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Review

Advances in process design, techno-economic assessment and environmental aspects for hydrothermal pretreatment in the fractionation of biomass under biorefinery concept

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HIGHLIGHTS

- Techno-economic parameters of this pretreatment are presented.
- Plant cell wall and composition of biomass are shown.
- Environmental aspects of sustainability for hydrothermal are discuses.
- Process design integration for hydrothermal pretreatment is presented.

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ABSTRACT

The development and sustainability of second-generation biorefineries are essential for the production of high added value compounds and biofuels and their application at the industrial level. Pretreatment is one of the most critical stages in biomass processing. In this specific case, hydrothermal pretreatments (liquid hot water [LHW] and steam explosion [SE]) are considered the most promising process for the fractionation, hydrolysis and structural modifications of biomass. This review focuses on architecture of the plant cell wall and composition, fundamentals of hydrothermal pretreatment, process design integration, the techno-economic parameters of the solubilization of lignocellulosic biomass (LCB) focused on the operational costs for large-scale process implementation and the global manufacturing cost. In addition, profitability indicators are evaluated between the value-added products generated during hydrothermal pretreatment, advocating a biorefinery implementation in a circular economy framework. In addition, this review includes an analysis of environmental aspects of sustainability involved in hydrothermal pretreatments.

1. Introduction

Nowadays, to accommodate the escalating demand for energy required by various sectors of the economy, the global energy grid now employs, on average, 80 % nonrenewable fossil fuels. Due to the finite supply of fossil fuels and the serious concern regarding global warming, many countries' economies are changing dramatically, increasing the need for renewable energy supplies. Second-generation biorefineries are

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working for the production of renewable energy resources using agricultural residue. Because of its sustainable source and economic effectiveness. LCB, such as agricultural wastes, forestry residues, and energy crops, should be the major raw material for renewable biofuel and high added value compounds production (Liu and Chen, 2016; Silva et al., 2018).

LCB may be broken down into its constituent carbohydrate components through biochemical conversion processes, which microbes can then ferment to generate fuels and other high value-added chemicals (bioproducts), this because LCB are resistant to biodegradation, there is the necessity to follow up the pretreatment before enzymatic hydrolysis to change or eliminate structural and compositional barriers and increase cellulose accessibility to enzymes (Shiva et al., 2022a).

In biomass processing applied under the concept of biorefinery there are many types of processes from chemical, physicochemical and biological, however few processes have been developed from laboratory, pilot, demonstration and industrial scale (Ruiz et al., 2021). For biorefinery platforms, whether biochemical or thermochemical, it is necessary to take into account today aspects of integration of different unit operations, energy integration, economic and environmental aspects. In this case, hydrothermal pretreatment, also known as autohydrolysis or hot water extraction, is a potential low-impact pretreatment technology that focuses on removing the hemicellulose barrier to allow for enzymatic cellulose hydrolysis by the relocation of lignin fraction.

Enzymatic hydrolysis of pretreatment raw material to depolymerize its holocellulose into reducing sugars, followed by fermentation of the reducing sugars to produce bioethanol or other product of interest through biochemical platform. Due to its use of mild and noncorrosive working conditions, the enzyme-based application is preferable to hydrothermal treatments. Furthermore, compared to acid or alkaline hydrolysis, the process conditions using water during the pretreatment are quite mild, resulting in potentially high yields. The complex matrix structure of cellulose, hemicelluloses, lignin, and pectin in plant cell walls is primarily responsible for biomass enzymatic hydrolysis recalcitrance (Shiva et al., 2022b). The efficiency of biomass hydrolysis is determined mainly by the enzyme cocktail provided. It has recently been demonstrated that a combination of hydrothermal pretreatment and enzymatic hydrolysis of pretreated solids by cellulase and hemicellulase can boost saccharification efficiency. Furthermore, higher solids content restricts cellulose conversion, necessitating the use of additional enzymes to maintain the target yield (referred to as the “solids impact” in the following) could be an effective step. Furthermore, due to their differing compositions and physical qualities, a single cellulase combination is ineffective for all materials with varied pretreatments, necessitating the creation of a tailor-made cellulase mixture (Cintra et al., 2020; Nitsos et al., 2019). To completely deconstruct the complex structure of plant cell-wall polysaccharides, the adequate fractionation of biomass through pretreatment and complementary activity of enzymes with diverse activities is required. This review aims to show aspects related to the composition of biomass, fundamentals, design, technoeconomic and environmental aspects applied for hydrothermal pretreatment as a consolidated process in the development of biorefineries and impact on the circular bioeconomy strategies.

2. Architecture of the plant cell wall and composition of plant-based side-streams as feed stock for hydrothermal pretreatment

Plant-based agricultural, forest or food-industrial side-streams are largely composed of compounds originally forming the structure of the plant cell wall (Carpita and McCann, 2020; Lannuzel et al., 2022). This cell wall material comprises mainly polysaccharides in addition to the aromatic polymer lignin and, to a lesser extent, structural proteins (Ana et al., 2022; Carpita and McCann, 2020; Kabel et al., 2021).

The primary cell wall is the outer layer surrounding the plant cell and structured by cellulose microfibrils set in a matrix of pectin and hemicelluloses (e.g., xyloglucan). On the inside of the primary cell wall layer, the secondary cell wall can be found, mainly comprised of cellulose, hemicellulosic xylan (and mannan) besides lignin (Fry, 2018; Voiniciuc et al., 2018; Zhong et al., 2019). These plant cell wall polymers form a strict network via non-covalent and covalent bonding, and has been shown to permit mechanical strength and to protect against pathogenic or environmental stress (Voiniciuc et al., 2018). Worth to mention is that in particular lignin is resistant, and in pretreatment processing its presence shields the plant polysaccharides from carbohydrate degrading enzymes to reach their substrate (Yao et al., 2022).

2.1. Cellulose

The main polysaccharide in cell walls of photosynthetic higher plants is cellulose, which is a linear polymer of β-(1 → 4)-linked glucan chains (Fig. 1a) forming microfibrils via hydrogen bonds and van der Waals forces (Carpita and McCann, 2020). Cellulose varies in crystalline forms and chain length, i.e. a very high degree of polymerization (DP; 10,000–14,000) has been found in cotton cell walls (Timpa and Triplett, 1993). In contrast, cellulose in primary cell walls, is generally shorter (DP 500–8,000) (Mohnen et al., 2008).

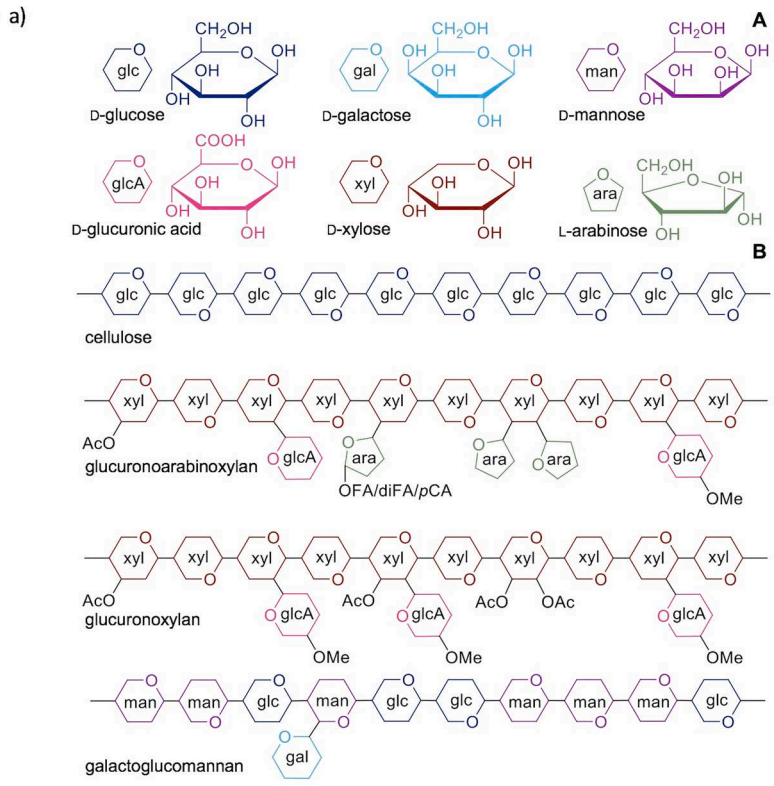
2.2. Hemicellulose

Hemicellulose is composed of heterogeneous polysaccharides, and its structure is highly varied across plant species (Ebringerová et al., 2005). In both grasses and cereal brans, the major hemicellulose is glucuronoarabinoxylan (GAX) (Kabel et al., 2021; Li et al., 2022) (Fig. 1a). GAX has a backbone of β-(1 → 4)-linked xylopyranosyl residues, which can be substituted at the *O*-3 or *O*-3 and *O*-2 position (di-substitution) with α-L-arabinofuranosyl residues, and/or at the *O*-2 position with (4-*O*-methyl-) glucuronosyl units. To a limited extent the xylosyl backbone can at *O*-2 and/or *O*-3 positions esterify to acetyl groups. For example, varying plant species and tissue types, the degree and pattern of substitution varies for GAX, likewise for the total composition of the cellulose, hemicellulose and lignin (Gírio et al., 2010; Vuong and Master, 2022). In GAX, the arabinosyl residues can be further esterified via the *O*-5 position to ferulic acid or diferulic acid (Underlin et al., 2020). As further discussed in the section “lignin-carbohydrate complexes,” these ferulate substructures form crosslinks between GAX molecules and between GAX and lignin.

In hardwoods, the hemicellulose glucuronoxylan (GX) is predominant (Fig. 1a). Like for GAX, the backbone consists of β-(1 → 4)-linked xylopyranosyl residues, which via the *O*-2 position can be substituted to 4-*O*-methyl-α-D-glucuronosyl units and is generally much richer in acetyl substituents than GAX (Ebringerová et al., 2005; Kabel et al., 2021; Li et al., 2022). Grasses and hardwoods additionally contain hemicellulosic mannans and glucomannans, composed of a β-(1 → 4)-linked mannosyl and β-(1 → 4)-linked mixed mannosyl-glucosyl backbone, respectively, and *O*-2 and/or *O*-3 acetylation (Carpita and McCann, 2020; Ebringerová et al., 2005). In softwoods, the main hemicellulose is (galacto) glucomannan having a similar mannosyl-glucosyl backbone, but with additional *O*-6 substitution to D-galactosyl units (Fig. 1b). Softwood hemicellulose also include GAX, although structurally different from GAX in grasses in terms of substitution pattern and degree. Specifically, 4-*O*-methyl-D-glucuronosyl and L-arabinosyl substituents are more abundant in softwood GAX, whereas acetyl esters are less prevalent (Ebringerová et al., 2005; Gírio et al., 2010).

2.3. Lignin

The aromatic plant cell wall polymer lignin is a highly heterogeneous structure built from 4-hydroxyphenylpropanoids (Vanholme et al., 2019). P-coumaryl, coniferyl, and sinapyl alcohol are the “monolignols” that participate in combinatorial radical coupling processes to biosynthesize lignin; when integrated into the polymer, these provide the corresponding p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S)



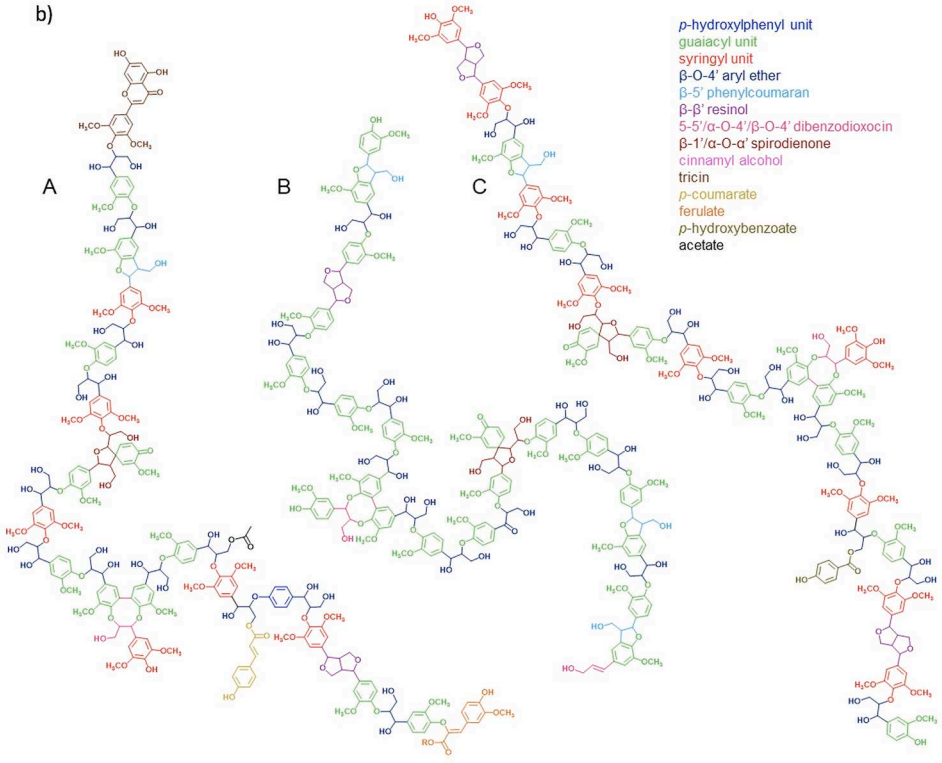


Fig. 1. (a) Structural representation of constituent monosaccharides (A) and polysaccharides (B) of the secondary plant cell wall. Me = methyl, Ac = acetate, FA = ferulate, diFA = diferulate, *p*CA = *p*-coumarate. (b) Model structures representing native lignin from grasses (A), softwood (B) and hardwood (C), based on Ralph et al. Note that even though we attempted to represent the individual substructures at levels according to those reported in the literature, model structures of 18–20 subunits cannot fairly represent all structures perfectly. In the grass model lignin ferulate R = H or arabinose. For simplicity, γ-acylation is only shown on β-*O*-4 aryl ethers.

units, respectively (Fig. 1b). The detailed underlying biosynthetic pathways (for example extensively reviewed in Dixon and Barros, 2019) are considered to be out of the scope of this review.

The resulting lignin subunit composition mostly rely on the taxon, and can vary further for species, tissue type, cell wall layer, transition phase, and even may depend on environmental circumstances (Liu et al., 2018). Overall, softwood lignin is predominantly built from G-units, whereas both G- and S-units, with traces of H-units, make up the majority of hardwood lignin. Although grass lignin is often higher in H-units, it further has the same subunits as hardwood (Vanholme et al., 2019). Between subunits, different aryl-ether and carbon–carbon interunit linkages exist, formed via the aforementioned combinatorial radical coupling, although the most abundant in lignin is the β-*O*-4′ aryl ether linkage (Ralph et al., 2019) (Fig. 1b). In addition to these β-*O*-4′ aryl ethers (i.e., generally about 80 % of all interunit linkages), other linkages found are resinols (β-β'), phenylcoumarans (β-5′), dibenzodioxocins (5-5′/α-O-4′/β-O-4′) and spirodienones (β-1′/α-*O*-α') (Ralph et al., 2019) (Fig. 1b). Condensed carbon–carbon linkages formed via coupling of free 5′-carbon ring-positions, is influenced by the degree of methoxylation. Therefore, condensed phenylcoumaran (-5′) and dibenzodioxocin (5–5′/-O-4′/-O-4′) substructures are more prevalent in softwood lignin (Ralph et al., 2019). These assumingly 'intersection points' (Crestini et al., 2011) via dibenzodioxocin, 5-5′ and 4-*O*-5′ linkages, have to date only been detected in their free-phenolic form and consequently, the lignin polymer might be more linear than generally considered (Ralph et al., 2019).

Further, the 'traditional' lignin subunits can be accompanied by incorporated monolignols with γ-acylated acetate/*p*-coumarate (i.e., for grasses) and *p*-hydroxybenzoate (i.e., for hardwood) (del Río et al., 2008; Mottiar and Mansfield, 2022). In some grass species that are rich in γ-acylated moieties, tetrahydrofuran substructure linkages in place of resinol connections form (Lu and Ralph, 2008). Yet, since the β-*O*-4′ aryl ether linkage is most abundant, here γ-acylation is mostly found.

More recently, other substructures than the typical monolignols described above have been described to participate in lignin biosynthetic routes. Examples include the flavonoid tricin found in grasses, hydroxystilbenes found in the endocarps of palm fruit and spruce trees, and diferuloylputrescine found in maize cobs (del Río et al., 2022, del Río et al., 2020).

For grass lignin, even, tricin is nowadays considered to be a starting point for the further biosynthesis (Lan et al., 2016, Lan et al., 2015), which previously has only been suggested for ferulates.

In addition to having consequences for the lignification process, these examples show the virtually limitless variety that may exist within lignin. Indeed, it has long been known that different lignin structural characteristics respond differently to pretreatment; as a result, a thorough knowledge and study of lignin structure are crucial for biorefinery incentives aimed at lignin removal or conversion (Hilgers et al., 2020; Van Erven et al., 2019).

2.4. Lignin-carbohydrate complexes

Lignin-carbohydrate complexes (LCCs), also known as covalent links between lignin and hemicellulose, have long been proposed and discussed in previous studies (Giummarella et al., 2019). Five main LCC linkage types have been proposed for woods: α-ether, α-ester, γ-ester, phenyl glycoside and acetal linkages. But only recently explicit evidence of one of these linkages was shown (Giummarella et al., 2019; Nishimura et al., 2018). Via multidimensional NMR analyses, inJapanese red pine, a mannosyl unit in glucomannan directly linked to the benzylic carbon of a β-*O*-4′ aryl ether via an α-ether bond (Nishimura et al., 2018).

Grass and cereal bran LCCs are considered to exist via ferulate and diferulate 'bridges' between GAX and lignin (Ralph et al., 2004; Underlin et al., 2020). The (di) ferulates (i.e., esterified to the *O*-5 position in arabinosyl units) can directly participate in the combinatorial coupling reactions during lignin biosynthesis as described for the monolignols and their conjugates (Ralph, 2010). Alternatively, these ferulates may also be 'passively' incorporated if their phenolic hydroxyl groups participate in nucleophilic addition to the quinone methide intermediates to yield ferulate α-ethers (Lam et al., 2001; Ralph et al., 1995). Various diferulate structures have been identified and further contribute to the complex, and heterogenous, grass lignin structures (Ralph, 2010; Underlin et al., 2020).

3. Process design for hydrothermal processing

Hydrothermal processing or pretreatment is a thermochemical platform to transform biomass into valuable products, using only water at subcritical and supercritical conditions (Ruiz et al., 2021). The term "hydrothermal" proceeds from a geological origin, which simulates the natural phenomenon of fossil fuels formation using reactors in a very short time (Ayala-Cortés et al., 2021). Depending on the operation conditions used during the process, several products can be obtained from biomass during this pretreatment as biofuels and high added value compounds (Ruiz et al., 2013) (Fig. 2). At temperatures ranging from 150 to 220 °C [~4.76 to ~23.19 bar] (a process known autohydrolysis) in subcritical conditions, the solubilization and hydrolysis of hemicellulose is initiated by the mildly acidic environment provided by the protonation of water molecules (hydroxonium ions, H_3O^+) at the elevated high temperatures scale, which is further aided by the in situ released acetic acid upon gradual decomposition of the hemicellulose (Ruiz et al., 2021, Ruiz et al., 2017). Recalcitrance property of biomass due to lignin, which works as a barrier and nonproductive absorbance of cellulase enzyme during the hydrolysis process, makes it necessary to remove lignin. During the hydrothermal pretreatment, lignin relocates, this is an aromatic Klason lignin positive substance from carbohydrate and hemicelluloses, providing more accessibility to the enzyme to work on internal units of the biomass (Hernández-Beltrán and Hernández-Escoto, 2018; Liang et al., 2020; Wang et al., 2019). Ilanidis et al. (2021) reported that under acid conditions can be formed a pseudo-lignin. Also, at these operational conditions the water hydrolyses the glycosidic bonds of hemicellulose and cellulose to produce xylooligosaccharides (XOS), glucooligosaccharides (GOS), arabinooligosaccharides (AOS), acetyl groups, phenolic compounds, xylose, glucose, arabinose, acetic acid, hydroxymethylfurfural, furfural (Ruiz et al., 2020). The challenge of any pretreatment is to reduce the resistance of the LCB to biological processing with low operating costs, high yields of cellulose recovery and no generation of inhibitory byproducts (Song et al., 2021). The resistance of LCB to enzymatic hydrolysis is due to both the physical structure and its chemical composition (Mankar et al., 2021). The highly organized architecture of secondary cell walls and the presence of hemicellulose and lignin creates physical barriers that limit the accessibility of enzymes to cellulose (Martín et al., 2022).

In a search in the SCOPUS database in 2022 using as keyword hydrothermal pretreatment, 2,096 documents were found, which the first one was published in the 1960s, however, the topic gained relevance at the beginning of the 21st century, mainly in the bioenergy, chemical engineering, and environmental topics. Hydrothermal pretreatment of LCB is found in literature as autohydrolysis, hot-compressed water pretreatment, liquid hot water (LHW) and steam explosion (SE) pretreatment (Ruiz et al., 2020). Hydrothermal pretreatment resembles a diluted acid pretreatment in many of the chemical reactions that occur during pretreatment (Yue et al., 2022). The pH of the water changes under thermal stress conditions, when the temperature increases of 25 to 250 °C, respectively, the pH decreases of 7.0 to 5.5, respectively (Yang et al., 2018). As the water is heated, the hydrogen bonds are broken increasing the ionization constant (Kw) from 10^{-14} mol^2/L^2 at 25 °C to 10–11 mol^2/L^2 at 300 °C (Chen et al., 2022). Drastic changes in the properties of water under subcritical conditions (Kw, density, viscosity and dielectric constant) favor the dissolution of organic matter and thus accelerate chemical reactions (Cheng et al., 2021). The acetyl groups of hemicellulose can form organic acids (formic acid, acetic acid and

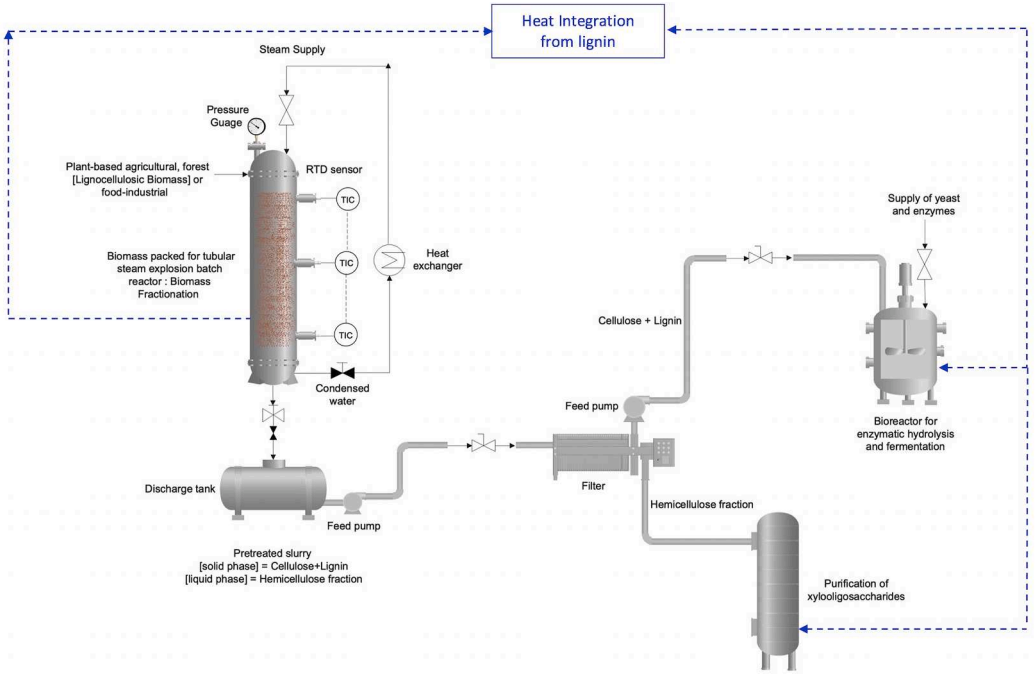


Fig. 2. Biorefinery process for lignocellulosic biomass fractionation using pilot-scale tubular steam explosion batch reactor in the production of high added products and biofuels and heat integration.

levulinic acid) and the H_3O^+ ions generated, increases ionization which promotes greater depolymerization of polysaccharides (Singh et al., 2019).

If water is mixed with LCB in a stainless-steel reactor, different reactions can occur, which depend on the temperature and heating time (Singh et al., 2021). Hydrothermal pretreatment removes firstly pectins and arabinogalactans, followed by hemicellulose and amorphous cellulose, causing a disorder in the cell wall and higher porosity and cellulose accessibility (Ruiz et al., 2020). Although hydrothermal pretreatment increases the fraction of lignin and crystalline cellulose, physical modification counteracts this effect and increases enzymatic digestibility (Ríos-González et al., 2021). Hemicellulose and amorphous cellulose are completely hydrolyzed at temperatures ranging from 220 and 230 °C, respectively. However, at these temperatures, xylose and glucose released can be dehydrated and converted to furfural and 5-hydroxymethyl furfural (HMF), respectively (Sun et al., 2022). Since glucose is more difficult to dehydrate than xylose under the same conditions, the yield of HMF is generally lower than that of furfural (Sarker et al., 2021). Crystalline cellulose is depolymerized above 220 °C, while proteins present, which play an important role in cell wall structure can be hydrolyzed to amino acids at temperatures that range from 250 to 400 °C, respectively (Bhatia et al., 2020). Lignin components (p-coumaryl, coniferyl and sinapyl alcohols with aromatic groups p-hydroxyphenyl, guaiacyl and syringyl) are usually depolymerized to phenols, cresols, syringols, guaiacols, and catechols, and the degree of which depolymerization depend on process conditions (Sethupathy et al., 2022). Inhibitory lignin-derived molecules that can be found in hydrolysates depending on pretreatment conditions are mainly syringic, ferulic, and 4-hydroxybenzoic acids, syringaldehyde, vanillin, and 4-hydroxybenzaldehyde (John et al., 2022). These compounds, along with furfural, HMF, acetic acid and formic acid can significantly inhibit fermentation and other biological processes (Tramontina et al., 2020).

3.1. Hydrothermal pretreatment under subcritical conditions: Steam explosion and liquid hot water

Steam explosion pretreatment (SE) and liquid hot water (LHW) are the most studied hydrothermal pretreatment processes for LCB. This can be corroborated with the analysis carried out in the SCOPUS database in which 606 documents related to LHW and 2-fold (1,211) of steam explosion pretreatment were found. Although the two methods are similar due to that both use only water as solvent, they differ in some features such as equipment and operating conditions and costs (Sarker et al., 2021).

LWH pretreatment is considered more affordable and simpler as it does not require specialized reactors which commonly are fabricated in 316 stainless steel tubes (Ruiz et al., 2021). As the main operational difference, SE consists of a sudden decompression of biomass treated with steam at temperatures in the range of 180 °C to 240 °C (10–33.5 bar) for short periods (3–20 min) (Yu et al., 2022). While in LHW the biomass and liquid water suspension is maintained at high pressure to avoid boiling at temperatures in the range of 150 to 260 °C, respectively (Chen et al., 2022). Utility costs and economic margin vary according to the pretreatment method used. LHW consumes more energy and water (6.7 MJ/ton biomass and 3.01-ton water/ton biomass) compared to SE (1.9 MJ/ton biomass and 1.3-ton water/ton biomass). da Silva et al. (2019) reported a higher economic margin in the ethanol production from corn stover biomass pretreated by LHW. However, in recent years, SE pretreatment has gained attention, as it is an efficient method with low environmental impact (Antczak et al., 2022).

Although numerous studies on LCB pretreatment using LHW and SE have been published, less than 60 documents were found comparing LHW vs SE. Table 1 summarizes recent work indicating the ideal pretreatment method in each study and the advantages for each case.

3.2. Severity factor on biomass pretreatment

In order to understand the correlation between temperature and time during the hydrothermal pretreatment of LCB, in 1987 the research group of Prof. Esteban Chornet proposed the famous model known as severity factor o index [$\log_{10}(R_o)$] (Chornet and Overend, 2017; Overend and Chornet, 1987). Severity factor combines these two variables as a single parameter, assuming a behavior of a first order reaction (Lachos-Perez et al., 2022). "Ro" was based on models applied in softwood kraft cooking process (H-factor), aqueous-steam prehydrolysis of Kraft (P-factor), coal liquefaction process (severity index) and cracking reactions

Table 1
Main results obtained in recent studies comparing LHW vs SE pretreatment of LCB.

Biomass	Purpose/ Application	Operational conditions	Main advantages	Sugar concentration/ glucose yield	Reference
Populus trichocarpa wood	Saccharification	SE/ 190 °C, 15 min	*Higher hemicellulose depolymerization *Less inhibitors formed *Similar enzymatic hydrolysis yield	676.4 mg/g pretreated biomass	Antczak et al. (2022)
Olive tree pruning	Ethanol production	SE / 200 °C, 5 min	*Higher sugar recovery *Lower temperature used *Similar ethanol production	80.4 % (sugar recovery)	Romero-García et al. (2022)
Sugarcane bagasse	Saccharification	LHW/ 195 °C, 10 min	*Higher hemicellulose hydrolysis *Higher sugars released during enzymatic hydrolysis	~ 37.5 g/L (glucose release in the enzymatic hydrolysis)	Bianquini et al. (2020)
Sugarcane bagasse	Ethanol production	LWH/ 195 °C, 10 min	*Higher glucose released during enzymatic hydrolysis *Lower temperature used *Higher ethanol production	~ 23 g/L (glucose production)	Florencio et al. (2019)

(cracking index) (Ruiz et al., 2021).

$$\mathrm{Log}_{10}[R_o] = \int_0^{tf} \exp\left[\frac{(T(t)-100)}{14.75}\right] \bullet dt \quad (1)$$

where (Log[R_o]) is the severity factor (min), t_f is the operation time (min), *T(t)* is the temperature of process (°C), 100 °C is the base of operational temperature during the hydrothermal pretreatment (In theory, this is where the reactions in the biomass begin), and 14.75 is an empirical parameter with activation energy for the breakdown of glycoside bonds of carbohydrates in the hydrothermal processing (Aguilar et al., 2018; Rosero-Chasoy et al., 2023). If the hydrothermal process is carried out under non-isothermal conditions, the above equation can be modified as (Pino et al., 2021, Pino et al., 2019).

Severity factor for non-isothermal regime considers the heating and cooling profiles and the isothermal process. However, in some works the isothermal regime is not considered, and therefore the reactor is only heated to the desired temperature and immediately cooled (Díaz-Blanco et al., 2018). The effects of temperature and time on hydrothermal processes can be combined with acid concentration when an acid catalyst such as H_2SO_4 or HCl are used (Sun et al., 2022). This combined factor (CSF) is calculated considering the pH of the reaction medium according to the following equation:

$$\log \mathrm{CSF} = \log_{10}[R_o] - \mathrm{pH} \quad (2)$$

3.3. Process integration and technological maturity of hydrothermal pretreatment

The integration of unitary operations in the development of second generation biorefineries is essential with the aim of reducing and optimizing equipment and making the energy of the process more efficient. According to Chaturvedi et al. (2020), first it is necessary to list all the unit operations and processing path and their level of depth. Second, by classifying these process designs based on the type of biomass, and list the operating conditions of each operating unit, such as feed input, product quantities, and their yields. They concluded that the multiple raw materials or multiple product process designs are taken as the minimum satisfactory condition to be considered a biorefinery, it is also necessary to write more details of the operation of each unit, which allows more comprehensive techno-economic comparisons between processing pathways and lead to more robust process designs for biomass utilization. In addition to the integration design processes in biorefineries, energy integration plays a very important role. Ruiz et al. (2020) reported a process flowsheet that include hydrothermal pretreatment in terms of biorefinery integrated process design and heat integration. They mentioned that the hydrothermal pretreatment reactor should not be evaluated in isolation from the other unit operations in the process flow, mainly if bioprocesses are involved in downstream processing. In a recent work Singhania et al. (2021) reported a process flowsheet in the development of a second generation biorefinery with the integration of energy and enzyme production using hydrothermal pretreatment. They showed the integration of energy (co-generation of electricity from lignin), production of enzymes, ethanol, and high added value compounds (oligomers, organic acids, furans) in 2 scenarios: 1) producing only ethanol (cellulose fraction) and electricity and 2) producing ethanol, electricity, and high added value compounds (oligomers, furfural, acetic acid, and formic acid from hemicellulose fraction). The Fig. 2 shows the design proposal and energy integration in the development of second generation biorefineries using hydrothermal pretreatment as a central process.

On the other hand, the technology readiness level (TRL) was developed by NASA and is the maturity level of a technology or the process. The TRL is based on a scale from 1 to 9, being the scale of 9 the most mature technology. Okolie et al. (2022) reported that the TRL of biochemical platform for biomass conversion and valorization is in the range of 4–5, while for thermochemical are expected to reach a TRL of 9 in the next decades. In a recent work, González-Gloria et al. (2022) showed different advantages of the hydrothermal process, including the biorefinery process, they reported that hydrothermal has been applied from demonstrative to industrial levels.

4. Techno-economic assessment of hydrothermal technology

The pathways of LCB deconstruction and fractionation with hydrothermal technology for biofuel and value-added product production have been widely studied (Ahmed et al., 2022; Preethi et al., 2021; Sarker et al., 2021). This section focused on the techno-economic assessment of the application of hydrothermal technology to the solubilization and fractionation of LCB and the production of biobased products, such as oligosaccharides, sugars, amino acids, bioactive compounds, and bio-oil. In some cases, hydrothermal technology was used as a pretreatment for biofuel production. Techno-economic assessment (TEA) plays an important role in the scale-up and large-scale implementation of hydrothermal technology. TEA has been widely used as a crucial tool in understanding cost benchmarks, potential feasibility, required research, and decision-making that may be necessary for scale-up (Mishra et al., 2022). The most critical parameters evaluated in a techno-economic analysis are capital investment, operating cost, cost of manufacturing, and profitability indicators. However, the first approach before starting an economic analysis of laboratory-scale processes is the determination of the scalability of the process. Fig. 3a shows a schematic diagram of the steps for conducting a techno-economic analysis of hydrothermal processes.

4.1. Scale-up of hydrothermal pretreatment

The scale-up of the process (from the laboratory to pilot and industrial scales) should be evaluated to determine the probable implementation costs, considering the equipment cost and equipment attribute. Until the moment, hydrothermal pretreatment of LCB has been

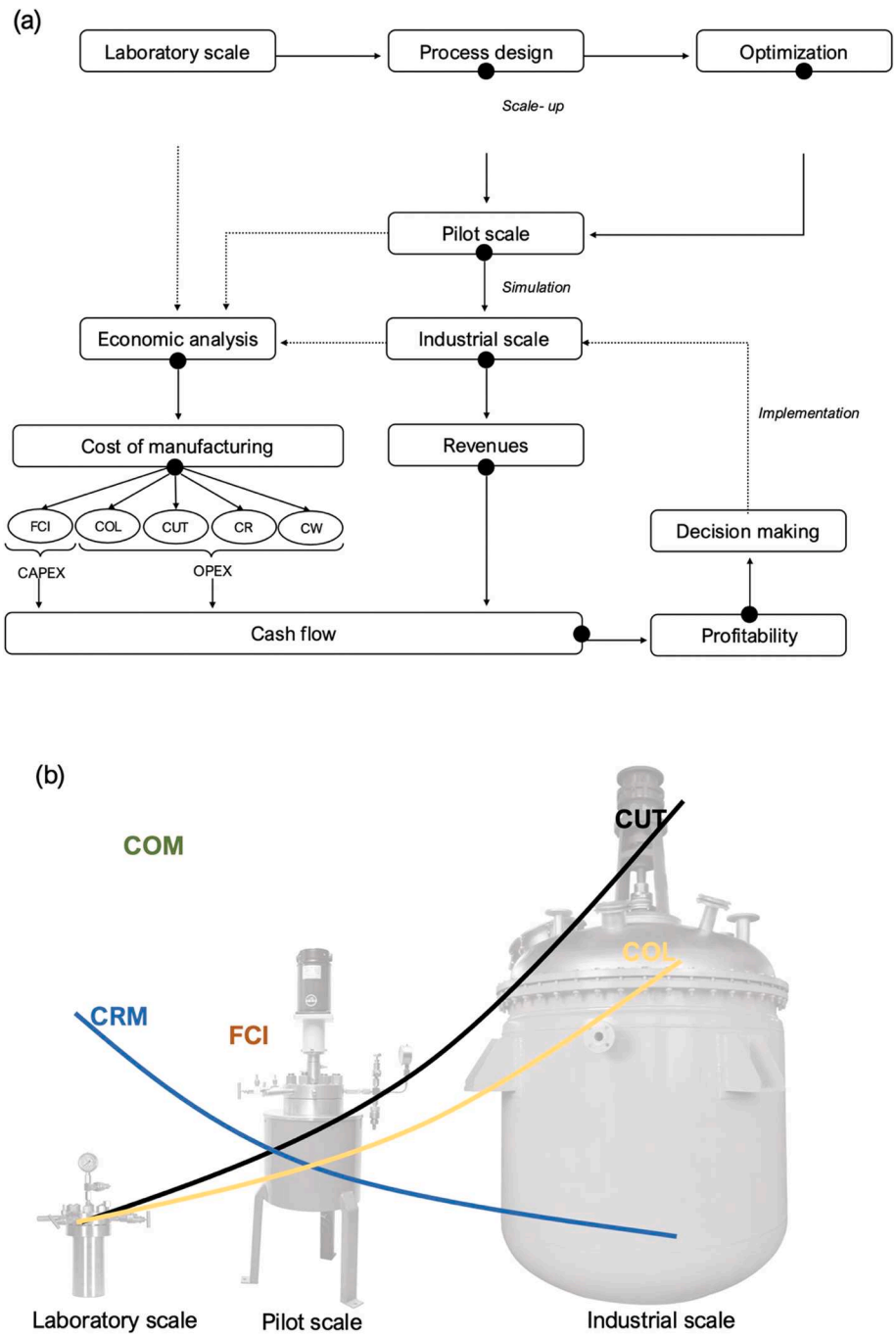


Fig. 3. a) Schematic diagram of the steps for conducting a techno-economic analysis of hydrothermal pretreatment under biorefinery concept; b) scale-up of hydrothermal pretreatment- operational cost labor and the cost of utilities.

studied from the laboratory to the pilot scale but is still in a very early stage of development (Jimenez-Gutierrez et al., 2021). The study of pilot plant-scale processes might be performed to provide reliable stream compositions and insight into realistic process conditions (Jimenez-Gutierrez et al., 2021). Process intensification offers opportunities to reduce capital costs in industrial plants (van der Wielen et al., 2021). For this, considering the scale-up based on the laboratory study, the purchased cost of the equipment should be estimated according to the scaling exponent method (Eq. (3)). This method allowed the calculation of the purchase price of equipment with a different size when the cost of a given size was known (Okolie et al., 2021) adjusting with the scaling exponent for each equipment (Turton et al., 2003).

$$C = C_0 \times \left(\frac{S}{S_0}\right)^f \tag{3}$$

where C represents the calculated actual equipment (for the current base year), C_0 represents the base cost of the equipment, S is the equipment capacity, S_0 is the base capacity, and f is the empirical scaling exponent.

The equipment cost should be adjusted to the base year by using the Chemical Engineering Plant Cost Index (CEPCI) (Eq. (4)) (https://www.chemengonline.com).

$$C = C_0 \times \frac{CEPCI}{CEPCI_0} \tag{4}$$

where C is the adjusted cost for the proposed process (current base year), C_0 is the reference cost of the equipment, $CEPCI$ is the equipment price for the studied year (current base year), and $CEPCI_0$ is the equipment price associated with the year of the reference cost of the equipment.

The Eqs. (3) and (4) should be used to adjust the scale and consider the change in equipment cost over time to implement the pilot-scale process. In addition, there is a strong correlation between hydrothermal pretreatment at a laboratory and pilot plant scale, demonstrating that efforts should be conducted to implement the process at a larger scale (Jimenez-Gutierrez et al., 2021).

The process intensification of hydrothermal technology has been widely assessed by the optimization of operational parameters (temperature, pressure, solvent-to-feed ratio, flow, solvent, and residence time) under laboratory conditions (Sun et al., 2022). The operational conditions that promoted the highest yield of the desirable product (oligosaccharides, sugars, amino acids, bioactive compounds, among others) from LCB should be used for the scale-up study. For instance, Torres-Mayanga et al. (2019) designed a laboratory-scale (internal volume of 110 mL) flow-through hydrothermal process to produce hemicellulose sugars from brewer's spent grains, the main lignocellulosic by-product generated from the beer industry. The scale-up study evaluated the hydrothermal process under a pilot plant (reactor of 10 L) and an industrial plant (reactor with 500 L) (Sganzerla et al., 2021b). A pilot-scale continuous hydrothermal reactor for the pretreatment of biomass (sorghum, agave bagasse, corn stover, sugarcane bagasse, and wheat straw) was built with different capacities (from 3 to 8.3 kg/h of biomass) and volumes (from 12.56 to 24.19 L) (Table 2). A pilot-scale reactor for hydrothermal carbonization was built with a volume of 0.1 m^3 and has been designed to operate under a wide range of operating conditions (at 300 °C and 86 bar), indicating that this process is reliable and safe (Zaccariello et al., 2022). In general, the pilot-scale process consists of a fed hopper, open flight and full pitch equalizing screw feeder, a hydrothermal reactor connected with a condenser, and a section for receiving the pretreated biomass Cheng et al., 2019a; Cheng et al., 2019b). From an economic perspective, all the equipment necessary for hydrothermal pretreatment should be considered in determining the fixed capital investment.

4.2. Capital and operational costs of hydrothermal pretreatment

Hydrothermal technology still represents one of the most cost-effective pretreatment methods for the solubilization of LCB (Scapini et al., 2021). The cost-effective pretreatment methods are directly associated with the capital investment of the process but also with the demand for high temperature and pressure (Xu and Li, 2021). Therefore, the determination of capital expenditures (CAPEX) and operational expenditures (OPEX) and the possibilities for their reduction during the scale-up are necessary to obtain a profitable hydrothermal process. Considering the scaling up of a process from a laboratory- to a pilot-scale plant, the fixed capital investment of hydrothermal technology represents the highest cost.

In the case of hydrothermal pretreatment of sugarcane bagasse for second-generation ethanol production, the liquid hot water pretreatment (180 °C, 10 min, and 20 % (w/v) solids loading) represented 28.17 % (US$ 102 × 10^6) of the fixed capital investment of the process with a simulated annual capacity of 14.33 × 10^6 L (Cheng et al., 2019). Moreover, the subcritical water hydrolysis of sugarcane bagasse (200 °C, 15 MPa, and residence time of 8 min) in a simulated industrial process (310 tons bagasse/day) to produce 6740.5 kg ethanol/day presents a fixed capital investment of US$ 27.4 × 10^6, where 35 % (US$ 9.6 × 10^6) is associated with the cost for implementing the subcritical reactor (Sganzerla et al., 2022). The fixed capital investment for liquid fuel production from woody biomass via hydrothermal liquefaction (355 °C, 20 MPa) was US$ 488 × 10^6, where the cost of the reactor system represented 18 % (US$ 88.7 × 10^6) (Zhu et al., 2014). This fact demonstrated that in the simulated industrial process of hydrothermal pretreatment, the cost of the reactor vessel is the largest expense for process implementation.

The operating costs contain two components. One is variable operating costs, including raw materials, waste stream charges, and by-product credits. The other is fixed operating costs, including labor and other overhead costs (i.e., maintenance and property insurance) (Lan et al., 2021). During the scale-up of hydrothermal pretreatment, the cost of operational labor and the cost of utilities usually increase when discrimination is over the cost of manufacturing (Fig. 3b). The hydrothermal process demands a high amount of energy for the solubilization of the biomass. In the case of sugar production from brewer's spent grains, the heat required for the reactor was calculated as 610 kJ/kg (Sganzerla et al., 2021b). The semi-continuous operation for the hydrolysis of sugarcane straw demands 1096 × 10^6 kcal/day (Sganzerla et al., 2022).

In the case of hydrothermal pretreatment followed by anaerobic digestion, the electricity demand dominates as OPEX with values of approximately 70 % (Seiple et al., 2020). Therefore, strategies should be optimized to decrease energy consumption in the hydrothermal reactor. According to Cheng et al. (2019), higher solids loading (~50 %) in the hot water pretreatment could be an alternative for improving the energy efficiency in pretreatment. Renewable energy at the generation site should be recommended to achieve lower electricity prices, such as a wind farm dedicated to generate electricity for hydrothermal pretreatment (Zimmermann et al., 2020).

4.3. Cost of manufacturing of the products generated from hydrothermal pretreatment

The main advantage of hydrothermal pretreatment is the sustainable

Table 2
Characteristics of the pilot-scale continuous tubular reactors used for the hydrothermal pretreatment of lignocellulosic biomass.

Product	Yield (%)/(concentration)	Dimensions (diameter × long)	Volume	Biomass flow	Temperature/ Residence time	Pressure	Feedstock	References
Glucose and xylose	82.55 and 70.78	0.15 × 1.37 m	24.19 L	n.d.	180 °C/10 min	n.d.	Sorghum	Cheng et al. (2019a) Cheng et al. (2019b)
*		0.1 × 1.6 m	12.56 L	n.d.	180 °C/11.2–42.7 min	150 psig	*	Jaramillo and Sanchez, (2018)
Xylooligosaccharides	70	0.1 × 1.6 m	12.56 L	n.d.	180 °C/37 min	150 psig	Wheat straw	Rodríguez et al. (2019)
Bisabolene production with *Rhodosporidium toruloides*	514.1 mg/L	n.d.	n.d.	8.3 kg/h	180 °C/20 min	150 psig	Corn stover	Pérez-Pimienta et al. (2019)
Structural changes and functional groups of biomass	n.d.	n.d.	n.d.	3 kg/h	185 °C/30 min	10 bar	Wheat straw	Molina-Guerrero et al. (2018)
Ethanol production with *Saccharomyces cerevisiae*	42 g/L	0.1 × 1.6 m	12.56 L	5 kg/h	180 °C/35 min	147 psig	Wheat straw	Pérez-Pimienta et al. (2020)

Label: n.d., not described; *study of mass flow dynamic modeling; &, study focused on the physicochemical characterization of biomass during the hydrothermal process.

production of value-added biobased products. Compared with conventional processes based on chemical, alkali, and enzymatic hydrolysis, LCB can be upgraded into several marketable products with hydrothermal processes without using organic solvents, toxic chemicals, and catalysts (Ahmed et al., 2022; Preethi et al., 2021). However, for the application of hydrothermal processes on an industrial scale, the cost of manufacturing the biobased products generated should be lower or equivalent to the current market price of conventional products. Therefore, the study of the cost of manufacturing is one of the main essential parameters in the techno-economic analysis. Determination of the cost of manufacturing (Eq. (5)) considers all the fixed and operational costs on an annual basis (e.g., USD/year) associated with the annual production capacity of the process basis (e.g., ton/year) (Turton et al., 2003).

$$\mathrm{COM} = \frac{(0.204 \times \mathrm{FCI}) + (2.73 \times \mathrm{COL}) + [1.23 \times (\mathrm{CUT} + \mathrm{CWT} + \mathrm{CRM})]}{\text{Annual production capacity}} \quad (5)$$

where COM is the cost of manufacturing, FCI is the fixed capital investment, COL is the cost of operational labor, CUT is the cost of utilities, CWT is the cost of waste treatment, and CRM is the cost of raw material.

Several studies applying hydrothermal pretreatment to LCB have determined the cost of manufacturing biobased products. A simulated industrial hydrothermal reactor (capacity of 500 L) to produce flavanones and sugars from orange peel was designed, and the lowest cost of manufacturing was US$ 25.72/kg flavanone and US$ 1.43/kg sugar (Lachos-Perez et al., 2021). The cost of manufacturing arabinose obtained from subcritical water hydrolysis of brewer's spent grains decreased from US$ 64.10/kg in pilot plants to US$ 7.22/kg in industrial plants, demonstrating that the scale-up can reduce the production costs with the increase in the plant capacity (Sganzerla et al., 2021b). Moreover, Ashraf and Schmidt (2018) compared the production of monomeric sugars by separate and mixed processing approaches (hydrothermal pretreatment and enzymatic hydrolysis) for multi-feedstock LCB, and the lowest cost of manufacturing sugar was US$ 0.58/kg (Ashraf and Schmidt, 2018).

The hydrochar produced from hydrothermal carbonization using biomass from forest residues has proved economically profitable with the industrial production of 18 ton hydrochar/h, presenting a cost of manufacturing of US$ 900.54/kg (Carrasco et al., 2022). In addition, using avocado stone for biochar production by hydrothermal carbonization presented a cost of manufacturing of US$ 9.64/GJ_{HHV} ($HHV_{hydrochar}$ = 25.81 GJ/ton) (Sangaré et al., 2022). These values are similar to the hydrochar produced from hydrothermal carbonization of palm oil fruit bunches, with a cost of manufacturing ranging from 9.13 to 11.51 US$/GJ (Sangaré et al., 2022).

Hydrothermal pretreatment has been used to produce biofuels and bioenergy. The minimum fuel selling prices produced by hydrothermal liquefaction of sugarcane bagasse showed very high market competitiveness, estimated as US$ 0.44/L gasoline, US$ 0.48/ L diesel, US$ 0.51/L jet fuel, and US$ 0.37/L marine fuel (Deuber et al., 2021). The production of renewable jet fuel from different biomasses through hydrothermal liquefaction emerged as one of the best technologies, with an estimated jet fuel cost ranging from 0.79 to 1.09 US$/L (de Jong et al., 2015). The technical–economic feasibility of integrating hydrothermal pretreatment with anaerobic digestion has been studied in the literature. Anaerobic digestion can improve biogas quality and contribute to decarbonizing the heating industry, storing long-term energy, and providing network balancing services (Medina-Martos et al., 2020). The economic analysis revealed that the dominant cost is associated with the energy demand, while the cost of equipment purchased from pretreatment steps predominates (Michailos et al., 2020). A study integrating hydrothermal carbonization and anaerobic digestion of sewage sludge showed a 14 % increase in the gross energy efficiency of anaerobic digestion. The CAPEX increased 37 % with pretreatment when compared with the control reactor. The minimum selling price of biomethane ranged between 135 and 183 £/MWh (Michailos et al., 2020). In addition, Seiple et al. (2020) studied hydrothermal pretreatment for biomethane production, and the results indicated an increase in energy recovery by 188 % and a decrease in the solids disposal costs by 43 %. Kang et al. (2020) studied liquid hot water pretreatment for biomethane production. The study achieved a 32.9 % increase in methane production with pretreatment.

Finally, the production costs of the hydrothermal process still need to be reduced to fall within the range of conventional products and fuel. In the future, the advance in reactor performance, economies of scale, technological breakthroughs, and biomass price dynamics can have a decisive impact on the economic performance of conversion pathways for biobased products with hydrothermal technology (de Jong et al., 2015).

4.4. Profitability indicators of hydrothermal pretreatment

A combined analysis of the technical (laboratory/pilot optimization) and economic aspects is essential to define a project implementation strategy, with the primary objective of obtaining a feasible technology for industrial application (Campos et al., 2020). The feasibility should be analyzed from the following profitability indicators: gross margin; net margin; return on investment (ROI); net present value (NPV); internal rate of return (IRR); and payback time. These indicators are the most used for profitability analysis, representing greater security for investors and decision-making, such as the scale of industrial plants (Sganzerla et al., 2021a).

The hydrothermal liquefaction of forest residues could break even if the capital costs associated with the reactor system are reduced by 30 %. In addition, the break-even prices of the co-products under existing market conditions were found to be 1.03 €/kg gasoline, 2.46 €/kg hydrogen gas, or 51.4 €/MWh biochar (Magdeldin et al., 2017). The integration of the hydrothermal pretreatment with a sugarcane ethanol distillery has significantly increased the IRR compared with the stand-alone, moving from 8.1 % to 12.6 % per year, indicating that hydrothermal technology has the potential of being economically feasible if integrated into a sugarcane mill (Deuber et al., 2021). Notwithstanding, the implementation of hydrothermal technology followed by separation systems for the purification of value-added biobased products can be an advantage in the industrial-plant process to become a process with positive profitability indicators (Zabot et al., 2018). The profitability of the production of purified sugars from subcritical water hydrolysis on an industrial scale was estimated at a payback of fewer than two years, an ROI of approximately 80 %, and an NPV of US$ 121 × 10^6 (Sganzerla et al., 2021b). In the case of the integration of hydrothermal pretreatment followed by anaerobic digestion, the process is still not attractive for large-scale investments due to the high electricity demands, and future standardization of the application of carbon credit could provide benefits to produce negative carbon emissions, leading to an expanding biorefinery industry (Dutta et al., 2022). The acquisition of electricity at a lower cost is a key factor in the profitability of hydrothermal processes (Medina-Martos et al., 2020).

5. Environmental aspects of sustainability involved in hydrothermal pretreatments

Hydrothermal pretreatments are considered environmentally advantageous because they do not require the addition of chemical compounds except water, either in the liquid or vapor phase, and they present minimal generation of residual materials. However, these environmental advantages compared to other pretreatments should be evaluated to confirm their validity. In general, the different pretreatments have been developed basically oriented to obtain high yields, both for the recovery of components and for the enzymatic hydrolysis of the pretreated material, or to obtain low production costs. Few studies

have been carried out considering operating conditions that consider not only high yields or low costs but also low environmental impacts.

Life cycle assessment (LCA) is a commonly accepted tool to assess the impact of the environmental aspects involved in a product placed on the market or in the process that produces it, including its total or partial life cycle according to the previously defined limits of the system (Rathore et al., 2013). LCA methodology quantifies the environmental impact of using natural resources and the emissions generated based on information obtained from the inputs and outputs of materials and energy involved during the production of biomass, biomass transportation, industrial conversion, distribution and use of the product, according to the considered limits of the system. Among these are Cradle to Grave, which includes raw material cultivation, transportation to the production facility, product and co-product production, distribution and use (also referred to as Well to Wheel (WtW) for biofuels); Cradle to Gate, which includes raw material cultivation, transportation to the production facility, product and co-product production (Well to Gate (WtG) for biofuels); Gate to Gate, which includes product and co-product production and Well to Tank (WtT) (for biofuels WtG plus fuel distribution).

Table 3 summarizes the global warming potential (GWP), expressed as greenhouse gas (GHG) emissions, reported by different authors that performed LCA analyses of different biorefineries configurations based on hydrothermal pretreatment (liquid hot water, LHW and steam explosion, SE, without catalyst addition), which in some cases are compared to other pretreatments. Comparison between processes must be done carefully as there are many differences in processes, conditions, yields, system boundaries, functional units and locations. Most of the studies shown in the table refer to biofuels. When this was the case and calculation was possible, GHG emissions per MJ of biofuel were calculated from author data, assuming in some cases the lower heating value (LHV). All the values associated to biofuels produced using hydrothermal pretreatment are lower than the fossil fuel reference of 93.3 g CO2/MJ gasoline for the EU and the US, but only some of them would meet the goal of 60 % GHG savings for US and 65 % GHG savings for UE (respect to the gasoline baseline value), set for biofuels produced in new facilities that produce cellulosic biofuels.

Several authors compared hydrothermal pretreatments with other pretreatments in terms of GHG emissions Table 3. The main contributors to the environmental differences between the pretreatments are the use of chemicals and conversion yields. Pretreatments that generate higher conversion of cellulose have higher product yields, which implies lower consumption of raw material per quantity of product obtained. Consequently, the environmental aspects corresponding to the agricultural phase have less impact. However, the pretreatments that generate greater conversion, are also frequently carried out under more severe conditions. Therefore, the environmental aspects corresponding to the industrial phase have a greater impact. Analyzing the GWP, better environmental performance of hydrothermal pretreatments was reported for different processes. Prasad et al. (2016) studied the environmental impact of the production of fermentable sugars from corn stover, which could be further processed to high value co-products in several possible biorefinery configurations. They found that for this process both LHW (190 °C, 20 min) and SE (190 °C, 5 min, acid) had lower GHG emissions than dilute acid (120 °C, 40 min, 1.1 % HCl), alkaline (10 % lime, 60 °C, 12 h) and organosolv pretreatments (120 °C, 40 min, EtOAc:EtOH:H2O 36.99:26.31:37.70 (all wt. %) + H_2SO_4 0.49 wt%). For the production of butanol from corn stover, SE showed better results than sulfuric acid, AFEX, ionic liquid, and biological pretreatments (Baral et al., 2018). In a sugarcane biorefinery, LHW had lower emissions than dilute acid pretreatment for two different configurations (producing only ethanol or ethanol and syrup) (Gnansounou et al., 2015). Analyzing bioethanol production from miscanthus, Lask et al. (2019) found that conversion-related emissions were significantly lower for LHW (200 °C) than for dilute acid (150 °C, 0.73 %wt H_2SO_4) and dilute alkaline (105 °C, 2.5 wt% NaOH) with differences mainly due to the reactants added in the other pretreatments. Bioethanol produced from grass straws SE (180 °C and 5 min) and enzymatic hydrolysis conducted at high solid loading (30 %) had lower GHG emissions than LHW (180 °C, 15 min, and 20 % solids), dilute acid (180 °C, 15 min, and 1 % acid) and dilute alkali (180 °C, 15 min, and 1 % alkali) (Kumar and Murthy, 2012). For bioethanol production from wheat straw, SE (180 °C, 10 min) and LHW (188 °C, 40 min) showed lower GHG emissions than the other pretreatments (SE with sulfuric acid (180 °C, 10 min, 0.9 % H_2SO_4) and dilute acid (121 °C, 90 min, 2 %w/v H_2SO_4) (Wang et al., 2013). Bioethanol production from bamboo had the best environmental profile involving GHG emissions when LHW (190 °C, 10 min) pretreatment was applied; other pretreatments analyzed were soaking in aqueous ammonia (15 % NH_4OH in pressure tubes 100 °C, 24 h) and dilute acid (0.2 % H_2SO_4, 160 °C, and 15 min) (Wang et al., 2014). Zhao et al. (2019) analyzed data from several authors for the production of bioethanol from corn stover using different pretreatments. They found that SE was the pretreatment with lower GHG emissions out of seven categories of pretreatments analyzed (acid, alkaline, solvent based, steam explosion, ammonia based, fungi and combi (combinations of physical, chemical, and thermochemical pre-treatment). Nevertheless, Khoshnevisan et al. (2016) found that the hydrothermal pretreatment of SE (190 °C, 2 min) had worst environmental performance than *N*-methylmorpholine-*N*-oxide (NMMO) based pretreatment (85 % NMMO solution at 120 °C for 3 h) in terms of human health, ecosystem quality, resources, and climate change. Some of the authors included both types of hydrothermal pretreatments (SE and LHW) on their environmental analysis. Most of the LCA that compared both hydrothermal pretreatments showed better results in terms of GHG emissions for SE. Different authors have reported that SE had lower CO_2 emissions than LHW for ethanol produced from corn stover (Zhao et al., 2019), grass straws (Kumar and Murthy, 2012) and wheat straw (Wang et al., 2013).

Several authors compared the environmental performance of hydrothermal pretreatments with other pretreatments through LCA using other impact categories in addition to GWP (Cherubini and Jungmeier, 2010; Gnansounou et al., 2015; González-García et al., 2018; Khoshnevisan et al., 2016; Prasad et al., 2016; Vaskan et al., 2018; Wang et al., 2013; Zhao et al., 2020). In general, it is observed that based on LCA and using different impact categories, hydrothermal methods, LHW and SE without catalyst, have better environmental performance than other pretreatments commonly used for eventual industrial scaling. The results are strongly dependent on the product yield generated by the processing of the pretreated material and the recovery of the resulting liquid fraction. Wang et al. (2013) evaluated the environmental performance of five pretreatment techniques (LHW, SE with and without sulfuric acid as catalyst, dilute sulfuric acid, and wet oxidation with compressed oxygen) with respective process configurations to produce ethanol and electricity from wheat straw by LCA comparing with petrol. The limit of the system was 'well-to-wheel' including the production of wheat and straw, making the allocation based on the economic value of each raw material. The impact categories considered were abiotic resources depletion, acidification, eutrophication, GWP (100-year horizon, GWP100), ozone layer depletion, photochemical-oxidants creation, human toxicity, and freshwater aquatic ecotoxicity. Credits from the surplus electricity were considered. LHW, SE without catalyst and wet oxidation showed the lowest values in most impact categories evaluated. SE, LHW and wet oxidation pretreatments were environmentally favorable over petrol particularly in abiotic resources depletion, GWP100, ozone layer depletion potential, ecotoxicity and photochemical-oxidants creation potential impacts. Prasad et al. (2016) the environmental performance of four pretreatments considered the most common techniques with high scalability potential (LHW, SE with 2 % wt sulfuric acid, dilute hydrochloric acid, organosolv) in four impact categories (GHG emission, terrestrial and aquatic eutrophication, acidification, and water depletion) using life cycle analysis of fermentable sugar obtained from corn stover. They included the agricultural production stage within the system boundaries, including the activities of

Table 3
GHG emissions reported by different authors for different biorefineries configurations based on hydrothermal pretreatment (LHW and SE without catalyst addition).

Pre-treatment	Raw material	Main product	Co-products	System boundary	Functional unit	GHG (g CO_2 eq./ functional unit)	GHG (g CO_2 eq./MJ)	Comments	Reference
SE (210 °C, 11 min)	Cardoon stalks	Yeast biodiesel	Surplus energy	Cradle to gate	1 MJ biodiesel	−1.5	−1.5		(Barbanera et al., 2021)
SE (200 °C, 5 min)	Corn stover	Butanol Acetone and ethanol Acetone, ethanol, electricity	Without co-products	Cradle to gate	1 MJ butanol	54.49 41.14 18.09	54.49 41.14 18.09	Comparison with other pretreatment methods using a probabilistic LCA method.	(Baral et al., 2018)
SE (160–260 °C, 2 min)	Corn stover	Ethanol	Phenols, electricity, biogas	Cradle to grave	477 corn stover kt dry/a	$137x10^9$	46.3	Comparison to fossil reference system. Includes other impact categories.	(Cherubini and Jungmeier, 2010)
LHW (190 °C, 20 min)	Corn stover	Fermentable sugars		Cradle to grave	1 kg of fermentable sugar	940 (LHW), 14,300 (SE)	N/A		(Prasad et al., 2016)
SE, LHW [a]	Corn stover	Ethanol	Surplus electricity, biogas	Cradle to grave	1000 kg dry matter	−65000 (SE) 367,000 (LHW)	20 (SE)59 (LHW)	Comparison with other pretreatment methods	(Zhao et al., 2020, Zhao et al., 2019)
SE (160–260 °C, 2 min)	Wheat straw	Ethanol	Phenols, electricity, biogas	Cradle to grave	477 kt wheat straw dry/a	$130x10^9$	49	Comparison to fossil reference system. Includes other impact categories.	(Cherubini and Jungmeier, 2010)
SE (180 °C, 10 min), LHW (188 °C, 40 min)	Wheat straw	Ethanol	Surplus electricity	Cradle to grave	to drive 1 km in a Flexible-fuel vehicle (FFV)	134 (SE) 156 (LHW)	42.88 (SE)49.92 (LHW) (0.32 km/MJ)	Comparison with other pretreatment methods. Includes other impact categories.	(Wang et al., 2013)
SE (160–260 °C, 2 min)	Switchgrass	Ethanol	Phenols, electricity, biogas	Cradle to grave	477 kt switchgrass dry/a	$60.5x10^9$	———	Includes other impact categories.	(Cherubini and Jungmeier, 2010)
LHW (200 °C, 5 min)	Switchgrass	Ethanol	Surplus electricity, furfural, acetic and formic acid	Well to wheel	1 MJ ethanol	2	2		(Larnaudie et al., 2021)
LHW (200 °C) [b]	Miscanthus	Ethanol	Surplus electricity	Well to wheel	1 GJ	28,960 (Stuttgart) 37,840 (Aberyswyth)	29.0 (Stuttgart) 37.8 (Aberyswyth)	Comparison with other pretreatment methods.Two locations analyzed (UK and Germany) .	(Lask et al., 2019)
SE (180 °C, 5 min), LHW (180 °C, 15 min)	Grass straws	Ethanol	Surplus electricity	Well to tank and well to wheel	10,000 MJ energy	−237695 (LHW) −555396 (SE)	–23.8 (LHW) −55.5 (SE)	Comparison with other pretreatment methods.	(Kumar and Murthy, 2012)
SE (190 °C, 2 min)	Pinewood	Ethanol	Biogas	Cradle to gate	105,263 tonnes pinewood input to the biofuel plant	78,932,801	11	Comparison with other pretreatment methods. Analyzes different production scenarios	(Khoshnevisan et al., 2016)
LHW (180–200 °C, 5–15 min) [c]	Sugarcane	Ethanol	Animal feed, sugar, energy	Well to tank (WtT) and well to wheel (WtW)	For WtT: 1 ton of sugar-cane; for WtW: 1 km of car operation in the case of ethanol (vs gasoline)	WtT: 100,000 (ED FF) 70,000 (SM FF)	WtT: 45.5 (ED FF)108.8 (SM FF)	Analyzes different production scenarios. ED FF (only ethanol, LHW) SM FF (produces sugar,	(Gnansounou et al., 2015)

(*continued on next page*)

Table 3 (*continued*)

Pre-treatment	Raw material	Main product	Co-products	System boundary	Functional unit	GHG (g CO_2 eq./ functional unit)	GHG (g CO_2 eq./MJ)	Comments	Reference
								LHW)	
LHW (185–195 °C) [b]	Sugarcane	Ethanol (1G and 2G)	Surplus electricity	Cradle to grave	1 MJ of anhydrous ethanol	21.52 (1G); 19.98 (1G + 2G)	21.520(1G); 19.980(1G + 2G)	Analyzes different production scenarios (1G, 1G + 2G)	(Elias et al., 2021)
LHW (180 °C) [b,c]	Palm empty fruit branches	Ethanol	C5 syrup (as feed for cattle), electricity	Cradle to gate and well to wheel	1 t of palm empty fruit branches	25,000	16.2	Comparison with other pretreatment methods. Includes other impact categories.	(Vaskan et al., 2018)
LHW (190 °C, 10 min)	Bamboo	Ethanol	Surplus electricity	Cradle to grave	1 kg ethanol produced from bamboo', and '1 km travelled in a flexible fuel vehicle (FFV)' 1 MJ ethanol	−1830	68.3 (LHV 26.803)	Comparison with other pretreatment methods.	(Wang et al., 2014)
LHW (210 °C) [b]	Brewery waste (barley straw from cereal cultivation and brewer's spent grains)	Ethanol	Xylooligosaccharides (XOS)	Cradle-to-gate	Production batch (74.22 tonnes of lignocellulosic stream), 1 kg of value product obtained (ethanol and XOS)	88.2 t CO_2 eq./ batch; 4.21 kg CO_2 eq./kg XOS; 7.39 kg CO_2 eq./kg ethanol	280	Includes other impact categories.	(González-García et al., 2018)
LHW (210 °C) [b]	Corn stover/ swine manure in the Portuguese case and wheat straw/ swine manure in Chilean case	Isobutene and *xylo*-oligosaccharides	Surplus electricity	Cradle to gate	1 kg corn stover (Portugal) or wheat straw (Chile); 1 kg isobutene or GJ isobutene	0.796 kg CO_2 eq./kg corn stover (Portugal) 0.760 kg CO_2 eq./kg wheat straw (Chile)	60.7 (Portugal)48.8 (Chile)	Includes other impact categories. Two locations analyzed.	(Lopes et al., 2019)

[a] The authors used 17 datasets and 11 datasets from different references for SE and LHW, respectively.
[b] Reaction time not reported.
[c] "IBUS" process with residual acid stream. GHG: greenhouse gas; LHW: liquid hot water; SE: steam explosion; LHV: lower heating value.

growing corn and harvesting the residue, considering that 50 % of the residue produced remains in the field. The authors concluded, based on the results of the LCA and the assumed sugar yields (80 %), that LHW is the most suitable technique for the pretreatment of corn stover. In particular, the LHW pretreatment showed the lowest values of GHG emissions, aquatic eutrophication potential and water depletion, and intermediate values of acidification and terrestrial eutrophication potentials. Zhao et al. (2020) evaluated ten environmental impact categories in the bioethanol production from corn stover using seven process configuration comprising different pretreatment technology: acid. alkaline, ionic liquid/organic solvent, SE, LHW, ammonia fiber expansion fungi. Using data from literature and through the integration of environmental aspects from a statistical perspective, they classified the technologies evaluated in terms of priority (high, medium, low) for their further development. SE and ammonia fiber expansion technologies were classified as high priority. They concluded that SE produces good ethanol yield and presents a low contribution in the environmental impact categories evaluated, such as GHG emission, acidification, eutrophication, photochemical ozone formation, particulate matter, ecotoxicity, and human toxicity. LHW pretreatment was classified as low priority. Its minor environmental performance is mainly attributed to the low ethanol yield assumed in this study, in comparison with the other techniques evaluated. It should be noted that most of the studies analyzed biorefineries that can be considered "basic", meaning that the other co-products generated are limited to the energy (heat and electricity) that comes from the burning of lignin and residual biomass. Biorefineries that consider the use of the hemicellulose fraction or lignin for the production of other chemicals could show greater environmental advantages in the form of credits for the avoided burden of the traditional production of said chemicals (Larnaudie et al., 2021). In these scenarios, the higher recovery of the different fractions associated to hydrothermal pretreatments would have a greater impact on the environmental benefits.

6. Perspectives for hydrothermal technology in a biorefinery

The valorization of biomass plays a significant role in the production of biofuels and biobased chemicals. Hydrothermal pretreatment can be applied in a biorefinery, and biological processes can enhance pretreated biomass to produce value-added products. An interdisciplinary bioeconomy approach can optimize the potential of biomass in terms of the environmental perspective and circular bioeconomy (Erythropel et al., 2018). The biorefinery based on the complete valorization of biomass contributes to the reduction of greenhouse gas emissions, bordering economic sustainability and environmental safety within of green chemistry and circular bioeconomy (Dutta et al., 2022). However, hydrothermal pretreatments can show operational disadvantages (types of biomasses, it is necessary to grind the biomass), sustainability (it is necessary to look for alternatives for the use of water for the process), and reduction in equipment costs. Undoubtedly, these are important challenges that process engineering must take into account for the development of biorefineries. The design and continuous operation for biomass processing, and the use of seawater can be a great alternative to improve the process.

7. Conclusions

Hydrothermal pretreatment is one of the most mature processes for biomass fractionation, and the development, integration design, as well as the technoeconomic analysis are fundamental for the scaling-up to different levels. Also, the hydrothermal pretreatments have a good environmental performance (lower GHG emissions than fossil reference for biofuels). The LCA studies focused on more diverse biorefineries (with higher value co-products and maximum use of the different lignocellulosic fractions and biofuels production) should be done in order to determine the full potential of these pretreatments in the development of biorefineries and circular bioeconomy.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

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