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Hydrothermal refining of biomass — an overview and future perspectives

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ABSTRACT: Biomass is a promising alternative for the production of energy, novel materials, chemicals, and other valuable products. A certain degree of processing is required to achieve those results. Hydrothermal processes offer a unique way to obtain a wide range of biorefinery products. They can be considered as environmentally friendly processes, using solely water at different temperatures as a process medium to convert abundant and inexpensive biomass into products. We provide a short overview on hydrothermal processes that use water in its liquid state, including hot water extraction, pressurized hot water extraction, liquid hot water pretreatment, hydrothermal carbonization, and hydrothermal liquefaction. We also provide examples of current research and real-world findings. We then present a novel hydrothermal biorefinery concept for sequencing these single processes, giving concrete examples of possible raw materials and products. Sequencing gives new possibilities for biorefineries to exploit all the biomass components as valuable products with zero losses. The added value comes from the increased efficiency of the bio-based products' value chain, by reducing losses and generating higher-value products and services.

Application: This paper describes potential opportunities for using hydrothermal processing for upgrading biomass into value-added products.

Biomass has been used for providing food, feed, and utilities of necessity and comfort. From an early stage it was discovered that a certain degree of processing is required to achieve a desired result: meat requires heating to make it more edible; fruits get a new dimension after being processed biochemically to produce alcohol; flax requires retting and mechanical processing to provide textile fibers; wood and crops require mechanical refining in aqueous conditions to provide fibers for papermaking, etc. All these early processes include simple ingredients that are readily available, the most important one being water. Liquid water is very efficient as a processing medium, even at temperatures below the boiling point, where plenty of components can be extracted from the processed materials, resulting in a slightly modified solid phase and a liquid phase containing dissolved components. At some stage, when equipment allowed an increase in pressure and better chemical resistance, higher processing temperatures could be used and the treatment could be made more efficient, resulting in better yields or even totally new products. Hydrothermal processes are currently widely used for biomass converting and as pretreatment methods to recover valuable components.

In the first part of this paper we give an overview of general aspects of hydrothermal processes using liquid water as a process medium in creating versatile products at different temperatures. Hydrothermal processes using steam, such as steam pretreatment of biomass, are outside the scope of this paper. In the second part, we present a novel hydrothermal biorefinery concept in which the single hydrothermal processes are sequenced in order to exploit all the biomass components as valuable products with minimal residue. Three examples of the sequencing are presented, giving an idea on the opportunities of the concept.

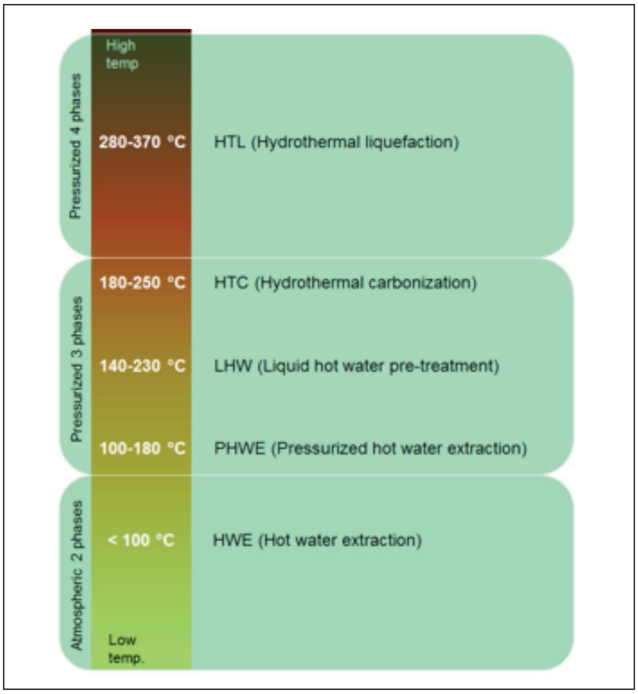
HYDROTHERMAL PROCESSES

Hydrothermal processes that use water in its liquid state can be divided into five categories, based on the temperature range used: hot water extraction (HWE), pressurized hot water extraction (PHWE), liquid hot water pretreatment (LHW), hydrothermal carbonization (HTC), and hydrothermal liquefaction (HTL) (**Fig. 1**). Those can be further grouped by temperature range: low temperature (<100°C), medium temperature (100°C-250°C), and high temperature (>280°C).

Low temperature (<100°C)

Hot water extraction

Temperatures below the boiling point of water are often enough to extract many components from biomass. Unpressurized HWE is a useful method to gently extract and separate water-soluble hydrophilic components from biomass. For botanical herb extracts, mild extraction conditions are especially important to conserve the bioactivity of the extract. Mild pH adjustment or low concentrations of some chemicals may be used to enhance the efficiency of extraction. Typical water-extractable biomass components are certain polysaccharides and polyphenolic compounds, such as pectin and tannin.



1. Hydrothermal processes categorized by the temperature range.

Pectins can be extracted from citrus peel and apple pomace by acidified water at 70°C [1]. The global production of pectin is about 50,000 tons [2]. Some glucomannans may partially be extracted with water in unpressurized conditions [3], but more commonly they are extracted in pressurized conditions, above 100°C. The same applies for arabinoxylans, which in some cases can be partially extracted from green plant leaves by boiling water [4]. Agar, a galactose-based gelling polysaccharide is industrially extracted using water at 80°C-95°C and some sodium carbonate to increase the pH [5]. Microwaves and ultrasound can be used to improve the efficiency of unpressurized hot water extraction of polysaccharides [6].

Tannins are polyphenolic compounds present in many fruits, berries, legumes, nuts, and barks. They are traditionally used in the tanning of leather, but also as animal feed additives, industrial dispersants and coagulants, and as additives and clarifiers in the wine, brewing, and beverage industries. Commercial tannins are produced by HWE (unpressurized or slightly pressurized), mainly from the bark of wattle (*Acacia mollissima* and *A. mearnsii*), the wood of quebracho (*Schinopsis lorentzii* and *S. balansae*), and the wood of the chestnut tree (*Castanea sativa*) [7]. The industrial production volume is in the range of 160,000–200,000 tons/year [8,9]. Tannins could be used to replace fossil-based phenol in wood adhesives and insulating foams, in the production of particle boards, and in many other applications. The low price of phenol has hindered the applicability of renewable tannin as a phenol replacement, but the situation is changing, and interest in tannin as an industrial chemical is growing. Thus, new sources of tannin, such as softwood bark, especially spruce bark [10] and radiata pine bark [11], have become industrially interesting.

Softwood bark is an example of a woody biomass that can be used hydrothermally under relatively mild conditions. Bark has been used for tanning leather since ancient times, initially by adding pieces of bark to a water solution and soaking the raw hides in the solution to allow the dissolved tannin to tan the hides. Kemppainen et al. [10] extracted spruce bark with water in unpressurized conditions and studied the effect of temperature (60°C-90°C) and solids loading (5%-15%) on total and component-based extraction yields during a 2 h extraction. The temperature was reported to positively affect the total extraction yield and also the extraction yield of tannins and bound carbohydrates. The extraction yield of free monosaccharides was not affected by the extraction temperature or solids loading. An increase in solids loading slightly reduced the extraction yield of tannin but not the extraction yield of carbohydrates. The extraction procedure was scaled up to pilot scale, and 10 kg of crude tannin extract was produced, containing 51% tannin and 22% carbohydrates, out of which less than 10% were in monosaccharide form. Soto et al. [12] were able to solubilize up to 25% of radiata pine bark with hot water at 70°C, whereas Hill et al. [13] reached 20% extraction yield at 90°C for the same material. Condensed tannins may condensate into water-insoluble unreactive phlobaphenes in low pH and high temperature [14], which is why higher temperatures may be detrimental for tannin extraction. Sulfites, carbonate, and urea can be used to increase the solubility and stability of tannins during and after the extraction.

HWE can, in certain cases, also function as a pretreatment for the production of fermentable sugars from biomass. Kemppainen et al. [15] reported that spruce bark, hot water extracted at 80°C, could be efficiently hydrolyzed to sugars if an enzyme mixture containing pectinase activity was used in the hydrolysis. Hydrolysates could also be fermented to ethanol without any signs of significant yeast inhibition. The results show that spruce bark could be considered as a new source of condensed tannin, and that the extracted residue could be used to produce fermentable sugars, and therefore sugar-based fuels and chemicals. However, for many other types of biomass, an unpressurized HWE is not sufficient to reduce the recalcitrance of the biomass matrix for enzymatic hydrolysis. Wan and Li [16] reported that HWE at 80°C slightly improved the fungal pretreatment and the subsequent enzymatic hydrolysis of wheat straw, whereas it had little or no effect on corn stover or soybean straw.

Medium temperature (100°C-250°C)

Pressurized hot water extraction

In PHWE, water is kept in liquid form by keeping the system under sufficiently high pressure. Applied temperatures are typically between 150°C and 180°C. The possibility to use PHWE conditions using dilute sulfuric acid as a catalyst for the extraction of larch wood arabinogalactan has been reported [17]. PHWE has been described as a stage before kraft pulping by Brasch and Free [18]. It is used as a pretreatment in the dissolving pulp process [19]. The integrated forest biorefinery [20] uses the prehydrolysis concept to reduce the hemicellulose content in black liquor and produce a hemicellulose-rich stream. The objective is to decrease the load of the recovery boiler while maintaining the quality and quantity of kraft pulp [21]. Suitable conditions for the integrated forest biorefinery deliver mainly oligomeric hemicelluloses [22]. Next to an additional stage in traditional pulping, PHWE-extracted wood is used for dissolving pulp production. Different conditions for PHWE of mixed southern hardwood were studied by Brash and Free in 1965 [18]. They showed the value of the prehydrolysis factor concept using a wide range of temperatures and prehydrolysis times in laboratory scale. More detailed analysis has been performed for a series of extracts obtained from pilot-scale extractions from birch wood, including furanic compounds and carbolic acids [23].

Recently, efforts have been made in many laboratories to use PHWE as a pretreatment process for biomass fractionation, delivering cellulose-rich biomass as a solid stream and oligomeric or polymeric hemicellulose together with some lignin and extractives in the extract. The motivation is that the potential of oligomeric and polymeric hemicelluloses has been shown for many applications, including cosmetics, pharmaceuticals, textiles, films, coatings, and adhesives, as well as alimentary and health products [24-36]. Therefore, the production of these hemicelluloses is the focus in the present overview.

Rissanen et al. conducted a larger set of laboratory scale, prehydrolysis experiments using spruce wood [24]. In their work, the molar mass of the extracted hemicellulose galactoglucomannan was studied in detail. Lower molar mass of approximately 20 kg mol^{-1} were obtained with larger chips at 130°C, compared to molar mass as high as 60 kg mol^{-1} at either 120°C or 170°C with smaller chips. Rissanen's work was supported by the work of Kleen et al. who studied the effect of physical form and size of the wood raw material in a pilot scale batch PHWE process [37]. Their study was performed on fresh birch wood. The amount of carbohydrates dissolved from the sawdust was 3 to 4 times higher, compared with that from chips after 30 min extraction. Both studies indicate that smaller particle size and the higher surface area lead to higher reactivity. Kleen et al. [37] demonstrated for sawdust that the extraction time of 30 min or less was enough for producing high-molecular-mass xylan (Mw >10 kDa) with a yield of 10 weight % calculated on dry sawdust, while the chips only released 3% polysaccharides in the same conditions, but with a higher Mw (13-15 kDa). High-molecular-mass material with Mw 10 kDa and a xylan yield of 5-7 weight % calculated on dry wood could be extracted at 160°C from birch chips in 60 min. Compression of the chips before extraction resulted in a release of higher amounts of high-molecular-mass material, with an Mw of about 10 kDa.

Kleen et al. [38] reported the concept of stepwise batch PHWE of birch sawdust in pilot scale. They defined stepwise PHWE as a process where certain material is extracted in several steps after each other in increasing temperatures. To dissolve xylan with a high yield, but also to keep the average molecular mass of the dissolved xylan as high as possible, stepwise PHWE followed by a relatively mild alkali extraction was applied to fresh industrial birch sawdust in pilot scale. The total extraction process dissolved 99% of the native xylan. The main effect was obtained at 160°C, where 27% of sawdust was dissolved, of which the main part had a high molecular mass of about 11 kDa.

Flow-through PHWE of dried birch sawdust in pilot scale has been reported by Kilpeläinen et al. [39]. They showed the possibilities to control amounts of extracted polysaccharides, oligosaccharides, and monosaccharides by using different temperatures and water flow rates. A high yield of xylan (13-18 weight % of dried wood) combined with a low yield of lignin (10 weight % of dried wood) was obtained at an extraction temperature of 180°C.

Compression of the residue after a PHWE extraction of fresh spruce chips at 150°C has been studied as a potential means to increase the amount of dissolved polysaccharides [40]. The extraction residue was compressed after collection of the primary filtrate using 100 bar pressure. Carbohydrates accounting for 2.9 weight % calculated on dry wood were obtained in the primary extract and carbohydrates accounting for 3.6 weight % calculated on dry wood were in the filtrate from the compression. More detailed analyses of the filtrate from the compression of spruce chips showed that it measured 94% polysaccharides of Mw of 8230 Da. This is a remarkable purity for polysaccharides from PHWE extraction. Of the polysaccharides, 67% was galactoglucomannan (GGM), with smaller amounts of xylan and pectic compounds. This result is surprising, because the primary filtrate contained a typical composition of 73% polysaccharides, 26% ultraviolet-absorbent lignin, and small amounts of extractives.

Liquid hot water pretreatment

LHW pretreatment uses similar conditions as PHWE, but the target of the treatment is different. LHW pretreatment is carried out to reduce the recalcitrance of lignocellulosic biomass toward hydrolytic enzymes and enable the hydrolysis of cellulose and hemicellulose and the fermentation of the released monosaccharides to biofuels and biochemicals. Biomass, typically agricultural residues or hardwood, is treated as a slurry with pressurized water for up to 20 min at temperatures of 140°C-230°C in a batch, with co-current flow, counter current flow, or a flow-through reactor [41,42]. Hemicelluloses are at least partially solubilized together with some lignin, leaving a cellulose- and lignin-enriched solid residue with better enzymatic accessibility. Higher temperature and prolonged treatment time promote cellulose digestibility in enzymatic hydrolysis, but may reduce the recovery of hemicellulosic sugars because of degradation reaction [43]. However, the risk of yield loss of sugars as degradation products is lower compared to steam pretreatment, because the concentration of solubilized hemicellulose and lignin products is lower in the liquid phase [44]. The liquid, which typically contains xylan and some lignin, and its degradation products may be recovered and subjected to a separate hydrolysis and fermentation of the C5 sugars. The lignin remaining in the insoluble solids may be able to migrate within and out of the cell wall in liquid hot water treatment [45]. Acetic acid liberated from hemicellulose during the treatment plays a role in catalyzing the hydrolysis of hemicellulose to oligosaccharides and monosaccharides. However, keeping the pH between 4 and 7 during the treatment helps to avoid the formation of inhibitors, which potentially could be harmful in the fermentation step [44,46].

LHW could be used to remove 86% of xylan from sugar cane bagasse and increase the enzymatic hydrolysis yield of glucan to 72% [45]. From soybean straw, it was possible to remove 80% of xylan and increase glucan hydrolysis yield to 71% in a treatment at 210°C for 10 min [47]. A two-step process may be beneficial for the reaching both a high hydrolysis yield and a high recovery of sugars. Yu et al. [48] treated *Eucalyptus grandis* first at 180°C for 20 min and then at 200°C for 20 min and obtained 82% yield in enzymatic hydrolysis and 97% total sugar recovery. Mosier et al. [42] were able to reach 90% hydrolysis yield for cellulose after LWH pretreatment of corn stover at 190°C for 15 min. Fermentability of the undiluted enzymatically hydrolyzed slurry at 16% dry matter content was found to be a good indicator that little or no fermentation inhibitors were released or formed in the treatment. The examples show that after the treatment temperature is raised closer to 200°C, plain water cooking can make many different kinds of lignocellulosic feedstocks amenable to enzymatic hydrolysis.

Hydrothermal carbonization

HTC is a technology developed in the early 20th century for converting biomass to coal-like material. The first experiments were done by Bergius, who in 1913 described the hydrothermal transformation of cellulose into coal-like products [49]. More systematic investigations were performed by Berl et al. [50], varying the source of biomass and treating the different samples in the presence of water at different temperatures. The influence of pH on the outcome of the reaction was analyzed and large differences in the decomposition schemes were later discovered [51]. Renewed interest in HTC has recently been established. The purpose of these new investigations is very different from the previous ones. The aim is to produce novel carbonaceous materials with specific structure (e.g., shape, size, porosity) and properties (e.g., heating value, adsorptive capacity, conductivity). The possibility to use the fast, simple, and climate-friendly carbonization process makes HTC an interesting alternative for bio-based carbon generation for a wide range of applications in a larger scale.

In the HTC process, wet biomass is processed at moderate temperatures (about 180°C-250°C) in self-generated pressures at approximately 20-30 bars for couple of hours. As a result of numerous chemical reactions, including hydrolysis, dehydration, decarboxylation, polymerization, aromatization, and recondensation [52], three easily separable phases are formed: a solid hydrophobic carbonaceous product, a liquid phase containing varying amounts of organics and inorganics, and a minor gas phase. The carbonaceous product is dark brown or black powder consisting of spherical particles with different shapes and size having aromatic carbon network structure and oxygen containing functional groups on the surface [53-55]. In general, this carbonaceous product has a potential to serve, for example, as a soil amendment or a material for carbon dioxide sequestration [54,56,57], a fuel [58], or as a raw material for further upgrading. Higher value applications include, for example, use as an adsorbent, a novel carbon material for electrodes/supercapacitors, energy storage and catalysts, and hybrid materials [53,54,56,59-64]. The components in the liquid phase are the primary precursors of the solid carbonaceous product. In general, the HTC liquid phase has high content of degradation products such as sugars, organic acids, and aromatics. Eventually, the structure of the solid and liquid phase is dependent on the nature of the original biomass and the HTC process conditions, such as processing temperature, residence time, and pH.

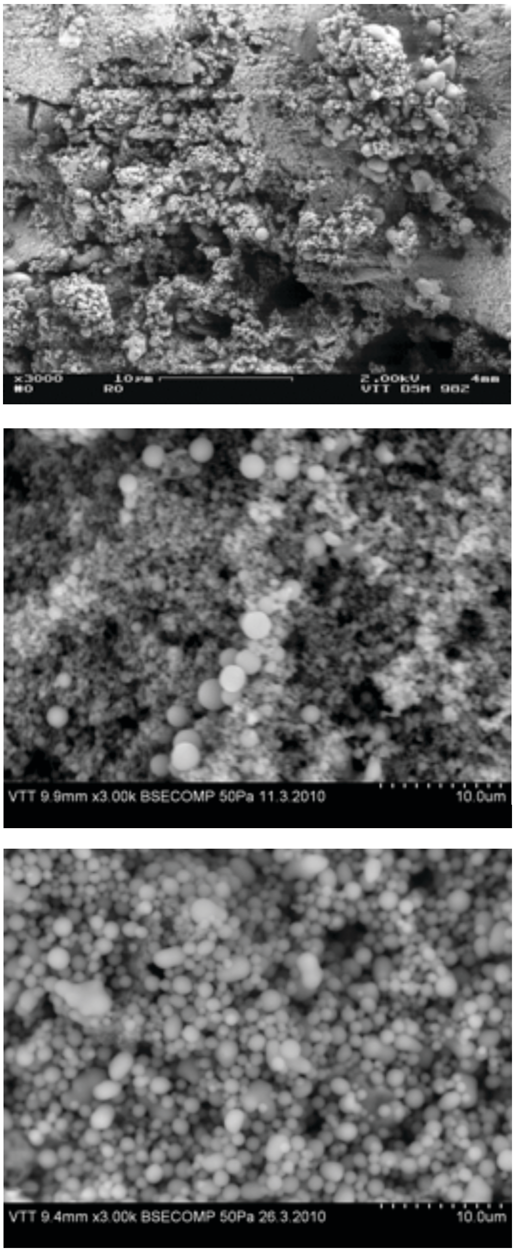
Several recent review articles on HTC have been published [52,54,56,57,59,65,66]. The research has focused on producing novel carbonaceous materials from pure raw materials, such as carbohydrates [53,67], and on lignocellulosic biomass of a more complex structure, such as wood, leaves, and rye straw [55,61,66,68]. In addition, HTC shows promise for treatment of waste materials, such as municipal sewage sludge [69,70].

By using pure raw materials, such as simple carbohydrates, products with rather uniform quality can be produced. Under acidic hydrolytic conditions, the hydrothermal process degrades sugars to furan-based (furfural or hydroxymethylfurfural [HMF]) intermediate, which finally forms the carbonaceous material [53,67]. Cellulose may also carbonize without complete hydrolysis to monosaccharides through intramolecular condensation, dehydration, and decarboxylation reactions, as described by Falco et al. [55]. Unlike saccharides, lignin is more complex, consisting of phenyl propane units. Lignin, however, provides an attractive alternative as raw material for HTC, because it is widely available and it has a high carbon content. Only few researchers have described the hydrothermal carbonization of pure lignin [71,72]. Lignin has a higher thermal stability, resulting in less conversion in the HTC and higher solid yields. Despite the different reaction mechanisms and dissimilar structure of the solid carbonaceous product originated from carbonization of carbohydrates and lignin, the final carbon content is rather similar. It usually varies between 65% and 70%, regardless of the original carbon content of the raw material, which is approximately 40% for carbohydrates and more than 60% for lignin [53,55,68,73].

When processing biomass consisting of several components, the product is affected by the composition of the mixture. Industrial side streams are not pure, but always contain mixtures of compounds. Forest industry side-streams, such as black liquor, contain for example lignin, hemicellulose and biomass degradation products, such as small organic acids and ash. When hydrothermally carbonizing mixtures, the product will be affected by the raw material composition and the process conditions. According to Lu and Berge [72], the prediction of functional groups in the solid HTC residue is difficult and inaccurate for mixtures, although energy content and yield can be predicted to a certain level. Black liquor has been carbonized to obtain fuel, but also value-added chemicals, such as aromatic aldehydes [71]. Formaldehyde can be added to the reaction as a polymerization agent for increasing the solid yield. When black liquor, which has been fractionated by ultrafiltration, was hydrothermally carbonized at 200°C in 1% consistency for 6 h, the resulting carbonaceous products had distinct differences in their particle structure, size, porosity, composition, and surface properties, differing from those of the corresponding original black liquor (**Fig. 2**) [64]. Ultrafiltration is a fractionation method where a membrane prevents molecules of a certain size in a pressurized water solution from penetrating the membrane into the permeate fraction, resulting in a high molecular weight concentrate and a low molecular weight permeate. Hence, the structural dissimilarities resulted mainly from the difference in the molecular weight of the fractions.

Another impure biomass stream that can be processed with HTC is biosludge from industrial wastewater treatment units. Traditional municipal and industrial wastewater treatment units bind inorganics and residual organics into biologically active wastewater sludge. The produced biosludge is an organic matrix that is difficult to dewater. It contains heavy metals, nutrients, pathogens, and persistent organic pollutants, the disposal of which represents a major cost. Sludge used to be landfilled or spread on agricultural fields, but, because of recent environmental, health, and economic concerns, anaerobic digestion, composting, and incineration are now favored [74]. As society has grown more resource-minded in recent decades, biosludge is increasingly seen as a resource and technologies to obtain value from sludge have emerged.

HTC has many benefits as a method for sludge treatment. The HTC process is rapid (hours) compared to biological treatment options (days to months). Continuous biosludge HTC can process a sludge stream in 3 h, be turned on and off instantly, and is not sensitive to biological disruptors, such as temperature, toxins, or process fluctuations [75]. HTC breaks the organic matrix and forms a hydrophobic carbonaceous product, biochar, enabling 60%-70% dry matter content (compared to 30% dry matter content for raw sludge) [76,77]. HTC's high temperature and pressure disinfects the often pathogenic sludge, and also reduces the levels of many organic pollutants typically present in wastewater sludge [78]. Produced biochar is a hydrophobic, stable carbonaceous product that can be stored and transported [69,70]. All these aspects contribute to making HTC an attractive biosludge treatment alternative to the current practice of anaerobic digestion or simple dewatering [79].



2. HTC carbon from top to bottom: black liquor, ultrafiltration concentrate 1 (cut off 100,000) and ultrafiltration concentrate 2 (cut off: 20,000) [64].

HTC also shows promise as a means to extract value from biosludge. The most studied method of valorization is the production of incineration fuel from biosludge, which has a higher heating value and incineration characteristics more representative of brown coal, potentially allowing incineration in existing power plants [52,57,69,70]. The carbonized biosludge can be valorized as a low-cost adsorbent with strong sorption ability to different types of pesticides and other organic contaminants [80,81] and a number of heavy metals [82]. Biochar has been hypothesized as an important soil amendment, enhancing carbon content, structure, water adsorption ability, nutrient adsorption ability, air flow, and anti-weathering and anti-erosion characteristics of soil, as well as simultaneously acting as a carbon sink [83-86].

Biosludge also contains inorganic components, most notably nutrients (nitrogen, phosphorous, and potassium) and metals, and HTC provides a tool for accessing these resources. Ongoing research is focusing on controlling the migration of these components during HTC into the phase of preference. This enables the direction of nutrients into the reject stream, from which they can be recovered through controlled precipitation (e.g., struvite formation) or ion capture technologies, or into the biochar fraction, from which they can be extracted through leaching or in which they can act as a fertilizing component in biochar soil amendment products [87-91].

High temperature (>280°C)

Hydrothermal liquefaction

HTL is situated at the more severe end of the hydrothermal processing spectrum (Fig. 1). Rather than trying to selectively extract single components or fractions from the biomass feedstock, the fundamental objective of the HTL process is to achieve an optimal level of energy recovery into biocrude, an oil-like product. In contrast to the other techniques discussed in this paper, the development of HTL has so far been primarily geared toward energy applications. Although the biocrude from HTL also has potential applications as a fuel oil, its further upgrading into transportation fuels is in many instances considered the ultimate goal for this biofuel production pathway. However, before this stage can be realized, the HTL process itself needs to achieve a sufficient level of technological maturity. Several recent reviews provide detailed discussion of the subject [92-96].

The HTL concept originated in Germany before World War II. The process was used to convert coal to transportation fuels on an industrial scale. Most of the early research on the liquefaction of lignocellulosic materials has been guided by the development of coal liquefaction technology. The largest experimental unit so far was built in the United States in the 1970s. This pilot-scale facility, which was located in Albany, OR, was used for demonstrating two process concepts [97]. The PERC (Pittsburgh Energy Research Center) process used bio-oil recycling, coupled with a reducing gas atmosphere and a sodium carbonate catalyst. The otherwise similar LBL (Lawrence Berkeley Laboratory) process did not include bio-oil recycling, but additionally contained an acid pre-hydrolysis step. The main industrial effort in Europe was made by Shell in the 1980s, and the HTU (hydro-thermal upgrading) concept, a spin-off in the 1990s, was an aqueous process with no added alkali. These three processes and their products are further described by Elliott [98].

Although these initial scale-up efforts for biomass HTL did not result in any direct industrial developments, research efforts toward understanding and developing the HTL technology have been revitalized in recent years. The basic concept of HTL entails converting a solid biomass feedstock in the presence of hot compressed water, which in this case acts as a reactant and a catalyst. When operating conditions of temperature (T) and pressure (P) approach the critical point of water (T_c = 374°C, P_c = 22.1 MPa), the physical properties of water start to differ significantly from those of normal water. Hydrothermal liquefaction can be carried out at both subcritical and supercritical conditions. In practice, this means operating at a temperature range of 280°C-370°C and pressures between 10 MPa and 25 MPa. Subcritical water has a lower viscosity, a lower dielectric constant, and a higher ionic product than normal water. The combination of these factors results in a higher solubility of organic compounds and increased reaction rates of base- and acid-catalyzed reactions, which in turn makes subcritical water an excellent medium for converting biomass-derived organic molecules into value-added liquid products.

Because of the high ionic product of water and the consequently accelerated ionic reactions, one essential factor in HTL is maintaining a suitable pH in the liquefaction medium. Several studies have shown that operating at alkaline pH levels favors the formation of oil-like products, whereas an acidic pH promotes charring and formation of heavier tar-like material. Thus, alkaline salts are often added in the process for pH adjustment and catalytic functions [92,93,95]. The overall product selection from HTL is, however, never limited to just the biocrude. The actual oil product is always accompanied by water-soluble organics, and a certain amount of noncondensible gases [96]. From an energy efficiency point of view, it would be desirable to retain as much of the carbon and hydrogen of the original biomass feedstock in the biocrude. In contrast to this, the retention of oxygen in the biocrude is an unwanted phenomenon. Thus, to facilitate the formation of a biocrude that is rich in carbon and hydrogen, the oxygen in the original biomass should be “rejected” into the other product fractions: water, water-soluble organics, and noncondensible gases. In practice, this means that the water-soluble fraction consists of compounds that are richer in oxygen than the biocrude itself (i.e., low molecular weight oxygenates). For the gas-phase products, the rejection of oxygen takes place via the formation of carbon oxides [99-101]. A considerable amount of the research work that has been directed toward HTL has essentially examined how various factors such as temperature, pressure, biomass type, and catalyst affect the product distribution and properties of the products.

Although HTL is featured among several other hydrothermal processing techniques in this paper, from a process point of view, it actually bears closer resemblance to fast pyrolysis of biomass. Fast pyrolysis and HTL both directly liquefy solid biomass, thus forming an intermediate biocrude that can then undergo further upgrading to higher value products. Both of these processes have their advantages and shortcomings, but certain positive aspects in the HTL process have made it a widely pursued research area. In other thermochemical conversion processes (i.e., pyrolysis and gasification), the actual conversion process is typically preceded by an energy-intensive drying step. One of the key features of HTL is its ability to process wet biomass feedstocks. Processing of most conventional lignocellulosic feedstocks, such as forest and agricultural residues, requires additional water for slurry preparation, whereas some high-moisture feedstocks, such as algae, still need to be subjected to some dewatering before HTL. Recycling and reuse of the water is also essential for the low-moisture content feedstocks, as this helps to minimize the amount of waste water that needs further processing. The concentration of dry solids in the slurry has to be selected so that pumpability is still maintained. Depending on the feedstock in question, the applicable range is 5-35 wt%. The issue of pumpability is reflected in the use of continuous flow reactor systems, in which the biomass slurry needs to be introduced into a high pressure reactor on a continuous basis [98].

Compared to purely fluid-based processes, dealing with an aqueous slurry of solid biomass particles imparts its own challenges on carrying out experimental work. Because of this, most of the HTL research has been carried out using batch-type autoclave reactors, which offer simple operational characteristics. As a downside, however, only limited amounts of information pertaining to important factors such as scale-up or long-term operability can be obtained from such studies. A typical liquefaction procedure in an autoclave reactor consists of four distinct phases: initial heat-up, hold period at desired reaction temperature, cool-down, and product recovery. Depending on the size of the reactor, the initial heat-up period can be quite long, which can add uncertainty to studies focusing on the effect on reaction temperature, etc. [102]. The product recovery step is another crucial factor in the HTL process. In batch experiments, the recovery of the biocrude is typically carried out using a combination of solvent extraction and evaporation procedures [103,104]. This kind of approach, which adds to the complexity of the process, is necessary in instances where the HTL process does not result in the formation of separate oil and aqueous phases.

Any eventual scale-up of the HTL process will have to be carried out using continuous flow reactors rather than batch autoclaves. Pacific Northwest National Laboratory has been one of the main developers of continuous flow HTL technology for the conversion of lignocellulosic and algae feedstocks. Their studies have shown that both feedstock types can be readily converted into intermediate biocrude oils with carbon and energy recoveries of >50% [96,105,106]. The biocrude oils, which exhibited a fairly low heteroatom (oxygen, nitrogen, sulfur) content, could then be catalytically hydro-treated into hydrocarbon products with boiling points in the transportation fuel range. Although the oil yield from the primary liquefaction step is lower compared to fast pyrolysis, for example, the lower oxygen content and improved thermal stability of the HTL biocrude simplified the secondary catalytic upgrading process.

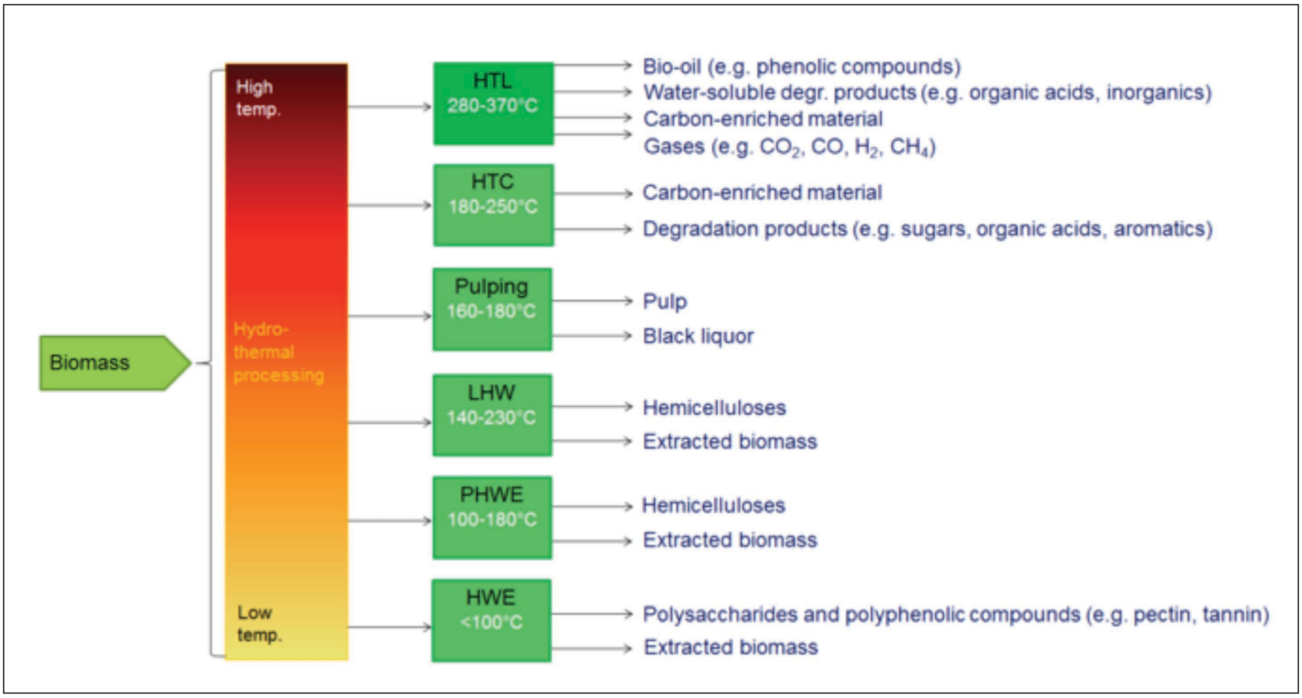
One key aspect that still warrants significant optimization efforts is minimizing the loss of organic matter into the aqueous product phase. Continuous flow HTL reactors have been constructed and are in use at other institutes as well. In Denmark, the University of Aalborg has been actively involved in the development of hydrothermal liquefaction processes. The first process, CatLiq (catalytic liquefaction), was originally developed by SCF Technologies, a Danish company [100]. This sub-critical liquefaction process used a combination of homogeneous and heterogeneous catalysts. The CatLiq technology was subsequently acquired by Altaca, a Turkish company [107], and is currently undergoing scale-up to a 200 tons/day capacity plant. More recently, Steeper Energy has built a continuous supercritical liquefaction unit at the University of Aalborg [108]. The University of Sydney has a continuous HTL pilot plant that has been used for studying the liquefaction of microalgae [109]. Sub-critical liquefaction of kraft lignin has been carried out at Chalmers University of Technology using a dual-catalyst approach similar to that of the CatLiq process [110].

In addition to the limited number of continuous flow reactor studies, a wide variety of feedstocks have been converted in studies using batch autoclaves. Algae conversion has been extensively studied at the University of Michigan [111,112] and at the University of Leeds [113,114]. HTL has also been used for converting different lignins. This can potentially open up new valorization opportunities for lignins that have been derived from either conventional pulping processes or 2nd generation cellulosic ethanol production. Lignin feedstocks that have been studied include kraft lignin [110], organosolv lignin [115,116], alkali lignin [117], and various lignin model compounds [118,119]. In addition to processing isolated lignin feedstocks, it is also possible to directly convert lignins contained in kraft black liquor [120,121]. Manure- and sludge-type feedstocks can also be converted using HTL [122,123].

HYDROTHERMAL PROCESS SEQUENCING — A NOVEL BIOREFINERY CONCEPT

Hydrothermal processes produce products in a wide range as described in the first part of this paper and summarized in **Fig. 3**. There are always, however, some residues formed during hydrothermal processing of biomass that can be considered as waste. The challenge is to better exploit resources in such waste material. Hydrothermal process sequencing offers a way to exploit all the lignocellulosic components of biomass with minimal residue. The added value comes from increasing the efficiency of the value chain of bio-based products by reducing losses and generating higher-value products and services. This new hydrothermal biorefinery concept, which we present here, is also cost-effective, because the size of the refinery can be tailored for specific input, making it easy to also use the concept in sparsely populated rural areas.

The logical approach to hydrothermal sequencing is to start at a low temperature and gradually separate fractions, causing

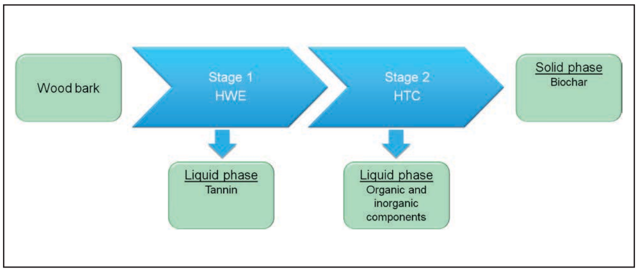


3. Main fractions produced by different hydrothermal processes (HWE = hot water extraction, PHWE = pressurized hot water extraction, LHW = liquid hot water treatment, HTC = hydrothermal carbonization, and HTL = hydrothermal liquefaction).

a minimum of thermal alterations in their composition. Part of the benefit of sequencing is that fractionation can be done without having to cool down the fractions before feeding them into the next stage, which minimizes the energy demand. The fractions also can be conveniently separated locally, which improves the economy of the process by eliminating unnecessary transport costs. It is worth noting that sequencing refers to using only the necessary hydrothermal steps for achieving a desired product range. Three examples are presented below to demonstrate the sequencing principle.

Example 1: HWE followed by HTC for bark

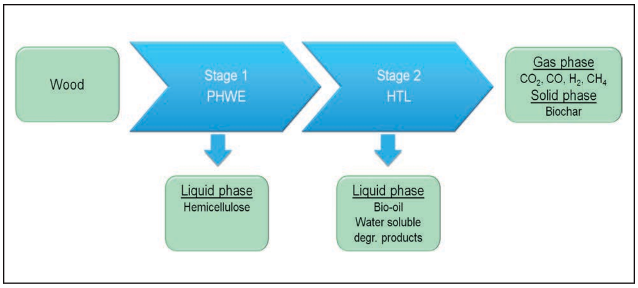
In this case, the biomass would be bark from a process that uses wood. Bark is a low-value side stream that is either composted or combusted to generate energy, but because the material is wet, its heat value is relatively low. Bark, on the other hand, contains tannin, which can be recovered using HWE. The crude tannin from this process can be used either as such, or it can be further purified for conventional tanning or adhesive applications, or it can be converted to novel products, such as insulation or packaging foam [124]. The crude tannin is recovered from the HWE liquid phase, whereas the remaining solid fraction can be further processed in an HTC stage to improve dewatering and increase its carbon content (**Fig. 4**). The solid biochar can then be used as improved fuel, soil amendment, or as a base material for further upgrade into higher value carbon material, such as activated carbon [53,54,56-64]. The liquid HTC fraction can be recycled in the process or potentially used for recovering organic and inorganic components.



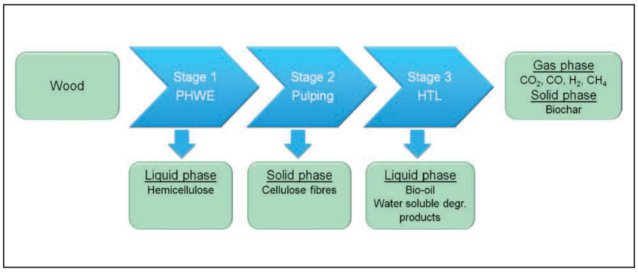
4. Process sequencing hot water extraction-hydrothermal carbonization.

Example 2: PHWE followed by HTL for wood (e.g., forest residue, sawdust)

Another potential sequence is the upgrade of wood by initially removing the hemicellulose fraction using PHWE, with an additional HTL stage to convert the remaining extracted solids into bio-oil, aqueous products, gas, and carbonaceous solids (**Fig. 5**). Hemicelluloses have been suggested for many applications, including cosmetics, pharmaceuticals, textiles, films, coatings, and adhesives, as well as alimentary and health products [24-36]. Elliott et al. [96] and Zhu et al. [106] have discussed the use of HTL product streams. The bio-oil from the HTL process could be catalytically hydro-treated into a transportation fuel, whereas the organic molecules, which are dissolved in the aqueous phase, could be used in an anaerobic digestion or a catalytic hydrothermal gasification process. A part of the aqueous phase would also be recycled back into the HTL process. Any carbon-containing gases could be fed into a



5. Process sequencing pressurized hot water extraction-hydrothermal liquefaction.



6. Process sequencing pressurized hot water extraction-pulping-hydrothermal liquefaction.

steam reforming unit, which would be used for generating the hydrogen that is required for hydro-treating the HTL bio-oil. The wood material in this example could potentially be lower grade forest residues or sawdust that is less suitable for producing fiber products. Sawdust will also provide a better PHWE yield of hemicellulose.

Example 3: PHWE followed by pulping followed by HTC or HTL for wood chips

A potentially interesting sequence is to extract hemicellulose (especially xylan) from wood chips in a PHWE stage and feed the extracted wood material into a pulping process to produce fibers for paper or board production (**Fig. 6**). The pulping process will produce spent liquor that can be converted to carbon-rich material in an HTC treatment or bio-oil and organic and inorganic compounds in an HTL process. Chemical pulping has not been included in this paper, as it requires chemicals other than just water and catalyst. Hydrothermal processing stages can be easily integrated in both chemical and mechanical pulping processes, providing an option of fractionating and separating more useful components from the wood material.

CONCLUSIONS

Liquid water can be used as the sole process medium to convert biomass into valuable solid, liquid, and gaseous products using hydrothermal processing at different temperatures. Each process has its unique characteristics regarding the process conditions and product application spectrum.

HWE is operated below the boiling point of water. It is most suitable for the separation of sensitive water soluble compounds that degrade or react further in higher temperatures. Typical water-extractable biomass components are certain polysaccharides and (poly)phenolic compounds, such as pectin and tannin. Tannins, for example, could be used to replace fossil-based phenol in wood adhesives and insulating foams and in the production of particle boards. In some cases, HWE may also facilitate process steps in a biorefinery, such as enzymatic hydrolysis of carbohydrates.

In PHWE, water is kept in liquid form by keeping the system under sufficiently high pressure. Applied temperatures are typically between 150°C and 180°C. PHWE has been used as a pretreatment stage before kraft pulping and the production of dissolving pulp. Recently, efforts have been made in many laboratories to use PHWE as a pretreatment process for biomass fractionation, delivering cellulose-rich biomass as a solid stream and oligomeric or polymeric hemicelluloses. Extracted hemicelluloses have been suggested for many applications, including cosmetics, pharmaceuticals, textiles, films, coatings, adhesives, and alimentary and health products.

LHWP uses similar process conditions as PHWE, but the target is to make the cellulose in the feedstock more amenable to enzymatic hydrolysis and subsequent fermentation of the hydrolysate to biofuels or chemicals. Temperatures may be as high as 230°C, but treatment time is typically less than 20 min. Hemicelluloses and lignin are partially dissolved in the treatment, but the formation of potential inhibitors from the dissolved components is reduced compared to steam pretreatment of biomass because of the lower concentration of soluble components in the system.

In HTC, wet biomass is processed for a couple of hours at moderate temperatures, normally between 180°C and 250°C, in self-generated pressures at approximately 20-30 bars. HTC has been used to produce inexpensive and sustainable carbonaceous materials with interesting nanostructure and functionalization patterns for a wide range of applications, including materials for adsorption, catalysis, and energy storage. The possibility to use a fast, simple, and environmentally friendly process for wet biomasses makes HTC very attractive for the generation of bio-based carbon products in larger scale. HTC also shows promise for dewatering and valorizing biosludge. The produced biochar is a hydrophobic, stable carbonaceous product that can be easily stored and transported. Its higher heating value makes it suitable for incineration.

In HTL, the operating temperature range is normally 280°C-370°C, denoting pressures between 10 MPa and 25 MPa. HTL is a technology that can be used for converting various biomass feedstocks into biocrude, an oil-like liquid product that can be further upgraded into transportation fuels. This technique is particularly attractive for wet feedstocks (e.g., algae and sludges) because extensive drying of the biomass can be avoided. In addition to the primary oil product, water-soluble organics are also produced alongside noncondensible gases.

We also presented a novel biorefinery concept in which individual hydrothermal processes were combined in sequences to obtain tailored products with maximum yield and efficiency. This concept will enable fractionation in one location, resulting in savings in energy and transport costs. This includes large and small standalone units. The use of water as the only process medium will also minimize the environmental impact caused by harmful chemicals. Hence, the added value comes from the increased efficiency of the sequential processing chain of bio-based products, loss reduction, and generation of higher-value products and services. **TJ**

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The biorefinery concept has a very high priority in today's research landscape. Hydrothermal processing, on the other hand, is very well fitted for carrying out a breakdown of biomass into value-added products, starting from low-temperature processes, such as hot water extraction and pressurized hot water extraction, to high temperature processes such as hydrothermal carbonization and hydrothermal liquefaction. Hydrothermal biorefinery offers a concept of using hydrothermal processes for producing bioproducts and sequencing the processes for obtaining energy and logistics benefits. Hydrothermal processing requires no or minimal chemical process additives and can be considered to be very environmentally friendly.

To maintain a straightforward approach on the subject, we decided to focus on processing in the liquid phase.

The conventional way of using hydrothermal processes is to apply them individually for fractionating and isolating chemical components. The processes have been extensively studied at VTT, which provides a solid basis for further development. Combining different hydrothermal processes into sequences brings a new dimension into biorefinery.

The processing itself involves ordinary issues related to yield and quality, whereas the real challenges in this study are more related to combining the different technologies into efficient sequences for producing a spectrum of products in an integrated unit.

Because individual hydrothermal processes normally focus on producing single products, there has been only minor interest in the past in the variety of different components that are actually formed. A more detailed review of the component spectrum in the solid and liquid phases demonstrates that interesting products are formed and can be recovered.

Mills may want to recover single products (tannin, hemicellulose, organic acids, carbon, etc.), or use hydrothermal processing as a step for producing bioethanol or other types of fuel. Sequencing hydrothermal processes or integrating them in pulp and paper mills may provide new opportunities for using their side streams and waste materials.

Interesting application opportunities for hydrothermal upgrading are side streams from mills that process biomass. The dissolved material contained in the liquid phase needs focus in the future, because it represents an economic opportunity as well as an environmental benefit.

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