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Recent advances and challenges of inter-disciplinary biomass valorization by integrating hydrothermal and biological techniques

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ABSTRACT

Biomass valorization for the production of various value-added biochemicals and biofuels plays a significant role in modern biorefineries/bioenergy towards a climate neutrality future. Among the developed valorization techniques for biorefining, hydrothermal and biological treatments have been demonstrated to valorize raw biomass materials or upgrade biorefinery intermediate products to afford respectably desired product yields. From the perspective of both green chemistry and circular bioeconomy, whether the inter-disciplinary approach could achieve complete biomass valorization with balanced energy and extra profits remains questionable. This review is presented to provide an overview of the opportunities combining both hydrothermal and biological techniques for biomass valorization. Combinations including (1) hydrothermal pretreatment followed by biological valorization (such as enzymatic hydrolysis, fermentation, anaerobic digestion, or composting) and (2) hydrothermal valorization of substrates generated from biological techniques (such as enzymatic hydrolysis pretreated food waste, or anaerobic digestion produced digestate) for the production of biochar, biocrude or syngas are comprehensively reviewed. The recent advances regarding treatment conditions, synergies between hydrothermal and biological techniques, and optimal performances are summarized and compared. Assessment of the energy balance and economic feasibility of different integrated options reported in previous studies is also compared. Finally, challenges and perspectives for advancing integrated hydrothermal and biological techniques toward complete biomass valorization are concluded.

1. Introduction

The past decades have witnessed a prosperous development of biorefining to produce value-added biochemicals (such as alcohols, furfurals, and organic acids) and fossil fuel substitutes (such as hydrogen, methane, ethanol, and butanol) [1]. The implementation of bio-based technologies continues to nurture the growth of a sustainable bioeconomy. In the European context, bioeconomy needs to have sustainability and circularity at its heart, enabling the transition from a linear economy to a circular one [2]. The International Energy Agency predicted the global bioenergy demand will increase significantly by almost 3-fold by 2060 [3]. For such a drastic increase, sustainable biomass resources (such as algae, crops and wastes) have to be used as efficiently as possible. Furthermore, this necessitates the development of innovative bio-cascading and circular approaches to meet future targets of bioenergy and biochemicals.

The product portfolio of bioenergy and biorefinery is vastly diverse as biomass valorization techniques become increasingly inter-

Abbreviations: LCB, lignocellulosic biomass; FPU, filter-paper units; DM, dry matter; HCW, hot-compressed water; TRS, total reduce sugar; SB, sorghum bagasse; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; GVL, gamma-valerolactone; 5-HMF, 5-(hydroxymethyl)furfural; IL, ionic liquid; DES, deep eutectic solvent; VS, volatile solid; VFA, volatile fatty acid; AD, anaerobic digestion; TS, total solid; LNP, lignin nanoparticle; NER, net energy ratio; HHV, higher heating value; AAEM, alkali and alkaline earth metallic; TEA, techno-economic assessment.

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disciplinary, bridging various physical, chemical, and biological technologies together [4–6]. Among these techniques, hydrothermal treatment is applicable to overcome the recalcitrant nature of raw biomass to enable subsequent treatments, or to transform them into valuable biochemicals [7]; while biological techniques can be used to treat various biomass feedstocks including a wide range of biodegradable wastes (such as agricultural, industrial, municipal, and kitchen wastes) for waste management and biomass valorization [8–11]. Nonetheless, both hydrothermal and biological techniques have their drawbacks: hydrothermal treatment typically requires a high energy input and the addition of catalysts or solvents [12]; while biological treatment requires long processing time and tends to be less effective to breakdown recalcitrant feedstocks.

The combination of hydrothermal and biological techniques can thus be promising for biomass valorization by combining the advantages of both treatments to overcome the diversified and recalcitrant nature of biomass for specific platform biochemical/biofuel production [13]. A proposed scheme is presented in Fig. 1 to illustrate the opportunities that arise from the combination of hydrothermal techniques with various biological treatments. Compared to biological treatment, hydrothermal treatment is less susceptible to feedstock type and reaction environment and is applicable as either pretreatment or post-treatment to biological processing. On the other hand, the efficiency of any biological treatments is heavily influenced by the survival and performance of the microorganisms, which often require careful monitoring of conditions. Using hydrothermal techniques for biomass pre-treatment under proper conditions is plausible to prepare suitable feedstock for their subsequent biological treatments with high processing efficiencies and ideal product yields; while using biological methods for the pretreatment of raw materials has the potential to enhance the performances of subsequent hydrothermal treatment [14]. With that said, challenges still exist during the integration of both techniques. Selection of suitable hydrothermal technique is especially important when biological treatment is applied at the subsequent stages, due to the following reasons: (1) the solvents or catalysts used during hydrothermal pretreatment may be toxic to enzymes and microorganisms, (2) hydrothermal pretreatment may produce several inhibitors (such as furfural) for biological processes [12], and (3) the integrated process may lead to extra costs in energy and economy due to the addition of an extra step to the existing system.

Numerous reviews have discussed the advances in biomass valorization via hydrothermal or biological techniques [15–24]. These reviews focused on the advances of either hydrothermal treatments (such as hot-compressed water treatment, water/catalyst treatment, solvent/water treatment) or biological treatments (such as anaerobic digestion, enzymatic hydrolysis) individually. There is a lack of discussion on the possibilities of integrating hydrothermal and biological techniques. Recent reviews shed light on the integration of hydrothermal and biological treatments that mainly focused on the integration of hydrothermal treatment with a single biological treatment or a specific hydrothermal pretreatment technology for biological pretreatment. However, these reviews lack comparisons between various biological techniques or hydrothermal treatments under different conditions. For instance, Karthikeyan et al. [25], Wahlstrom et al. [26], Carrere et al. [27], and Cesaro et al. [28] reviewed various pretreatment techniques for anaerobic digestion (AD) of various biomass. Alvira et al. [29] mainly reviewed various pretreatment techniques for subsequent fermentation for bioethanol production. The use of deep eutectic solvents (DESs), ionic liquids (ILs), and organic solvents for biomass pretreatment has been reviewed by Tan et al. [30], Usmani et al. [31], and Ferreira et al. [32], respectively. Abraham et al. [33] and Millati et al. [34] focused on reviewing pretreatment strategies for lignocellulosic biomass pretreatment for AD valorization. Pecchi et al. [35] and Deng et al. [36] reviewed the combination of AD and thermochemical technologies for biomass valorization.

This review considers feasible combinations using both hydrothermal and biological techniques for biomass valorization. An overview of previous studies using integrated hydrothermal and biological techniques for biomass treatment has been conducted. The treatment parameters of both hydrothermal and biological stages, as well as the key results, are summarized. Energy balance and economic assessment are also discussed to assess the sustainability of different combinations. The principles for complete biomass valorization, challenges and perspectives are also concluded and proposed. This work provides a comprehensive understanding of the current advances and defects of the interdisciplinary studies, thus helping future studies to select proper scenarios for biomass valorization.

2. Hydrothermal pretreatment followed by biological valorization

The conception of hydrothermal treatment can be broadly defined based on a variety of temperature and pressure. With water as an example, the treatment condition can be classified into: (1) supercritical water treatment (temperature $>$ 374 °C, P $>$ 22 MPa); (2) subcritical water treatment (temperature could be varied from 100 to 374 °C with pressure ranging from saturated steam pressure to 22 MPa to maintain

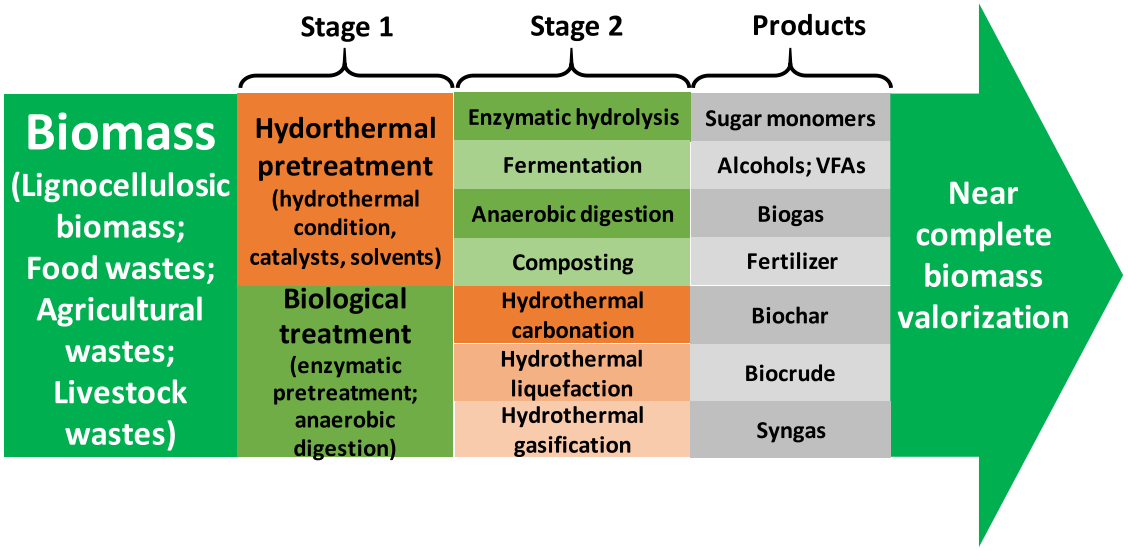


Fig. 1. A schematic diagram for biomass valorization via hydrothermal and biological treatment techniques.

water in liquid form); and (3) ambient liquid water treatment (25–100 °C, ordinary pressure 0.1 MPa) [37,38]. The definition could be variable when different fractions of co-solvents are presented as the critical properties of fluids vary drastically [39]. This review considers all applied treatments using water, water/catalysts, and water/solvents under temperature above ordinary conditions (25 °C, 0.1 MPa) as hydrothermal treatments.

2.1. Combination of hydrothermal pretreatment with subsequent enzymatic hydrolysis

The combination of hydrothermal pretreatment and enzymatic hydrolysis aims to saccharify lignocellulosic biomass (LCB) to its sugar monomers (such as glucose and xylose). With raw LCB, the efficiency of enzymatic hydrolysis is limited due to the following reasons:

- Cellulose is surrounded by both hemicellulose and lignin, forming a complex lignocellulosic matrix, which blocks the access of enzymes (mainly cellulase) to cellulose [40,41].
- The presence of hemicellulose-derived xylooligomers suppresses the effectiveness enzymatic hydrolysis of cellulose [42]. Moreover, lignin can absorb cellulase and comparably divert the amount of enzymes loaded on cellulose, therefore the rate of enzymatic digestibility of cellulose is reduced [43].
- The rigid crystalline structure of cellulose is highly resistant to hydrolysis; therefore, the crystalline index of cellulose is correlated to the initial hydrolysis rate during the enzymatic hydrolysis of cellulose [44,45].

To overcome the recalcitrance of LCB, it is necessary to eliminate the adverse impact of lignin and hemicellulose to improve the hydrolysis performance of enzymes. As reviewed by Mosier et al. [46], an effective pretreatment should be assessed based on several criteria including size reduction, sugar recoveries, inhibitors formation, and cost-effectiveness. They compared various early (before 2005) pretreatment methods including steam explosion, liquid hot water (or HCW), acid/water, lime, and ammonia pretreatments as potential cost-effective methods for LCB pretreatment. More recently, hydrothermal pretreatment has become a key technique that has been widely applied for LCB pretreatment to achieve selective fractionation of major compositions (lignin, cellulose, and hemicellulose) and high sugar recovery during enzymatic hydrolysis [24,47]. The previous decades have experienced evolutions in conducting hydrothermal pretreatment of LCB with sustainable and recyclable solvents, lower temperatures and high fractionation selectivity, suggesting that hydrothermal pretreatment is a more promising technique for the enzymatic hydrolysis of LCB. Some of the representative studies are listed in Table 1 with conditions of both hydrothermal (stage 1) and enzymatic (stage 2) treatments presented. In this review, these studies are classified into different categories based on their reaction medium during the hydrothermal pretreatment stage.

2.1.1. Hot-compressed water pretreatment & enzymatic hydrolysis

Hot-compressed water (HCW) pretreatment uses sub-critical/supercritical water to break down the components of LCB under various temperatures and reaction times. The combined effect of reaction temperature and time can be quantified by the severity factor R_0 (Eq. (1)) [72].

$$\log(R_0) = \log\left(t \cdot \exp\left(\frac{T-100}{14.75}\right)\right) \quad (1)$$

where t represents the reaction time (min) and T represents the reaction temperature (°C). Different R_0 can result in various changes in pretreated biomass compositions, thus influencing the enzymatic hydrolysis of pre-treated LCB [49,52,57]. A typical example was given in Fig. 2 to show the correlations between HCW pretreatment severity and enzymatic sugar yield. The effect of HCW pretreatment on LCB composition and its influence on the subsequent enzymatic hydrolysis of pre-treated biomass are concluded as follows.

First, HCW pretreatment significantly removes the hemicellulose component of LCB. As demonstrated by Dogaris et al. [49] after pretreatment at 210 °C for 20 min ($\log R_0 = 4.54$), the majority of hemicellulose was removed. The removal of hemicellulose can enhance the enzymatic hydrolysis of cellulose in LCB, as hemicellulose-derived sugar oligomers (such as xylose and arabinose) are inhibitive to the activities of cellulase [42]. The inhibitory effect of hemicellulose derived sugars was further investigated by Rajan et al. [57], and a decrease in enzymatic efficiency from 100 to 66% for cellulase hydrolysis was observed when xylose concentration was raised to 1 g/L. To this extent, the removal of hemicellulose via hydrothermal pretreatment can enhance the biodegradability of cellulose [73]. Larnaudie et al. [74] optimized the pretreatment conditions via the response surface methodology and suggested that multiple factors including the water/solid ratio, initial pH, and enzyme dosage were responsible for the final glucose yield.

Second, some glucan is inevitably released during pretreatment, thereby increasing the crystallinity of the resulting cellulosic residues. For instance, a previous study by Xiao et al. [55] suggested that the hydrothermal pretreatment (140–200 °C for 10–120 min) of bamboo resulted in a loss of glucan of up to 15%, while the crystalline index slightly increased from 45 to 50% with the increase of severity factor. Another study by Nitsos et al. [56] indicated that the crystalline index of cellulose in poplar wood increased from 72.2 to 83.4% after pretreatment at 220 °C for 15 min. However, the increase in the crystalline index does not directly affect the final glucose recovery. For example, the enzymatic digestibility and conversion rate of cellulose were shown to be increased after HCW pretreatment despite the increase in crystallinity [13,54], indicating that the crystallinity of cellulose may not be the main factor influencing the performance of enzymatic hydrolysis of LCB.

Third, lignin may decompose and dissolve into the liquid phase, generating various substituted phenolics in the product stream. Even though only a small fraction of lignin decomposes in HCW, compared with hemicellulose [56,75], the removal of lignin-derived chemicals before enzymatic hydrolysis is of critical importance because the resulting phenolics are potential inhibitors affecting the enzymatic performance of cellulase. For instance, phenolics at 1 g/L significantly reduced the enzymatic hydrolysis rate by 92% [57]. A high treatment severity is typically needed to remove lignin in LCB, while this may be accompanied with a high loss of cellulose component as shown in Fig. 3 (b). Li et al. [54] demonstrated that the majority of lignin (>80%) still remained in the solid residue after hot-compressed water pretreatment with a considerable loss of glucan (>20%). However, under proper conditions, the lignin/cellulose (L/C) loss ratio could be optimized and reduced, which is preferable to the enzymatic hydrolysis of LCB [43].

Fourth, HCW pretreatment also alters some physical properties of LCB, and some of these changes may affect the digestibility of enzymes. The most obvious change after pretreatment is the darkening of color (from brown to black) of the LCB feedstock, mainly due to the solubilization, re-condensation, and concentration of lignin-derived compounds during hydrothermal reactions [13,56,57,76]. Another change is the structure of particles. It has been shown that HCW pretreatment can cause the collapse of the cell wall structure of LCB [54]. Moreover, the porosity and specific surface area also increase after pretreatment. These changes are preferred for the loading of enzymes onto the surface of solids for enzymatic hydrolysis [56,77].

Besides lignin degradation, carbohydrates themselves are also susceptible to produce substrates that can inhibit the enzymatic activity or alter the local pH during the HCW treatment as shown in Fig. 4. With the further decomposition of hemicellulose, cellulose and lignin, common biomass platform chemicals, such as furfural, 5-hydroxymethylfurfural, acetic acid, and formic acid, could be produced via various reaction pathways [49,50]. A recent study investigated the inhibitory effect of these chemicals, and demonstrated they exhibited variable inhibitory

Table 1
Previous studies combining hydrothermal pretreatment and enzymatic hydrolysis for biomass valorization.

Feedstock	Hydrothermal stage	Enzymatic hydrolysis stage	Results	Reference
Poplar wood	water/sulfuric acid; 190 °C for 1 min	cellulase loading at 15 to 60 FPU/g glucan for 120 h	•An integrated study with hydrothermal pretreatment, enzymatic hydrolysis, and ethanol fermentation, •The addition of acid enhanced the release of hemicellulose during the pretreatment.	[48]
Various agriculture waste	water; 160–210 °C; 10–30 min	cellulase loading at 10–30 FPU/g DM for 90 h	•Conversion of cellulose was enhanced by 15% after pretreatment, •Inhibitors were produced as the treatment severity factor increased.	[49]
Eucalyptus grandis	water; first stage at 180 °C for 20 min; second stage at 200 °C for 20 min	Cellulase loading at 40 FPU/g dry matter for 72 h	•A two-stage hot-water method was used for biomass pretreatment, •The enzymatic digestibility of pretreated residues was significantly enhanced.	[50]
Eucalyptus barks	water/carbon dioxide; 150–200 °C; for 1–4 h	cellulase and xylanase at 12.5 FPU/g DM for 24 h	•10% of the overall glucose was lost during pretreatment, •Enzymatic digestibility was enhanced to > 90% after pretreatment.	[51]
Sugar-beet pulp	water; 120–170 °C for 52 min	mixed enzyme (C1-G1) loading at 7.5 FUP/g DM for 48 h	•More than 90% of the cellulose was degraded under optimal conditions, •No toxic compound was produced at a temperature lower than 140 °C.	[52]
Wheat straw	water/acetic acid; 190–200 °C for 10 min	mixed enzyme (CTec2 and HTec2) at 15 FPU/g DM for 48 h	•The majority of hemicellulose was removed during pretreatment, •The highest glucose yield was achieved at 195 °C with a yield of 93%.	[53]
Beech wood	water; 130–220 °C for 15–180 min	cellulase loading at 60 FPU/g DM for 72 h	•Glucose enzymatic yield was enhanced from 7 to more than 70%, •The increase of treatment severity enhanced the loss of hemicellulose and the production of toxic chemicals.	[13]
Bamboo	water; 120–240 °C for 60 min	cellulase loading at 20 FPU/g DM for 96 h	•Bamboo was first de-waxed before hydrothermal treatment, •The enzymatic conversion was enhanced up to ~ 80% after pretreatment and its rate increased with the increase of hydrothermal severity.	[54]
Bamboo	water; 140–200 °C for 10–120 min	cellulase loading at 14.5 FPU/g DM for 120 h	•Bamboo was first de-waxed before hydrothermal treatment, •~2–15% of glucan loss was achieved during pretreatment; cellulose crystalline index was increased.	[55]
Poplar, grapevine, pine	water; 170–220 °C for 15–180 min	cellulase loading at 60 FPU/g solution for 72 h	•Correlation between treatment severity and various parameters was studied, •The severity parameter was also correlated to the yield of products.	[56]
Rice straw	water; 220 °C for 52 min	cellulase loading at 41.7 U/mL solution for 3 h	•Inhibitors of cellulase were characterized and classified, •The inhibition of enzymatic hydrolysis by chemicals was studied.	[57]
Wheat straw	ionic liquid/water; 80 °C for 6 h	cellulase and xylanase at 11 FPU/g and 50 CBU/g	•~50% of lignin was extracted by ILs pretreatment, •Enzymatic digestibility of raw material was enhanced to ~80% after pretreatment.	[58]
Rice straw	ionic liquid; 90 °C for 6 h	cellulase at 14.3 mg protein/g glucan for 24 h	•Different ionic liquids were employed for lignin extraction, •A correlation between enzymatic digestibility and lignin content was obtained.	[59]
Safflower straw	Water/sodium carbonate; 180 °C for 5 h	cellulase loading at 10–50 protein/g glucose for 72 h	•Cellulose accessibility of untreated and treated samples was characterized, •DES treatment enhanced the accessibility was responsible for the enhanced digestibility.	[60]
Sugarcane bagasse	water/sulfuric acid; 140–180 °C for 10–40 min	cellulase loading at 15 FPU/g glucan for 48 h	•The enzymatic digestibility of feedstock was increased from ~40 to 96% under optimal conditions, •Correlations between reaction conditions and glucan content/digestibility were obtained.	[61]
Wood chips	water/ethanol/sulfuric acid; 170 °C for 1 h	mixed enzyme (Novozym 22C) at 5 FPU/g glucan for 72 h	•Esterification of lignin was characterized in ethanol/water, •Ethanol/water pretreatment suppressed the affinity of lignin to the enzyme and enhanced the digestibility of cellulose.	[43]
Corn stover	water/ethanol/organic amine; 140 °C for 40 min	cellulase at 15 FPU/g DM for 48 h	•Lignin removal (from ~50 to 82%) were enhanced after pretreatment, •Overall sugar recovery (from ~40% to 81%) was enhanced.	[62]
Cotton stalk	GVL/water/sulfuric acid; 170 °C for 60 min	cellulase at 15 FPU/g DM for 72 h	•The cellulose-enriched fractions displayed a homogeneous and porous network structure, •Glucose yield from pretreated residue was enhanced from 40 to 78%.	[63]
Corncob	water/solid acid; 120–160 °C for 4–6 h	cellulase loading 20–40 FPU/g DM for 96 h	•~78% of hemicellulose was released during hydrothermal treatment, •The enzymatic hydrolysis of cellulose was enhanced after pretreatment.	[64]
Bamboo	sodium xylene sulfonate/water, ethanol/water, water; 160 °C for 60–90 min	cellulase at 20 FPU/g DM for 72 h	•Pretreatment influences the enzyme adsorption capacity of biomass, •An optimal 80% glucose yield from treated bamboo was achieved by acidic salt pretreatment, •Correlation between pretreatment and enzyme adsorption was discussed.	[65]
Sugarcane bagasse	ethanol/water; 190 °C for 50–150 min	cellulase at 10 FPU/g DM for 72 h	•The combination of water and water/ethanol treatment was applied, •The majority of hemicellulose and lignin was removed, which resulted in the enzymatic hydrolysis of cellulose being enhanced from 22 to 72%.	[66]
Akebia residues	organic acids derived DESs/water; 80–120 °C for 8 h	cellulase at 10–40 FPU/g dry matter for 72 h	•Herbal wastes were pretreated in different biomass derived DESs, •Optimal conditions for the removal of lignin and retaining of glucan was achieved.	[67]
Switchgrass	DESs/water/sulfuric acid; 130 °C for 30 min	cellulase and xylanase at 20 and 2 mg protein/g solid for 48 h	•The system was suitable for biomass pretreatment with high solid loading (20–27%), •The addition of acid enhanced the treatment performance of DES.	[68]
	DESs/water; 80–150 °C for 0–5 h			[69]

(*continued on next page*)

Table 1 (*continued*)

Feedstock	Hydrothermal stage	Enzymatic hydrolysis stage	Results	Reference
Sugarcane bagasse		cellulase at 10–50 mg protein/g glucan for 120 h	•Different DES were prepared for lignin extraction, •Ionic liquid and DES were shown to have better performances (i.e., cellulose accessibility and fermentable sugar yields) than other solvents for sugarcane pretreatment.	
Sugarcane bagasse	ILs/water; 120–160 °C for 2–7 h	cellulase at 2–40 FPU/g glucan for 72 h	•Respond surface methodology was employed to optimize the pretreatment of selected ionic liquids, •Enzymatic digestibility of feedstock was enhanced from ~23 to 80% after ionic liquid pretreatment.	[70]
Rice straw	various organic solvents/water; 110 °C for 60 min	Cellulase at 20 FPU/g dry matter for 72 h	•Different organic solvents/water were applied for lignocellulosic biomass pretreatment, •Correlations between the Hansen's solubility parameter of solvents and the lignin extraction of solvents were discussed.	[71]

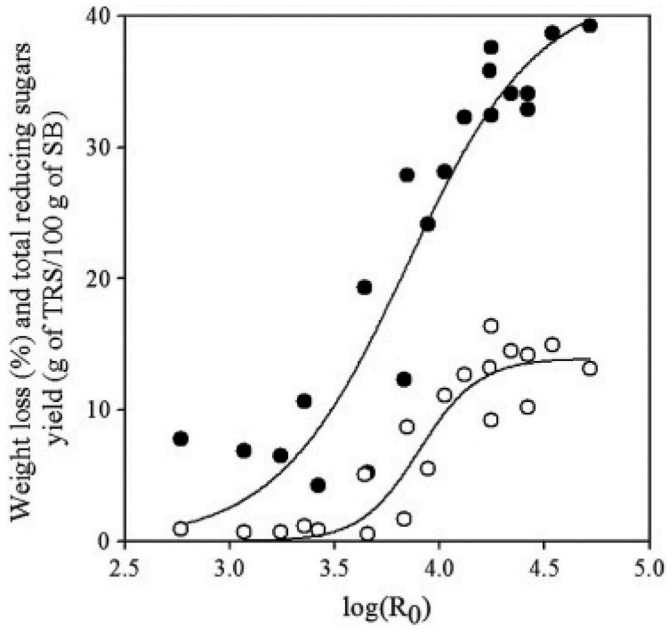


Fig. 2. Effect of severity factor on (●) solid removal and (○) total reducing sugar (TRS) release during hydrothermal treatment of sweet sorghum bagasse (SB). Although the reaction conditions (severity factor) are variable in different studies, it is apparent that the decomposition rate of feedstock increases as the treatment severity increases. Adapted from reference [49] with permission.

effects on cellulose hydrolysis, the presence of acetic acid and phenolics at 1 g/L can significantly decrease the enzyme efficiency of cellulase by ~87 and 92%, respectively [57]. Herein, the produced inhibitors in the liquid phase need to be removed before the subsequent biological applications.

2.1.2. Acid-catalyzed HCW pretreatment & enzymatic hydrolysis

Acid-catalyzed HCW (such as sulfuric acid and acetic acid) has also been reported to deliver comparable LCB degradation yield at lower temperatures [48,51,53,60,61,64]. Lloyd et al. [78] conducted an integrated study with dilute sulfuric acid pretreatment (140–200 °C for 2–80 min, corresponding to treatment severity at 0.93 to 1.55) with a subsequent enzymatic hydrolysis for the saccharification of LCB. In contrast, the control experiment without acid was conducted at 150–210 °C for 2–107 min (corresponds to treatment severity at 3.5 to 4.5). The result showed the addition of an acid showed a significantly higher xylan removal (maximal 34.5%) compared to a hot water-only pretreatment (maximal 12.5%). A further study compared the effect of dilute acid (2% of sulfuric acid) with other pretreatment techniques, such as SO_2 steam explosion, lime, ammonia fiber expansion, etc., and demonstrated that the use of dilute acid was more effective to produce monosaccharides for the subsequent bio-ethanol production [48]. More recently, Djioleu and Carrier [61] demonstrated that the digestibility of pretreated residues from Switchgrass was significantly enhanced by 90% under optimized conditions (i.e., 180 °C for 10 min with 0.5% sulfuric acid, or 160 °C for 20 min with 1.0% sulfuric acid). The study also suggested that undesirable degradation of glucan occurred during the pretreatment, leading to more than 20% of glucan loss even at mild conditions. In addition to the over-degradation, the use of strong acids also induces equipment corrosion and requires post-processing neutralization before enzymatic hydrolysis. Therefore, weak acids are often preferred over strong acids [79,80]. Petrik et al. [53] employed acetic acid (2.4 g/L) as a catalyst to pretreat wheat straw at 190–200 °C, which broke down almost 80% of the hemicellulose and enzymatic hydrolysis of the pretreated solid residue achieved glucose yield at > 90%. Another study by Matsushita et al. [51] used water/CO_2 as a weak acidic system for *Eucalyptus* bark pretreatment; the following enzymatic hydrolysis assessment suggested that water/CO_2 pretreatment significantly enhanced the enzyme accessibility to the pretreated LCB and increased the digestibility of glucan to >90%.

A major issue of using acids as catalysts is that the homogeneous character of acids makes them difficult to be recovered or reused, thus extra steps are needed for the neutralization and removal of acids-related byproducts. The use of heterogeneous acids (i.e., solid-supported acids) was developed to immobilize the acidic components on solids, such as biochar and other carbon-based materials [81]. Qi et al. [64] prepared a carbon-based solid acid for corncob pretreatment; the method significantly enhanced the enzymatic digestibility by more than 40% compared with that of the unpretreated samples. In general, the presence of acid catalysts improves the efficiencies of HCW, but most of the lignin remains intact in the residue and needs to be further separated to enhance the efficiency of enzymatic hydrolysis.

2.1.3. Organic solvent/water pretreatment & enzymatic hydrolysis

Organic solvents have also been widely studied for biomass pretreatment [12]. The use of organic solvents is commonly applied to dissolve lignin, thus enhancing the accessibility of enzyme to cellulose. The dissolution of lignin in various solvents can be assessed by Hansen's solubility parameter as suggested in a recent study by Zhang et al. [71]. The selective removal of compositions results in the variety of the biodegradability of biomass [65]. The organic solvents used for biomass hydrothermal pretreatment can be classified into polar aprotic and polar protic solvents based on their physicochemical properties. Herein, a review of the studies applying hydrothermal polar aprotic solvent/water and polar protic solvent/water pretreatment for the enzymatic hydrolysis of biomass is conducted.

The most highlighted polar protic solvent/water system is ethanol/water because ethanol is a biomass-derived value-adding chemical that can be obtained from LCB by ethanologenic fermentation [82]. Some early studies combining ethanol/water pretreatment and enzymatic hydrolysis for LCB treatment were conducted by Pan et al. [83,84], in which the hydrothermal pretreatment using ethanol/water/acid for wood biomass fractionation (153–187 °C, 43–77 min, sulfuric acid

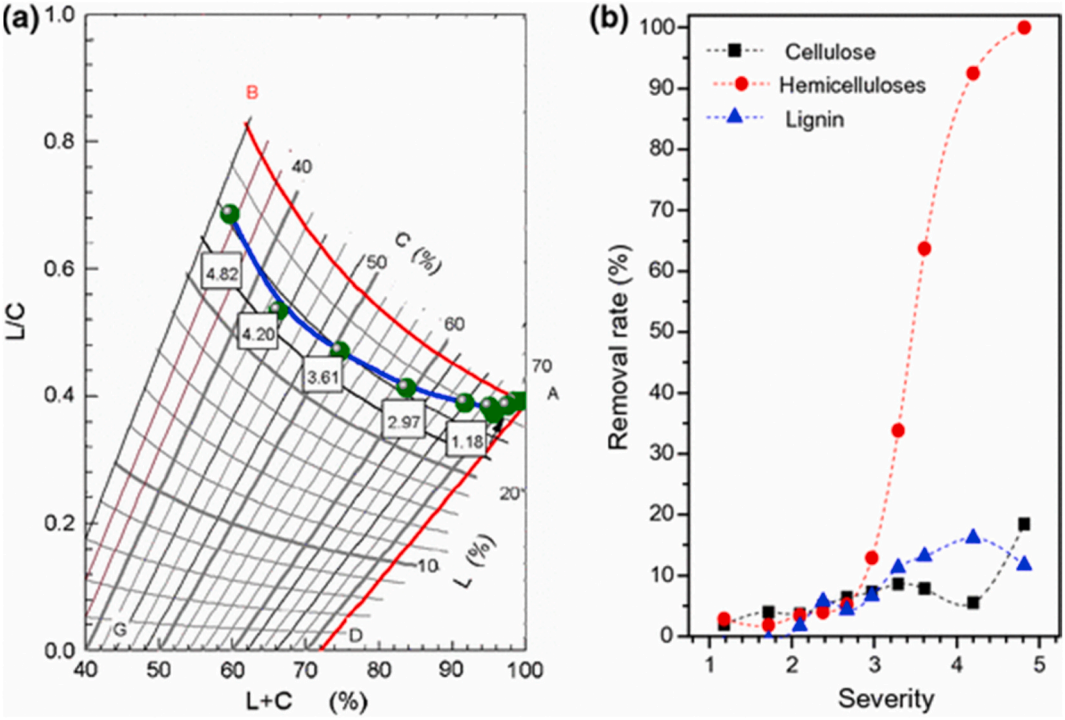


Fig. 3. Effect of severity on the removal of hemicelluloses, lignin and cellulose. (a) Ross diagram, and (b) removal of hemicelluloses, lignin and cellulose. Adapted from reference [54] with permission.

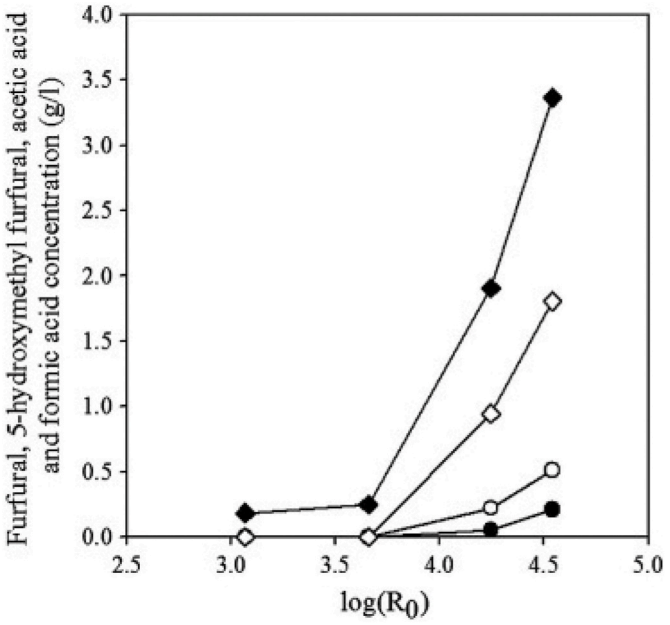


Fig. 4. Effect of severity factor on (●) 5-HMF, (○) furfural, (◆) acetic acid, and (◇) formic acid formation during hydrothermal treatment of sweet sorghum bagasse. Adapted from reference [49] with permission.

content 0.76–1.44%, ethanol 48–82%) was optimized via surface response methodology and achieved the removal of both lignin and hemicellulose from wood chips, following enzymatic hydrolysis of the pretreated residue almost completely recovered glucose within 12 h. Later on, Brosse et al. [85] established a two-step hydrothermal pretreatment: for the first step, dilute acid was used for LCB soaking at near 100 °C, which recovered the majority of hemicellulose; the second step used hydrothermal ethanol/water pretreatment and recovered more than 90% of lignin; enzymatic hydrolysis of the pretreated residue almost recovered 100% of glucose. The following studies expanded this technique to the treatment of various LCB feedstocks and optimized the performances with various catalysts; subsequent enzymatic hydrolysis was employed for the further treatment of residues obtained after pretreatment [62,86–89]. More recently, Santo et al. [66] investigated the solvent effect of ethanol/water on LCB decomposition, indicating that the use of ethanol/water mainly enforced the dissolution and partial removal of lignin from LCB, which was believed to be the key reason for the enhanced enzymatic digestibility of pretreated residue; while water only rearranged the structure of lignin, which likely contributed to the increased access of enzyme to cellulose. Moreover, Lai et al. [43] studied the alkylation of lignin during ethanol/water pretreatment and demonstrated that the etherification of lignin functional groups with ethanol reduced the affinity of enzymes onto lignin, which is another reason for the enhanced enzymatic hydrolysis of LCB after pretreatment by ethanol/water. Other aqueous protic solvents such as glycol/water, butanol/water, propionic acid/water were also studied for LCB pretreatment [90].

As to polar aprotic solvent/water systems, gamma-valerolactone/water (GVL/water) has attracted wide interests recently. Compared with other aprotic solvents (such as acetone, DMSO, and THF), GVL presents higher lignin dissolution [91]. Moreover, GVL can be produced from biomass-derived sugars. More interestingly, GVL may be used as the solvent or co-solvent for all the treatment steps from the beginning of LCB pretreatment [92] to the further conversion of LCB derived sugars for levulinic acid production [93], and to the final synthesis of GVL from levulinic acid [94]. Moreover, the recovery of GVL and products in GVL/water treatment system have also been proved to be feasible [92,95]. The integration of GVL/water pretreatment and enzymatic hydrolysis was primarily studied by Luterbacher et al. [92] in 2014, when a GVL/water/sulfuric acid solvent system was established for wood pretreatment, and its effect on subsequent biological treatment (enzymatic hydrolysis and fermentation) was investigated for the further valorization of LCB. This method combining GVL/water/sulfuric acid pretreatment and biological conversion for LCB valorization was patented in

2016 [96]. The enzymatic digestibility of GVL/water pretreated biomass was further studied by Shuai et al. [97] and suggested that GVL/water was more suitable for biomass pretreatment compared with THF, dilute acid, alkali, and ethanol/water, under the same reaction condition (120 °C for 1 h). Moreover, the alkaline incubation of samples was mentioned as a method to further enhance the enzymatic hydrolysis. A further study by Wu et al. [63] demonstrated that GVL/water pretreatment (170 °C for 1 h) removed lignin and hemicellulose and amended the structure of cellulose with higher porosity for enzyme loading. Other studies by Song et al. [98–100] investigated the solvent effect of GVL on the isomerization reactions of cellulose and its derived sugars, the addition of GVL could suppress the isomerization reactions of sugar compounds, which would suppress the production of side products (5-HMF) and benefit the enzymatic hydrolysis. Pretreatment with other aprotic solvent/water systems with subsequent enzymatic hydrolysis such as acetone/water [101], THF/water [102], IBMK/water [103], and imidazole/water [104] was also studied.

2.1.4. Ionic liquid pretreatment & enzymatic hydrolysis

The use of ionic liquids (ILs) or ILs/water as solvents for the pretreatment of LCB has been demonstrated as one of the effective ways for lignin removal. The preparation and application of ILs as solvents have been long studied in the area of chemistry as reaction media for various synthesis and catalysis reactions [105]. In 2007, Fort et al. [106] and Kilpelainen et al. [107] first investigated the dissolution of woody biomass in ILs. The following enzymatic hydrolysis suggested that the glucose recovery was enhanced by 48%, showing the potential of IL treatment for LCB pretreatment. Later, Brandt et al. [108] prepared various ILs with different solubilities for cellulose and pinewood pretreatment, and the results suggested that the Kamlet-Taft solvent parameters were correlated to the swelling and dissolution of LCB. The use of ILs for LCB fractionation can take advantage of the differences between lignin, hemicellulose, and cellulose in solubilities (Fig. 5), enabling selective fractionation of different components of biomass.

The use of structural design to tune the selectivity of ILs for LCB dissolution has been reported in-depth in a previous study [109]. The diversified inventory of cations ($[A]^+$) and anions ($[X]^-$) [110] provides researchers countless options to design and optimize the performances of ILs to maximize efficiency for biomass treatment, while keeping toxicity at minimal for any subsequent biological treatments. Some of the representative studies with the combination of ILs pretreatment and enzymatic hydrolysis are reviewed as follows. Several studies on chloride- and acetate-based ILs were investigated as a biomass pretreatment process due to their intrinsically lower toxicity compared to other common ILs counter anions, such as [X-] or [X-] [58,70]. Zhao et al. [111] assessed the solvent effect of chloride- and acetate-based ILs on the enzymatic hydrolysis of Avicel cellulose, and found that ILs pretreatment could enhance the enzyme adsorption and enzymatic digestibility of cellulose through decreasing the crystallinity of cellulose by >50%. It should be noted that certain types of ILs might be toxic to enzymes. Hou et al. [112] tested the performance of cholinium- and amino acid-based ILs on the treatment of rice straw and found the enzymatic hydrolysis of the pretreatment biomass was significantly enhanced from 20.4% for raw materials to 84.0% after pretreatment. Furthermore, An et al. [113] pretreated rice straw with cholinium argininate at 90 °C for 12 h, and the LCB was fractionated into hemicellulose-rich, lignin-rich, and cellulose-rich fractions; following enzymatic hydrolysis of the cellulose-rich fraction achieved the glucose recovery of 58–75%. The study reused the IL for 8 rounds and demonstrated that the property of IL was stable with a slight loss (less than 8%) between cycles. The performance of cholinium-based ILs was further studied by Xu et al. [59], the enzymatic digestibility of cellulose-rich fraction was shown to be positively correlated to the removal of lignin content, the surface area of particles, and pore volume, indicating that ILs pretreatment enhanced lignin removal, and optimized the physical properties of solid residues for enzyme loading. To achieve better fractionation performances and nearly complete glucose recovery during the enzymatic stage, the combination of ILs and various catalysts has also attracted interest [114–116].

Compared to the hydrothermal pretreatment with water or water/acid, ILs offers a milder treatment condition without compromising fractionation yield. However, the use of ILs as a pretreatment method for enzymatic hydrolysis is also criticized due to the following concerns. First, the product recovery from ILs can be complicated since it involves multiple stages of washing and extraction (Fig. 6) [117]. In brief, after the IL pretreatment, the system was separated into a cellulose-rich solid fraction and a hemicellulose & lignin-rich liquid fraction; the cellulose-rich fraction was collected via filtration and flushing, while the lignin and hemicellulose were concentrated respectively by extraction with different solvents. Second, a large volume of solvent and lots of energy are required to isolate and purify the products and the IL, which translates into greater processing cost and environmental footprint. Given most ILs are toxic to enzymes, product purification is of critical importance to avoid enzyme deactivation [26]. Third, the high cost of ILs compared to other common solvents, such as ethanol and acetone, poses a great financial barrier to upscale the use of ILs. Until recently, only triethylammonium hydrogen sulfate, reported by Brandt-Talbot et al. is proven as a cost-effective solvent for the scale-up of LCB pretreatment for enzymatic hydrolysis. This was considered as the closest to scale-up [118,119].

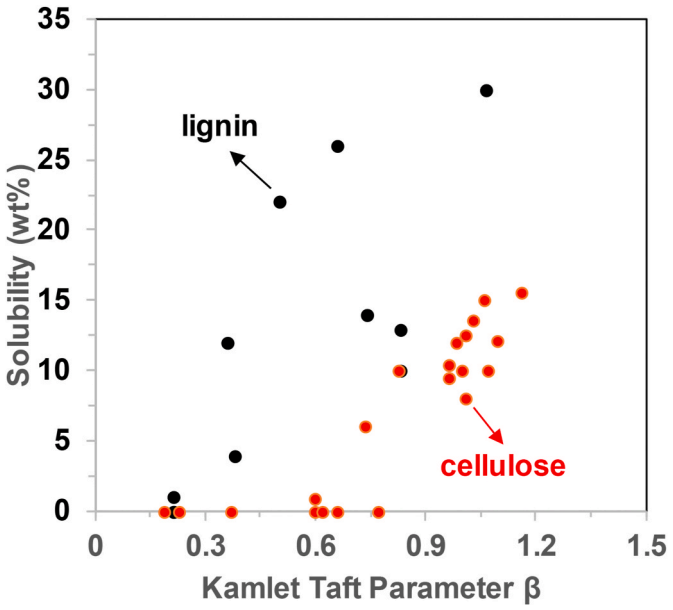


Fig. 5. The solubility of cellulose and lignin in ionic liquids as a function of the Kamlet–Taft β value of the ionic liquids. The figure was plotted based on the data concluded in the previous review by Brandt et al. [109]. The measurements of data were performed under a variety of conditions (such as different temperature, dissolution time, cellulose degree of polymerization, moisture content, ionic liquid purity), which affect the maximum solubility, a clear difference in solubility between cellulose and lignin can be observed. The solubility of hemicellulose was not presented due to the lack of data.

2.1.5. Deep eutectic solvent pretreatment & enzymatic hydrolysis

Deep eutectic solvents (DESs) are similar to ILs in their preparation and application for LCB pretreatment. DESs can be prepared facilely by mixing selected solid compounds that can form strong hydrogen bonds with each other [120]. Interestingly, DESs can be prepared with various natural compounds, especially, biomass-derived chemicals such as glucose, xylose, and sucrose, which makes these solvents promising for the sustainable treatment of LCB [67,121]. The toxicity of these DESs on enzymes can be neglected as these biomass-derived chemicals are biodegradable. The use of DESs for biomass pretreatment only started

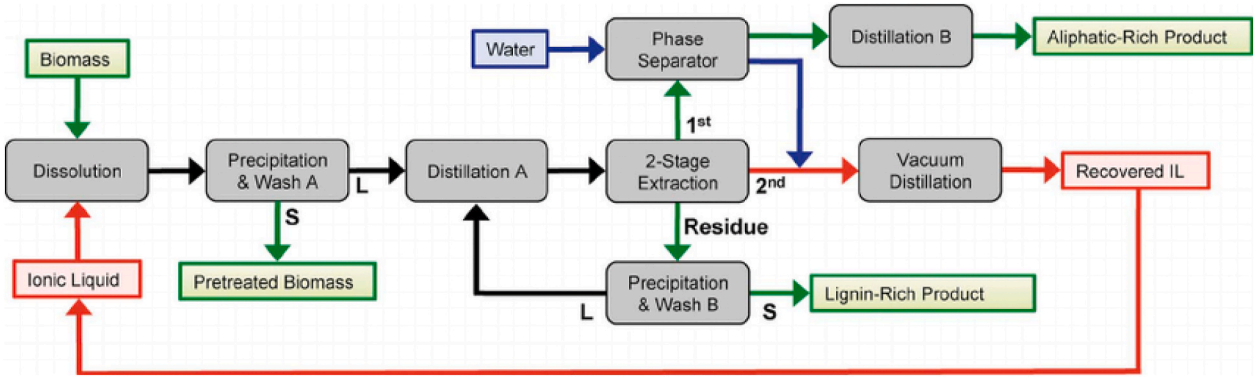


Fig. 6. A proposed ionic liquid pretreatment system with the recovery of solutes from used ionic liquid. The first stage is for the extraction of hemicellulose-rich fraction. The second stage is for the extraction of lignin-rich fraction. S = Solid, L = Liquid. Adapted from reference [117] with permission.

recently and has attracted large interest [122]. Kumar et al. [123] prepared two types of lactic acid-based DESs and applied them on rice straw pretreatment under mild conditions (60 °C for 12 h) and achieved a lignin removal at approximately 60%; following enzymatic hydrolysis with cellulase achieved a saccharification efficiency at approximately 36%. Procentese et al. [124] pretreated corncob with DESs (choline chloride mixed with glycerol, urea, and imidazole, respectively) under severer conditions (80–150 °C for 15 h), the pretreatment removed the majority of hemicellulose and lignin under optimal conditions; the enzymatic hydrolysis for the solid residue was significantly enhanced and resulted in a glucose yield at 86%. Chen et al. [68] prepared another choline chloride-based DES for switchgrass pretreatment at 130 °C for 30–40 min, and the enzymatic digestibility of the residue was enhanced to more than 90%. Kim et al. [125] developed a class of new DESs based on lignin-derived phenols for biomass pretreatment, followed by enzymatic hydrolysis of pretreated residues, this study accentuated the sustainable future of DESs in biorefinery. Another study was recently conducted by Satlewal et al. [69], in which 10 renewable DESs were prepared for sugarcane bagasse pretreatment and subsequent enzymatic hydrolysis, the pretreatment performances were compared with other methods including dilute alkali, dilute acid, and ILs pretreatments. The result of the subsequent enzymatic hydrolysis indicated that DESs/water is superior to dilute alkali/water and acid/water pretreatments, but less effective than ILs/water. More recently, Chen et al. [126] developed a lignin-derived DES (choline chloride and *p*-coumaric acid) for the pretreatment of herb residue, the facile pretreatment (160 °C) significantly enhanced the release of sugar to 84.62% compared with that at 48.08% for the control. However, the technique of using DES for LCB valorization is still at the laboratory research level and needs to be further optimized [127].

In general, compared with HCW and water/acid pretreatments, ILs and DESs provide a more efficient environment to fractionate lignin and can achieve a higher enzymatic degradability for LCB. However, the scaling up of using these solvents for LCB pretreatment needs to be further investigated. Based on the current advances, the combination of ILs pretreatment and enzymatic hydrolysis with subsequent conversion technologies (such as fermentation and AD) is highlighted as a promising step for LCB valorization; while the use of DESs pretreatment and enzymatic hydrolysis is relatively underexplored, more studies are encouraged to investigate the use of DESs for LCB pretreatment, their influences on enzymes, and scale-up techniques.

2.1.6. An assessment of various hydrothermal solvent systems for enzymatic hydrolysis

Hydrothermal pretreatment for LCB enzymatic hydrolysis has experienced an evolution in the solvent system. Hot-compressed water pretreatment generally requires higher treatment severities (4.0 or higher) to achieve the removal of hemicellulose and structural modification of lignin. In contrast, the addition of acid can significantly enhance hemicellulose removal even with a low treatment severity (<2.0). The application of novel solvents such as GVL, ILs, and DESs has taken advantage of the selective dissolution properties of the solvents to isolate the specific components in LCB at ambient conditions (~100 °C). The development of novel solvent systems has driven the advance of LCB biorefinery towards the valorization of all components. Based on the above discussions, the advantages and challenges of the representative pretreatment techniques, i.e., water, acid-catalyzed water, ethanol/water, GVL/water, ILs/water, and DESs/water are summarized and

Table 2
Advantages and challenges of various solvent systems for biomass hydrothermal pretreatment.

Solvent systems	Advantages	Challenges
water	•less or no pollutants, •feasible to remove the majority of hemicellulose.	•unable to remove lignin fractionation, •lower sugar recovery compared with other methods, •produce of inhibitors, •high energy input (treatment severity).
Acid-catalyzed water	•lower energy consumption than that of water, •high efficiency for hemicellulose removal.	•toxicity of catalysts, •corrosive to facilities, •unable to remove lignin, •recovery and reactivation of catalysts.
ethanol/water	•feasible to remove the majority of hemicellulose and partial removal of lignin, •ethanol is easier to be recovered compared with catalysts such as acids.	•the use of ethanol increases the progress cost, especially the recovery progress, •lignin is not well concentrated compared with GVL/water, ILs, and DESs, •treatment severity is higher than that for catalysts and other organolsov.
gamma-valerolactone/water (GVL/water)	•economically feasible, •good fractionation of LCB, •high sugar recovery, •simple solvent recovery techniques	•high progress cost on GVL recovery.
ionic liquids/water (ILs/water)	•good fractionation of LCB, •high sugar recovery, •mild pretreatment condition (from 80 to 150 °C).	•toxicity of solvents, •higher progress cost on solvent recovery compared with other methods, •the cost-effectiveness is questionable.
deep eutectic solvents/water (DESs/water)	•promising alternatives for ILs, •biodegradable.	•higher viscosity compared with other solvents, •currently on infancy level.

presented in Table 2. In brief, water and water/catalyst are preferably beneficial to the removal of hemicellulose, but the removal of lignin is limited. Ethanol/water may be considered sustainable as ethanol is a commonly produced biorefinery product, but lignin is not typically less soluble in this solvent system. In contrast, GVL/water and ILs/water are highlighted as these two solvent systems can selectively dissolute lignin and hemicellulose, thus enhancing the enzymatic hydrolysis of cellulose. These two solvents systems are the most studied and likely the closest to large-scale applications, although some ILs are toxic and generally costly [128]. More studies on DESs/water for biomass pretreatment are encouraged, as these solvents are less expensive and less toxic compared to ILs.

2.2. Combination of hydrothermal pretreatment with other biological techniques

2.2.1. Hydrothermal pretreatment & anaerobic digestion (AD)

AD aims to degrade wet organic feedstocks (such as food waste and sludges) to generate energy-condensed biogas, which typically consists of approximately 60% methane and 40% carbon dioxide. Hydrothermal pretreatment has been studied as an applicable method to enhance biodegradation efficiency of typical bio-feedstocks, such as food waste, yard waste, or other putrescible biomass [129]. The use of hydrothermal solvents depends on the variation of feedstocks. For instance, food waste is generally pretreated with HCW without the addition of solvents such as ILs, organic solvents, or DESs to avoid their toxicity on AD microorganisms; while for LCB, solvents are generally required to achieve the delignification because lignin is a key component that can suppress the degradation of carbohydrates in LCB. Some of the representative studies are summarized in Table 3.

An early study by Qiao et al. [130] assessed the feasibility of hydrothermal pretreatment on the AD treatment of various feedstocks for biogas production, and indicated that hydrothermal pretreatment of fruit/vegetable, sludges, and pig manure enhanced biogas yield; while that for cow manure and food wastes decreased. More recent studies by Hesami et al. [131], Hashemi et al. [60], Kang et al. [132], Yu et al. [133], Wang et al. [134], Phuttaro et al. [135], and Wei et al. [136] further studied the valorization of different LCB feedstocks via hydrothermal pretreatment & AD. Similar to the enzymatic hydrolysis of LCB, the removal of lignin by hydrothermal pretreatment accounted for the enhanced methane yields and the decrease in digestion time. The mixing ratios of multiple feedstocks also influence the subsequent AD for methane production, as the mixing ratios are correlated to the generation of water-soluble carbohydrates during hydrothermal pretreatment [137]. Hydrothermal pretreatment of food waste mainly increases the dissolution of carbohydrates and protein, thus enhancing the digestibility of feedstocks and the yields of target products (such as methane and volatile fatty acids) during AD valorization. Jia et al. [138] studied the effect of hydrothermal pretreatment (90 °C for 30 min) on the performances of AD for food waste valorization. The study suggested that hydrothermal pretreatment could achieve an increase in net energy gain by 83.1% compared with untreated food waste. Moreover, hydrothermal pretreatment with subsequent AD of microalgae was studied by Passos et al. [139] and the methane yield was significantly enhanced by 40%. More recently, AD of waste sludge with hydrothermal pretreatment was studied by Yang et al. achieving the dissolution of >60% protein and 80% of polysaccharides in the liquid phase, and an increase of methane yield at > 31% [140]. Obviously, hydrothermal

Table 3
A summary of previous studies combining hydrothermal pretreatment with anaerobic digestion for biomass valorization.

Feedstock	Compositions	Hydrothermal stage	AD stage	Results	Reference
Various wastes	varied to different feedstocks	water; 170 °C for 60 min	mesophilic; seed sludge from a pilot-scale reactor	•Methane yield was enhanced after pretreatment except for food waste and cow manure, •The yields varied to different feedstock.	[130]
Sunflower stalks	glucan, xylan, lignin at 34.1, 24.4, and 26.8%	isopropanol/water/sulfuric acid; 140–200 °C for 30 or 60 min	mesophilic; 45 days	•The pretreatment removed the majority of hemicellulose and part of lignin, •Methane yield was enhanced to 278 mL/g VS, compared with that at 124 mL/g VS for control.	[131]
Microalgae	protein, lipids, and carbohydrates at 58, 19, and 22%	water; 110–130 °C for 15 min	Mesophilic; 30 days.	•Methane yield was increased by 41% compared with control, •Damages of algae cells were evidenced by microscopic images.	[139]
Safflower straw	glucan, xylan, lignin at 32.2, 18.9, and 20.8%	water/sodium carbonate; 120–180 °C for 1–5 h	mesophilic; 45 days	•The pretreatment removed the majority of both hemicellulose and lignin at 180 °C, •Methane yield was significantly enhanced, •The gasoline equivalent of hydrothermal pretreatment & AD was calculated.	[60]
Energy grass	cellulose, hemicellulose, and lignin at 33.9, 20.7, and 18.4%	alkaline solution; 35–121 °C for up to 24 h	mesophilic; seed sludge from a wastewater treatment plant	•Lignin removal enhanced the methane yield by 60 mL/g VS and decreased the digestion time to 10 days, •Correlation between lignin removal and methane yield was discussed.	[132]
Grass	cellulose, hemicellulose, and lignin at 42.6, 34.6, and 6.53%	calcium hydroxide/water; ultrasonic-assisted; 75 °C for 30 min	mesophilic; 12 days	•Cellulose/lignin ratio was enhanced after pretreatment, •VFA production was more than doubled compared with control, •Solid-liquid separation of pretreatment sample was highlighted for high VFA production.	[134]
Napier grass	Cellulose, hemicellulose, and lignin at 40, 32, and 12%	water; 125–200 °C for 15 min	mesophilic; seed sludge from a wastewater treatment plant	•Methane yield was improved by 35% with optimal pretreatment •Inhibitors were generated at 200 °C.	[135]
Energy grass	Cellulose, hemicellulose, and lignin at 36.2, 19.7, and 16.6%.	GVL/water; 135–180 °C for 90 min	mesophilic; lab-cultivated seed sludge	•GVL/water pretreatment achieved the removal of 33% lignin and maintained >80% of hemicellulose and >90% of cellulose •Co-production of biomethane and lignin nanoparticles were achieved	[148]
Food waste	lipid and protein at 27 and 20%	water; 90 °C for 30 min	mesophilic; 21 days; pig manure inoculum as seed sludge	•Methane yield was enhanced after pretreatment, •Energy efficiency was assessed for different scenarios.	[138]

pretreatment is widely applicable to various feedstock to enhance their AD performance. However, one of the key challenges in this combination is the production of inhibitors during hydrothermal pretreatment, especially under conditions with high severity. For example, almost all sugar derived chemicals such as 5-HMF, furfural and acids can pose inhibition to biological treatments [141]. Also, hydrothermal pretreatment of food waste can cause the production of toxics through the Maillard reaction, which may influence its subsequent AD treatment [142]. Thus, developing pretreatments with low pretreatment severity to avoid the generation of these toxics and methods for the removal of toxics are encouraged [143].

Given the proper hydrothermal pretreatment and detoxification of inhibitors, it is predictable that an increase in methane production could be achieved. Also, an energy gain could be obtained under optimal pretreatment conditions with ideal heat exchange between the hydrothermal and AD sectors, as the heat used for hydrothermal pretreatment can be used for the energy supply to maintain AD conditions. To gain some in-depth understandings of hydrothermal pretreatment, a comparison between this method and other pretreatment is required. However, the microorganism species of different AD systems are hard to be united because of the nature of AD seed sludges. To minimize this variety, a brief discussion on some studies from the same research group using the same feedstocks is presented. Sun et al. conducted a pretreatment of an energy grass (*Pennisetum hybrid*) via microwave (200 g feedstock, 1180 W for 3 min) [144], NaOH/water pretreatment (35–121 °C; 1–24 h) [132], hot water (160–200 °C for 20–60 min) [145], mechanical pretreatment (grinding for 1 min followed by sieving for size fractionation) [146], acetic acid/sodium chlorite/water pretreatment (80 °C for up to 200 min) [147], and GVL/water pretreatment (130–180 °C for up to 2 h) [148] for subsequent AD valorization. These treatments resulted in maximal biomethane yields at 169.3, 301.7, 290.6, 291.9, 228.0 and 287.6 mL/g VS, respectively, suggesting that hydrothermal pretreatment with hot water is likely a reasonable method for the AD of LCB. Mirmohamadsadeghi et al. investigated hot water pretreatment (120–180 °C for 30–50 min) [149], NaOH/water pretreatment (0–100 °C for 10–60 min) [150], and sodium carbonate/water (120–180 °C for 1–5 h) pretreatment [60] for the AD of safflower straw, achieving corresponding maximal methane yield at 245.28, 191.4, and 139.6 mL/g VS. Hot water pretreatment is preferable as compared to methods such as alkaline solution and sodium carbonate/water pretreatment for methane production from LCB. Considering a complete valorization for all compositions, other treatments for selective removal of lignin are likely a better solution to achieve the valorization of feedstocks to their maximum. For instance, a recent study by Wu et al. [148] using GVL/water pretreatment slightly enhanced the biomethane yield but achieved the co-production of lignin nanoparticles (LNPs) via precipitation of the pretreatment liquid waste. Given the variety in both compositions and microbial species in other wastes such as food waste and sludges, their AD performances could be highly variable. Thermal pretreatment at a lower temperature (<110 °C) has been recommended as a more cost-effective method for the AD of these wastes [141]. Further energy balance and techno-economic assessment of hydrothermal pretreatment and AD are discussed in Section 4.

2.2.2. Hydrothermal pretreatment & fermentation

Fermentation has also been widely used in biorefining, especially for the conversion of LCB-derived sugars to bulk products, such as ethanol, acetone, and butanol. Compared with other biological treatments, such as composting, enzymatic hydrolysis and AD, fermentation is more demanding in feedstock properties, microorganism seeds, and inoculum conditions [151]. Because of its requirement on feedstocks, fermentation is generally employed as a subsequent step after enzymatic hydrolysis of LCB. However, with proper pretreatment, the direct integration of hydrothermal pretreatment and fermentation is also possible for LCB. For instance, the study by Remon et al. assessed the direct production of fermentable species via microwave-assisted hydrothermal treatment (160–210 °C for 0–5 min) with model compounds (i.e., cellulose, hemicellulose, and alginic acid). The fermentability of hydrolysates was assessed by *M. pulcherrima* for 2-phenylethanol (2 PE) production, and the results demonstrated that fermentable species (cellulose, hemicellulose and alginic acid derived monomers and oligomers) could be produced via a direct hydrothermal treatment [152]. The hydrothermal pretreatment of both hardwood and softwood with acid-catalyzed GVL/water could achieve the direct production of nonenzymatic sugars with yields at 70–90% [92], which can be circulated to fermentation for ethanol production without enzymatic hydrolysis. A more recent study by Binder et al. used ILs for the direct saccharification of corn stover, achieving glucose and xylose recoveries at ~94 and 88% under 105 °C for 4 h, respectively [153]. In brief, the direct production of nonenzymatic sugars from LCB is a significant innovation of the conventional "pretreatment – enzymatic hydrolysis – fermentation" model, but requires a cost-effective process for product extraction and solvent recovery after hydrothermal pretreatment [154]. Also, as only part of the feedstocks (primarily cellulose and hemicellulose) is utilized via fermentation, cost-effective approaches are required for the valorization of non-fermentable fractions (mainly lignin) to achieve complete feedstock valorization. In the current LCB industry, lignin is often burned for its energy value. However, this undermines the chemical potential of the biopolymer to produce a variety of aromatic chemicals. Many reviews have discussed the valorization of lignin through different catalytic methods. The discussion focused on lignin is beyond the scope of this review, but readers are welcome to refer to some of the recommended reviews [155–158].

Hydrothermal pretreatment can also be integrated with biohydrogen production via dark fermentation (or acidogenic fermentation) of LCB. Eskicioglu et al. [159] conducted hydrothermal pretreatment of wheat straw, biomass sorghum, rice straw, corn stover, and Douglas fir bark with CO_2/water for 30 min under 25–175 °C. The obtained liquid fraction was used for dark fermentation to produce hydrogen, while the solid fraction was directly fed into an AD system to produce methane. This integration of hydrothermal pretreatment, dark fermentation and AD achieved energy yields at 9.5–11.7 MJ/kg biomass, 41% higher than the integration of hydrothermal pretreatment and AD. Murphy et al. [160–162] conducted a set of comprehensive studies using hydrothermal pretreatment for the subsequent dark fermentation and AD of seaweeds. In brief, hydrothermal pretreatment of *Saccharina latissima* at 100–180 °C for 20 min, led to hydrogen and methane yield at 6.9–13.7 and 278.7–345.1 mL CH_4/g VS, respectively. The energy balance assessment suggested a maximal energy conversion efficiency of 72.8% [160]. The performance of acid/water pretreatment was compared with acid/stream pretreatment for the dark fermentation and subsequent AD of algal bloom [161]. With both treatments conducted under 135 °C for 15 min, the hydrothermal pretreatment could achieve a higher production of soluble metabolite products (~360 mM) than stream pretreatment (~320 mM). One of their recent studies was a hydrothermal pretreatment (140 °C for 20 min) of *Laminaria digitata* with acid/water (sulfuric acid at 1 v/v%) [162]. Subsequent dark fermentation and AD achieved hydrogen and methane yield at 44.8 and 282.2 mL/g VS with total energy yield increased by 26.7% compared with unpretreated feedstock.

The integration of hydrothermal pretreatment and fermentation has also found its application for food waste valorization. For instance, Orozco et al. [163] pretreated starch under hydrothermal conditions (185–235 °C for 15 min) for the dark fermentation with *E. coli*. The integration achieved a maximal hydrogen yield at 0.38 mol H_2/mol glucose, compared with that for pure glucose at 0.35 mol H_2/mol glucose. Matsakas et al. [164] used water/acetic acid for the hydrothermal treatment of solid food waste, and subsequent fermentation showed that the pretreatment enhanced the ethanol yield by 13–16%. Ding et al. [165] conducted hydrothermal pretreatment (100–200 °C for 5–30 min) for the integrated dark fermentation and AD of food waste. The optimal pretreatment conditions (140 °C for 20 min) achieved

hydrogen and methane production at 43 and 511.6 mL/g VS, resulting in an energy conversion efficiency at 78.6%, compared with untreated food waste at 31.7%. Hydrothermal pretreatment can also promote the production of volatile fatty acids (VFAs) via anaerobic fermentation. Yin et al. [166] conducted hydrothermal pretreatment of food waste at 100–220 °C for 30 min for its subsequent anaerobic fermentation for VFAs production. The study achieved maximal VFA yields at 0.294–0.411 g per gram of food waste, but suggested that fermentative toxics (such as furfurals) could be produced when the temperature was increased to 200 °C and higher. Based on the optimal condition obtained by Yin et al. [167] the study combined pre-fermentation (25 °C for up to 21 day with indigenous microorganisms) and hydrothermal pretreatment (160 °C for 30 min) for fermentative VFAs production from food waste. This combination increased the VFAs yield by 21%.

Moreover, hydrothermal treatment has also found its application as a pretreatment for food waste composting. The study by Nakasaki et al. [168] pre-treated food waste at 180 °C for 30 min with subsequent composting with the addition of inoculated activating bacteria. The results suggested that hydrothermal pretreatment shortened the required composting time. However, the use of hydrothermal pretreatment to accelerate the process of composting seems economical inviable because composting is normally deemed as the cheapest form of organic material processing, which makes it difficult to justify the cost of hydrothermal pretreatment.

3. Hydrothermal valorization of enzymatic pretreated biomass or AD digestate

Hydrothermal treatment offers a technological option that can be used for further valorization of by-wastes (such as digestate generated from AD) generated from the biological valorization of biomass. Herein, post-treatment of biotreated feedstocks aims to avoid the disposal of organic wastes and produce some possible valuable products such as biochar or biocrude to achieve green valorization and a zero-emission end in an integrated circular bioeconomy [169]. The hydrothermal valorization of biological treatment derived byproducts primarily includes two modes: (1) hydrothermal valorization of enzymatic pretreated biomass and (2) hydrothermal valorization of solid digestate from AD. A review is given as follows based on the current research progress.

3.1. Hydrothermal valorization of enzymatic pretreated biomass

The combination of enzymatic hydrolysis with hydrothermal post-treatment has been seldomly studied. Obama et al. [170] conducted enzymatic hydrolysis of *Miscanthus*, leading to a slight disruption to the lignocellulosic matrix. This pretreatment was preferred for the following pulping process with ethanol/water hydrothermal treatment [170]. However, this method was not further studied, likely due to its high process cost and low benefit output. Another study was recently conducted by Kaushik et al. [171] for the valorization of food waste. The study used enzymatic hydrolysis with mixed enzymes and enhanced the concentration of organic monomers in the liquid phase. This process enhanced the quality of biochar and bio-oil produced by following hydrothermal treatment. The enzymatic pretreatment with subsequent hydrothermal post-treatment was further studied by Kannan et al. [172] for the valorization of seafood waste for hydrochar and biocrude production.

3.2. Hydrothermal valorization of anaerobic digestion-derived digestate

The valorization of AD-derived digestate has attracted wide interest recently, because the fast-growing AD industry is overproducing digestate; while the traditional land application of digestate is less desirable as it neglects the chemical potential of the organic materials and may pollute local land and water [173]. Agricultural wastes and manure-derived digestate contained a considerable amount of lignin and cellulose, both of which are potential feedstocks to produce phenols, glucose, and other value-added chemicals. Recent studies have considered the hydrothermal treatment of these digestates for the production of biochar or biocrude as fuels [174–180]. After hydrothermal treatment, the biochar or biocrude showed lower H/C and O/C atomic ratios as presented in Fig. 7 [180]. A brief review of some representative studies is given as follows.

3.2.1. Hydrothermal carbonization of digestate for biochar production

Hydrothermal carbonization of digestate follows the similar treatment conditions for the carbonization of lignocellulosic biomass that requires low temperatures and long reaction times (temperatures at < 300 °C, and treatment time at > 2 h) [181]. This method is preferred mainly because digestate is formed with high moisture content (>90%) due to the nature of AD, while other carbonization treatment such as pyrolysis requires minimizing the moisture content of feedstocks [35]. The hydrothermal treatment of maize silage derived digestate was conducted by Mumme et al. [180], achieving the highest biochar yield with ~85% of the initial carbon in digestate at 190 °C for 2 h. The higher heating value (HHV) of obtained biochar increased from 25.4 to 35.7 MJ/kg with the increase of treatment severity from 190 °C for 2 h to 270 °C for 10 h, suggesting that this biochar can be used as a solid biofuel. However, the char showed poor physical structure with less mesopore area, surface area, and micropore compared with cellulose char, suggesting that this digestate is unlikely suitable to be used as an absorbent. A later study by Reza et al. [174] studied the different structures of digestate-derived biochar and raw biomass-derived biochar via Optical microscopy. Briefly, digestate-derived biochar was granular, while raw biomass-derived biochar was spherical. Further studies from the same group (Mumme et al.) investigated the changes of lignocellulosic compositions with the enhancement of treatment severity and considered using a zeolite catalyst to improve the hydrothermal carbonization performances [175,176]. More studies on the hydrothermal carbonization of digestate are summarized in Table 4.

The application of digestate-derived biochar could be further expanded with the increasing interest of using biochar as an additive in AD systems, which could enhance the AD performance and achieved higher biogas yield [182]. Besides, with the progress of technologies for nano-biochar preparation, the low specific surface area and poor porous structure of digestate-derived char could be improved via reducing the size of the digestate-derived biochar to a nanoscale [183,184]. The land

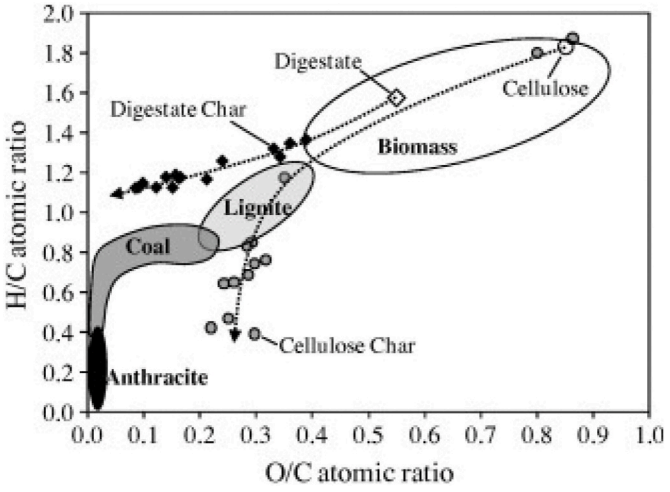


Fig. 7. Van Krevelen diagram showing changes in the atomic ratios of digestate and cellulose during hydrothermal carbonization. The course of the arrows indicates harsher process conditions. Adapted from reference [180] with permission.

Table 4
A summary of previous studies considering hydrothermal valorization of AD digestate.

Feedstock	AD stage	Composition of digestate	Hydrothermal stage	Results	Reference
Maize silage	thermophilic (55 °C)	37.6% lignin, 25.5% cellulose, crude fiber 25.9%	water; 190–270 °C; 2–10 h	•The mass yield of biochar was 55–85% of the initial carbon, •Changes of C, O, H during the hydrothermal treatment were studied.	[180]
Maize silage	thermophilic (55 °C)	ash 11.4%, cellulose 25.5%, lignin 37.6%	water; 230–250 °C; 6 h	•The mass yield of biochar was 40–50%, •Transformations during the formation of char were optically studied.	[174]
Wheat straw	thermophilic (55 °C)	5.6% ash, 18.9% hemicellulose, 44.6% cellulose, 21.4% lignin	water; 180–260 °C; 2–8 h	•The mass yield of biochar was 50–70% after 8 h, •Degradation of compositions during the process was studied.	[175]
Cow manure and maize straw	40.5 °C	C, H, and O at 47.6, 7.07, and 32.62	water; 190–270 °C; 2 h	•O/C and H/C ratios were decreased in biochar, recovery of various elements was studied, •Hydrothermal treatment performance was enhanced with the addition of zeolite.	[176]
Cow manure	room temperature	C, H, and O at 19.9, 2.8, and 60.8	water; 350 °C; 30 min	•Biocrude yield was increased from 24 to 44%, •Energy recovery of biocrude was 50–72%	[177]
Wheat straw/corn silage & cow manure	thermophilic (55 °C)/mesophilic (39 °C)	C, H contents were at 47.1 and 6.9/39.7 and 6.5	water; 200–240 °C; 10–360 min	•Distributions of N, S, P were traced during the treatment, •Nutrients were recovered after carbonization.	[178]
Sewage sludge	Not given	P content (20% solid, 65% inorganic, 15% organic); N content (60% solid, 35% inorganic, 5% organic)	water; 160–250 °C; 30 min	•Organic contents in the liquid were enhanced, •Inorganic N and P were decreased, organic N and P were increased.	[191]
Corn silage, grass silage, and cattle manure	mesophilic	cellulose 35.8%, hemicellulose 4%, lignin 24.9%	water; 190–250 °C; 3–6 h	•Mass yield at 60–70%, •Activated carbon was produced after activation of the hydrothermal product.	[179]
Cow manure	Local farm digester	C, H and O at 34.3, 3.7 and 25.9%	Phosphoric acid/ water; 300 °C; 40 min	•Acid addition enhanced the biocrude yield to maximal at 61% of carbon recovery, •Acid addition enhanced dehydration reactions and the production of cyclic furan compounds.	[187]
Cow manure	Local farm digester	Not given	Water; 300 °C; 60 min	•Considered membrane distillation for the treatment of biocrude, •75% of the initial water could be recovered from biocrude.	[194]
Hydrolyzed air flotation sludge	Mesophilic (37 °C)	C, H and O at 28.64, 4.45, and 24.6%; Ash content 39.53%	Water; 250–350 °C; 0–60 min	•7% of biocrude (based on dry basis of digestate) could be generated, •Hydrothermal treatment of digestate significantly reduced the cost for digestate treatment.	[190]
Digestate from a local plant	Not given	Not given	423 °C; 28 MPa; 8 min	•A methane rich syngas was produced, and salts were recovered, •A positive energy balance would be reached with throughput of 100 kg/h and carbon at more than 4 wt%.	[185]

use of digestate-derived biochar is also encouraged as the recent study by Funke [178] suggested that hydrothermal carbonization of N and P rich digestate could enhance the availability of phosphate and potassium ions in biochar. The alkali and alkaline earth metallic (AAEM) species in biochar can be collected via acid-leaching and be used as fertilizer [185].

3.2.2. *Hydrothermal liquefaction or gasification of digestate for biocrude or biogas production*

Compared with carbonization, the liquefaction of biomass and digestate requires higher temperature (280–380 °C) and shorter treatment time (<1 h) to achieve fast hydrolysis, dehydration and condensation of major components in their liquid forms [23,186]. A recent study by Eboibi et al. [177] conducted hydrothermal liquefaction of digestate obtained from the AD of cow manure at 350 °C for 30 min. The obtained biocrude recovered 76% of the initial energy with HHV at 28.4–31.2 MJ/kg. A more recent study by Posmanik et al. [187] suggested that the hydrothermal liquefaction (at 300 °C for 40 min) of digestate could be altered by the addition of acid that enhanced the dehydration reactions and suppressed the formation of carboxylic acids. The acid-catalyzed liquefaction of digestate achieved the increase of biocrude carbon yield from ~35 to 61% and the enhancement of HHV from 33.4 to 34.8 MJ/kg compared with acid-free process. The produced biocrude from hydrothermal liquefaction can then be used for further upgrading [188]. Okoro et al. and the corresponding research group conducted a set of works using hydrothermal liquefaction for the treatment of digestate with high ash content (>39%) and produced biochar, biocrude and biogases [189,190]. Moreover, hydrothermal treatment could also be used to re-collect digestible organics from digestate for AD treatment. Aragón-Briceño et al. [191] conducted hydrothermal treatment of sewage sludge digestate to extract organics containing C, P and N, the obtained liquid was rich in organics that could be re-circulated into the AD system for biogas production.

Under supercritical conditions, digestate can also be hydrothermally gasified into syngas like the treatment for biomass and other organic wastes [192]. The gasification of digestate was recently studied by Boukis et al. [193] with a well-established catalytic hydrothermal gasification system (6 wt% of total solids, 423 °C, 28 MPa, residence time 8 min, and carbon-supported ruthenium as the catalyst). The treatment achieved a syngas rich in methane (~0.31 mol gas/mol

carbon in feed) and hydrogen (~0.14 mol gas/mol carbon in feed), while the salt content was collected as liquid by-products. The study suggested that the integration of AD and hydrothermal gasification of digestate can achieve complete valorization of organic wastes.

4. Energy and economic assessment of combined hydrothermal and biological treatments

Hydrothermal treatment is applicable to enhance the yield of ideal products, shorten the reaction time, and generate high-value products from biological wastes. However, the combined process is inevitably accompanied by extra energy consumption and process cost. Therefore, the energy and economy assessment of the combined systems are needed to evaluate the possibilities for large-scale applications.

4.1. Energy balance assessment

The combination of hydrothermal and biological methods for biomass valorization requires extra energy input, especially for hydrothermal processing. However, more energy may be generated because hydrothermal treatment may result in increased production of bioenergy. Thus, assessment of the differences between the extra energy input of hydrothermal treatment and the energy output from enhanced products can be used to quantify the energy efficiency of the combined system. The assessment of energy input for hydrothermal treatment needs to take various factors such as liquid/solid ratio, desired hydrothermal temperature, and treatment time into consideration [12,195]. To compare the gained energy from different scenarios, the gasoline equivalent value or energy output through combustion is used for the assessment energy yields from products such as methane and ethanol [60,196]. The energy balance assessments of various hydrothermal and biological treatment scenarios are discussed in the following sections.

4.1.1. Energy balance assessment for processes combining hydrothermal pretreatment for enzymatic hydrolysis or fermentation

For "hydrothermal pretreatment – enzymatic hydrolysis", the pretreatment energy efficiency (η), primarily defined by Zhu et al. [195] can be employed to assess the effectiveness of different hydrothermal pretreatment methods.

$$\eta_{pretreatment}(kg\ sugar\ /\ MJ) = \frac{Total\ monomeric\ sugar\ yield\ (kg)}{Total\ energy\ consumption\ (MJ)} \quad (2)$$

However, the overall energy balance for the combination of hydrothermal pretreatment and enzymatic hydrolysis should be incorporated with "hydrothermal pretreatment – enzymatic hydrolysis – fermentation" as heat transfer between hydrothermal, enzymatic hydrolysis and fermentation might be required to save net energy cost. Another key presumption to conduct the energy assessment of this combined process is that the produced final products are all used for energy purposes, which is unlikely true for practical applications. Moreover, the integration also suggests costs for solvent and catalyst, while the valorization of byproducts including fractionated lignin and hemicellulose would add some extra values to the system. Based on these concerns, the feasibility of conducting hydrothermal pretreatment with enzymatic hydrolysis and fermentation generally requires an overall techno-economic assessment. A brief review of the techno-economic assessment is given in section 4.2.

4.1.2. Energy balance assessment for processes combining AD and hydrothermal treatment

For both "hydrothermal pretreatment – AD" and "AD – hydrothermal treatment for digestate valorization". This review recommends Net Energy Ratio (NER, shown in Equation (2)) as a united parameter to discuss the energy balance of integrated hydrothermal and AD processes [197].

$$NER = \frac{Energy\ output}{Energy\ input} \quad (3)$$

For the combination of hydrothermal and AD treatment, lower hydrothermal temperature, shorter retention time, higher solid/liquid ratio are preferred to save energy input. Energy transfer between the hydrothermal and biological sectors is critical to save energy. Moreover, the production of biogas should be optimized to achieve the highest energy gain. In a system with dilute sulfuric acid pretreatment for sunflower stalk at 170 °C for 5 min with heat recovery rate at 80% from the hydrothermal section, the solid load should be at least 200 g TS/L (total solid/liter) to achieve the energy balance (NER = 1) with the conversion rate of biogas to heat and electricity at 50 and 35%, respectively [198]. Passos et al. [139] studied that pretreatment of microalgae (2.0–2.5 w/w%) at 130 °C for 15 min could increase the final methane yield by 41% and achieve energy balance (NER = 1) given that the solid ratio of microalgae was thickened to 7.4%. Another study from the same group suggested that a facile pretreatment of microalgae at 75–90 °C for 10 h could enhance the methane yield by 70% and achieve positive energy gain. The NER values were at 1.19 and 1.27 for pretreatment at 90 and 75 °C, respectively, compared with those of 1.01–1.09 without pretreatment [199]. Optimizing the AD system is also of critical importance. A study by Jia et al. [138] proposed that a facile pretreatment of food waste (50 w/w%) at 90 °C for 30 min followed by a two-stage AD (hydrogenogenic stage and methanogenic stage) could achieve the highest net energy gain (NER = 1.21) compared with a process using the same pretreatment but AD by a single-stage reactor (NER = 0.76). A recent study by Kang et al. [145] used response surface analysis and optimized the hydrothermal pretreatment condition (175 °C 35 min) for the AD of a grass. They could achieve a NER at 2.07 given that the heat transfer efficiency was 90%, while mechanical pretreatment and acetic acid/sodium chlorite/water pretreatment for the same feedstock achieved final NERs at 1.7 and 2.2, respectively.

For the hydrothermal treatment of digestate, the energy gain is the heat value of the target products (hydrochar or biocrude), while the major energy cost is consumed during the hydrothermal treatment. The solid/water ratio is also critical to determine the final NER. A recent study by Okoro et al. [200]. conducted hydrothermal liquefaction of digestate for biocrude treatment. The energy assessment showed an NER of less than 0.75, which could be increased to 1 and higher if the solid/water ratio could be increased to 1/3 or higher. Whereas, a simulation study by Hoffmann et al. [201] conceptually integrated an AD plant with a hydrothermal liquefaction sector for digestate treatment to achieve the recovery of 62–84% of the biomass energy (corresponds to the NER at 1.63 to 3.25) in the form of both liquid and gaseous biofuels.

4.2. Techno-economic assessment

Currently, the scale-up applications of techniques combining hydrothermal and biological treatments are still limited, mainly due to the high capital cost, high energy consumption, and use of chemicals for the pretreatment [141]. Herein, the economic assessment of three integrations, i.e., "hydrothermal pretreatment – enzymatic hydrolysis – fermentation" for bioethanol (or other chemicals) production, "hydrothermal pretreatment – AD" for biomethane production, and "AD – hydrothermal valorization of digestate" are reviewed because these approaches are considered to have a relatively higher technology readiness level for industrial-scale biorefinery.

4.2.1. Techno-economic assessment for combined hydrothermal and fermentation for biomass valorization

The techno-economic assessments on the production of ethanol from LCB (i.e., corn stover) was conducted by Nation Renewable Energy Laboratory (NREL) on a "water/sulfuric acid pretreatment –enzymatic hydrolysis – fermentation" approach [202]. The NREL TEA suggested a minimum ethanol selling price (MESP) 2.15 USD/gal and a

gasoline-equivalent MESP 3.27 USD/gal to achieve the economic balance (plant life 30 years). Feedstock and enzymes were regarded as the major contributors, taking ~50% of the overall cost. A later study by Kumar et al. compared this water/sulfuric acid method with other pretreatments (dilute alkaline, steam explosion, hot water) [203]. Pretreatment using hot water was more cost-effective with the ethanol production cost at 3.07 USD/gal, while that for the other considered methods was 3.14–3.33 USD/gal (plant life 20 years). The organosolv process "ethanol/water/sulfuric acid pretreatment – fermentation" was assessed by Kautto et al. and suggested that lignin price was a major contributor to the MESP of their proposed scenario [204,205]. Increasing the price of lignin from 450 to 1000 USD per metric ton could drop the MESP from 3.1 to 2.0 USD/gal, suggesting that valorization of lignin is of great significance (plant life 30 years). Another study by Viell et al. also suggested that the price of lignin is a key factor for the valorization of wood chips via THF/water pretreatment – fermentation" for ethanol production. If lignin price is less than 500 USD per metric ton, the plant was unlikely to achieve economic balance [206]. The "GVL/water/sulfuric acid pretreatment – fermentation" scenario could achieve a MESP at 4.87 USD/gal of gasoline equivalent [92], which is comparable to the study conducted by Kazi et al. at 5.13 USD/gal with dilute acid pretreatment [207]. The scenario of "ILs/water pretreatment – fermentation" has two key factors, IL price and lignin selling price, that determine the MESP of bioethanol. As discussed by Klein-Marcuschamer et al., the MESP price could be less than 4 USD/gal, given that the IL price was 2.5 USD/kg (99.6% of the IL could be recycled), even if the lignin has 0 selling price; while the MESP could be 6.6 USD/gal when the IL price was increased to 50 USD/kg [208]. Another study by Baral et al. [209] suggested the recovery of IL at 97% and the recovery of waste heat at 90% was required to achieve a comparable MESP to the NREL method. Because of the high cost of most ILs, it is recommended that developing ILs or substitutes (DESs) with lower prices at 2.5 USD/kg or less is required [210].

4.2.2. Techno-economic assessment for combined hydrothermal and AD for biomass valorization

Integrating hydrothermal pretreatment and AD requires high energy input during the pretreatment sector, which is the key challenge for achieving the profitability of the whole hydrothermal and AD system. Xiao et al. [211] suggested using solar energy for the pretreatment that could achieve lower selling pricing at 0.0245 USD/kWh, lower than that at 0.0317 USD/kWh using conventional hydrothermal pretreatment and that at 0.0432 USD/kWh without pretreatment. Conducting pretreatment under lower temperatures could be another option. For instance, "dilute alkaline pretreatment – AD" is a plausible means to enhance the methane yield with less process cost mainly due to the lower energy input. The study by Monlau et al. assessed a dilute alkaline pretreatment & AD system, in which the dilute NaOH pretreatment was conducted at 55 °C for 24 h. This scenario was assessed to be economically beneficial with varieties to different feedstocks and local prices for biogas energy (extra net gains could reach 4.61, 14.98, and 18.44 USD per ton of TS in France, Germany, and Italy, respectively) [198]. They also recommended pretreatment with CaO at 35 °C for 2 days was also proposed as a cost-effective pretreatment to enhance the net gains of pretreatment – AD systems [212]. When both nitrogen-rich and carbon-rich feedstocks are available, co-digestion is regarded as a simpler and more cost-effective way to enhance the net gain compared with hydrothermal pretreatment [213]. Solé-Bundó et al. [214] demonstrated that the methane yield of microalgae could be enhanced by 77% by simply co-digestion with 50% of wheat straw, while pretreatment with 10% CaO at 75 °C for 24 h only enhanced the methane yield by 15%. Orive et al. [215] suggested that co-digestion could enhance the net present value by more than 5 times and shorten the payback period from 9.2 to 6.7 years for an AD plant considering co-digestion of olive oil mill pomace and pig slurry.

Considering hydrothermal valorization of digestate not only achieves near-complete valorization of biomass, but also increases the overall economic profits. Kassem et al. [216] assessed the techno-economic performance of adding a hydrothermal liquefaction sector to an AD plant for the treatment of digestate, and the whole system (with a lifetime 40 years) was levelized to electricity cost. The study suggested a minimum electricity selling pricing at 0.07 USD/kWh (local price at 0.06 USD/kWh), suggesting that the profitability is sensitive to local electricity prices. Bringing in the carbon credit based on low carbon fuel standard (LCFS) into account, the study by Kassem et al. [217] assessed that integrating AD and hydrothermal liquefaction could achieve a competitive levelized cost of energy of 10 USD/GJ (corresponds to 0.036 USD/kWh of electricity levelized cost). Medina-Martos et al. [218] assessed the integration of AD and hydrothermal carbonization. Compared with singular AD treatment, the addition of a hydrothermal sector enhanced the treatment cost by 42%, while the CO_2 emission was reduced from 72 to 18 kg per ton sludge. The feasibility of integrating AD and hydrothermal valorization of digestate is likely promising given a standardized and internationalized carbon credit system [219].

5. Challenges and perspectives

The integration of hydrothermal and biological treatment for biomass valorization has made a tremendous breakthrough over the past several decades, but many challenges still remain. Some of the current challenges and future perspectives are summarized below.

First, the concept of complete valorization of biomass has been emphasized as a principle for the future biorefinery, which is consistent with the principles of green chemistry and the development of a circular bioeconomy [220]. To this end, valorization of various byproducts generated from different treatments should be considered to ensure a sustainable flow of biomass materials. For instance, hydrothermal pretreatment of LCB with water and acid/water mainly generates a water solution rich in hemicellulose-derived compounds as the byproduct, while the subsequent enzymatic hydrolysis generates solid byproducts rich in lignin and cellulose. The hemicellulose-rich fraction can be fed into fermentation or AD systems to generate high-value products, while the lignin and cellulose-rich residue can be valorized via fractionation with selective solvents, or hydrothermal valorization through carbonization, liquefaction, or gasification.

Second, the combination of hydrothermal and biological treatments for biomass valorization requires interdisciplinary knowledge from both chemistry and biology. The chemistry of biomass composition under hydrothermal conditions varies due to the changes in treatment conditions and the use of different catalysts and solvents. For instance, the formation of pseudo-lignin during the hydrothermal pretreatment of lignocellulosic biomass has been proved to alter the enzymatic hydrolysis of biomass [221–223]. Also, the Maillard reaction happens during the hydrothermal treatment of food waste, and generates biological toxics, such as melanoidins, which adversely affect the subsequent AD performance [224]. Other biomass hydrothermal reaction pathways, such as the isomerization of sugar oligomers and polymers, and the self-assembly nature of lignin are likely to create a polymeric structure that adds challenges to the biological valorization of biomass [225,226]. Research on the fundamental mechanisms during hydrothermal treatments is essential to achieving an optimized integration of hydrothermal and biological treatment.

Third, conventional hydrothermal pretreatment of biomass with water or acid/water is neither energy-efficient nor cost-effective because of their high energy cost and low fractionation efficiency. The evolution of organic solvents, DESs and ILs has provided solutions to achieve high fractionation efficiency with less energy cost. However, the higher processing cost induced by these advanced liquid systems will pose great financial challenges to their implementations, and the scenario is exacerbated by the energy needed for product extraction and solvent recycling after the reaction. Therefore, this review calls for more studies

in developing cost-effective ways for product separation to facilitate their transitions into the current biorefinery scheme.

Fourth, bringing techniques from other disciplines such as material science into the hydrothermal and biological integrations can widen the spectrum of value-added products available from biomass. For instance, lignin nanoparticles (LNPs) have been successfully produced from lignocellulosic biomass via simple processes of dissolution and precipitation, whilst achieving the recycling of solvents [148]. Another emerging interest considers producing biochar (hydro-char or pyro-char) from the hydrothermal and biological treatments of biomass, and apply them in different environmental applications, such as pollutant absorption, soil pH remediation, and animal feed binder [184].

Finally, the integration of hydrothermal and biological treatments for biomass valorization means to achieve higher economic outputs compared to practicing them individually. Thus, a clear line should be drawn between "viable" and "profitable" to divide the consideration between energy expenditure and techno-economic assessment. Current progress indicates that integrating hydrothermal and biological techniques for biomass valorization may be profitable in some cases, but lacks attraction for large-scale investment due to relatively low technology readiness level. Considering that complete biomass valorization can achieve negative carbon emission, the standardization and application of the carbon credit conception in the near future will witness a booming biorefinery industry, when the integration of hydrothermal and biological techniques can be more attractive.

6. Conclusions

This work reviews the inter-disciplinary studies combining hydrothermal and biological techniques and assesses their prospects for biomass valorization. To this end, the effectiveness of different technology combinations is evaluated in terms of their current advances and challenges, based on the results of up-to-date studies. Importantly, hydrothermal treatments have been used widely as both pretreatment and post-treatment methods: (1) hydrothermal pretreatment with subsequent enzymatic hydrolysis, AD, fermentation, or composting for biomass valorization; and (2) hydrothermal post-treatment of enzymatic pretreated or anaerobic digested biomass.

Among the reviewed combinations of hydrothermal and biological techniques, saccharification of LCB through hydrothermal pretreatment and subsequent enzymatic hydrolysis has attracted the most research interests. Moreover, the applications of biomass-derived organic solvents and ILs are highlighted, as these solvents are the most studied solvents for biomass fractionation to prepare cellulose-rich compositions for glucose production via enzymatic hydrolysis. To deploy these techniques in biorefining, the effect of hydrothermal pretreatment on biomass fractionation, recyclability, toxicity to both human and enzymes, and cost-effectiveness need to be further understood; and also, new solvent systems with better fractionation performance, easier recycling process, less cost and lower toxicity than the currently available solvents are encouraged.

Hydrothermal pretreatment with subsequent AD is currently not cost-effective, mainly due to its high energy consumption during hydrothermal pretreatment, and its comparably lower net energy gain from the enhanced biomethane yield; especially, compared with proper co-digestion methods, hydrothermal pretreatment is shown to be redundant with higher process cost. More studies on the energy balance and economic assessment are encouraged to further understand the limits and opportunities of this combination.

Hydrothermal post-treatment of the solid fraction of AD-derived digestate is also highlighted in this study, as an alternative method to reduce the secondary environmental pollution of AD digestate. The current studies are mainly on the carbonization of digestate for biochar production. Given the specific compositions (such as lignin, cellulose and ash) of solid digestate, it is encouraged that more studies of different fractionation and valorization techniques need to be conducted. Other technology combinations including hydrothermal pretreatment coupled with subsequent fermentation, composting, and hydrothermal carbonization of enzymatic pretreated biomass are shown to be less feasible in terms of their energy efficiency.

Finally, to develop practical technologies for future scale-up biomass valorization using combined hydrothermal and biological techniques, multi-dimensional analysis (such as carbon footprint, environmental loads, sustainability of energy use, and economic benefits) need to be conducted.

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.

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