closed Reflux Titrimetric Method, and Closed Reflux Colorimetric Method [272].

4. Routes to add value to WTCP aqueous fractions and resulting products

Until recently, the aqueous fraction after biomass pretreatment was considered of low value and too complex for practical applications [78]. The complex nature of this aqueous stream (i.e., the presence of several chemical compounds that accompany hemicellulose-derived products) makes it challenging its direct use through routes developed for hemicelluloses transformation. According to Abejón [53], the literature search using the terms “hemicellulose” and “valorization” showed results only after year 2003. Therefore, most works dealing with the valorization of these aqueous fractions are based on the rich experience working with isolated (pure) hemicelluloses. Despite these challenges, there is an increasing interest in this aqueous byproduct as it offers opportunities to produce several value-added products [273]. [53] Hemicelluloses valorization includes the production of high-value chemicals such as xylose and xylitol [17] and other products after chemical modification, including nutritional supplements, packaging materials, emulsifiers, encapsulating agents, adhesive components, sugars [274], and fuels and lubricants [20]. Qaseem et al. [59] presented an updated review on the use of hemicelluloses for these applications. Therefore, this section only summarizes findings reported in the literature.

Hemicelluloses are highly water-soluble and heterogeneous materials, with low degree of polymerization (in the 80–200 range), which could limit specific conversion routes. Modification of hemicelluloses has been employed to produce derivatives, resulting in, for example, benzylated hemicelluloses, carboxymethylated hemicelluloses, butyrylated hemicelluloses, acylated hemicelluloses, lauroylated hemicelluloses, and stearoylated hemicelluloses. Modification requires using different types of solvents such as ethanol/water, N, N-dimethylformamide/lithium chloride, anhydrous DMSO-d_6, and 1,2-dimethoxyethane [47]. Fig. 12 presents possible routes for hemicelluloses modification. Four routes have been identified: etherification, esterification, graft copolymerization, and crosslinking. The valorization of hemicelluloses and/or hemicellulose-derived fractions obtained via WTCP operations are in part based on these concepts. Fig. 13 shows three possible paths for using or transforming the aqueous byproducts from WTCPs into value-added products; i.e., 1) recovery and direct use, 2) separation of nutrients and chemicals, and 3) conversion into fuels and chemicals. These pathways agree with those identified by Leng et al. [62]. Table 12 shows examples of works reporting the composition of the aqueous byproduct of WTCPs using different types of raw materials, which allows using the fraction for a specific targeted product. It is seen that the composition of the aqueous byproduct largely depends on raw materials and process. As a common trend, the constitution of the aqueous byproduct directs the targeted use. For example, ethanol production is carried out using liquids richer in sugar precursors, and fertilizers can be produced mainly from liquids richer in nutrients.

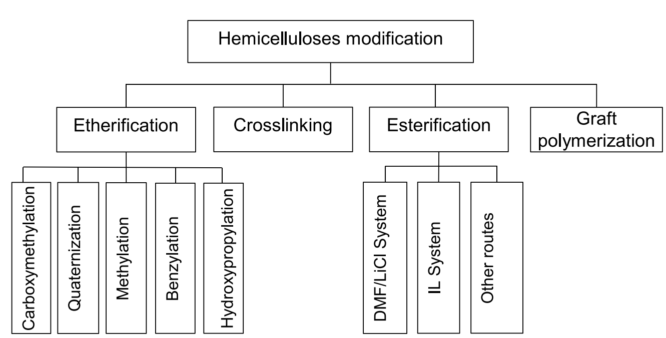

Fig. 12. Routes for the modification of hemicelluloses (DMF – N,N-Dymethylformamide; IL – Ionic liquid) [275].

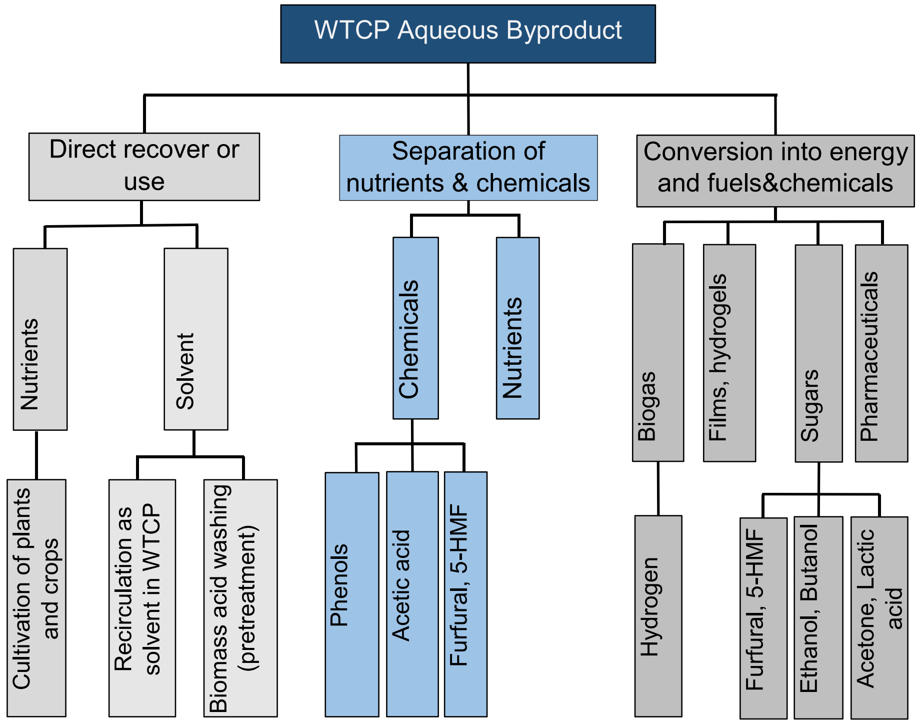

Fig. 13. Pathways for the valorization of the aqueous phase resulting from biomass WTCPs and some expected products. Adapted in part from [49].

4.1. Sugars for chemicals and biofuels

4.1.1. Chemicals

Hemicellulose-derived sugars serve as raw materials for producing liquid biofuels for the transportation sector and lubricants [20], succinic acid, lactic acid, ethyl lactate, adipic acid, polylactic acid (PLA), PHA, 1,4 butanediol, and acrylic acid [93], intermediate chemicals (e.g., pyridine, pyrazine, and their alkyl derivatives) for agrochemicals and drugs [224], xylitol for pharmaceutical products and other uses [19], and packaging and adsorbent materials [69]. The possibilities of using xylan for producing chemicals have been reviewed by Rafiqul et al., Umai et al., and Naidu et al. [16,18,21]. Galactoglucomannans (GGMs) can be used in the food, health products, papermaking, textile, and cosmetic industries [89,94,277,278]. Mannans can also serve as stabilizers of oil-in-water beverage emulsions [279] and to produce conductive biocomposites [280]. Specific works on the use of the hemicellulose-rich aqueous byproduct from WTCPs for chemicals and fuels are summarized following.

4.1.1.1. Furfural and HMF as platform chemicals. Furfural and HMF (C_5 and C_6 molecules, respectively) are two platform molecules that can serve as intermediates for the transformation of biomass into chemicals (e.g., fertilizers, plastics, paints, and fungicides) and fuels in biorefineries [56,281,282]. Furfural is a precursor of furan-based chemicals and jet- and diesel–fuel-range hydrocarbons that are of interest in the transportation sector [46,283]. Under specific conditions, the liquid byproduct of WTCPs should result in high yields of xylose (the pentose that serves as the source to produce furfural). The conditions of the WTCPs, however, could also allow the direct formation of furfural and HMF [93,95,112], but the corresponding yields can be too low to be considered of practical interest. Therefore, the conversion of hemicelluloses to furfural requires a) hydrolysis of the polysaccharide into xylose, and b) dehydration of xylose to obtain furfural by removing three molecules of water [284]. Ntimbani et al. [285] showed that producing furfural from biomass (after a steam explosion pretreatment) is more economically promising than producing ethanol alone or a combination of ethanol with furfural in biorefineries. Steinbach et al. reviewed the possibilities of producing furfural and HMF using specific biomass WTCP, i.e., steam explosion, HWE, diluted and concentrated acids, and alkaline solutions [52]. The authors presented a detailed discussion on the selection of raw materials, mechanisms of furfural formation, catalysts used, challenges, and the formation of byproducts of furfural synthesis. An economic and environmental assessment of furfural production has been presented by Contreras-Zarazúa et al. [286]. Thus, this section presents only a short discussion on the main findings of works that used the aqueous byproduct of WTCP for furfural.

Some works related to WTCPs have intentionally optimized the conditions of the process to obtain high yields of furfural and other platform chemicals. For example, Jung and Oh [46] carried out a low-acid hydrothermal treatment of pine wood, intending to fractionate wood's constituents into furfural and acetic acid (See Table 12). The xylose in the aqueous fraction was converted into furfural using 0.73 M of $ZnCl_2$ (as a catalyst). The reaction happened at different temperatures (160, 170, and 180 °C) using a molten salt bath for 30 min. The process reaction was terminated by rapid quenching in an ice-water bath. Then, solvent extraction with ethyl acetate allowed furfural separation. The reaction at 170 °C for 30 min resulted in the highest yields (7.93 g/L) of furfural, with a conversion of xylose into furfural of 93.7 %. Longer reaction times reduced furfural yields due to furfural decomposition, as previously found by Köchermann et al. [276].

The aqueous byproduct of the organosolv processing of eucalyptus wood was used in another work to produce furfural [176]. The organosolv process was conducted at 140–170 °C with 1 % H_2SO_4 (Section 2.3). Organosolv lignin was precipitated from the aqueous fraction, and the remaining fraction was subjected to hydrolysis before producing furfural using, again, an acidic medium in the same reactor employed for the organosolv process. Furfural yields up to 7.9 mass% were obtained from combining the organosolv process at 160 °C and acid hydrolysis at 180 °C.

4.1.1.2. Xylitol for pharmaceuticals and other products. Xylose from the aqueous fraction of WTCPs can be isolated and used for producing xylitol, which is of interest in the food, cosmetic, deontological, and pharmaceutical industries [19,21,287]. Xylitol is commercially

Table 12
Examples of works on the valorization (targeted product) of hemicelluloses-rich aqueous byproducts from WTCPs.

Targeted product	WTCP	Hemicelluloses origin	Main compounds/materials in the aqueous stream	References
Biogas	HWE	Sewage sludge	Acids (Acetic, Benzene Acetic, Butanoic, Pentanoic, Propanoic). Alkenes, Phenolic and Aromatic Compounds, Aldehydes, Furans, Pyrroles, Pyrazines, and Pyridines Ammonia Nitrogen	[123,124]
	Organosolv	Sweet sorghum stalks	Free Sugars (Sucrose, Fructose, Glucose, Xylose), Alcohols	[182]
	HTC	Sewage sludge	Proteins, Volatile Fatty Acids (Acetic Acid, Propionic Acid, Isobutyric Acid, Butyric Acid, Isovaleric Acid,And Pentanoic Acid), Ammonia Nitrogen, Amino Acids (Alanine, Glutamate, Glycine, Aspartic Acid, Valine, Leucine And Threonine) Mg^{2+}, Phosphorus And Carbohydrates, Tryptophan-Like, Fulvic Acid-Like And Humic Acid-Like Compounds. Organic Species: Pyrazines, Pyrimidines, Ketones, Phenols, Amides, Pyridines	[73,121,122,193,196,205,212]
	HTC	Swine manure	Ammonium Nitrogen, Micro-Nutrients (K, Na, Ca, Mg), Organic Nitrogen, C.	[206]
	HTL	Sewage sludge	Organic Carbon, N, Phenolic Compounds, Acetate, Propionate, Butyrate, Na, Ammonium, K, Mg, Ca, Chloride, Phosphate, Sulfate	[122,230]
	HTL	Swine manure	Organic Acids (Lactic, Acetic, Propionic, Butyric, Valeric), Ammonia Nitrogen, N, P.	[227]
	HTL	Spirulina	N, Ammonia Nitrogen, P	[222]
Fertilizer	HWE	Palm oil empty fruit bunches	Macronutrients (N, P, K, Ca, Mg), Ba, Fe, Mn, Zn (Not detected: Pb, Cd and Cr)	[126]
Ethanol	HWE	Sugarcane bagasse	Xylan, Xylose, Glucan, Furfural, Glucose, 5-HMF	[117]
	Acid thermal pretreatment	Corn stover	D-Xylose, Glucose, Acetic Acid, Furfural, 5-HMF, Phenolic Compounds	[255]
Sugars	HWE	Hardwood and softwood	Monomeric Sugars (Xylose, Mannose, Galactose), Xylo-Oligosaccharides, Acids (Acetic, Formic, and Levulinic), and Furans (Furfural, 5-HMF)	[103]
Hydrogen (from CH_4 via AD)	HTL	Terrestrial biomass	Carboxylic Acids (Acetic, Glycolic, Propionic), Ketones, Alcohol (1,3-Butanediol; Methanol. Ethanol; And 1-Butanol), Ethylene Glycol.	[218]
Chemicals (xylitol)	Steam explosion	Poplar wood	Monomeric Sugars (Xylose, Glucose, Mannose, Galactose, Arabinose), Xylo-Oligosaccharides, Phenolic Compounds, Furan Derivatives (Furfural, 5-HMF), and Acetic Acid	[172]
Chemicals (furfural)	Organosolv	Eucalyptus	Pentoses (Xylose, Mannose, Galactose), Glucose Lignin, Klason Lignin, Acid Soluble Lignin	[176]
	Organosolv	Beech wood	Glucose, D-Xylose, Arabinose, Xylooligosaccharide, 5-HMF, Furfural, Acetic Acid, Ethanol	[276]
Chemicals (polyhydroxybutyrate)	HWE	Hybrid poplar	Glucose, Xylose, Galactose, Arabinose and Mannose, Acetic Acid, Furfural	[93]
Chemicals (lactic acid)	HWE	Hardwood species mix	Glucose, Mannose, Galactose, Xylose, Arabinose, Lactic Acid, Formic Acid, Acetic Acid, Furfural	[116]

produced using a chemical route by catalytic hydrogenation of pure xylose through five steps: 1) acid hydrolysis of xylan, 2) purification of xylose, 3) catalytic hydrogenation of xylose, 4) purification of xylitol obtained, and 5) crystallization of xylitol [288]. New processes (i.e., microbial and enzymatic conversion) are being developed to produce xylitol as an alternative to chemical processes [19,172,287].

Vithanage et al. [172] used the aqueous byproduct from steam-exploded poplar woodchips for xylitol production. The aqueous fraction was a mix of the liquid directly obtained after the steam explosion process (purge liquid) and the liquid resulting from squeezing the solids. This aqueous phase was constituted by monomeric sugars, *xylo*-oligosaccharides, phenolic compounds, and organic acids. The aqueous phase was then hydrolyzed to monomeric xylose + other sugars using H_2SO_4 at different concentrations (0.3 – 1.0 % w/v) at 121 °C for 1 h. The pH of the hydrolysates was adjusted to 5.5 using 2.0 M NaOH and used as a fermentation substrate employing both batch and fed-batch fermentation modes in shake flasks (~10 g/L of *Candida guillermondii* FTI 20037). Results showed conversion of xylose to xylitol of 0.30 g xylitol/g xylose (equivalent to 4.9 g/L) in the batch process, which occurred with a 2-fold diluted prehydrolyzate (i.e., aqueous phase). This result was lower than that using pure xylose (i.e., 0.53 g xylitol/g xylose or 9.9 g/L). The process was improved by removing inhibitors (responsible for low xylitol yields). Detoxication of the aqueous phase was employed (Amberlite IRA-400 resin, chloride form)) to remove inhibitors before fermentation. After detoxication, the yield of xylitol increased to up to 8.9 g/L. The fed-batch fermentation further increased the yield of xylitol to 22.0 g/L when the detoxified hydrolysate was employed. Therefore, acid hydrolysis of the aqueous stream after WTCPs, followed by detoxication and fed-batch fermentation, offers an attractive way for xylitol production.

4.1.1.3. Hydrogen. Hydrogen is one of the targeted products from biomass SCWG. Hydrogen yields depend on the conditions of the SCWG process and the type of catalyst employed [242,245]. The aqueous byproduct from other lower-temperature WTCPs can also be subjected to SCWG for hydrogen production [245]. Other processes to produce hydrogen from the aqueous byproduct from HTL of biomass have been proposed, for example, by Davidson et al. [218]. The carboxylic acids present in the aqueous phase can be upgraded using three approaches: 1) catalytic upgrading into chemicals via condensed-phase ketonization reaction, 2) catalytic upgrading to H_2 via direct steam reforming, and (3) catalytic upgrading to H_2 via anaerobic digestion (to CH_4) followed by steam reforming. One of the problems for direct catalytic upgrading is the deactivation of the catalyst, which makes it necessary to clean up the aqueous phase before the process using activated carbon, followed by liquid–liquid extraction. The potential of converting the cleaned aqueous fraction into hydrogen was demonstrated by using condensed-phase ketonization (for ≈100 h) and steam reforming. Steam reforming employed a dual-bed catalyst configuration (to reduce coke deposition) in which carboxylic acids were subjected to ketonization over CeO_2 (in vapor phase) followed by steam reforming of the ketone intermediates over Co/CeO_2. A techno-economic analysis was included by the authors [218].

4.1.1.4. Other chemicals. Other chemicals produced using the aqueous fraction from WTCPs include levulinic acid [111,289], polyhydroxybutyrate [93], lactic acid [116], and acetic acid [46], among others. Levulinic acid (a low molecular weight carboxylic acid) can serve as a platform chemical [111] to produce: 1) chemicals such as tetrahydrofuran (which serves as solvent), succinic acid (as chemical intermediate), δ-Aminolevulinic acid (as a herbicide), N-alkyl pyrrolidone (as a solvent or for fine chemicals), and diphenolic acid (for polymers production), and 2) liquid fuels and additives (e.g., levulinic acid esters, valeric acid and pentenoic acid and their esters, γ-valerolactone, 2-methyl-tetrahydrofuran, n-Octane, and aromatics) through different routes [290,291]. The conversion of hexoses (glucose and fructose) to levulinic acid is accompanied by the formation of formic acid through a mechanism in which HMF serves as an intermediate. HMF is formed by hexoses dehydration [111].

Rivas et al. [111] used the aqueous fraction from HWE pine to produce levulinic acid. In the process, the aqueous fraction was processed in acidic media (by adding H_2SO_4 at different concentrations) for longer times (up to 10 h) using an autoclave at 120, 130, and 140 °C. Levulinic concentrations close to 50 mmol/L were obtained at high process severity. Resulting byproducts included acetic acid and formic acid. A model was proposed to predict the concentration profiles of these compounds. In the model, major steps included: conversion of oligomers into monosaccharides, conversion of hexoses into HMF, decomposition of HMF into levulinic and formic acids, dehydration of pentoses into furfural, and conversion of furfural into formic acid. Under the best conditions assayed, the yield of levulinic acid accounted for 66 % of the stoichiometric value.

Lactic acid is a chemical of interest in the pharmaceutical and food industries. Lactic acid was produced from the aqueous fraction of HWE of a mix of hardwood chips [116]. The extraction process used either water or 2 % total titratable alkali (TTA) of green liquor (containing 0.88 g/l NaOH, 2.57 g/l Na_2S, and 8.16 g/l Na_2CO_3) with a W:B = 4 and added anthraquinone (0.05 %) to improve delignification. The process was conducted at 160 °C. A hydrolysis step (with H_2SO_4 to reach a pH of 1) was conducted prior to the production of lactic acid. Fermentation was performed at 50 °C under agitation, using *Bacillus coagulans* MXL-9. Results showed that the liquor containing 45 g/L of total monosaccharides (mainly galactose and arabinose) produced 33 g/L of lactic acid and consumed the sugars entirely.

4.1.2. Liquid biofuels

The prospects of producing biofuels, specifically ethanol, from hemicelluloses have been reviewed in previous publications of Girio et al., Kuhad et al., Avanthi et al., and Chandel et al. [292–295]. Other works have reviewed the impact of thermal pretreatment of biomass on biofuels and chemicals production [40,41,248]. Transforming hemicelluloses into ethanol requires that hemicellulose-derived sugars are readily available for fermentation [296]. Sugars can also be used to produce furfural that can subsequently serve to produce other fuels such as renewable diesel and jet fuel [297]. Since the intensity of the WTCP could not guarantee that enough sugars are available in the aqueous byproduct to make the process attractive, a hydrolysis step is frequently necessary to transform hemicellulose-derived products into sugars. After sugars production, ethanol production only requires a fermentation step.

Ethanol production from sugars is a very well-known process, which explains why only a few works report the whole process to obtain ethanol from hemicellulose-derived sugars using the aqueous byproduct from WTCPs. Among these works, Agbogbo and Wenger [255] used the aqueous byproduct of dilute acid treatment of corn stover (see composition in Table 11) for ethanol, using a pilot scale process. The aqueous byproduct was neutralized with NH_4OH to pH 6 and sterilized. Fermentation was carried out in an air-shaker incubator at 30 °C at 100 and 150 rpm (for 48 to 96 h) in containers with 50 mL of sugar media, 1 mL of a nutrient solution, and 1 mL of inocula (i.e., cell concentration of 2 g/L). A buffer (1.5 mL of 1 M KH_2PO_4/NaOH, pH 6) was added to some fermentation media to obtain a final buffer concentration of 27.5 mM. Results showed yields up to 0.37–0.44 g ethanol/g (glucose + xylose), equivalent to 10.4–15.1 g/L. Treatments with higher concentrations of inhibitors (HMF and furfural) produced a lag of up to 6 h in the fermentation process.

Butanol is another drop-in fuel of increasing interest in the transportation sector [298,299]. Production of butanol (i.e., biobutanol) from hemicelluloses can be inefficient due to the expensive pretreatment of lignocellulosic biomass [300]. However, it is expected that the process can become more attractive when hemicelluloses are available as a byproduct from WTCPs, as demonstrated by Kudahettige-Nilsson et al. [301], who used xylan recovered from hardwood Kraft black liquor to produce butanol. In the work, Acetone–butanol–ethanol (ABE) fermentation was conducted after an acid-hydrolysis step (using H_2SO_4) to recover xylan and a detoxification process (using activated carbon). Xylose yields of up to 18.4 % were reported, and the detoxification process effectively removed phenolics and HMF. Butanol yields up to 7.3 g/L were achieved. As shown by [301], the most important industrial production strains for butanol are *clostridia*, which are advantageous for treating different types of sugars such as pentoses (xylose and arabinose), hexose (glucose, fructose, mannose, and galactose), disaccharides (lactose, sucrose, maltose and cellobiose), and polysaccharides (starch) [299].

4.1.3. Biogas

Biogas production from the liquid byproducts of thermochemical processes of carbonaceous materials has been a topic of interest for a long time. Early studies on HTC of peat suggested that this liquid could be anaerobically digested, resulting in the production of a “methane-rich fuel gas” [190]. Literature is abundant on later works describing the use of the aqueous phase from WTCPs for AD. A recent review by Ipiales et al. presents a comprehensive discussion on integrating HTC with AD of the HTC aqueous byproduct [58]. Therefore, this section provides only a synthesis of relevant studies on this topic. Table 13 presents studies on using the aqueous byproduct from WTCPs to produce biogas and biohythane. The interest in using the aqueous fractions from WTCPs for biogas arises from the necessity of expanding routes for biogas production. The volatility of NG prices and the need for local solutions for waste treatments justify such necessity. Sewage sludge is an abundant byproduct of wastewater treatment plants. Although sometimes used in agricultural applications, this material is often discarded in landfills or incinerated, resulting in greenhouse gas emissions, polluting local water resources, and negatively impacting the environment [302]. Sewage sludge can be alternatively treated through thermochemical processes such as pyrolysis and incineration, typically with lower energy efficiencies compared to HTC for treating, for example, fecal sludge [303].

Although HTC research has traditionally concentrated on a narrow selection of feedstocks, primarily pure substances, other studies have explored using more complex materials such as wood [306]. This expansion in the research scope has unveiled HTC as a promising method for enhancing digestate, leading to the generation of solid hydrochar and process water (aqueous byproduct) enriched with organic carbon. These HTC-derived products can serve as valuable soil amendments and have possess potential for energy recovery [307]. Parmar and Ross [307] assessed the effectiveness of HTC in enhancing the valorization of four distinct digestates generated from the AD of agricultural residue, sewage sludge, residual municipal solid waste, and vegetable, garden, and fruit waste. The findings of the study provide evidence that HTC can effectively be combined with AD to enhance the valorization of digestate, as supported by Ferrentino et al. [205]. The authors explored the recycling of HTC aqueous product and hydrochar generated from digested sludge back into the AD process, testing different compositions and individual substrates. Results showed that the biomethane yield almost doubled when the HTC liquor was cycled back to the AD and treated alongside primary and secondary sludge, reaching 102 ± 3 mL CH_4/g COD. Furthermore, when both the HTC

Table 13
Summary of works on AD of the aqueous byproduct from WTCPs.

Raw material	Process type and conditions	Biogas yield /composition	Reference
Sewage digestate	HTC (240 °C, 30 min)	max CH_4 production yield of 0.325 L/g COD / CH_4 content of 74–80 %	[193]
Primary and secondary sludge	HTC-ANUNCIO	max CH_4 production yield of 0.187 L/g COD / Not reported	[205]
Sweet sorghum stalks	Improved organosolv – AD	max CH_4 production yield of 0.271 L/g VS / Not reported	[182]
Dewatered sewage sludge	HTC – AD (208 °C; 1 h)	max CH_4 production yield of 0.177 L/g COD / Not reported	[196]
Sewage sludge	Hydrothermal/Alkali hydrothermal pretreatments – AD (140–220 °C; 30–120 min, pH: 9–11)	Not reported	[124]
Primary sewage sludge	HTC at different temperatures and retention times	Not reported	[123]
Oil palm empty fruit bunches (OPEFB)	AD with NaOH pretreatment	0.35 L/g VS / CH_4 content of 60 %	[304]
Winter rye, oilseed rape straw, faba bean straw	Wet oxidation pretreatment (195 °C; 15 min)	CH_4 production yield of 0.36 L/g VS	[305]
Sewage sludge	HTC (200–300 °C)	254 mL CH_4 /g volatile solids obtained from the treatment at 250 °C for 4 h	[122]
Sewage sludge	HTC (208 °C)	177 ± 5 mL CH_4/g COD	[212]
Cornstalk	HTL (260 °C) followed by AD of the aqueous phase using a UASB reactor	CH_4 content of 60–70 % and biohythane production yield of 0.18–0.22 L/g COD	[228]
Microalgae	HTC (150 °C) followed by AD using a multistage anaerobic hythane reactor (MAHR) and a UASB reactor	Average methane production rate was ~ 8.6 and ~ 6.2 L/L/d for MAHR and UASB, respectively. Methane content was ~ 70.2 % and ~ 54.5 %, respectively	[209]

liquor and hydrochar were fed to the AD process with primary and secondary sludge, the biomethane yield increased even further, reaching up to 187 ± 18 mL CH_4/g COD when 45 % of hydrochar (with respect to the total feedstock) was added. This study demonstrated the potential of coupling HTC with AD for sewage sludge treatment and its effectiveness in improving biomethane production. AD of the aqueous byproduct from HTC of algae has shown that the COD removal rate of improved AD reactors can be higher than processes using other types of raw materials for HTC [209].

An interesting approach to improve the methane yields of biomass during AD is via the integration of the aqueous and the solid phases. AD from both HTC products and the aqueous byproduct from other WTCP processes can be a viable and promising approach to improve biomass methane yields in sewage sludge management. Mao et al. [231] conducted a study that examined the integration of hydrothermal treatment and AD for the recovery of both bioenergy and struvite. The research used an HTL reactor and an AD reactor for the system integration of wet biomass valorization, exploring various hydrothermal conditions and determined that a treatment temperature of 220 °C for 3 h yielded the highest recovery of struvite from the dewatered sewage sludge mixture. Furthermore, a significant increase of 38 % in biomethane production was observed compared to the control.

De La Rubia et al. [212] conducted a study to examine the impact of inoculum source and initial concentration on the AD of the aqueous byproduct from sewage sludge HTC. During the study, three different inocula were collected from full-scale industrial anaerobic reactors operating under mesophilic conditions. The inocula tested were granular biomass from industrial reactors treating brewery and sugar beet wastewaters and flocculent biomass from a full-scale municipal sewage sludge digester. Two initial inoculum concentrations (IC) were used, 10 and 25 g COD/L. The study found that the effect of IC was different for each inoculum studied, with an increase from 10 to 25 g COD/L increasing the CH_4 yield by 23 % for brewery waste, achieving the highest value obtained (177 ± 5 mL CH_4/g COD) while declining to 99 ± 2 mL CH_4/g COD for sugar beet. The authors found that the inoculum-to-substrate ratio of 1 on a COD basis was optimal to improve the CH_4 production from the aqueous fraction of HTC of sewage sludge. The study concluded that the AD process was significantly affected by the inoculum source and initial concentration. Similarly, Chen et al. [122] conducted a study on the hydrothermal conversion of sewage sludge using a lab-scale reactor and various reaction conditions: 200-300°C, reaction time from 1 to 8 h, and a liquid:solid ratio of 10:1 under a nitrogen atmosphere to prevent oxidation. The study revealed that the corresponding aqueous products had a high chemical oxygen demand (COD) and a low pH. The CH_4 yields of the aqueous byproducts were found to be influenced by the reaction temperature and time, with the highest CH_4 yield (254 mL CH_4/g VS) obtained from the aqueous fraction processed at 250°C for 4 h.

4.2. Bioplastics, films, and hydrogels

Hemicelluloses can serve to produce bioplastics, films, hydrogels, packaging materials, and other bio-based materials for a long list of applications [252,308–319]. Hansen and Plackett [308] reviewed works on films and coatings production from hemicelluloses. The first step towards producing these materials is the fractionation of lignocellulosic biomass to obtain hemicelluloses [320], in which the positive role of WTCPs is evident. An excellent review about the production of bioplastics from hemicelluloses can be found at Brodin et al. [320]. According to the authors, the production of bioplastics normally follows routes practiced in the pulp and paper industry (i.e., biomass fractionation) and in the plastics industry (i.e., polymer polymerization). Commercially available bioplastics include PLA (polylactic acid), BioPE (bio-polyethylene), and PHA (polyhydrohyalkanoates) [320].

Ruiz et al. used the aqueous fraction resulting from HWE of wheat straw (treated at 180 °C for 30 min) to produce reinforcing κ-carrageenan/locust bean gum (κ-car/LBG) polymeric blend films [142]. The aqueous fraction was primarily constituted by xylan (82.2 mol%) and arabinan and glucan in less amounts. The process for producing the κ-car/LBG film is described in the referred work. Tested properties of the films included barrier properties (water vapor permeability), mechanical properties (tensile strength and elongation-at-break), moisture content, and opacity and thermal properties. The decrease of water vapor permeability and increase in tensile strength suggested that the aqueous fraction after HWE has positive effects as reinforcing materials in polymer blend films [142].

4.3. Fertilizers

P and N are essential nutrients for food production and plant growth. WTCPs (especially HWE, steam explosion, and HTC, conducted at mild temperatures, i.e., at up to ~ 200 °C) are promising approaches for reclaiming P, N, and other nutrients from biomass sources (e.g., animal manure) [34]. In HWE and steam explosion, P and N are partly solubilized/removed in the treatment water (the rest is retained in the solid products). A review of interest on the fate of P and N during HTC and the mechanisms of N transformation has been carried out by Aragón-Briceño et al. [321]. As expected, the findings associated with HTC apply, at least in part, to HWE and steam explosion.

Novianti et al. reported a work on the recovery of N, P, and K in the aqueous fraction of EFB during HWE [126]. Although the concentrations of macronutrients in the aqueous fraction were below those of commercial liquid fertilizers (resulting mainly from the relatively low N, P, and K content in the raw materials), it is expected that this fraction will serve as a fertilizer for agricultural applications if extra N, P, and K elements are added to the liquid (as required). The concentrations of harmful components in the liquid (i.e., Pb, Cd, and Cr) were low (or below the equipment's detection limits), which is important for using the liquid as a fertilizer. The presence of micronutrients (e.g., Ba, Fe, Mn, and Zn) was also detected, with a positive correlation with increased treatment temperature. The authors also presented a detailed procedure for phytotoxicity analysis of the liquid byproduct via seed germination and plant growth bioassay. The phytotoxicity tests showed positive results on the germination of seeds when the liquid resulting from treatment of EFB at temperatures up to 180 °C was used. However, no germination of seeds was observed when the aqueous fraction from the 220 °C treatment was tested, which could result from phenols, furfurals, and derivatives. Despite the positive results on the germination using the aqueous fraction from the lower temperature thermochemical treatments, it was suggested that dilution of the liquid is necessary for better phytotoxicity results. As the authors concluded, further work could provide a better picture of the potential and limitations of WTCP liquid byproducts for agricultural applications. In a related work, Nurdiawati et al. showed that the aqueous fraction from HWE of similar feedstock (i.e., EFB) can remove up to 37 % of N, 65 % of K, and ~ 10 % of P in the treatments at 220 °C [125].

Studies on the solubilization of N, P, and organics from swine manure in the HWE aqueous byproduct have been reported by Yuan et al. [27]. Treatments above 200 °C can convert > 98 % N into soluble form. Germination tests using the aqueous product from treatment at 150 °C for 60 min allowed seeds germination indices of ~ 100 %. An advantage of using this fraction from WTCP as fertilizer is that it is free of pathogens [189]. However, a concentration of nutrients appears necessary before using this liquid as a fertilizer. Recirculation of the water process during HTC (using a pilot-scale reactor) allowed increasing N, P, and K concentrations in the liquid up to 5400, 397, and 23300 mg/L, respectively, after three recirculation cycles [189]. The liquid was then assessed for lettuce growth, with results comparable to those obtained with commercial fertilizers. Combining water process recirculation and its use as a fertilizer can be a suitable approach for recycling nutrients back to soils and helping the viability of HTC. According to Ferrentino et al. [206], integrated use of the aqueous fraction (containing nutrients) as a fertilizer with AD of the solid product from HTC appears promising for producing liquid fertilizers and energy from swine manure.

The aqueous byproduct from steam explosion of pine wood has also been tested for growing lettuce. Jung et al. [171] prepared mixes of the liquid extract with commercially available nutrients (ascorbic acid, magnesium sulfate, citric acid, potassium nitrate, amino acid, and seaweed extract) and used to assess their influence on the growth of lettuce. Plant height, number of leaves, and leaves length were measured during the growing process. Fresh weight and dry weight of separated shoots and roots were also measured. Results showed that the mix of nutrients with hemicellulose-derived compounds in the liquid extract positively impacted (to a greater or lesser degree) all the variables measured. These positive results were partly attributed to sugars in the extracts.

It is important to note that the solid fraction resulting from WTCP also offers potential as a fertilizer. Nakhshiniev et al. [98] suggested that this solid, after aerobic digestion (composting), can serve as an organic fertilizer. The role of WTCP is to prepare the material for accelerated microbial degradation. However, only materials treated at relatively low temperatures appear adequate. The solid product of HWE at 160 °C shows potential for adequate composting, but aerobic digestion of materials resulting from treatment at higher temperatures (i.e., 200 °C and 220 °C) appears inefficient. Materials with high N and P content, processed at such relatively high temperatures are, nevertheless, hydrochars that can potentially be used as biochar for soil amendment.

Implementing strategies for nutrients recovery from the WTCPs aqueous streams is vital for producing sustainable fertilizers. Technologies such as ion exchange, precipitation, and membrane filtration can be employed to recover valuable nutrients for agricultural applications [322], thereby contributing to a circular economy in the valorization of WTCP aqueous fractions. The recovery and utilization of nutrients from the aqueous byproducts contribute to the circular economy by recycling essential nutrients back into agricultural systems.

5. Challenges and prospects for scaling up WTCPs and processing the corresponding aqueous byproducts

5.1. Challenges for scaling up WTCPs

Lignocellulosic biomass is a complex mixture of organic matter with inorganic impurities [323]. Biomass is also heterogeneous in particle size, origin, moisture and ash content, bulk density, anatomy, and chemical and elemental composition. Therefore, an inherent challenge before biomass chemical or thermochemical processing, both under dry and wet conditions, is to deal with this heterogeneity of characteristics. Pretreatment operations help to partially homogenize properties [10,11,324–327].

The pretreatment of biomass using WTCPs offers several challenges, primarily related to operational issues [56,79,245,319,328]. Operational issues in HTL and SCWG have been reviewed by Toor et al. and Ghavami et al. [79,245]. These issues include: a) process safety risks that result from mechanical stresses in the reactors and plugging due to solid deposition, b) difficulties of pumping the feedstocks, especially at high concentrations (i.e., low W:B ratios), c) catalyst deactivation, d) difficulty of controlling products quality and yields, e) corrosion, and f) operational costs. Operational costs of WTCPs are linked to the energy requirements and the need for expensive catalysts that are often deactivated in the process [319]. Catalysts used for HTL and SCWG include alkali metals, transition metals, activated carbon, and metal oxides, some of which can be expensive [245,329]. Cheaper catalysts used for other processes (e.g., H_2SO_4 used in low acid treatment) or processes with no catalysts (e.g., HWE and steam explosion) may be advantageous for some targeted products. The necessity of expensive solvents can be a limitation for adopting, for example, organosolv. Moreover, choosing an environmentally friendly solvent is necessary to prevent pollution. High investment costs [79], high production costs, and a lack of products that can be sold with profits can also be barriers to processing biomass using WTCPs at commercial scale [147]. The economics of WTCPs deserves more study because there is a lack of publications devoted explicitly to the use of the aqueous byproduct. The works of [60,232,330,331] can serve to expand this topic. Thus, a careful analysis of the advantages and disadvantages of each WTCP considering specific products and limitations should be conducted before designing biomass pretreatment and processing.

Some of the mentioned challenges for HTL and SCWG are also unavoidable in other processes such as HTC, steam explosion, and HWE because the aqueous byproduct in these processes is usually acidic and can contain salts, which result in corrosion of metallic components (i.e., reactors' walls and pipelines) exposed to acidic flows, char, and alkali salts [79,328,332]. Corrosion has been largely recognized as a problem that results in higher investment costs for WTCPs [43]. Pumping and plugging in continuous WTCPs is also difficult to avoid; thus, high W:B ratios are generally required for WTCPs such as HWE and organosolv [325] (see Sections 2.1 and 2.3). Methods for addressing WTCP challenges include reactors' configurations to reduce plugging and manage operational conditions to minimize other related issues [245]. Therefore, scaling up WTCPs requires the development of adequate equipment and infrastructure to ensure that the process is able to both maintain its efficiency at larger scale and keep product quality.

5.2. Challenges and prospects for the valorization of the WTCPs' aqueous byproduct

Despite the importance and opportunities of using the aqueous streams from WTCPs (See Section 1), several challenges need attention toward the valorization of these streams. These challenges are related to:

a) The low concentration of chemicals and nutrients of interest, mainly due to the necessity of using high W:B relationships in WTCPs. The valorization of the aqueous byproduct from WTCPs is challenging because these streams are usually dilute [218]. Thus, long and expensive processes for isolating/concentrating compounds from the aqueous byproduct in WTCPs (for example, via liquid–liquid extraction) are needed. Recirculation of the aqueous byproduct has proven as a viable strategy for concentrating chemicals and, thus, helping to partially solve these challenges [217,232]. Recirculation of water also reduces water consumption and decreases water contamination, an essential requirement toward biorefineries' sustainability. However, a careful selection of the upgrading strategies is required, depending on the concentration of chemicals of interest and economic factors [218].
b) The relatively complex chemistry behind the processes for the valorization of the aqueous fraction will require specialized personnel for designing, scaling up, and operating these processes. For example, Narisetty et al. [44] mention that xylose's low metabolic capabilities (compared to glucose's) and other process limitations need improvement toward transforming xylose into bioproducts at an industrial scale. More efficient xylose transporters are expected to facilitate the simultaneous fermentation of mixed sugars.
c) The requirements of devoted catalysts as some catalysts can deactivate during the aqueous stream upgrading process [218].
d) The difficulty of controlling inhibitors and undesired chemical compounds in the aqueous byproduct stream. Maximizing xylose production and minimizing inhibiting degradation products is a key challenge [61]. For instance, furfural, HMF, and acetic acid could be of interest for some applications, but biofuels production is negatively affected by the presence of these compounds [4,44].
e) The necessity of developing dedicated storing system to temporarily storing large volumes of non-processed acidic aqueous byproducts. Temporarily storage of the aqueous product can help the management because processing larger volumes could make the recovery of compounds more economical.
f) The necessity of adequately disposing of or using final wastes [4,44].
g) Lack of tools to predict the yields and composition of the aqueous byproducts from WTCPs, considering the conditions of different raw materials and processes.
h) Lack of sufficient data about the yields of the aqueous, solid, and gas fractions in WTCPs, which is understandable because most studies have been conducted at laboratory and pilot scales, and only a few processes have reached industrial scale (See examples in Sections 2.5 and 2.6).
i) Lack of data on the environmental and economic impacts of integrating methods for the valorization of the aqueous stream. Prospective valorization pathways for aqueous byproducts from WTCP suggest economic and environmental benefits that enhance biomass economic and sustainable utilization. However, more work on techno-economic assessment (TEA) and life cycle assessment (LCA) to appraise the economic and environmental sustainability of proposed valorization methods are necessary [223]. TEAs, specifically devoted to valorizing the aqueous stream from WTCPs, are not available, making it difficult for engineers and companies to decide about economically viable technological routes to obtain products that fulfill market expectations. TEAs focused mainly on the leading products obtained via WTCPs in biorefineries (see, for example, Ruiz et al. [60]) can serve to advance TEAs centered on the byproducts of these processes.

The potential of the WTCPs' aqueous fraction to produce an array of products, resulting in economic and environmental benefits, is a strong argument to adopt existing and/or to-be-designed processes for using such aqueous byproducts in biorefineries. This approach may also be part of the solution to managing an increased availability of residues from industries processing lignocellulosic materials due to stricter environmental legislation [63] and help enhance the sustainability and efficiency of biofuel production processes [218]. However, designing and optimizing processes for industrial-scale high productivity with low environmental impacts is challenging due to the many variables that need to be considered. Design of experiments (DOE) should be used to optimize the production of chemicals and products of interest.

Future research and industrial applications may rely on interdisciplinary and multidisciplinary work and new technological tools to solve these challenges. Computational tools that integrate the results obtained by different laboratories are necessary. Artificial intelligence (AI) is seen as a tool that can contribute to the advancement of biorefineries considering this large number of variables [333–337] and the different types and yields of byproducts. AI, through machine learning and predictive modeling, can serve for process optimization using available experimental datasets. This approach is expected to avoid time-consuming tasks to predict the product's quantity, quality, characteristics, and required resources (e.g., water, energy, and chemicals) [335]. Nevertheless, the necessity of numerous experimental datasets to generalize machine learning tools is a factor that can delay the adoption of AI in biorefineries [338].

6. Conclusion

WTCPs are used for processing biomass with high moisture content, resulting in pretreated solids, aqueous byproducts, and gases. Although WTCPs differ in the process conditions, the common aqueous byproduct is rich in sugars or oligomers (readily transformable into sugars through hydrolysis), furfural, HMF, acetic acid, and other compounds of interest. The hemicellulose-rich derived products offer the potential for producing fuels, fertilizers, and several chemicals and intermediate chemicals using different technological routes. The advance of biorefineries requires process integration for the complete use of biomass resources (including the aqueous byproduct) to reduce waste, as the circular bioeconomy requires. However, several challenges must be solved to ensure biomass is utilized to its fullest potential. The complex chemistry of the aqueous byproduct and the low concentration of chemicals and products of interest are among the challenges to using the aqueous byproduct better. Despite the challenges of scaling up the WTCPs and designing and operating processes for using the aqueous fractions, the findings reported in the literature offer enormous prospects, from an engineering viewpoint, for integrating technological routes in biorefineries. New technological tools, including artificial intelligence, are expected to contribute to better design processes and predict yields and properties of the aqueous stream, with reduced experimental work, to advance biorefineries under the circular bioeconomy framework.

CRediT authorship contribution statement

Manuel Raul Pelaez-Samaniego: Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Conceptualization. **Sohrab Haghighi Mood:** Writing – review & editing, Writing – original draft. **Juan F. Cisneros:** Writing – review & editing, Writing – original draft. **Jorge Fajardo-Seminario:** Writing – review & editing, Funding acquisition, Conceptualization. **Vikram Yadama:** Writing – review & editing, Supervision. **Tsai Garcia-Perez:** Writing – review & editing, Writing – original draft, Validation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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