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Hydrothermal liquefaction: exploring feedstock for sustainable biofuel production

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Abstract

A number of technological strategies utilizing various types of biomass for the production of hydrocarbons have been put forth but their energy intensive methods are a concern for improved efficiency of biofuel production. Hydrothermal liquefaction (HTL) has emerged as a promising and feasible technology towards utilization of lignocellulosic biomass. The suitability of different biomass feedstock for HTL is intricately tied to their macromolecular composition and process parameters. The comprehensive analysis of feedstock for hydrothermal liquefaction (HTL) signal towards the immense potential of various biomass feedstock, such as corn stover, Miscanthus, pine biomass, *Spirulina*, sugarcane bagasse, rice bran etc. in contributing significantly to renewable energy production. The study emphasizes that the composition of biomass is critical in influencing bio-oil yield during the HTL process. Biomass components like cellulose, hemicellulose, and lignin, each play distinct roles in determining the efficiency of conversion. Specifically, feedstock with higher cellulose and hemicellulose content, such as *Miscanthus* and sugarcane bagasse, demonstrate superior bio-oil yields. The analysis of proximate factors affecting HTL efficiency reveals that moisture content, ash content and high heating value (HHV) are pivotal in optimizing the process. In addition to composition and physical characteristics, the article underscores the significance of growth conditions and nutrient utilization in cultivating biomass feedstock. Integrating HTL with biomass cultivation can create a sustainable, closed-loop system where nutrients from the HTL process are recycled back into cultivation. Biomass offers a renewable energy alternative, however it also poses challenges related to land use and potential competition with food production. Sustainable practices, such as utilizing agricultural and forestry residues and optimizing collection as well as storage processes, can alleviate some of these concerns. By optimizing feedstock selection, process parameters, and integrating sustainable practices, HTL can play a decisive role in advancing biofuel production and contributing to a more sustainable energy future. The interplay between biomass composition, processing efficiency, environmental impacts, and economic feasibility is essential for realizing the full potential of HTL technology in the bio-economy. The current analysis sheds light on the relationship of bio-oil yield with macromolecular components including cellulose, hemicellulose, and lignin as well as process parameters like ash content, moisture content, higher heating value, fixed carbon and volatiles. Focusing on process optimization, this study embodies a closer analysis of literature aimed at defining optimum strategies for enhancement of HTL.

Key words: biomass, biofuels, hydrothermal liquefaction, renewable energy.
Abbreviations: HHV, higher heating value; HTL, hydrothermal liquefaction.

Introduction

Humans started using fossil fuels a little more than 150 years ago for various energy requiring processes and since then they have been substantially extracted and utilized for various purposes, principally transportation. It is a well-known fact that there is a limit to the crude oil present in the earth's crust to support the growing energy needs. Therefore, bringing in sustainable and cleaner energy alternatives is one of the major needs and challenge. Exponentially increasing energy demand and problems associated with climate change are posing serious challenges to mankind necessitating exploration into novel methods of energy production. Biomass trumps the available sustainable alternatives in this quest for energy due to its heterogeneous chemical composition, minimal environmental effect and high abundance in nature. Biomass is the largest global contributor of renewable energy (Singh et al. 2014). The potential of biomass for the production of electricity and fuels for transport is immense, and a careful deployment of this resource can address the global primary energy supply and mitigation of greenhouse gas emissions (Bauen et al. 2009).

However, one of the major constraints in the social concurrence of biomass-based energy is the food vs fuel dilemma (Prasad, Ingle 2019). In this context, a feasible source of renewable energy is inedible plant materials including wheat stems, corn stover, wood shavings, other wood biomass, and other agricultural waste. According to a report 40 million tonnes of such inedible plant material is discarded every year, which upon proper utilization may offer a huge source of bioenergy (Sanderson 2011). Such biomass may provide quantitatively sufficient substrates like cellulose, hemicelluloses, lignin, water-soluble sugars, amino acids, aliphatic acids, and many more that can be utilized for production of bioenergy using high efficiency processes like hydrothermal liquefaction (HTL). HTL is a thermochemical process for converting wet biomass into biocrude oil and chemicals at moderate temperatures and high pressures.

The comprehensive analysis of various biomass feedstock, such as corn stover, Miscanthus, pine biomass, Spirulina, sugarcane bagasse, rice bran etc. for HTL signal towards the immense potential in contributing significantly to renewable energy production while addressing challenges of food security, sustainability and climate concerns. Rapid and high-efficiency reactions are piloted in the presence of critical water parameters like suitable temperature (250 to 400 °C) and pressure (10 to 25 MPa) conditions. The process can be divided into five major steps: (i) hydrolysis and depolymerization wherein the water molecules break the bonds of complex macromolecular structures such as cellulose, hemicellulose, lignin, and proteins, resulting in the formation of smaller, water-soluble compounds, including sugars, phenols, and amino acids (Kruse, Dinjus 2007); (ii) decarboxylation and dehydration remove carboxyl groups from organic acids, releasing carbon dioxide (CO_2) and eliminating water molecules respectively, leading to the formation of alkenes and other unsaturated compounds (Biller, Ross 2016); (iii) condensation and polymerization propel the intermediates to re-polymerize into larger, more complex higher order molecules using reactions like aldol condensation and other polymerization approaches that contribute to the bio-crude oil phase (Toor et al. 2011; Jensen et al. 2017); (iv) gas formation and aqueous phase reactions lead to the formation of gases like CO_2, CH_4, H_2, and NH_3 from decarboxylation and deamination; (v) the water phase, containing various organic acids, alcohols, and ammonia, plays a critical role in further reactions that stabilize or alter the composition of the bio-crude oil (Funke, Ziegler 2010; Vardon et al. 2011); and (vi) solid residue (biochar) formation principally comprised of unreacted carbon, inorganic materials, and some stable organic compounds. Biochar formation is an outcome of the incomplete breakdown of lignin and other impervious biomass components, which are condensed into solid form (Funke, Ziegler 2010).

HTL yield largely depends on the nature of the feedstock, process parameters, and catalysts involved (Singh et al. 2014). Biomass feedstock and water are key components that drive the reaction and have dynamic outcomes based on process conditions like heating rate, temperature, pressure, and pH (Castello et al. 2018). Biomass composition is central to the process yield and variations can affect the outcomes significantly. Fig. 1 presents a HTL process flow diagram describing the parameters and methods crucial for feedstock collection, storage, treatment and processing. HTL can integrate bio-oil production with nutrient recovery, generally during the phase separation step and contains nutrients (N, P, K) and CO_2. Depending on the biomass feedstock used, the process begins with cultivation or collection of biomass followed by the pretreatment step to optimize feedstock properties for conversion. The pretreatment step involves methods like steam explosion and enzymatic hydrolysis that enhance the biomass prior to the HTL process. The quality of bio-oil is influenced by several factors, including the composition of hydrocarbons and phenolic compounds produced (Fig.1).

A diverse array of biomass sources that can be utilized for HTL, including lignocellulosic, aquatic, and waste-derived feedstock, highlights the versatility and potential of this technology to contribute to a sustainable bio-economy. Careful consideration of feedstock composition, availability, treatment and cost are important factors when selecting appropriate biomass resources for HTL. Biomass feedstock sources comprise lignocellulosic biomass, such as forest and agricultural residues (Mosier et al. 2005; McKendry 2002a). Microalgae and macroalgae are few aquatic biomass types that have also been explored as HTL feedstock (Biller, Ross 2011; Neveux et al. 2014). High photosynthetic efficiency, rapid growth rates, and alternative culture methods make them a suitable for HTL (Jena, Das 2011). These abundant algal species do not compete with food crops for land, and therefore are considered as promising feedstock for HTL (Anastasakis, Ross 2011). Organic wastes and residues from various industries have also been investigated for HTL, including sewage sludge, manure, food processing wastes, and lignocellulosic residues from the pulp and paper industry (Vardon et al. 2011; Pedersen 2015). Waste feedstocks are advantageous as they are often available at low or negative cost, and their conversion via HTL can provide both energy recovery and waste treatment benefits (Biller, Ross 2011; Mourtzinis et al. 2014).

Biomass compositional analysis has been a buzzing area of interest for the past few decades and many laboratories have assessed the various biomass parameters critical to efficient biofuel processes. Biomass substrates like *Miscanthus* (van der Weijde et al. 2017), rapeseed (Karaosmanoğlu et al. 1999), corn stover (Mathanker et al. 2020), wheat straw (Templeton et al. 2016), sugarcane bagasse (Singh et al. 2014; Rocha et al. 2015), rice bran (Amissah et al. 2003), microalgae (Alvarenga et al. 2011), pinewood (Viana et al. 2018), sugarcane bagasse (Singh et al. 2014) and many more have been studied. The composition of biomass is critical in influencing bio-oil yield during the HTL process. Biomass components like cellulose, hemicellulose, and lignin, each play distinct roles in determining the efficiency of conversion. Specifically, feedstock with higher cellulose and hemicellulose content, such as *Miscanthus* and sugarcane bagasse, demonstrate superior bio-oil yields.

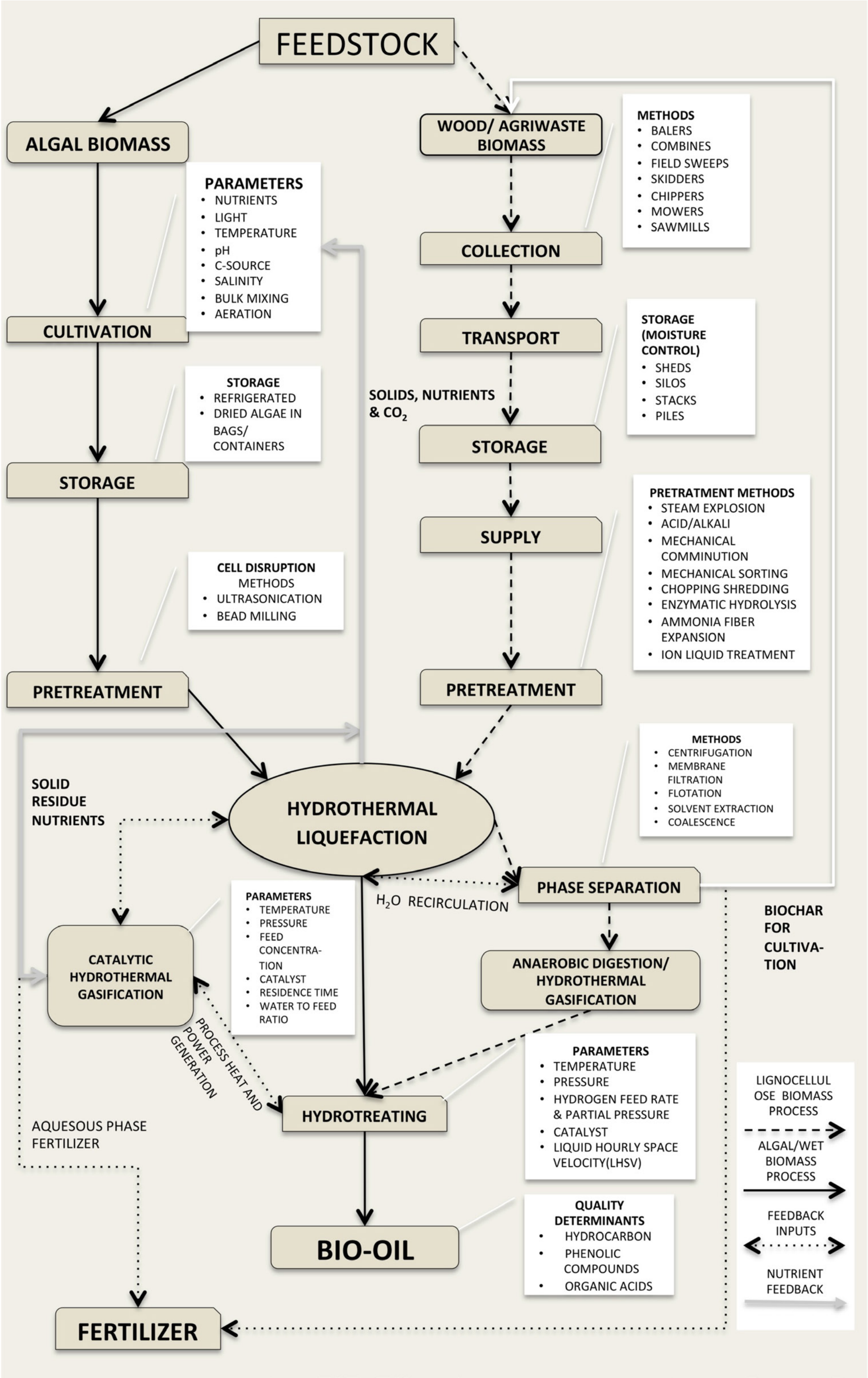

Fig. 1. Process flow diagram explicating hydrothermal liquefaction and allied processes. Modified from Gollakota (2018) and Biller, Ross (2016).

The analysis of proximate factors affecting HTL efficiency reveals that moisture content; ash content and high heating value (HHV) are pivotal in optimizing the process. Smaller particle sizes enhance heat transfer and reaction rates, while lower moisture content reduces energy consumption during HTL. The relationship between volatile matter and bio-oil yield is also emphasized, with higher volatile content is associated with improved yield.

In addition to composition and physical characteristics, the significance of growth conditions and nutrient utilization in cultivating biomass feedstock are equally noteworthy. Integrating HTL with biomass cultivation, particularly algae, can create a sustainable, feedback system where nutrients from the HTL process are recycled back into cultivation. A plethora of biomass types, characteristics and compositions that are employed in the HTL process and evaluating their fitness for economical, efficient and sustainable biofuel production can yield greater dividends for sustainability. An analysis of the relationships between bio-oil yield and key feedstock attributes like biomass composition and HTL biomass process parameters of different feedstock is necessary in this pursuit. Simplicity of the HTL process and technology has the potential to evolve into more energy efficient methods for biofuel production. Utilizing agricultural waste and organic discard with potential product development routes to higher quality product attributes can be a boon to the existing concerns of the fuel crisis, agronomy, anthropogenic waste and discard methods, as well as climate related trepidations.

Feedstock characteristics influencing HTL process

The macromolecular composition and interactions between various constituents can considerably impact the bio-oil yield and its characteristics when produced through HTL (Zhong, Wei 2004; Demirbas 2005; Bhaskar et al. 2008). Biomass feedstock is primarily composed of three major macromolecular components: cellulose, hemicellulose, and lignin (Perlack et al. 2005). Cellulose is a linear polymer of glucose linked by β-1,4 glycosidic bonds, forming a highly crystalline structure that is resistant to depolymerization (Lee, Fan 1982). The crystallinity of cellulose is an important factor in HTL, as it affects the accessibility and reactivity of the material (Möller et al. 2013). During HTL, cellulose undergoes rapid hydrolysis to form glucose and other saccharides, which are then further degraded. Feedstock with higher cellulose content generally yields higher bio-oil in the absence of a catalyst (Zhong, Wei 2004; Demirbas 2005; Bhaskar et al. 2008). Hemicellulose, a branched polymer of various pentose and hexose sugars, typically accounts for 20 to 30% of biomass (McKendry 2002a; McKendry 2002b). It has a weak polymerization and crystalline behavior (Pérez et al. 2005). This makes hemicellulose more susceptible to hydrolysis (Garrote et al. 1999) than cellulose under hydrothermal conditions, producing a variety of monosaccharides (Belkacemi et al. 1991; Pińkowska et al. 2011).

Lignin is a highly complex, cross-linked aromatic polymer that provides structural support and rigidity to the plant cell wall (Sarkanen, Ludwig 1971). The recalcitrant nature of lignin makes it resistant to de-polymerization, and its presence can inhibit the conversion of cellulose and hemicellulose during HTL (Bhaskaret al. 2008). However, the high aromatic content of lignin-derived compounds can contribute to the energy density and chemical diversity of the HTL bio-oil (Brebu, Vasile 2010). It accounts for 20 to 30% of most biomass feedstock (McKendry 2002a). Lignin is more resistant to hydrolysis compared other macromolecules, and its decomposition under HTL conditions can lead to char formation (Zhang et al. 2011; Yong, Matsumura 2012). However, at alkaline conditions, higher lignin content can give increased bio-oil yield (Minowa et al. 1998a; Zhong,Wei 2004; Bhaskar et al. 2008).

The interactions between macromolecular components are significant to HTL performance. Forest biomass typically contains 40 to 45% cellulose, 15 to 35% hemicellulose, and 20 to 35% lignin (Wegener et al. 1983), and agricultural waste with an empirical composition of 40% cellulose, 20 to 25% hemicellulose, and 15 to 20% lignin (Alvira et al. 2010). Cellulose exhibited synergistic interactions with lignin for HTL mediated bio-oil production, whereas it is negatively impacted by hemicellulose (Zhang et al. 2011). The yield of bio-oil is negatively correlated to lignin content, whereas a positive relationship is seen with cellulose and hemicellulose content (Minowa et al. 1998a). An analogous trend was also noted while observing the decline in the bio-oil yield from biomass under alkaline conditions, wherein the incremental cellulose content negatively affected the yield, although higher cellulose content increased the bio-oil yield (Demirbas 2005). Lignin content can be a key factor in HTL and specific conditions along with lignin content can meaningfully influence the yield and related outcomes. However, the increase in the hemicellulose content paralleled a decrease in the yield of bio-oil. The complex nature of biomass and the diverse reactions that can occur during liquefaction processes make it challenging to fully understand the impact of biomass composition (Minowa et al. 1998b; Balat et al. 2008). The yield and properties of bio-oil produced through HTL are greatly affected by the composition and interactions, and delineating these complexities is essential to optimize the HTL process for enhanced yield of bio-oil and byproducts from various feedstock.

Growth conditions of biomass feedstock and collection

The growth conditions of biomass feedstock, such as algae and lignocellulosic materials, can have a substantial impact on the biochemical composition and, consequently, the HTL product yields and properties (Valdez et al. 2014; Tian et al. 2015). Algae grown under different nutrient regimes, light intensities, and temperatures can exhibit varied lipid, protein, and carbohydrate contents, which are known to have distinct behaviors during HTL (Biller, Ross 2011; Eboibi et al. 2014). For example, it was found that *Chlorella vulgaris* grown under nitrogen-limited conditions had a higher lipid content and produced biocrude with a higher energy density compared to nitrogen-replete conditions (Biller, Ross 2011). Similarly, the HTL of algal biomass harvested from a eutrophic lake, with a high ash and low lipid content, resulted in a lower biocrude yield and quality than that of microalgae cultivated in a controlled environment (Tian et al. 2015). It was discovered that the biocrude produced during the HTL of *Scenedesmus* (algae) contained higher nitrogen content compared to *Spirulina*, mostly due to the higher protein content of *Scenedesmus* (Vardon et al. 2011). Similarly, the HTL of macroalgae, which typically have higher ash and lower lipid contents than microalgae, resulted in lower biocrude yields and higher char formation (Toor et al. 2011).

The methods of collection of biomass feedstock and subsequent processing before HTL can also influence the yield and quality of the biocrude (Minarick et al. 2011; Sintamarean et al. 2017). For example, the dewatering and drying of algal biomass can affect the biochemical composition and the ease of pumping the feedstock into a HTL reactor (Sintamarean et al. 2017).

HTL coupled biomass cultivation and nutrient utilization

The success of HTL of biomass relies heavily on the availability and efficient utilization of nutrients by the cultivated biomass feedstock (Biller, Ross 2011; Toor et al. 2011). The primary nutrients required for biomass growth are nitrogen (N), phosphorus (P), and potassium (K) (Hirel et al. 2011). Coupling HTL with algae cultivation can create a symbiotic system where the nutrient-rich aqueous phase from the HTL process is recycled to cultivate more algae (Gao, McKinley 1994; Jena, Das 2011). It was demonstrated that the nutrients in the HTL aqueous phase can be recycled three to 10 times to amplify algal biomass production (Jena, Das 2011). This approach not only enhances the biomass yield but also reduces the need for external nutrient inputs, thereby improving the overall sustainability and economics of the HTL process.

For lignocellulosic biomass, the nutrients are primarily supplied through fertilizers applied during cultivation (Robbins et al. 2012). However, the efficiency of nutrient utilization by the plants is often low, leading to nutrient losses and environmental pollution (Hirel et al. 2011). The HTL process can help recover these nutrients from the aqueous phase and recycle them back to the biomass cultivation system, improving the nutrient use efficiency (Toor et al. 2011; Biller, Ross 2011). Additionally, the solid residue (biochar) generated during HTL can be used as a soil amendment, improving soil fertility and water-holding capacity, further enhancing the sustainability of the overall process (Marris 2006; Barrow 2012). The integration of HTL with biomass cultivation, nutrient recycling, and biochar utilization can create a closed-loop, energy-efficient system that maximizes the utilization of available resources.

Feedstock analysis and impact on bio-oil yield

The efficiency and outcome of the HTL process can be modulated by process parameters of feedstock biomass that are studied using a proximate analysis (Table 1). Particle size plays a crucial role in heat transfer and reaction rate, as smaller particles typically allow for more uniform heating and faster reactions (García-Núñez et al. 2016). Smaller particle sizes can enhance the surface area-to-volume ratio, improving the mass transfer and reaction kinetics during HTL (Mani et al. 2004). Bulk density is another important factor, as it affects the mass and energy density of biomass, which has direct implications for transportation and storage costs (Bridgwater 2004). Moisture content is particularly critical because water must be heated to high temperatures in HTL, and excessive moisture can lead to increased energy consumption, thereby reducing the overall efficiency of the process (Elliott et al. 2015). Higher bulk density can facilitate the handling and transportation of biomass feedstock, while lower moisture content can

Table 1. Various feedstock parameters for proximate analysis to optimize the HTL process for efficient conversion of biomass into valuable biofuels and chemicals. DM, dry mass

Parameter	Significance	Unit	Reference
Particle size	Affects heat transfer, reaction rate, and the uniformity of the HTL process	μm or mm	García-Núñez et al. 2016
Bulk density	Influences the overall mass and energy density of the biomass, affecting transportation and storage	kg m^{-3}	Bridgwater 2004
Moisture content	Impacts the energy required for HTL, due to modulation in reaction temperatures	%	Elliott et al. 2015
Fixed carbon	Represents the solid carbonaceous residue after volatiles are removed, essential for biochar yield	% DM	Demirbas 2004
Ash content	Higher ash content can result in catalyst poisoning and operational issues during HTL	% DM	Vassilev et al. 2010
High heating value (HHV)	Indicates the energy content of the biomass, crucial for evaluating the efficiency of the HTL process	MJ kg^{-1}	Parikh et al. 2007
Volatile matter	The proportion of biomass that converts to gas and liquid during HTL, impacting product distribution	% DM	Shen et al. 2010

reduce the energy required for drying prior to HTL (Acharjee et al. 2011).

The parameters of feedstock proximate analysis include fixed carbon, ash content, and volatile matter, which play meaningful roles in the HTL process. Fixed carbon represents the solid residue left after volatile compounds are removed and is important for biochar production (Demirbas 2004). Ash content is a key consideration because high ash levels can lead to operational challenges and catalyst poisoning during HTL, making the process less efficient (Vassilev et al. 2010). Thus, a combination of low ash and higher volatiles can be an indication of better suitability as feedstock biomass. Volatile matter impacts product distribution during HTL, as it consists of the portion of biomass that converts to gas and liquid phases, thereby influencing the yield of bio-oil and other by-products (Shen et al. 2010).

A significantly positive relationship can be observed between bio-oil yield and volatiles, with *Miscanthus* showing higher bio-oil yield of 69.2% using the fast pyrolysis method and with 3.5% ash content, 4.9% moisture content, fixed carbon at 20.4%, and high volatiles at 78.2% (Table 2). Volatiles and ash content are associated inversely with yield and higher volatiles with values of 85.7, 75.6, 79.4 and 84.8% are offered by pine, rapeseed straw, *Spirulina* and sugarcane bagasse, respectively. However, oil yield from pine biomass is low and needs to be investigated for drawing conclusions. Rice bran with modified HTL methods for biomass has a low yield of bio-oil at 10.48%, making it unsuitable for HTL mediated biofuel production. Moisture content displays a weak relationship with yield of bio-oil in *Miscanthus*, pine and rapeseed straw, whereas sugarcane bagasse with 42% moisture content has a strong positive association.

The high heating value (HHV), a measure of the energy content of the biomass, is another essential parameter for evaluating the potential energy output of the HTL process (Parikh et al. 2007). A higher HHV value is preferred for HTL as it is potentially associated with higher yield of bio-oil and other valuable products. The HHV relationships with bio-oil yield are most pronounced in case of *Miscanthus, Spirulina* and sugarcane bagasse feedstock with yields and HHV values of 69.2% (20 MJ kg^{-1}), 34.51% (22.56 MJ kg^{-1}) and 35% (16.1 MJ kg^{-1}), respectively (Table 2). These parameters collectively help in optimizing the HTL process to ensure efficient conversion of biomass into valuable biofuels and chemicals.

The heatmap in Fig. 2 includes parameters such as ash content, moisture content, fixed carbon, volatiles, high heating value (HHV), cellulose, hemicellulose, total lignin, glucose, xylose, arabinose, galactose and bio-oil yield. The correlation coefficient between ash and bio-oil yield is $r = -0.31$, indicating a moderately strong inverse relationship. Moreover, a strong negative correlation ($r = -0.94$) is evident between ash content and cellulose content. Ash content also shows a significant negative correlation with total lignin ($r = -0.69$) and glucose($r = -0.65$). These negative correlations suggest that higher ash content is associated with lower cellulose, lignin, and glucose content in the biomass feedstock. Higher ash content generally results in lower bio-oil yield during HTL processing. For example, corn stover with 7.0% ash has a bio-oil yield of 29.3%, while rice bran (21.1% ash) tends to have lower bio-oil yields of 10.5%. This is also comparable to feedstock with lower ash, like pine biomass (2.0%) and *Miscanthus* (3.5% ash). Additionally, the correlation heatmap shows a strong negative correlation ($r = -0.46$) between ash

Table 2. Proximate and compositional analysis of feedstocks parameters for bio-oil yield in hydrothermal liquefaction process. DM, dry mass. Data sources: Shekharam et al. 1987; Karaosmanoğlu et al. 1999; Amissah et al. 2000, 2003; Ross et al. 2008; Templeton et. al. 2009; Wilson et al. 2011; Brosse et al. 2012; Mtunzi et al. 2012; Sunphorka et al. 2012; Niu et al. 2013; Wu et al. 2014; Rocha et al. 2015; Svard et. al. 2015; Chagas et al. 2016; Govindasamy et al. 2018; Viana et al. 2018; Jaichakan et al. 2019; Jamilatun et al. 2019; Seghiri et al. 2019; Funda et al. 2020; Mathanker et al. 2020; Mensah et. al. 2021; Szyszlak-Bargłowicz et al. 2021; Kumar 2022; Obeid et al. 2022; Cui et al. 2023; Yadav et al. 2023; Tirumareddy et al. 2024; Wancura et al. 2024)

Parameter	Corn stover	Miscanthus	Pine biomass	Rapeseed straw	Rice bran	Spirulina	Sugarcane baggase	Wheat straw
Ash (% DM)	7.0	3.5	2.0	5.9	21.1	14.6	5.6	17.1
Moisture content (%)	5.4	4.9	11.7	12.6	7.8	12.7	48.0	11.0
Fixed carbon (% DM)	16.8	20.4	18.7	18.6	13.4	12.51	11.8	15.0
Volatiles (% DM))	71.0	78.2	85.7	75.6	23.9	79.4	84.8	68.5
Cellulose (% DM)	37.7	54.2	50.0	41.3	15.5	27.2	42.2	31.8
Hemi-cellulose (% DM)	20.62	38.61	22	24.11	31.1	33.47	27.6	31.27
Total lignin (% DM)	30.5	21.3	29.0	18.5	11.1	10.0	24.4	21.7
Glucose (% DM)	31.9	52.8	45.0	48.7	–	54.4	40.5	33.6
Xylose (% DM)	18.9	30.9	4.6	18.4	3.2	7.0	22.0	19.3
Arabinose (% DM)	2.8	3.3	1.3	1.4	3.4	0	1.5	2.2
Galactose (% DM)	1.5	0.3	2.4	17.6	–	2.6	0.3	0.6
High heating value (MJ kg^{-1})	17.8	20.0	21.6	17.6	13.9	22.6	16.1	16.
Bio-oil yield (%)	29.3	69.2	10.0	27.0	10.5	34.5	35.0	32.3

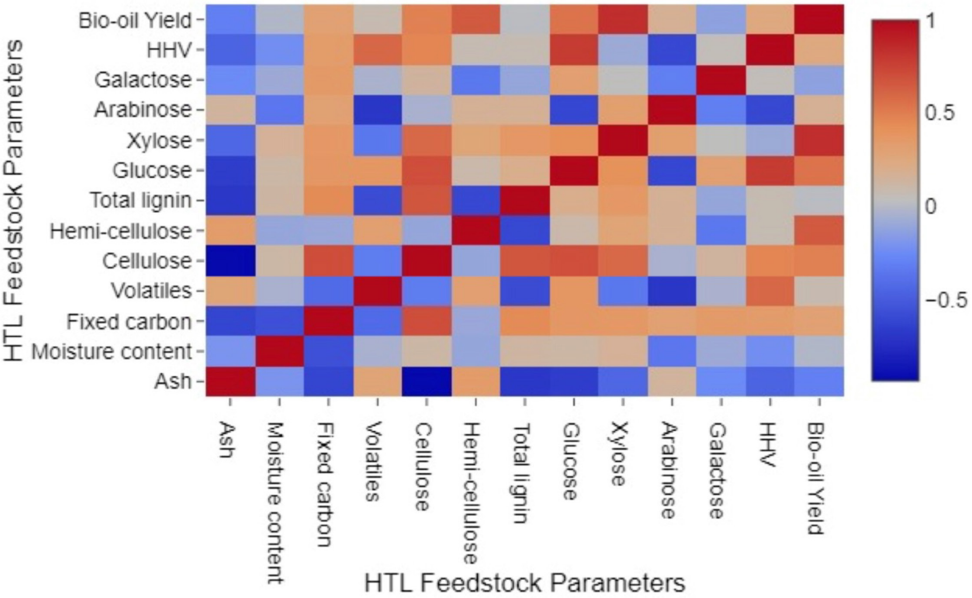

Fig. 2. Reconstructed heatmap for correlation analysis of HTL feedstock parameters by using data from various sources (Shekharam et al.1987; Karaosmanoğlu et al. 1999; Karaosmanoğlu et al. 2000; Amissah et al. 2003; Ross et al. 2008; Templeton et. al. 2009; Wilson et al. 2011; Brosse et al. 2012; Mtunzi et al. 2012; Sunphorka et al. 2012; Niu et al. 2013; Wu et al. 2014; Rocha et al. 2015; Svard et al. 2015; Chagas et al. 2016; Govindasamy et al. 2018; Viana et al. 2018; Jaichakan et al. 2019; Jamilatun et al. 2019; Seghiri et al. 2019; Funda et al. 2020; Mathanker et al. 2020; Szyszlak-Bargłowicz et al. 2021; Mensah et al. 2021; Kumar 2022; Obeid et al. 2022; Cui et al. 2023; Yadav et al. 2023; Tirumareddy et al. 2024; Wancura et al. 2024).

content and HHV. Higher ash content dilutes the energy-rich organic components of the biomass, thereby reducing the overall heating value. HHV also displays a moderately positive correlation (r = 0.25) with bio-oil yield directly. This indicates that biomass with higher HHV tends to have higher bio-oil yield during the HTL process. HHV shows a strong positive correlation (r = 0.79) with glucose content suggesting the association of higher glucose content in the biomass with higher HHV, which can contribute to higher bio-oil yield. This also indicates that as the ash content of the biomass feedstock increases, the high heating value tends to decrease, and also maintains coherence with literature as ash content is generally considered an undesirable component in biomass feedstock for energy applications.

Moisture content of the biomass feedstock does not appear to have a strong correlation (r = –0.01) with the bio-oil yield. In contrast, stronger positive correlations between bio-oil yield and other parameters like hemicellulose (r = 0.65), xylose (r = 0.84), and glucose (r = 0.54) indicate that the composition of the biomass, particularly the carbohydrate fractions, have a more significant influence on the bio-oil yield during HTL than the moisture content. Based on this heatmap, moisture content does not appear to be a strong driver of bio-oil yield in HTL processes. The composition and structural carbohydrates of the biomass seem to be more important factors. However, more contexts, in relation to process parameters like pH, catalyst, temperature etc. can further delineate the multi-factorial relationships.

The correlation between volatiles and bio-oil yield (r = 0.08) is very weak and positive (Fig. 2). This suggests that the content of volatiles in biomass does not significantly affect the yield of bio-oil produced through hydrothermal liquefaction (HTL). In the context of different feedstock, various materials exhibit varying volatile content, which may influence the overall bio-oil yield. For instance, corn stover has a volatile content of 71.0% dry mass and yields 29.3% bio-oil, while rice bran, with a much lower volatile content of 23.9% dry mass, yields only 10.5% bio-oil (Table 2). While volatiles may contribute to the chemical processes during HTL, their impact on bio-oil yield appears to be minimal based on the correlation data presented.

A moderately strong positive correlation (r = 0.30) between fixed carbon and bio-oil yield is indicative of higher fixed carbon content of the biomass feedstock positively influencing the bio-oil yield during HTL processes (Fig. 2). The fixed carbon content is a measure of the non-volatile combustible material in the biomass, which can contribute to the production of bio-oil during the HTL process. Higher fixed carbon typically implies a lower volatile matter content, which can lead to increased bio-oil yields as the less volatile components are more readily converted into the liquid bio-oil product. These relationships are tangible in the light of process chemistry, as the fixed carbon fraction of the biomass is more resistant to volatilization and can be more effectively converted into the desired bio-oil during the HTL reaction conditions.

A strong positive correlation of bio-oil yield with xylose content (r = 0.84) and a moderate relationship (r = 0.54) with glucose content, signify the importance of carbohydrates (Fig. 2). It appears that higher xylose content in the biomass feedstock, rather than glucose, is likely to produce more bio-oil. Arabinose and galactose exhibit weak relationships to the bio-oil yield. The correlation between bio-oil yield and hemicellulose is significantly positive (r = 0.65). A moderate positive correlation (r = 0.49) between bio-oil yield and cellulose implies that higher cellulose content can lead to an increase in bio-oil yield, although the relationship is not as strong as with xylose or hemicelluloses. The parameters that exhibit strong positive correlations with bio-oil yield are xylose, glucose, hemicellulose, and cellulose, while total lignin shows a very weak association. Delineating the behavior of feedstock compositional parameters can be significant for improved bio-oil yield through HTL processes.

The insights drawn from the patterns and trends observed in the heatmap are supported by literature, reinforcing the importance of selecting appropriate feedstock for optimal bio-oil production. These correlations suggest that feedstock composition, particularly the carbohydrate fractions (cellulose, hemicellulose, and their constituent sugars), play a meaningful role in determining the bio-oil yield from the HTL process. Feedstock with higher contents of these carbohydrate components is likely to produce higher bio-oil yields. However, it is important to note that this is based on the correlation analysis, and the strength of these relationships may vary depending on the specific biomass feedstock and HTL process conditions with due experimental validation.

Proximate and compositional analysis of feedstock parameters for bio-oil yield in the HTL process are presented in Table 2. Cellulose and hemicelluloses are very significant as core substrates for bio-oil yield. *Miscanthus*, rapeseed straw, *Spirulina* and sugarcane bagasse are the highest yielding feedstock. *Miscanthus* has high cellulose content of 54.2% and hemicellulose content of 38.6%, making it a potentially suitable feedstock for HTL (Table 2). Pine biomass has a moderate cellulose content of 46 to 50% and hemicellulose content of 19 to 22.0%. Rice bran has lower cellulose content at 15.5% and hemicellulose content at 31.1%, which might make it less suitable for HTL compared to *Miscanthus*. Sugarcane bagasse has high cellulose content of 42.2% and hemicellulose content of 27.6% whereas wheat straw has cellulose content of 31.8% and hemicellulose content of 31.3% (Table 2). For HTL, feedstocks with higher cellulose and hemicellulose content are more suitable as they can be converted into valuable products like bio-oil.

Monosaccharaides, especially glucose, xylose and galactose, also exhibit positive proclivities towards bio-oil yield. Corn stover, for example, has glucose, xylose, arabinose, and galactose values of 31.9, 18.9, 2.8, and 1.5%, respectively, with a bio-oil yield of 29.3%. In comparison, *Miscanthus* presents a higher concentration of glucose and xylose at 52.9 and 30.9%, respectively, and similar values of *Spirulina* glucose content at 54.4% make them promising feedstock for HTL. Similarly, sugarcane bagasse shows significant glucose and xylose content of 40.5 and 22.0%, respectively. Rice bran, however, exhibits lower monosaccharide content, especially in terms of glucose at 15.5%, which could impact the production efficiency of HTL processes. Overall, on the basis of the monosaccharide values, corn stover, *Miscanthus, Spirulina* and sugarcane bagasse appear to be favorable choices for hydrothermal liquefaction due to their relatively higher monosaccharide content, particularly glucose and xylose, and respective bio-oil yield.

Challenges and research gaps

The process parameters and biomass composition largely determine the product characteristics and distribution of the hydrothermal liquefaction process (Gollakota et al. 2018). However, it was noted that the effects of the operating parameters and biomass feedstock on wood based HTL are not so lucid because of structural and chemical complexities of wood (Jindal, Jha 2016).

Biomass composition can also regulate the chemical nature of the resultant biocrude generated during the processes using subcritical water technologies (Toor et al. 2011). The yield of bio-oil can be optimized with various biomass as well as process parameters during HTL that include rate of heating, particle size, solvents, residence time, temperature of liquefaction etc. (Akhtar, Amin, 2011). Biomass-water relations during HTL with changing physicochemical properties of water were elucidated (Tekin et al. 2014). Investigations for optimizing critical operating parameters like temperature and pressure that govern HTL, can yield higher bio-oil (Gollakota et al. 2018). Each type of biomass feedstock, whether algal, lignocellulosic, has unique characteristics and challenges that must be addressed for successful integration into biorefineries and biofuel production processes. Some of the other key challenges and considerations are discussed below.

Feedstock pretreatment and fractionation: for addressing the recalcitrance of lignocellulosic and algal biomass through effective pretreatment and fractionation methods and improving the accessibility of the desired molecular components for subsequent conversion processes (Mosier et al. 2005; Alvira et al. 2010).

Conversion technologies: the selection and optimization of appropriate conversion technologies, such as biochemical, thermochemical, or hybrid processes, are essential to maximize the yield and quality of biofuels and biochemicals from the diverse biomass feedstock (McKendry 2002a; McKendry 2002b; Gollakota et al. 2018).

Process integration and bio-refinery concepts: integrating biomass conversion processes into a biorefinery framework can improve the overall efficiency and economics by enabling the co-production of multiple value-added products from the various biomass components (Naik et al. 2010; Yue et al. 2014).

Feedstock availability and logistics: ensuring a reliable and consistent supply of biomass feedstock, while considering factors such as seasonality, geographical distribution, and transportation logistics, is crucial for the successful deployment of biofuel and biochemical production facilities (Bhutto et al. 2011; Cheng,Timilsina 2011).

Environmental and sustainability considerations: the environmental impacts and sustainability of biomass utilization, including greenhouse gas emissions, water usage, and land-use changes, must be carefully evaluated and addressed to ensure the long-term viability of biofuel and biochemical production from various biomass sources (Clarens et al. 2010; Gnansounou, Raman 2016).

Environmental impacts of biomass generation for HTL

Biomass utilization as a renewable energy source has gained momentum in the past few decades, especially for mitigating the challenges of energy security, fossil fuel depletion and climate change (Gollakota et al. 2018). There can be environmental concerns when employing biomass for energy production using HTL but not as substantial as the existing fossil fuel regime (Savage et al. 2010). One of the key environmental concerns associated with biomass feedstock production for HTL is the impact on land use and land use change (Pedersen, Rosendahl 2015). The conversion of land to grow specific crops used for feedstock can lead to direct and indirect land use changes, which can result in the release of stored carbon from vegetation and soils, with considerable disturbances to the diversity of the ecosystem and its services (Jensen et al. 2017). It was highlighted that the net greenhouse gas emissions of a biomass-to-biofuel supply chain are highly dependent on the specific land use changes involved (Savage et al. 2010).

Another environmental impact of biomass production for HTL is potential competition with food and feed production, which can have implications for food security and prices (Lynd et al.2009). It was suggested that the use of agricultural and forestry residues, as well as marginal lands, for biomass production can help to mitigate these concerns (Ioelovich 2015). The harvesting and transportation of biomass feedstock can also have environmental impacts, such as air pollution, water consumption, and ecosystem disturbance (Kabir, Hameed 2017). The importance of developing sustainable supply chain logistics and infrastructure to minimize these impacts was emphasized (Molino et al. 2016). Furthermore, the conversion of biomass to bio-oil and chemicals through HTL can have environmental implications, such as the generation of waste streams and the potential release of hazardous substances (Jensen et al. 2017). Careful process design and waste management strategies are necessary to address these concerns (Mortensen et al. 2011).

Economic viability and market potential for various biomass types

The economic viability and market potential of biomass feedstock used in hydrothermal liquefaction (HTL) processes are vital for the commercialization of this technology (Gollakota et al. 2018). A comprehensive techno-economic analysis is necessary to evaluate the production costs and identify the most cost-effective biomass sources (Pedersen, Rosendahl 2015). Lignocellulosic biomass, such as agricultural and forestry residues, is generally considered a low-cost feedstock for HTL (Zhu et al. 2014). However, the availability and quality of these feedstocks can vary significantly, affecting their suitability and pricing (Anastasakis et al.2018). Alternatively, dedicated energy crops, like fast-growing trees and grasses, offer more consistent biomass supply, but may require higher upfront investment for cultivation (Ou et al. 2015).

Wet organic waste streams, including municipal sewage sludge, animal manure, and algae, have gained attention as promising HTL feedstock due to their abundant availability and low or even negative cost (Vardon et al. 2011; Lavanya et al. 2016). The ability to process these high-moisture feedstock directly without the need for drying is a significant advantage of HTL over other conversion technologies (López Barreiro et al. 2013).

The market potential for HTL-derived products, such as biocrude oil and value-added chemicals, is also a crucial factor in determining economic viability (Biller, Roth 2018). The quality and composition of the biocrude can significantly impact its marketability and the required upgrading costs. Developing efficient upgrading and refining processes is essential to maximize the value of HTL products and improve the overall economic feasibility of the technology (Tekin 2015). The comprehensive analysis of feedstock for HTL signal towards the immense potential of various biomass feedstock in contributing significantly to renewable energy production while addressing challenges of food security, sustainability and climate concerns. Key findings emphasize that the composition of biomass is critical in influencing bio-oil yield during the HTL process. Biomass components and proximate factors are pivotal in determining the efficiency of conversion and optimizing the overall process. In addition, environmental considerations underscore that while there are challenges related to land use change and competition with food production, yet they offer an excellent renewable energy alternative. Sustainable practices, such as utilizing agricultural and forestry residues and optimizing collection as well as storage processes, can alleviate some of these concerns. Lastly, the economic viability of HTL is dependent on low-cost options for biomass and the market potential for HTL-derived products, including biocrude oil, and hinges on the quality of the outputs and the efficiency of upgraded processes. By optimizing feedstock selection, process parameters, and integrating sustainable practices, HTL can play a decisive role in advancing biofuel production and contributing to a more sustainable energy future.

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