



Review

Wet organic waste treatment via hydrothermal processing: A critical review



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H I G H L I G H T S

- The feasibility of handling wet waste via hydrothermal treatment was reviewed.
- Formation of value-added products and reduction of waste volume was proven.
- The mechanism and reaction pathways have not been developed enough.
- Hydrothermal processing suffers from immature technology, demanding innovations.

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A B S T R A C T

There are several recent reviews published in the literature on hydrothermal carbonization, liquefaction and supercritical water gasification of lignocellulosic biomass and algae. The potential of hydrochar, bio-oil or synthesis gas production and applications have also been reviewed individually. The comprehensive review on the hydrothermal treatment of wet wastes (such as municipal solid waste, food waste, sewage sludge, algae) covering carbonization, liquefaction and supercritical water gasification, however, is missing in the literature which formed the basis of the current review paper. The current paper critically reviews the literature around the full spectrum of hydrothermal treatment for wet wastes and establishes a good comparison of the different hydrothermal treatment options for managing wet waste streams. Also, the role of catalysts as well as synthesis of catalysts using hydrothermal treatment of biomass has been critically reviewed. For the first time, efforts have also been made to summarize findings on modelling works as well as techno-economic assessments in the area of hydrothermal treatments of wet wastes. The study concludes with key findings, knowledge gaps and future recommendations to improve the productivity of hydrothermal treatment of wet wastes, helping improve the commercial viability and environmental sustainability.

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1. Introduction

Biomass waste is considered to be an attractive alternative resource to decarbonise the world and reduce mankind's reliance on fossil resources. Biomass can be used for energy, fuel, chemicals and carbon materials production (Nonaka et al., 2011; Zhao et al., 2014; Hrnčić et al., 2016). The majority of biomass wastes are hydrophilic and contain large amounts of inherent moisture up to between 60 and 90 wt% (Hitzl et al., 2015), hence being generally referred as wet biomass waste. They have a paste-like consistency with high viscosity and thereby it is challenging to dewater and prepare for further processing due to their heterogeneous and non-Newtonian nature (Lee et al., 2016).

Production of huge amounts of wet biomass, including municipal solid wastes (MSW), aquaculture and algal residues, sewage sludge and paunch waste is the inevitable consequence of rapid urbanisation and population growth. According to the World Bank report, about 0.77 kg MSW is produced per capita per day, generating over 2 billion tonnes of MSW with inadequate treatment and recovery (Kaza and Yao, 2018). It is composed of various useful fractions including paper, food, green waste, plastics and rubber which can be a good resource for the production of energy, fuels, chemicals and carbon materials (El-Fadel et al., 2002). In a similar way, algae produced in lakes and wastewater treatment plants also contain very high levels of inherent moisture (i.e., >85%) and are generally considered problematic, as they directly affect the marine life and water quality. Algae can be considered a renewable resource as they are produced by consuming water and CO₂ through photosynthesis. Additionally, they contain very high amounts of lipids and therefore they can also serve as a promising source of energy (Yang et al., 2004). The main drawback of algae conversion is its high pretreatment cost for dewatering and drying, accounting for around 30% of the total product costs (Chen et al., 2015). The development and establishment of wastewater treatment plants have resulted in the production of a large quantity of sewage sludge in which moisture content exceeds 70 wt% (Xu et al., 2012). Other than moisture, sludge contains valuable organics such as protein, lipid and carbohydrates (Inoue et al., 1996). Paunch

waste, the undigested/semi-digested feed of cattle, is the main wet waste produced in abattoir having a moisture level as high as 95% and high levels of carbohydrates (Marzbali et al., 2020). The majority of the abovementioned wastes contain pathogens such as *E. coli*, *Salmonella* spp. and *Leptospirosis* spp. (Koutsoumanis and Taoukis, 2005) and therefore they carry biological risks. These wastes can contaminate the oceans and groundwater resources, cause diseases and health problems and create clogging in drain systems, when leachate level builds up (Rowe and Yu, 2012).

In the view of massive production of wet organic wastes from various industries such as animal farming, agriculture, housing and food processing, there is a need for a cost-effective route to convert undervalued resource into a sustainable and renewable energy resource, while emitting very low levels of greenhouse gases (GHG) (Delivand et al., 2015). Based on necessity for pre-drying the wet waste, strategies can be classified into two groups, as shown in Fig. 1.

The incineration, pyrolysis and gasification process require a drying step and handle a feedstock having a low moisture content. Therefore, requirement of energy-intensive pre-drying step for handling the wet wastes is the major challenge of these methods (Dunnigan et al., 2018). The pre-dried biomass waste has been subjected to various thermochemical treatments such as pyrolysis and gasification to produce biochar, bio-oil and gaseous products (Foo and Hameed, 2009; Bing et al., 2016). The presence of water decreases the temperature and hinders the complete cracking of molecules in the pyrolysis zone. Therefore, it is advised to lower the biomass moisture content to less than 10–15% prior to the process; otherwise this makes the ignition problem for the produced fuel (McKendry, 2002). Dong et al. (2016) also suggested that the moisture content of MSW should be decreased to up to 20–25% to ensure a good performance, syngas quality and energy efficiency during gasification. In case of incineration of a wet biomass, it was also shown that the mechanical dewatering and drying of sludge is needed before incineration to enhance the heat efficiency and diminish the need for auxiliary fuel (Li et al., 2014b). Despite the advantage of incineration in significant reduction of the volume of waste (10% of that of dewatered waste (Li et al., 2014b)), it is

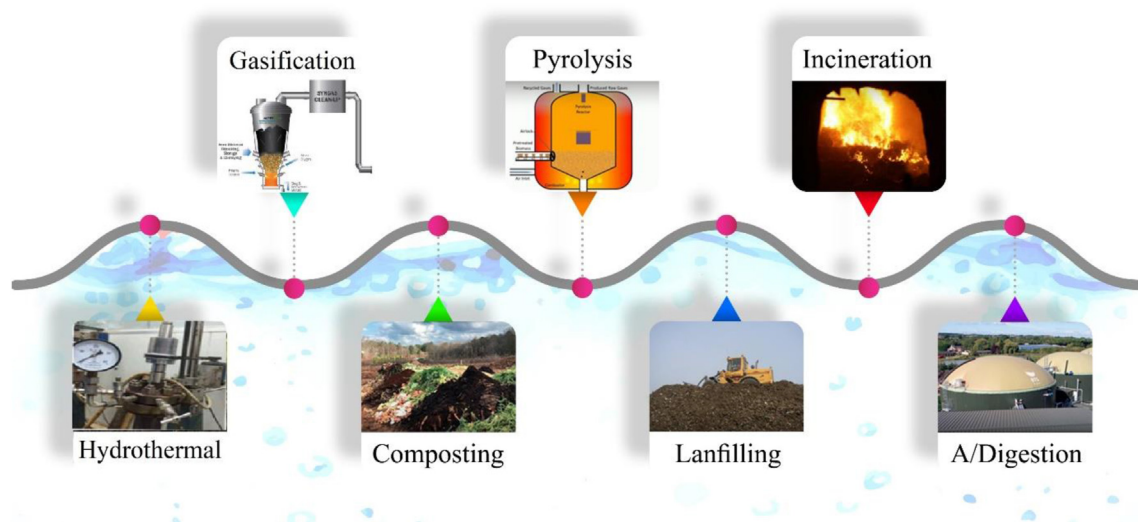


Fig. 1. Classification of different management strategies of wet wastes.

discouraged for waste management as it emits toxic gas such as dioxins and furans (El-Fadel et al., 1997; Schreck, 1998; Hoornweg and Bhada-Tata, 2012).

The methods, not requiring the pre-drying step such as landfilling and anaerobic digestion can save a great deal of energy. Around 53% of MSW in the U.S. end up in landfills (Satchwell et al., 2018). However, landfilling without gas capture is unfavourable as it releases methane, CO₂ and a small portion of H₂S to the ecosystem (Qiyong and Jiaoju, 2011). For example, annual methane emissions from MSW in China steadily increased and reached over 1850 Gg in 2013 (Du et al., 2017). Greenhouse gases, in particular methane and CO₂, contribute significantly to the global warming. Given these serious drawbacks, some countries have shown less interest for landfilling. For instance, Sweden prohibited the establishment of new landfill site from 2006 (Nges and Liu, 2010). The process of methane production is naturally occurring in the environment through decomposition of wet waste in an oxygen-free environment using a microbial consortium (Pain and Hephherd, 1985), which is referred to as anaerobic digestion (AD). AD has been widely put forward for converting wet waste to biogas (Jensen et al., 2016; Kiyasudeen et al., 2016; Ma et al., 2018; Milledge et al., 2019). Along with biogas, AD produces two additional by-products i.e., digested residue and effluent, which need proper treatment before discharging to the environment (Sawatdeenarunat et al., 2015). AD also demands a long processing time, from weeks to months as described in previous works (Appels et al., 2008; Lee et al., 2011). Therefore, the AD process requires a high capital investment for the digester which eventually undermines the commercial viability of the process.

The hydrothermal processing is a promising approach for wet organic waste conversion as it can circumvent the energy-intensive pre-drying stage required for the conventional treatments and produce a wide range of products. Other advantages reported in the literature are low activation energy requirement and flexibility in producing high quality char, oil and gas (Libra et al., 2011; Liu and Balasubramanian, 2014). This is because in this process, water itself can act as a reactant media and helps initiating the reaction via hydrolysis (Kruse and Dinjus, 2007). A comparison between hydrothermal liquefaction and slow pyrolysis of *Scenedesmus* and *Spirulina* algal biomass showed that the bio-oils produced from both processes have similar elemental composition; however, hydrothermal treatment was found to be more energetically

favourable in case of wet biomass with 80% moisture (Vardon et al., 2012). The energy consumption of hydrotreatment was nearly half of that of pyrolysis for wet biomass as pre-drying was required to remove the water content in the latter approach. Moreover, hydrothermal treatment eliminates all biological risks, including pathogens from the waste due to inherent autoclaving at above 121 °C (Hossain et al., 2012; Anbu et al., 2017).

There are several review articles published on hydrothermal treatments of biomass wastes (Pavlovic et al., 2013; Ruiz et al., 2013; Kumar et al., 2018). The most recent excellent reviews on the hydrothermal processing of waste biomass discuss the reaction mechanism of biomass constituents in hydrothermal media, effect of process conditions on products distribution, products characterization and applications as well as nutrients migration behavior with no to a very little focus on techno-economic aspect of the technology (Djandja et al., 2020; Yang et al., 2020; Zhang et al., 2020). Therefore, a state-of-the-art review is required for in-depth understanding on the process modelling and simulation as well as assessment of techno-economic constraints prior to the commercially more attractive process development, which is one of the main focus of the current review. Apart from these, this paper critically reviews the entire spectrum of hydrothermal processing (i.e., carbonization, liquefaction and supercritical water gasification) of wet organic wastes, including catalytic and non-catalytic reactions. There exist several drawbacks and research gaps, which require to be addressed for improving its commercial viability. At the end of the review, an attempt is made to summarize the challenges of hydrothermal process development for commercial-scale application.

2. Water properties and types of hydrothermal processes

As inferred from the terminology, hydrothermal processes convert organic feedstock into value-added products using the actions of water at elevated temperatures in a sealed vessel (Yoshimura and Byrappa, 2008). In the initial step, macromolecules of biomass are broken down into their building blocks (through hydrolysis), which are later reconstructed to form products. In other words, the presence of high-temperature water in a sealed vessel induces the hydrolysis of complex compounds in which cellulosic materials turn into subunits, namely glucose. High ionization constants of subcritical water create high concentrations of

ionic products of H_3O^+ and OH^- , providing a suitable medium for respective reactions (Wang et al., 2018a). Given the key role of water, many studies monitored and discussed the properties of water in such reactions. Tekin et al. reviewed the physicochemical properties of water under sub- and supercritical conditions to understand the hydrotreatment of biomass (Tekin et al., 2014). Fig. 2 shows the drastic change in water properties at elevated temperatures. Density slowly decreases with increase in temperature, while viscosity experiences a sharp decrease up to 100 °C. Dielectric constant can describe a solvent polarity where solvents with low dielectric constant, ϵ , represents non-polar solvent (Sarwono et al., 2016). Therefore, dielectric constants assist in classifying solvents: polar ($\epsilon > 50$), semi-polar ($20 < \epsilon < 50$), or non-polar ($1 < \epsilon < 20$) (Pharmaceutical Compounding Laboratory at the UNC Eshelman School of Pharmacy, 2019). The decrease of dielectric constant of water at elevated temperature makes it a non-polar solvent. This means that water at high temperatures can dissolve hydrophobic organic compounds such as free fatty acids which are non-soluble in water at ambient temperature (Nazari et al., 2015a). This has also been experimentally verified by a previous work (Yin et al., 2010). The high ionization constant and reduced density, viscosity and dielectric constant make water as a suitable solvent for the treatment of organic wastes at high temperatures.

Sevilla et al. examined the chemical transformation of cellulose employing characterization techniques (Sevilla and Fuertes, 2009). The study revealed that $T > 210$ °C was required to achieve any considerable conversion of raw material, signifying the importance of operational conditions on cellulose carbonization. Moreover, it was confirmed by XRD analysis that the sample obtained at 210 °C preserved the microcrystalline structure of the raw material. These observations conclude that the onset of the reaction happens after this threshold temperature. In the molecular level, the hydrogen bonds between polymeric chains resist the decomposition of the raw materials. It was found that when temperature increases, the average number of hydrogen bonds decreases, tending to zero at elevated temperatures (Kalinichev and Bass, 1997). The glucose as-

produced is consumed to yield either organic acid-based intermediate products such as levulinic acid (Licursi et al., 2018) and formic acid (Ding et al., 2018), or hydrochar after going through condensation and re-polymerization steps (Donar et al., 2016). At elevated temperature and pressure, hydrothermal liquefaction and gasification of biomass feedstock are expected to happen during which bio-oil and gaseous products can be mainly obtained, respectively (Texier et al., 2017). Pressure is self-generated as temperature increases inside the sealed reactor and therefore, the developed pressure is generally termed as autogenous pressure (Gao et al., 2016).

There are three forms of hydrothermal processing: hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL) and supercritical water gasification (SCWG). Fig. 3 illustrates the conditions and processing time range along with respective product spectra from those forms of hydrothermal processing (Kruse et al., 2013; Déniel et al., 2016). Operations in the temperature range of $180 \leq T \leq 250$ °C are usually defined as HTC and the favourable product in this case is the solid called "hydrochar". Treatments in the range of $250 \leq T \leq 370$ °C are considered as HTL which focuses on the production of bio-oil and chemicals. When $T \geq 400$ °C, the objective is to maximize gas production from the raw material, particularly hydrogen and methane. This gasification treatment is usually called supercritical water gasification (SCWG). This is because water needs to reach its supercritical state to perform the gasification of raw material.

2.1. Hydrothermal carbonization (HTC)

2.1.1. Features of HTC on the treatment of organic wastes

HTC is the mildest hydrothermal treatment with focus on energy efficiency improvement, when treating wet waste streams (Minaret and Dutta, 2016; Chen et al., 2018; Akarsu et al., 2019). Several studies interpreted the potential mechanism of hydrochar formation through either solid-solid conversion (for primary char formation) or nucleation-growth (for secondary char formation)

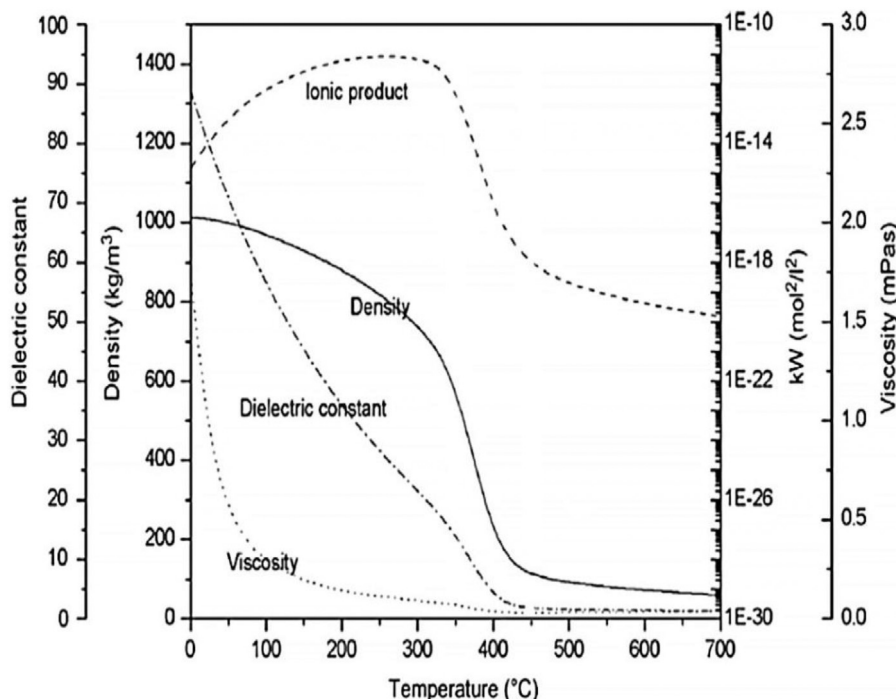


Fig. 2. The variation of water properties with the change of conditions sub-to supercritical, adapted from (Wagner and Pruf, 2002).

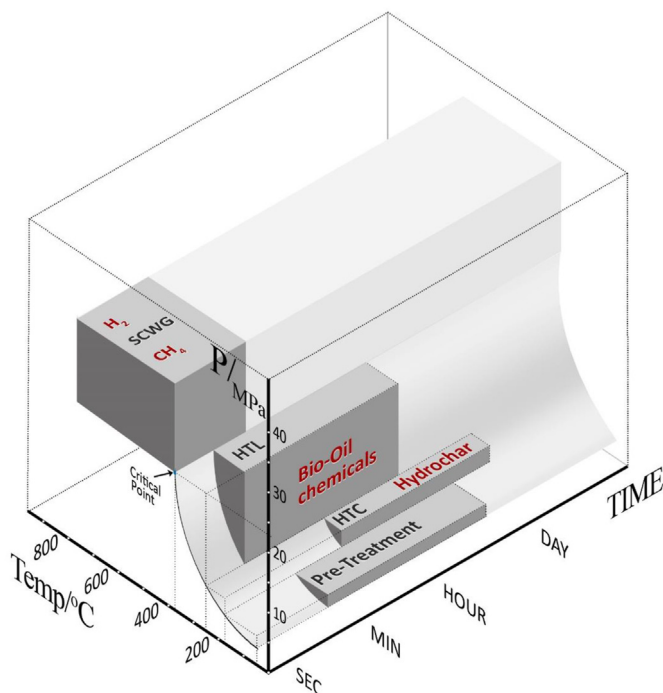


Fig. 3. P–T phase diagram of water along with different conditions of hydrothermal processes as well as the range of processing time required for various hydrothermal treatments.

pathways (Sevilla and Fuertes, 2009). For lignin-rich feedstock, it preferably follows the solid-solid change in HTC operational conditions (Funke and Ziegler, 2010; Jain et al., 2016). But secondary char particles form, when nano-sized nuclei are created through a sequence of reactions, including hydrolysis, isomerization, dehydration, condensation polymerization and finally aromatization, leading to the formation of larger particles. Along with hydrochar, HTC process can produce two other phases namely aqueous phases and gas phase. The aqueous phase is rich in organic carbon and nutrients, thus it can be utilized in many applications such as nutrient source for microalgal growth (Belete et al., 2019).

Although most of the phosphorus (P), present in the feedstock (i.e., microalgae, manure and digestate), are concentrated in the solid phase during the hydrothermal process, the aqueous phase after HTC treatment of these feedstocks also contains an appreciable level of nitrogen (N), P and potassium (K) (Ekpo et al., 2016b). In addition to the type of feedstock, the solubilization of these nutrients are highly influenced by the reaction severity. For instance, Sun et al. (2013) showed that the solubilization of P and N enhanced from 10 to 15% and from 40 to 70%, respectively, when the processing temperature increased from 180 to 240 °C during HTC of sewage sludge. They suggested to use this P and N rich aqueous phase as a liquid fertilizer. Belete et al. (2019) extracted the aqueous phase from HTC of activated sludge and used that as a source of nutrient for microalgal growth. The additional benefit of the aqueous phase is that it is already sterilized (the normal sterilization of contaminated samples is usually performed in an autoclave under 121 °C for 20 min) (Uguz et al., 2016) and therefore it is pathogen-free. Smith et al. (Smith and Ross, 2016) proposed two approaches to exploit and recycle valuable organics from the aqueous phase. The first approach is to reuse this water in HTC process after controlling and removal of concentrated acids and salts. The second approach is to ferment acids and sugars in the liquid phase employing anaerobic digestion to yield bio-methane

or bio-hydrogen. The gas phase from HTC is predominantly composed of CO₂ due to the decarboxylation reactions. A very low amount of gas, produced during the HTC treatment, cannot provide any economic value; however, this phase is important for understanding the underlying reaction mechanism during HTC.

2.1.2. Dependency of the type of waste on product formation under HTC conditions

In addition to processing temperature and reaction time (Mäkelä et al., 2015), the characteristics of feedstock significantly affects the quality and distribution of HTC products. Some wastes are of cellulosic in nature, while some other contain high amount of lipid or ash content. Fig. 4a shows the difference in atomic O/C vs H/C ratios of organic compounds via the Van Krevelen diagram for typical MSW (Berge et al., 2011), food waste (Lin et al., 2017), paunch waste (Marzbali et al., 2020), microalgae (Park et al., 2018; Liu et al., 2019), sludge (Wilk et al., 2019) and their respective hydrochars. The positions of wet wastes in this diagram indicate that carbohydrates, lipids and proteins are their main components of these wet waste. MSW, food waste and paunch waste are rich in carbohydrates, while microalgae species contain mostly lipids and proteins. The initial composition of the feedstock directly affects the properties and quality of the hydrochar. Data points for all wastes lie on the dehydration followed by decarboxylation lines, demonstrating their undoubtedly important role during HTC process. On the contrary, hydrochars, produced from the HTC process are between lignin and condensed aromatics regions. It is noteworthy that wet wastes containing more carbohydrates experienced a bigger drop in the atomic O/C ratio, compared to microalgae with high amounts of lipids and proteins. This means the latter requires harsher conditions to convert via hydrothermal treatment (Garcia Alba et al., 2012). This fact is also shown in Fig. 4b, describing the dependency of yield and higher heating value (HHV) of hydrochar on the type of wet waste. Generally, for less severe process (severity factor (SF) < 4), the hydrochar yield remains high because the processing conditions are not sufficient to decompose the biomass molecular structure into liquid products. Kim et al. (2016) revealed that the decomposition of lignin occurs at around 250 °C during HTC, while the onset of cellulose and hemicellulose conversion is at 220 and 180 °C, respectively. As a result, when the reaction severity intensifies in HTC process, the yield of hydrochar sharply decreases. Unlike sewage sludge and mixed MSW with ash content as high as 40% (Wilk et al., 2019) and 28.4% (Berge et al., 2011) respectively, food waste and paunch waste have soft nature due to high carbohydrate and low ash contents, thereby present a better conversion rate. On the other hand, the HHV of hydrochars also increases at high SF values for most wet wastes except sludge. This is because the O/C atomic ratio is reduced in the hydrochars as evidenced in Fig. 4a. For sludge, there is no much improvement in HHV value despite oxygen reduction, since the sludge derived hydrochar is heavily enriched with inorganic content (Wilk et al., 2019).

2.2. Hydrothermal liquefaction (HTL)

2.2.1. Features of HTL on the treatment of organic wastes

Hydrothermal liquefaction of organic waste is conducted at moderate temperature and pressure, during which feedstock is broken down into small molecules and majorly converted into liquid phase. Four phases are generally formed during HTL: solid residue (hydrochar), bio-oil (water insoluble organics), aqueous phase having high organic carbon content and light gas (primarily CO₂ with minor contents of CH₄, CO and H₂) (Cantero-Tubilla et al., 2018). Bio-oil is considered as the most favourable product in hydrothermal liquefaction of organic waste.

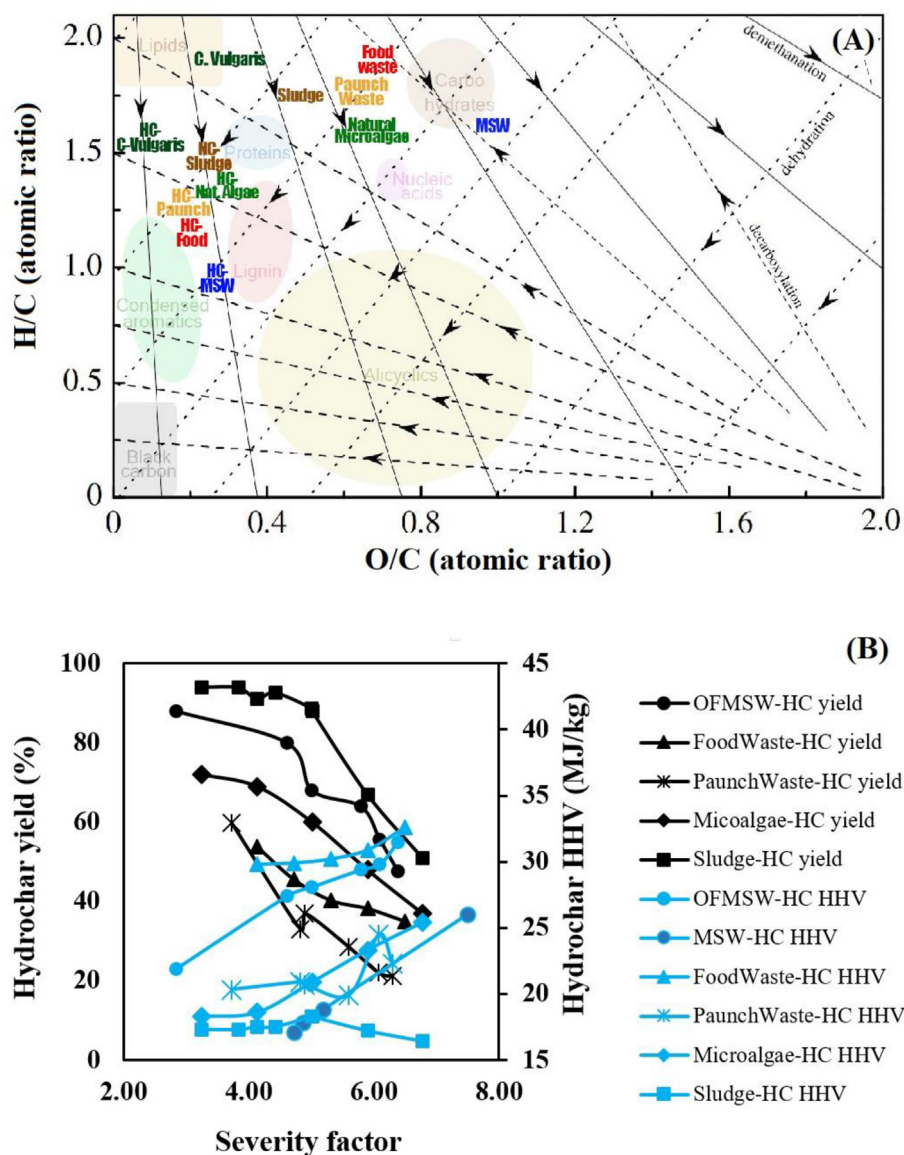


Fig. 4. (a) Van Krevelen diagram, illustrating H/C ratio against O/C ratio for different wet waste streams, (b) Dependency of the yield and HHV of hydrochar on severity factor and type of feedstock (Berge et al., 2011; Lu et al., 2011; Prawisudha et al., 2012; Kim et al., 2014, 2015; Lucian et al., 2018; Park et al., 2018; Wang et al., 2018b; Marzbali et al., 2020). The processing temperature and reaction time were combined into a single value called the reaction ordinate (RO), as introduced by Overend et al. [81]: $RO = t \times e^{\left[\frac{T}{14.75}\right]}$, where t stands for the reaction time (min) and T is the reaction temperature ($^{\circ}\text{C}$). The logarithm of RO is referred as the severity factor.

The main components of biomass, whether it is carbohydrate and lignin or lipid and protein, decompose into their building blocks to produce bio-oil during HTL (Li et al., 2014a). Carbohydrate are hydrolyzed to yield simple sugar molecules, which are then isomerized, dehydrated and rearranged to form different types of water-soluble compounds. Phenolic compounds are the indisputable products of hydrolysis of ether-bonds in lignin. The lipid content of biomass is responsible for production of glycerol and fatty acids via hydrolysis reaction (Yang et al., 2020). On the other hand, proteins go through the hydrolysis, decarboxylation, deamination and Maillard reactions to produce amino acids, low-polarity heterocyclic compounds and cyclic nitrogenous compounds (Huang et al., 2016; Cheng et al., 2018). Toor et al. reviewed the transformation of different biomass components in HTL to provide an insight into the molecular level reactions (Toor et al., 2011). It is worth noting that HTL is also able to produce diverse chemicals, thus, recent HTL based research works focus either on yielding high-grade transportation fuel or producing platform chemicals.

When compared to HTC, HTL enhances the deconstruction of the components like rigid lignin wall and results in higher fractional conversion of raw material into liquid phase. It has already been established that a higher conversion of feedstock can be achieved when reaction severity increases (Elliott et al., 2015). Pyrolysis process can also produce bio-oil from organic wastes. However, this process requires nearly dried feedstock (i.e. <15 wt% moisture) and an oxygen-free environment (Zhang et al., 2007). In addition, pyrolysis process usually requires high temperatures (at least 350°C) and the yielded liquid product is often regarded as a low-grade liquid fuel. A comparative study on microalgae liquefaction and pyrolysis for biofuel production conducted by Chiaramonti et al. (2017), revealed that HTL is more promising than pyrolysis based on energy yield and product quality. A couple of examples on the benefits of HTL are as follows: 1) HTL provides bio-oil with HHV of averagely 30 MJ/kg compared to 17 MJ/kg for bio-oil produced from pyrolysis and 2) HTL bio-oil is easier to upgrade compared to pyrolysis because of having less oxygen content

(Dimitriadis and Bezergianni, 2017). One obstacle affecting the HTL process viability is the acidic nature of produced bio-oil due to the formation of organic acids during liquefaction. Bio-oil of acidic nature causes corrosive problems for storage and this challenging area can open up various future research opportunities. Control of pH during HTL and additional acid neutralisation steps after HTL should be considered to avoid these issues.

There have been attempts to enhance the quality of bio-oil by means of organic solvents rather than water (so-called solvo-thermal process). However, apart from hydrothermal treatment of algae, no study has been found to investigate the feasibility of applying another solvent solely or when mixed with water for processing other wet wastes. Normally, dried or semi-dried biomass should be used to conduct solvo-thermal treatment. Higher conversion of sugarcane bagasse was achieved when ethanol was used as the solvent instead of water at high temperatures (Baloch et al., 2018), as ethanol shows its supercritical properties at HTL conditions. More specially, bio-oil yield was observed to increase approximately by 10% in the case of ethanol process. However, still, the HHV of the bio-oil was found to be up to 30 MJ/kg, which is considerably lower than that of conventional liquid fuels and this is mainly because of high oxygen content of initial biomass feedstock. There are also several co-solvent systems (i.e. binary solvent mixtures) reported in the literature, as highlighted in Fig. 5. In the case of HTL, alcohols are considered as a potential co-solvent with water. A study on hydrothermal liquefaction of microalgae *Chlorella pyrenoidosa* reported that the bio-oil yield increased from 46 to 57% when increasing alcohol/water mass ratio from 0 to 2.5, but decreased to 50% in pure ethanol medium (Zhang and Zhang, 2014). Therefore, it appears that the use of both solvents can provide an opportunity to take advantage of supercritical conditions of ethanol and subcritical conditions of water having extreme non-polarity and increased acidity at the same time (Peterson et al., 2008). With water-alcohol mixture, due to rapid conversion, temperature and residence time requirement of the HTL process can also be meaningfully reduced. The synergic effect of water-alcohol mixture was also demonstrated in a previous study (Cheng et al., 2010), signifying that supercritical ethanol/methanol intensifies lignin degradation and formation of lighter molecules, namely monomeric phenols. This is because the lower dielectric constant of alcohols than that of water enables them to

lower the surface tension of products, better diffuse into the lignin structure and dissolve the heavy compounds generated from the feedstock fractionation (Yamazaki et al., 2006). Different types of co-solvent can show different results, as shown in Fig. 5. For example, the bio-oil yield in the HTL of marine algae was enhanced by 14.5% when adding 10% isopropyl alcohol, while ethylene glycol was not able to change the yield (Han et al., 2019). Another study utilized glycerol as a co-solvent in HTL of rice straw (not a wet waste) and demonstrated that bio-oil yield increased continually to 68.4% when more glycerol was present in the process (Cao et al., 2016). Because glycerol has a long hydrocarbon chain, thereby being a suitable solvent for non-polar compounds in the bio-oil mixture. Although achieving the bio-oil yield as high as 68.4% with the aid of glycerol was appealing, high viscosity of final product mixture made the post-processing and product separation very challenging. Despite achieving promising results, given the difficulties in separation and related technical challenges, it remains unanswered whether mixing solvents is practical when dealing with wet waste or not. Because the solvent is not fully recovered and this would greatly impact the economic viability of the process.

Phase separation after HTL process is a critical step for improving the process viability and products distribution. A schematic of a proposed integrated system using evaporation was demonstrated in our previous study (Marzbali et al., 2020), where the final mixed product of HTL was separated into different phases with an emphasis on recycling the solvents, used in the post-process separation. Briefly, the products mixture is first vacuum filtered, separating filtrate and wet solid phases. The solid residue is then washed again with a solvent (for example ethanol) to remove all heavy bio-oil (HBO) compounds condensed on the hydrochar surface. The hydrochar is then dried, and the resultant filtrate undergoes rotary evaporation to recover the solvent and yield heavy bio-oil. The filtrate from the first filtration is assumed to contain light bio-oil (LBO) compounds, hence it cannot directly go through the rotary evaporation. This is because in an attempt to evaporate water, it is highly likely to lose lighter compounds from the mixture. As a result, the bio-oil is extracted with a solvent having a lower boiling point, like dichloromethane, then another rotary evaporation is carried out to recover the solvent and collect the light bio-oil. The selection of solvent employed for liquid-liquid extraction is dependent on the polarity of the solvent and targeted bio-oil samples. Table 1 shows the ability of different solvents in extracting bio-oil, showing that both polar and non-polar solvents can be applied. This is because the obtained bio-oil often contains both polar and non-polar compounds (Yang et al., 2014). Several researchers employed non-polar solvents for the primary bio-oil separation, as in (Wang, 2013). Yan et al. reported an opposite finding from HTL of duckweed, where bio-oil was more soluble in solvents with higher polarity (Yan et al., 2016). A similar observation was reported for bio-oil obtained from pyrolysis process (Izhar et al., 2012). It appears that depending on the composition of produced bio-oil, the polarity of solvent can enhance or mar the separation efficiency and products recovery. The use of a mixture of polar and non-polar solvents has been also suggested (Pragya et al., 2013; Yang et al., 2014). A proper solvent can preferentially separate the bio-oil or chemicals with a desired quality. For instance, a relatively high HHV (43 MJ/kg) was recently reported for the bio-oil, produced from the HTL conversion of digested sewage sludge at 275 °C, where the bio-oil was extracted with cyclohexane solvent (Saba et al., 2018). Nonetheless, employing toxic solvents such as benzene or toluene requires safety precautions, which may limit their use.

Separation of phases by the differences in their melting point is also possible; however, it has not been well studied in the literature.

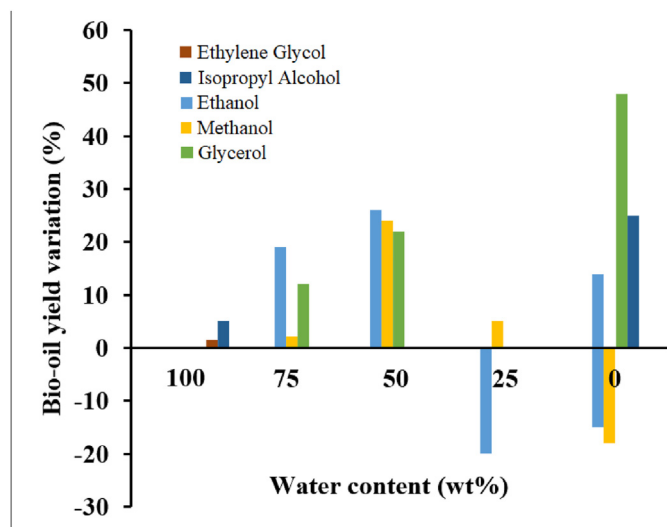


Fig. 5. Effects of solvent addition on the bio-oil yield in the HTL of biomass (Cheng et al., 2010; Cao et al., 2016; Baloch et al., 2018; Han et al., 2019; Cui et al., 2020; Yerrayya et al., 2020).

Table 1

Lists of potential solvents suitable for phase separation in HTL process (Di and Chang, 1996) and (Mao et al., 2016), along with bio-oil extraction yield (Yang et al., 2014).

Solvent	Melting point (°C)	Boiling point (°C)	Dielectric constant (F m ⁻¹) ^b	Bio-oil extraction yield (%)
Water ^a	0	100	80	—
Acetic acid	17	118	6.15	—
Petroleum ether	< -73 °C	42–62	0.01	12.7
Acetone	-95	56	20.7	30
n-Hexane	-95.3	69	0.1	8.3
Benzene	5	80	2.27	—
Dichloromethane	-95	40	8.93	26.5
Tetrahydrofuran	-108.4	66	4.2	45
Diethylamine	-50	56	3.6	—
Diethyl ether	-117	35	2.7	28
Ethanol	-114	78	24.5	—
Methanol	-97.6	64.7	6.6	23
Ethyl acetate	-84	77	6.02	30.2
Toluene	-95	111	2.38	38.3

^a Water was added for comparison.^b All values at 20 °C and 0.1 MPa.

This approach was first developed and patented by Henry (1942). In this technique a non-solvent material is added to the mixture of materials with different melting temperatures to create an emulsion; after that, the mixture is cooled down until one component begins to solidify which could be separated by normal filtration/separation scheme. At the end the non-solvent material is separated out. The inventor claimed that this method was able to separate different oils, wax and fatty acid range materials. It seems to be preferable over evaporation approach in special conditions, as it can preserve more volatile compounds during the separation.

2.2.2. Dependency of the type of waste on product formation under HTL conditions

Various types of materials have been subjected to HTL and the production of bio-oil or chemicals has been explored (Kim et al., 2019). Although due to the hydrophilic nature of the majority of biomass materials, liquefaction of wet wastes is favourable (Elliott et al., 2015). Wet organic wastes contain a wide range of moisture content, therefore it might be necessary to adjust it prior to the process in terms of pumpability and economic aspects. Elliott et al. state that mixtures with 65–95% moisture content favours efficient pumpability and helps in transporting slurry to the HTL reactor (Elliott et al., 2015). However, algal resources with typical water content above 99% (as they grow at very low concentrations) demand a pre-dewatering treatment for reducing the water content in order to ensure a more compact reactor design. Jena et al. (2011) performed the HTL of microalgae with the solid content between 10–50 wt%. Normally, the higher the water content the better it is for achieving higher process efficiency, but sometimes contradictory observations have been reported. For example, when water-to-sawdust ratio increased from 2 to 6, the bio-oil yield improved from 3.7 to 12.7 wt% (Jindal and Jha, 2016), explaining that at higher ratios, higher active hydrogens can stabilize the produced intermediates, thereby preventing the occurrence of secondary reactions. In a study on HTL of microalgae (Jazrawi et al., 2013), a different observation was reported, where higher solids content favoured the bio-oil yield which might be due to fragile nature and presence of high amounts of lipids when compared to sawdust which is more lignocellulosic in nature. Generally, higher water content would require higher reactor volume which may increase both capital and operating costs. Therefore, absolute minimum water requirement needs to be identified through experimental works and dewatering should be appropriately applied prior to HTL process to keep the volume, thus capital and operating costs of the HTL as low as possible. It appears that it is not plausible to generalize a particular value as the optimum waste-to-water ratio, and

the optimized ratio must be carefully determined for every feedstock, as correctly argued by Jazrawi et al. (2013).

The initial size of the solids may also play an important role in the HTL conversion. However, a study by Zhang et al. (2009) observed no appreciable improvement in the bio-oil yield in the processing of grassland perennials. It is believed the conversion should be expedited with a smaller size of solids. This is due to the fact that initially, the process runs in a diffusion-controlled regime until the solid particle reaches an equal concentration and temperature gradient from surface to the core of the particle. Some of the wet wastes such as sludge and microalgae have inherently lower particle sizes. Therefore, faster conversion can be achieved with them, thus the residence time is reduced. Sometimes feed formatting may be inevitable to allow for an appropriate pumpability. Akhtar et al. suggested that low-cost grinding of feedstock to a size ranging from 4 to 10 mm can help overcome mass and heat transfer limitations (Akhtar and Amin, 2011). Adjusting sizing prior to HTL process can be challenging especially with wet waste as grinding would be highly energy-intensive and inefficient in wet conditions, however, for woody biomass pre-drying and grinding might be possible (Mani et al., 2004).

Different feedstock yielded significantly different bio-oils and sometimes chemicals. HTL of MSW produced approximately 15% oil at 300 °C for 1 h (Minowa et al., 1995). It was shown that, among all feedstocks, microalgae should comparatively yield higher energy recovery which is probably due to its high lipid content and low oxygen content. Microalgae feedstock showed bio-oil yields between 15 and 55%, with HHV of 30–40 MJ/kg. It was reported that liquefaction of *Chlorella* at 350 °C for holding time as short as 3 min can produce bio-crude as high as 41.7 wt% (Jazrawi et al., 2013). In another study, *Nannochloropsis salina* was converted via HTL (Cheng et al., 2018) and produced over 54% bio-oil with HHV of approximately 38.8 MJ/kg which is comparable to that of petrodiesel fuel (~46 MJ/kg (Demirbas, 2008)). However, high viscosity and nitrogen content of bio-oil obtained from algal feedstock are problematic, requiring further upgrading. Processing sewage sludge at 325 °C with no holding time can yield bio-oil of approximately 26% with HHV of 27.7 MJ/kg (Prestigiacomo et al., 2019). HTL can also be used to extract chemicals from waste materials. Watermelon peel generated 5-hydroxymethylfurfural (HMF, a valuable platform chemical) with yield of less than 4% at temperatures as low as 130 °C for 5 min (Shao et al., 2019). Further research is needed to enhance the quality and quantity of bio-oil or chemicals produced through HTL process. Table 2 presents some of research works using HTL to convert different wet waste streams.

Table 2
Research works on non-catalytic HTL of various waste streams.

Feedstock	Total Solids (wt%)	Operating Conditions	Yield (wt%)	HHV (MJ kg ⁻¹)	Major observations	Reference
Municipal waste (artificial garbage)	6.5	300 °C 1 h	Oil yield: 15 (extracted by DCM)	ND ^a	Processing time had no profound effect. Only light bio-oil was obtained.	Minowa et al. (1995)
Microalgae <i>Dunaliella tertiolecta</i> cake	9 Size <150 µm	360 °C 50 min	Bio-oil yield: 22 (extracted by CHCl ₃)	Bio-oil HHV: 30.74	Low ash containing bio-oil was found. No appreciable increase in yield/conversion for holding times longer than 1 h.	Shuping et al. (2010)
Microalgae <i>G. sulphuraria</i>	5	350 °C 5 min	LBO: 20.1 (extracted by hexane) HBO: 8.9 (extracted by DCM)	LBO HHV:40.3 Hydrochar HHV:22.4	Ashy hydrochar and high yields of aqueous and gas phases were generated. Aqueous phase pH: 8.82. Shorter residence time and higher TS favoured bio-oil yield. Around 35 wt% of feed was distributed into aqueous and gas phases or lost. Ashy hydrochar and alkaline aqueous phase (pH:9) was derived.	Cheng et al. (2018)
Microalgae <i>N. salina</i>	5	310 °C 5 min	LBO: 49.6 (extracted by hexane) HBO: 9.4 (extracted by DCM)	LBO HHV: 40.1 Hydrochar HHV:22.4	Around 35 wt% of feed was distributed into aqueous and gas phases or lost. Ashy hydrochar and alkaline aqueous phase (pH:9) was derived.	Cheng et al. (2018)
Microalgae <i>C. vulgaris</i>	10	325 °C 0 min	Bio-crude yield: 28 (extracted by cyclohexane and acetone)	Bio-crude HHV:34.7	Most bio-crude was recovered from the reactor wall. Denitrification of biomass was suggested as N ₂ was observed in the gas phase.	Prestigiacomio et al. (2019)
Watermelon peel	7.7	130 °C 5 min	HMF yield: 3.8	HHV of hydrochar as a by-product (yield:-26 wt%):18.9 Oil HHV: 34.7	HMF, a valuable chemical (1520\$/ton) can be obtained at mild conditions.	Shao et al. (2019)
Swine manure	20	300 °C 30 min	Oil yield: 30.2 (extracted by DCM)	Oil HHV: 34.7	Oil yield was found to be highly dependent on feedstock composition. Phenolic- and lipid-derived compounds were identified to be generated from carbohydrate and lipid content.	Vardon et al. (2011)
Sewage sludge	10	325 °C 0 min	Bio-crude yield: 26 (extracted by cyclohexane and acetone)	Bio-crude HHV:27.7	The presence of micro-plastics was postulated from observing a new phase on top part of reactor. Given the bio-crude yield and quality, it was stated that sewage sludge can be a viable feedstock for HTL process.	Prestigiacomio et al. (2019)
Digested anaerobic sludge	20	300 °C 30 min	Oil yield: 9.4 (extracted by DCM)	Oil HHV: 32	Given the low oil yield, continuing the current disposal strategies was suggested. Unless bio-gas production from anaerobic digestion is sacrificed for higher yields of oil in HTL.	Vardon et al. (2011)

^a Not Determined.

2.3. Supercritical water gasification (SCWG)

2.3.1. Features of SCWG on the treatment of organic wastes

Moving from subcritical to supercritical conditions leads to drastic changes in water properties as is evident in Fig. 2. A supercritical fluid can completely dissolve solids and generate combustibles such as H₂ and methane as the primary products (Deniz et al., 2015). This process requires harsher conditions than HTC and HTL, usually at temperatures above 400 °C. These conditions promote secondary reactions where intermediate soluble components formed in case of liquefaction (such as acids, phenols, alcohols) are converted to gaseous products. Formation of hydrochar because of repolymerization and condensation was also reported during low-temperature SCWG (Azadi and Farnood, 2011). Temperature above 600 °C is needed to ensure complete solid carbon conversion (Matsumura et al., 2005).

Fig. 6 illustrates the conditions usually studied in the literature for gasification of different C6 sugars and sugar alcohols (products of biomass hydrolysis) (Paída et al., 2019). It shows that, except glucose, other sugars are gasified in varied conditions. In other words, depending on the feedstock characteristics which reflects on the initial composition of these produced sugars, the operational conditions profoundly vary.

Low concentrations of a model compound (glucose) can be completely gasified at 600 °C and 34.5 MPa in less than 30 s, leaving no trace of solid residues (Yu et al., 1993). Near-critical conditions are favourable to generate methane along with H₂ gas (Yoshida et al., 2004). The alternative method to obtain such gas consisting of methane and H₂ from wet biomass is the conventional

biological approach, namely anaerobic digestion, which, after a long processing time, leaves about 50% of initial biomass unconverted. This is because not all feedstock have enough nutrients to nourish the bacteria to evolve gas from the process (Chynoweth et al., 2001).

In addition to being a solvent, water is of pronounced importance in the SCWG process, as it participates as a reactant in several reactions, notably in the water-gas shift reaction. Unlike the conventional gasification where the final gas product is syngas (the mixture of H₂ and CO) (Cao et al., 2019), water in SCWG process helps converting CO molecules into H₂ and CO₂. Hydrogen produced in this treatment evolves either from biomass or water molecules. This can be inferred from the ideal reaction of converting glucose into hydrogen (C₆H₁₂O₆ + 6H₂O → 6CO₂ + 12H₂) (Kumabe et al., 2017).

Moreover, water in supercritical conditions behaves like organic solvents at ambient temperature (Reimer et al., 2017). As seen in Fig. 2, the dramatic change in the water properties under supercritical conditions provides a unique opportunity for hydrothermal gasification, as it serves as a good solvent for organic compounds. However, the natural inorganic ingredients of biomass like salts are less soluble in such conditions (Kruse, 2009). These insoluble salts can cause plugging and corrosion problems for the system; however, they can be separated as hydrothermal brine and used as fertilizer (Kruse et al., 2010).

In spite of the high rate of organic matter decomposition in SCWG, which potentially promises an efficient technology for converting watery biomass, the safety constraints and high costs of operation at elevated conditions remain a considerable challenge. A

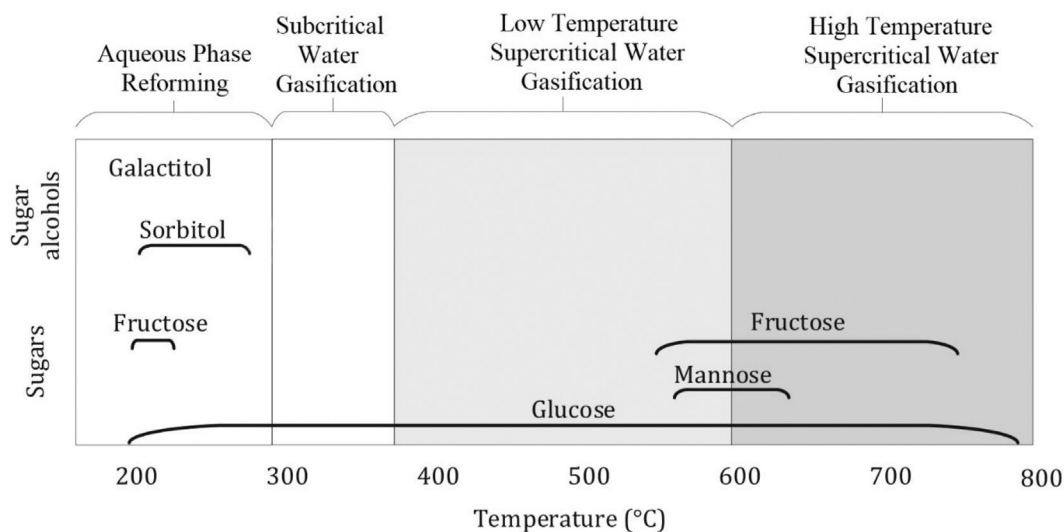


Fig. 6. Variation of sugar production at different temperature range in SCWG, adapted from (Paida et al., 2019).

case study in Tokyo indicated that the production of gas by means of SCWG was assessed to be 1.86 times more expensive than that of conventional route (Matsumura, 2002). Hence, establishing a cost-effective scenario such as utilizing solar energy (Chen et al., 2010) may be a practical solution for SCWG treatment of biomass in the longer run. The extreme temperature and pressure requirements have limited the efforts of conducting research in lab/pilot-scale, which is clearly evidenced by fewer research papers available on this topic when compared with HTC and HTL.

2.3.2. Dependency of the type of waste on product formation under SCWG conditions

Wet/dry biomass acquires high carbon and hydrogen content through various reactions such as photosynthesis, through which the naturally available CO_2 and H_2O molecules are utilized (Gollakota et al., 2018). Gasification aims to revitalize this carbon and hydrogen in the form of methane and hydrogen gases. In addition to the effects of operational conditions in the final gas distribution, the gas yield was found to be highly dependent on the composition of biomass and its C/H ratio, as explained by Salimi et al. (2016). They found a linear relation between the cellulose content and the total gas yield for agricultural wastes. However, the H_2 gas yield was inversely proportional to C/H atomic ratio. Safari et al. (2015) also showed that the higher cellulose content in biomass enhanced the total gas yield with an increase of H_2 but a decrease of CH_4 yield. The increased yield of methane was reported for the feedstock having a lower cellulose concentration (Möbius et al., 2013). Furthermore, the distribution of yield in the gaseous products depends on the operating conditions of SCWG. Higher temperature favours the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$), thus enhancing H_2 yield; while the longer residence time favours the methanation reaction ($\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$), thereby increasing methane yield (Amrullah and Matsumura, 2018). Table 3 shows a record of the findings in SCWG and provides an opportunity to compare the results obtained from different studies in the literature.

Supercritical CO_2 may also present a benefit in extracting valuable products from wet waste streams. CO_2 has a supercritical point well below water and thus requires much milder conditions compared to water. Baysal et al. (2000) showed that lycopene and β -carotene could be extracted from tomato waste employing supercritical CO_2 under 55 °C and 300 bar for 2 h. In another study

(Charest et al., 2001), 1 kg of crawfish tail shells was treated by supercritical CO_2 at 60 °C, 41% moisture content and 31.8 MPa which generated 207.6 mg of astaxanthin, a substance with several health benefits. This study suggests that treating wet waste streams in the presence of CO_2 can boost productivity.

3. Catalytic hydrothermal treatment

Hydrothermal processing of wet biomass has been predominantly successful in addressing the environmental concerns associated with their incineration and landfilling (Berge et al., 2015). However, there is still a range of opportunities to establish a system that is able to valorise waste into high value products by using catalysts. In other words, adjusting operational conditions such as temperature and pressure can lead to different products and chemicals, but it is not always possible to attain higher selectivity, therefore a catalytic approach is often needed.

A catalyst can be briefly defined as a substance that is able to expedite a specific chemical reaction while itself not being consumed. In the presence of catalysts, the reactants are firstly converted to intermediate species which are not produced in their absence. These intermediates are subsequently transformed into the final product. This is why catalysts can determine the reaction pathway of a particular process. In general terms, the catalytic conversions can be classified into two classes based on how it is applied to the process: 1) *ex-situ*: catalytic transformation occurs in a separate chamber to the main process and 2) *in-situ*: the main process and subsequent catalytic transformation occurs in a solo chamber. Catalysts are typically classified as homogeneous and heterogeneous. Despite the efficacy of homogeneous catalysis in many cases, its costly preparation and the issue of separation (due to being completely mixed with the reactants) have hindered its widespread application. Homogeneously synthesized catalysts are used in less than 20% of processes (Shylesh et al., 2010), such as in the synthesis of fine chemicals and pharmaceuticals (Torborg and Beller, 2009; Bender et al., 2018). In summary, the use of *in-situ* heterogeneous catalysis is preferable due to simpler operation.

Since a decade ago when Huber et al. published their pioneering works in catalytic biomass treatment (Huber et al., 2003, 2006; Chhedha et al., 2007), scholars' attention has been drawn toward heterogeneous catalysis in this area. Their recent work suggests that the selection of the best conversion pathway for the

Table 3
Research works on non-catalytic SCWG of various waste streams.

Feedstock	Conditions	Yield ^a	Major observations	Reference
Microalgae <i>C. vulgaris</i>	400–700 °C 1–15 min	1–2.5 mol H ₂ /mole feed <0.5 mol CH ₄ /mole feed	Gas is mainly composed of CO ₂ , CO; But more CH ₄ and H ₂ gases are obtained at higher temperature.	Chakinala et al. (2009)
Glucose	750 °C 19 s	4.78 mol H ₂ /mole feed	0.6 M glucose in water. H ₂ yield increased dramatically above 660 °C while CO yield decreased	Lee et al. (2002)
Glucose	600 °C, 25 MPa, 3.6 min	H ₂ fraction: 41.8%	Complete gasification by yielding an H ₂ -rich gas together with CO ₂	Hao et al. (2003)
Wheat straw soda black liquor	300–800 °C 10–50 min	Maximum H ₂ fraction: 63%	Higher temperature substantially favoured H ₂ yield but decreased the calorific value. Higher total solids significantly lowered H ₂ fraction in the resultant gas.	Cao et al. (2017a)
Sewage sludge	450 °C 2 h	H ₂ fraction: 49 vol%, CH ₄ fraction: 17 vol%	Direct production of hydrogen-rich fuel gas. Further treatment is needed due to the presence of CO ₂ and CO.	Schmieder et al. (2000)
Sewage sludge	480 – 540 °C Total solids: 4 – 12 wt%	Maximum H ₂ yield: 9.26 mol/kg of dry feed Maximum H ₂ molar fraction: 43.6%	H ₂ and CH ₄ yield increased when temperature increased. Increasing solid content decreased H ₂ and CH ₄ yield, however slightly increased CH ₄ fraction.	Chen et al. (2013)

^a HHV not reported in the literature. However, HHV of combustible gases is already known. For example, the gravimetric HHV of hydrogen and methane gas is 12.75 and 39.82 MJ/Nm³ respectively (Cao et al., 2017a). Therefore one can have an estimation of the HHV of the gas produced using the following equation (Cao et al., 2017a): HHV = 12.745 ω_{H_2} + 12.635 ω_{CO} + 39.816 ω_{CH_4} + 63.397 $\omega_{C_2H_2}$ + 70.305 $\omega_{C_2H_6}$ where ω is the weight percentage of any gas compounds in the products mixture.

deconstructed biomass feedstock is complex (Lin and Huber, 2009). However, once the preferred method is determined, catalysts can accelerate the rate of the desired reaction. Palladium over zeolite crystals has been reported to enhance biomass hydrogenation reaction with a furan selectivity as high as 98.7% (Wang et al., 2016). Similarly, Stöcker discussed the value of shape-selective cracking catalysts and highlighted their roles in decreasing process temperature while shifting the product distribution pattern to a desired one (Stöcker, 2008). Therefore, the synthesis of a catalyst having appropriate pore size and shape can effectively control the yield of a desired product by suppressing the route of those unwanted products formation. The lack of knowledge hinders tailoring the reaction pathways in hydrothermal conversion; nonetheless, substantial efforts have been devoted to the catalytic hydrothermal treatment of biomass, although the mechanisms for those catalytic reactions are mostly unknown. In the following subsections, catalysis concepts in each of the hydrothermal processes are separately discussed.

3.1. Possibilities of employing catalysts in HTC treatments of organic wastes

Generally, HTC is an autocatalytic process, given the presence of acidic intermediate compounds such as organic acids, which can promote the hydrolysis and dehydration reactions (Titirici et al., 2012). Table 4 summarizes some of the works done on catalytic HTC. The studies on the application of catalysts on HTC of organic matter can be classified into two different areas:

i) The use of catalyst to lower the energy consumption; Mumme et al. added a natural zeolite for HTC of digestate and observed an increase in the energy and carbon recovery in hydrochar (Mumme et al., 2015). Also, the use of appropriate catalyst in HTC can help to reduce the processing temperature and time as well as lower the amount of chemical agent and solvent. For example, sodium salts as catalyst were able to drastically speed up the HTC of biomass, where the time needed for the emergence of carbon colloids decreased from 2.5 to 1.4 h (Ming et al., 2013). The use of Lewis and Brønsted acid catalysts promoted the hydrolysis of biomass, thus reduced the processing temperature (Evcil et al., 2020). In this study, the yield of hydrochar in catalytic HTC at 225 °C was equal to that of non-catalytic HTC at 275 °C.

ii) Production of carbon materials via catalytic HTC (Titirici et al., 2012; MacDermid-Watts et al., 2020); Many researchers have found the HTC conditions as a favourable medium for the production of

engineering carbon materials (Hu et al., 2010). The main idea is to use the organic matter in biomass as a precursor during HTC (Titirici et al., 2007; Qi et al., 2014). Iron oxide nanoparticles and iron ions were active in catalysis of the HTC of starch and rice carbohydrates to create hollow and massive carbon microspheres (Cui et al., 2006), as seen in Fig. 7a. In a similar fashion, starch was hydrothermally carbonized in the presence of AgNO₃, leading to the formation of morphologically nanocables with silver encapsulated in the carbon structure, as illustrated in Fig. 7b (Yu et al., 2004). This treatment could also boost the starch conversion from 18 to 54 wt% and accelerate the reaction. This result is due to the ability of glucose (formed via starch hydrolysis) to reduce the silver ion from AgNO₃ to metallic silver in a phenomenon known as silver-mirror (Li et al., 2011). A catalyst may also enhance a particular chemical functionality in the hydrochar (MacDermid-Watts et al., 2020). A new carbon-based strong acid catalyst was synthesized through HTC and sulfonation of glucose, showing a high activity for the acetalization reaction (Liang and Yang, 2009). Sulfur and nitrogen doped carbon aerogels were also produced via a one-pot hydrothermal carbonization, demonstrating an improved electrocatalytic activity for the oxygen reduction reactions (Wohlgemuth et al., 2012). A core-shell composite, Tellurium(Te)/carbon, with a unique structure, applicable for photoluminescence was obtained through HTC of glucose and Te nanowires (Qian et al., 2006). The nanowires were first synthesized and found to act as nuclei in the solution, on which the carbon species were grown. These supporting nanowires were subsequently removed, leaving carbon nanofibers behind (Fig. 7c). In another study, a magnetic carbon nanocomposite with graphene on the surface was produced via microwave-assisted solvo-thermal carbonization of rice husk, which could enhance the bio-oil yield by 8%, as shown in Fig. 7d (Siddiqui et al., 2019). These findings suggest that catalytic HTC, as a versatile approach for producing nanoarchitectures, can be a potential strategy for managing wet waste streams.

3.2. Opportunities of adding catalysts in HTL treatments of organic wastes

The opportunities of applying catalysts in HTL process are immense, as many platform chemicals can be extracted from wet biomass in this process. A general view of all possible products attainable from hydrothermal treatments is presented in the literature (Kruse et al., 2013; Dénier et al., 2016). The bio-oil obtained from HTL needs further upgrading during or after the process to

Table 4
Catalytic conversion of biomass during hydrothermal processes.

Feedstock	Condition	Catalyst	Major observations	Reference
Pretreated coconut shell	HTC 275 °C	ZnCl ₂	Improved mesoporosity of the char	Jain et al. (2013)
Coconut shell	HTC 200 – 350 °C	ZnCl ₂	Enhanced mesoporous area, thereby increased phenol adsorption.	Jain et al. (2015)
Cellulose	HTC 150 °C	AC-SO ₃ H	Enhanced conversion of cellulose to glucose, due to strong acid sites of SO ₃ groups.	Onda et al. (2009)
Cellulose and fructose	HTC180 °C for ~ 6 h	HTC-SO ₃ H	Improved HMF selectivity	Wataniyakul et al. (2018)
Cellulose	HTC 170 °C	Nb/C composite	Improved HMF selectivity (~53%)	Li et al. (2018)
Glucose and cellulose	HTC120 °C for 3 h	PIL-supported metal (Cr, Al)	Improved HMF selectivity (65.8%). Expensive catalysts despite being Recyclable.	Liu and Chen (2013)
Fructose, glucose and cellulose	HTC 200 – 230 °C	α -Sr(PO ₃) ₂ CaP ₂ O ₆	Acidic catalysts Improved HMF selectivity (20–40%)	Daorattanachai et al. (2012)
Wheat straw, rice straw, biomass sorghum, corn stover and Douglas fir bark	HTC 26 – 175 °C	CO ₂	It could pre-treat and reduce lignin and hemicellulose content by 12 and 42%. Faster hydrolysis rate (20–172%) in the following biogas production.	Eskicioglu et al. (2017)
Water hyacinth	HTL 250 – 300 °C 15–60 min	KOH and K ₂ CO ₃	Alkaline catalysts upgraded bio-oil quality and yield.	Singh et al. (2015)
Municipal waste (artificial garbage)	HTL 340 °C	Na ₂ CO ₃	Increased bio-oil yield HHV = 36 MJ/kg	Minowa et al. (1995)
Algae strains viz. <i>Nannochloropsis</i>	HTL 250 – 350 °C	Na ₂ CO ₃	Increased bio-oil yield	Shakya et al. (2015)
Cyanidioschyzon merolae	HTL 180 – 300 °C	KOH, NaOH, CH ₃ COOH and H ₂ SO ₄	Increased bio-crude oil yield	Muppaneni et al. (2017)
Birchwood sawdust	HTL 300 °C	KOH, FeSO ₄ ·7H ₂ O, K ₂ CO ₃ , MgO, HT, and calcium borate mineral	Increased bio-crude oil yield, and reduced solid residue yield	Nazari et al. (2015b)
Beech wood	HTL 250 – 350 °C	Colemanite	Increased bio-oil yield, however no significant effect on HHV	Tekin et al. (2012)
Scotch pine wood	HTL 250 – 350 °C	NaBO ₃ ·H ₂ O	Increased bio-oil yield, and decreased solid residue yield	Tekin et al. (2013)
Wastewater generated from HTL of human faeces	SCWG 400 °C	NaOH and Raney Ni	Enhanced H ₂ production, and reduced liquid COD	Watson et al. (2017)
Microalgae	SCWG 430 °C	Pt/C, Pd/C and Ru/C	Increased yields of H ₂ and CH ₄	Jiao et al. (2017)
Olive-pomace	SCWG 300 – 600 °C	KOH, K ₂ CO ₃ and Trona	Increased H ₂ formation	Sert et al. (2018)
Potato waste	SCWG 719 °C	Activated carbon	Complete gasification with production of around 1 g gas per 1 g of organics. However, reactor plugging was an issue.	Antal et al. (2000)
Sewage sludge	SCWG 450 °C 2 h	K ₂ CO ₃	Catalyst decreased H ₂ and CH ₄ yield, while improved formation of CO ₂ .	Schmieder et al. (2000)
Sewage sludge	SCWG 480 – 540 °C 4 – 12 wt%	KOH, K ₂ CO ₃ , NaOH, Na ₂ CO ₃	Alkali catalyst enhanced the H ₂ yield (up to 15.49 mol/kg which comprised 55.96% of gas produced) mainly via water-gas-shift reaction, rather than steam reforming	Chen et al. (2013)

compete with conventional fuels. The focus of this review is on the *in-situ* catalytic HTL rather post-HTL upgrading of bio-oil. Depending on the composition of the feedstock, different types of catalyst may need to be used in the HTL process. In the case of algal biomass, noble metal catalysts often show good activity for decarbonylation reaction (Robota et al., 2013); however, they suffer from low selectivity and high cost. On the contrary, non-noble metal–nickel (Ni) based catalysts are also active for deoxygenating the algal lipids (Yang et al., 2016). Nanocatalyst Ni/SiO₂ was employed for HTL of *Nannochloropsis* sp., resulting in a higher bio-oil yield with decreased oxygen and nitrogen content (Saber et al., 2016). Different supported and unsupported catalysts such as

zeolite catalyst HZSM-5 (Nava Bravo et al., 2019), Na₂CO₃ (Shakya et al., 2015), Ru/C (Xu and Savage, 2017), CaO/ZrO₂ (Biswas et al., 2020), mesoporous SiO₂-based materials (Lu et al., 2020), NaOH, Palladium and Platinum-based materials (Yu et al., 2014) have been recently employed during HTL process. But for wet lignocellulosic wastes, containing higher carbohydrate, these catalysts may not be active enough. A list of catalysts, used in hydrothermal liquefaction, mostly homogenous, is presented in Table 4. However, given the difficulties of separating homogenous catalysts from HTL products and reusing them despite their positive effect on bio-oil formation, heterogeneous catalysis have come to the forefront of biomass HTL (Alper et al., 2019b). Addition of a low cost activated carbon helped

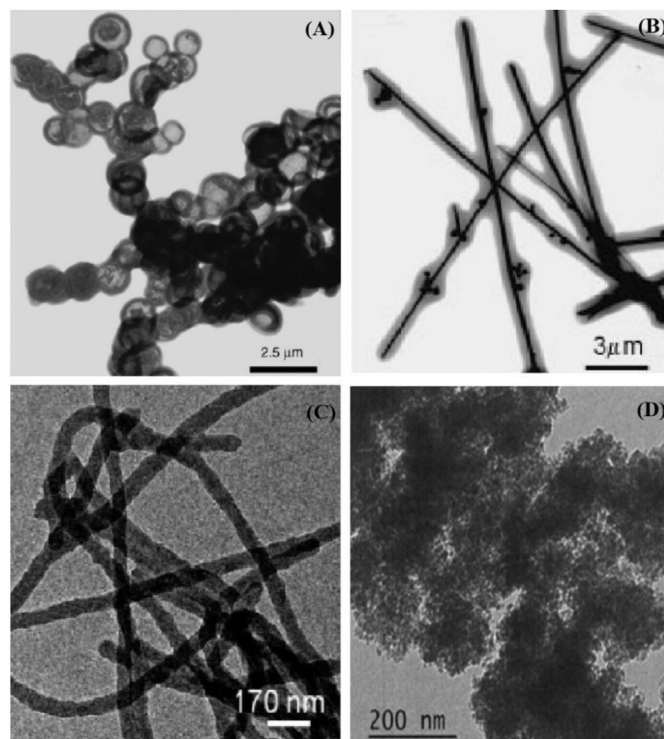


Fig. 7. TEM images of various carbon nanostructures produced from catalytic HTC of biomass or glucose: (a) hollow carbon microspheres, adapted from (Cui et al., 2006), (b) carbon nanocables with encapsulated silver nanowires, adapted from (Yu et al., 2004), (c) carbon nanocables, adapted from (Qian et al., 2006), (d) magnetic carbon nanocomposite, adapted from (Siddiqui et al., 2019).

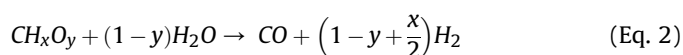
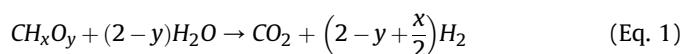
to enhance the quality of bio-oil during the sewage sludge HTL (Prestigiacomo et al., 2019). Among heterogeneous catalysts, transition metals and lanthanides oxides are more active for lignocellulosic biomass HTL in terms of bio-oil yield and quality (Scarsella et al., 2020). As an example, CeZrO_x catalyst showed activity for deoxygenating the water-soluble organic compounds and forming less oxygenated and oil-soluble products in the HTL of food waste (Maag et al., 2018). Acid catalyst, namely sulfonated activated carbon, can preferentially convert the cellulose to glucose at low temperatures in the range of 120–180 °C during the HTL process (Onda et al., 2009). The authors demonstrated that without catalyst, the concentration of glucose, produced from the hydrolysis of cellulose, dramatically decreased above 200 °C and converted to various products. Simple sugar molecules, namely glucose and fructose, are the precursors for HMF production (Shao et al., 2020).

HMF is referred to be the bridge between carbohydrate chemistry and industrial mineral oil-based organic chemistry as it can be derived from both sources (Lichtenthaler and Peters, 2004). HMF, an intermediate product formed by the dehydration of sugars, is one of the most favourable bio-refinery platform chemicals capable of producing diverse commercial products (Wang et al., 2014). The potential uses and applications of HMF in the industry, together with the challenges, opportunities and economic and environmental constraints are discussed elsewhere (Mukherjee et al., 2015). To achieve a high yield of HMF, the reaction pathways must be controlled. This is where catalyst comes into play and holds a prominent role in the future for HTL process (Ennaert et al., 2016; Robinson et al., 2016). Fig. 8 displays a possible pathway of converting sugars of biomass into transportation fuel using potential catalysts in hydrothermal systems. In the initial stage, usually, an isomerization pre-treatment is conducted over basic catalysts to

yield fructose since glucose is obtained more abundantly from biomass hydrolysis, and then the fructose is dehydrated to HMF in acidic conditions (Jin, 2014). Hydrothermal conditions provide both acidic and basic medium, therefore these two steps can be performed in a single pot (Srokol et al., 2004). The unwanted reaction at this preliminary stage is the formation of humins – a water insoluble organic compound – from both glucose and HMF and this is due to the low activation energy of this reaction (Shen and Wyman, 2012). In order to enhance the formation and extraction of HMF, a biphasic medium of water/organic phase has shown success (Román-Leshkov et al., 2006). In addition, a catalyst with Brønsted and Lewis acid sites can assist (Chen et al., 2016). HMF can be converted to levulinic and formic acids through rehydration (Girisuta et al., 2006). Hydrogenation of levulinic acid generates 4-hydroxypentanoic acid which is thereupon dehydrated to gamma-valerolactone (GVL) (Protsenko et al., 2017). The GVL is further transformed to a sustainable liquid energy carrier such as liquid alkenes (Bond et al., 2010). Given the recent progress in catalyst characteristics, it appears that catalysts can facilitate the control of reactions in the chamber, leading the process towards the favourable direction.

3.3. Prospects of using catalysts in SCWG treatments of organic wastes

Catalysts were often used in SCWG of organic materials. Vogel et al. reported the production of equimolar CH₄ and CO₂ with a small fraction of H₂ from the SCWG of ground wood slurry onto Ru/carbon catalyst (Vogel et al., 2007). Monitoring the evolution of the process confirms a gasification followed by methanation reaction pathway in the chamber wherein CO₂ and H₂ are produced and then react to form CH₄. Despite its unclear mechanism, the following general endothermic reactions are assumed to take place in the reactor (Safari et al., 2018):



Three exothermic reactions, including water-gas-shift and methanation, can also compete with the above-mentioned reactions as follows (Seif et al., 2016; Safari et al., 2018):



Depending on the desired product, whether it is hydrogen or methane gas, suppression or acceleration of undesired and desired reactions need to occur respectively. A suitable catalyst can effectively perform such a task. Fig. 9 illustrates the role of catalysis in achieving the desired product.

A number of works focusing on catalytic SCWG are presented in Table 4. Catalytic activity of Ru has been frequently tested in SCWG process and showed excellent results, but the cost associated with using noble metal-based catalysts remains a large obstacle. Especially when dealing with waste streams, catalysts must be inexpensive. Catalysts are generally used in this process to reduce the operational temperature via a cost-effective treatment, but when they contain metals, drawbacks such as gas poisoning, short durability and even sometimes reduced selectivity can limit their applicability (Cao et al., 2017b). Ni-based compounds were also

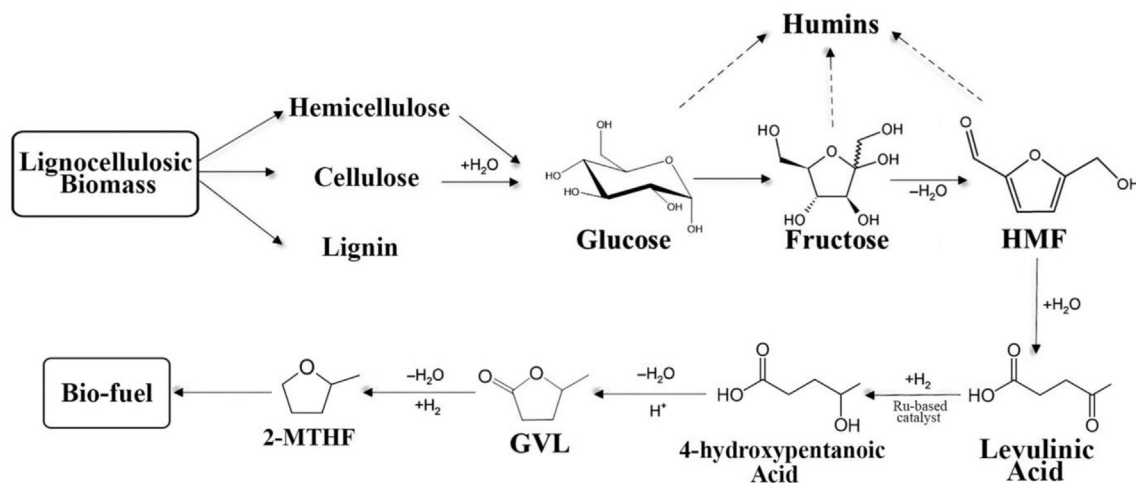


Fig. 8. Catalytic HTL of lignocellulosic biomass to HMF, GVL and finally to bio-fuel.

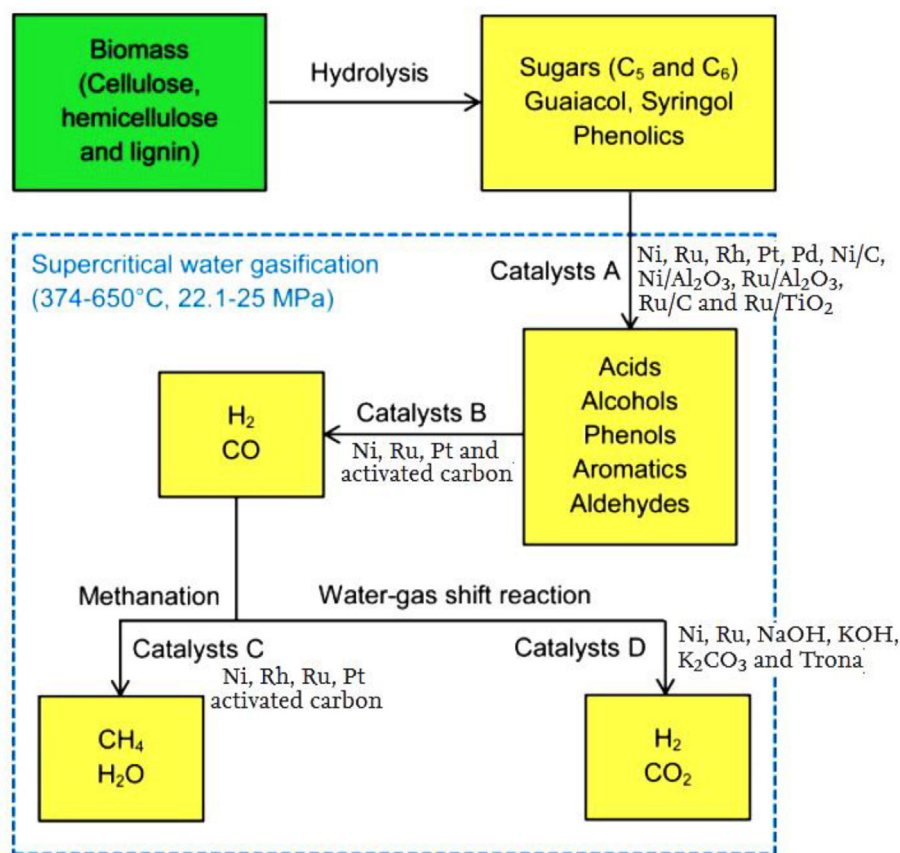


Fig. 9. Routes established with different catalysts for yielding various product distribution in SCWG of lignocellulosic biomass, adapted from (Reddy et al., 2014).

found to have significant catalytic activity for the steam reforming reaction (Zamzuri et al., 2017), therefore their reduced form are assumed to be beneficial for gasifying biomass under hydrothermal conditions (Elliott et al., 1993). It was reported that Ni remains reduced after hydrothermal treatment, proving its stability (Elliott, 2008). Despite being cheaper than noble-metal catalysts, deactivation as well as low H_2 yields of Ni-based catalysts (Yamamura et al., 2009) is a challenge, thus demanding further studies. Hydrogen gas was co-fed with biomass to the reactor in the

presence of Ru/C catalyst to maximize methane production, and a gas product composition near its thermodynamic equilibrium was attained (Reimer et al., 2017). Alkali metals are also found to assist in SCWG. A study showed that alkali compounds catalysed SCWG of food processing wastes with no tar/oil formation (Muangrat et al., 2010). However, in case of sewage sludge, these catalysts showed contradictory results in terms of combustible gas formation, as seen in Table 4. Most recently, carbon-based catalysts have shown significant improvement in terms of the final product distribution and

economic aspects. For instance, carbon-based metal-free compounds have been discovered to be effective catalysts, showing an acceptable degree of catalytic activity in several reactions (Liu and Dai, 2016). Safari et al. (2016) studied the catalytic effect of the SCWG derived hydrochar in the same process and reported an increase in the hydrogen gas yield and phenol yield in liquid product. The porosity and inorganic compound in the produced hydrochar were considered the reasons for this higher yield. The authors, in a different study, investigated the potential of employing solid residues, collected from the SCWG of *Cladophora glomerata* macroalgae and wheat straw (both rich in alkali and alkaline earth metals) as a catalyst for SCWG of almond shell. Unlike their previous work, only the inorganic compounds present in the nominated catalyst favoured the hydrogen production by a factor of 1.4 (Safari et al., 2018) and this enhancement was most likely due to the higher cracking of biopolymers (Muangrat et al., 2010).

The high preparation cost of catalysts, especially those containing transition metals, has dramatically hindered their commercialization, despite their promising activity and selectivity. There is still no well-defined investigation on how catalyst particles are supposed to be separated and reused in catalytic hydrothermal processes. The use of magnetic-based catalysts particle is one possible idea, in which the particles can be separated using a magnetic field and further reused.

4. Modelling efforts in hydrothermal processes

There are several aspects in hydrothermal treatment, which can be modelled in different ways such as processing the model compounds, kinetic modelling and predictive modelling. These areas will be briefly discussed separately in this section, and the description of some unique modelling ideas reported in the literature for hydrothermal processing of biomass are detailed in Table 5.

4.1. Processing model compounds

Needless to say that processing of model compounds provides the valuable and less-assumed modelling data, related to the mechanisms involved in the process for conversion of that specific reactant (Daorattanachai et al., 2012; Qi et al., 2014). Asghari and Yoshida explored the mechanism of dehydration of fructose, a product of glucose isomerization, to HMF in the presence and absence of acid catalysts in subcritical water (Salak Asghari and Yoshida, 2006). In other studies, the pathways of interconversion of D-glucose and other monosaccharides was postulated to happen via enediol transformations followed by the formation of liquid products through the key intermediate compounds like glyceraldehyde in subcritical and supercritical water (Kabyemela et al., 1999; Srokol et al., 2004) were developed from the controlled model treatment. In order to determine the pathways for char and tar formation, sewage sludge was modelled by five model compounds without considering the interactions between the compounds (Wang et al., 2020). Later, Teri et al. (2014) studied the HTL of biochemical components of biomass namely saccharides, proteins and lipids individually and their mixtures as well. They found that in most cases, the bio-oil yield from mixtures was very close to the average of the values for individual components, except for the mixture of saccharides and proteins. The model of compounds' mixture is a step forward to study a more complex system with interactions between components and get closer to the prediction of real biomass treatment (Yang et al., 2018). For example, Deniel et al. (Déniel et al., 2017) selected a mixture of model monomers (glucose, guaiacol, glutamic and linoleic acids) along with two polymeric compounds (microcrystalline cellulose, alkali lignin) to

represent the real blackcurrant pomace in HTL. In their study, the yields of bio-oil, hydrochar and gas were miscalculated only 1 wt%, 8 wt% and 3 wt%, respectively, demonstrating the fair representativeness. These steps are important, when moving from an ideal model on a lab-scale to processing of real biomass at large scale.

4.2. Kinetic modelling

Kinetic modelling is an important field of research that has attracted reasonable attention as it can provide a picture of mass conversion trend during the process and help perceive the mechanisms involved in the process. Given the complexity of the real biomass composition and numerous reactions occurring during hydrothermal treatment, kinetic study was initially limited to investigating the rate of mass loss i.e. feedstock consumption (Luo et al., 2011). A fundamental study on kinetics of HTC of primary sewage sludge and synthetic faeces showed that they follow the first-order reaction and the activation energy for decomposition of sewage sludge is 70 kJ/mol, slightly lower than that of faecal sludge decomposition (Danso-Boateng et al., 2013). This implies that conversion of sewage sludge to produce hydrochar needs a lower temperature than that required for faecal sludge. Jatzwauck et al. expanded the reaction scheme such that solid biomass was initially dissolved and then formed the final products (Jatzwauck and Schumpe, 2015). In their work, solid decomposition via hydrolysis had the highest activation energy and the formation of hydrochar was assumed to be an order of 1.53, while the rest followed the first-order reaction. Fig. 10 shows the full reaction network used in the latest efforts for calculating the kinetic data and predicting products yields in a setting, named as lumped kinetic modelling. In this network, the main products are interconnected with a number of reaction routes (Valdez, 2013; Valdez and Savage, 2013; Valdez et al., 2014). The rate of production and conversion of each product are formulated and the resultant set of ordinary differential equations are solved using computers to determine the kinetic parameters. Depending on the type of feedstock and operating conditions, many of the reaction routes in Fig. 10 may not exist. Obeid et al. (2019) proposed different simplified reaction networks for carbohydrate, lipid, lignin and protein, in which only four reaction pathways were considered and respective kinetic parameters were obtained. For a better kinetic modelling, having a more inclusive reaction network is imperative.

4.3. Predictive modelling

Numerical predictions of hydrothermal processing of real biomass have also been carried out for different purposes depending on the aim of the research. These models extract and utilize the relevant data from the literature, and accordingly develop a mathematical equation to usually predict the yield of hydrochar or bio-oil. They determine the response variable by feedstock characteristics through developing a linear correlation between bio-oil yield and the biochemical content of the biomass (Billar and Ross, 2011; Leow et al., 2015). In an extended effort, Yang et al. (2019) considered the HTL process variables in the regression modelling along with biochemical composition, and R-squared values of 94.6% and 93.2% were calculated for bio-oil and hydrochar yields predictions, respectively. In most cases these predictions lack accuracy, because a straight-line relationship is studied for a non-linear process. To overcome this, multi-linear approach and regression trees models have been recently applied for prediction of hydrochar yield and its calorific value based on feedstock reactivity index (ratio of reactive to inert components in biomass (Lynam et al., 2015)) and polarity index (ratio of N + O to C (Gai et al., 2016)) (Vallejo et al., 2020). In this work, the inclusion of

Table 5
Summary of novel modelling ideas applied to hydrothermal processing.

No.	Model type	Scope of modelling	Major observations	Reference
1	Kinetic model	It models precipitation in a continuous hydrothermal flow synthesis (CHFS), considering hydrolysis and dehydration reactions via population balance modelling technique.	- Model properly predicted TiO ₂ formation kinetic. - Higher temperature increases rate constants, especially under supercritical state, which is supported by the theory. - First-order reaction mechanism was considered, and linear relationship between $\ln k$ and $1/T$ was found.	Chen et al. (2011)
2	Thermodynamic model	- Reactor operates isothermally at 24.1 MPa. - A logarithmic form is assumed for equilibrium constant.	-At higher temperatures, it is easier to reach equilibrium, meaning high supersaturation level in the solution (as correctly predicted by model). -Saturation concentration value at the reactor conditions was attained, which could be further used in the population balance model to determine growth mechanism.	Chen et al. (2011)
3	Nucleation model	- Classical homogenous nucleation rate expression in supercritical solution.	-The model calculated that the nucleation occurs at approximately 1.07×10^{-6} s, verifying the theory of burst nucleation.	Chen et al. (2011)
4	Population balance model	- Assuming continuous mixed solution mixed product removal (MSMPR) crystallizer - Constant system temperature and pressure - Solving by backward finite difference discretised method.	-The model calculated the crystal size distribution by use of kinetic, thermodynamic, nucleation, growth and aggregation equations. - It also determined the time to reach steady-state in 90 s, with average particle size of 25–30 nm. -It showed that particle size distribution is dramatically affected by aggregation phenomenon.	Chen et al. (2011)
5	Multiscale modelling of hydrothermal pretreatment	- Diffusion of steam/liquid into biomass occurs. - A simplified equation for the hydrolysis rate of hemicellulose is considered, due to complexity of mechanism.	- The processing time for diffusion of steam/liquid into the feed was found to be a function of biomass chip radius. - The optimized feed particle size enhanced the energy efficiency up to 50%.	Hosseini and Shah (2009)
6	Thermodynamic property model	- Considering the ternary H ₂ O–CO ₂ –CH ₄ system. - Extending the binary models of H ₂ O–CO ₂ and H ₂ O–CH ₄ mixtures to the ternary mixture using activity coefficients regression.	-The model results led to providing a viable process design for polygeneration of fuels, power and heat from lignocellulosic biomass gasification with conservative hypotheses (solid content of up to 20% and hydrolysate loss of 10%). -Catalyst deactivation was found to be an important drawback. This has to be considered in the model.	Gassner et al. (2011)
7	Kinetic model of HTC of cellulose	- First-order reaction rate model and Arrhenius equations are employed - Heating was modelled by finite elements software COMSOL. - Kinetics and heat transfer equations were solved simultaneously.	- After initial slow induction period, the reaction rate elevates quickly thus cellulose was mostly transformed. - The important role of temperature was proven.	Álvarez-Murillo et al. (2016)

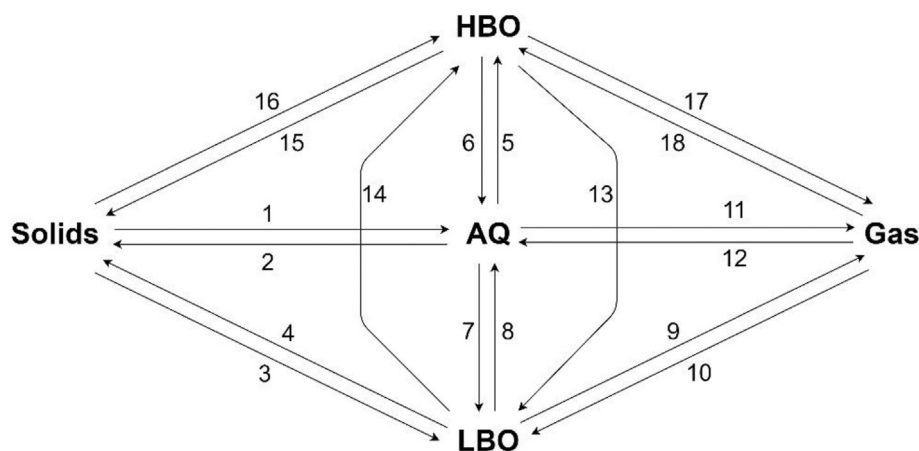


Fig. 10. A general reaction network proposed for lumped kinetic modelling. (HBO: heavy bio-oil; AQ: aqueous phase; LBO: light bio-oil).

reactivity index as an input parameter could enhance the adjusted R-squared value by 10%. Also, a logarithmic curve fit was proposed by Suwelack et al. for hydrochar yield and degree of carbonization (Suwelack et al., 2016). In order to consider the non-linearity of the process, advanced predictive models were employed. An artificial neural network model was developed to predict the carbon and inorganic phosphorus recovery during HTC by studying the process conditions as inputs (Ismail et al., 2019). They found that at low temperatures, the carbon and phosphorous recovery is more dependent on residence time than temperature. The accuracy of

these models can be developed by collecting more experimental data points from literature and considering all effective input parameters including process variables and feedstock characteristics.

5. Techno-economic analysis (TEA)

Most of the published works related to hydrothermal treatment of biomass are limited to lab-scale investigations (Baskoro et al., 2017; Phasee and Areeprasert, 2018; Mosqueda et al., 2019; Yan et al., 2019; Miliotti et al., 2020). The lab-scale investigation's

results along with a full complement of engineering data such as mass and energy balances, process modelling, detailed reactor design and cost estimation are needed to study the technical feasibility and economic viability prior to scaling-up the process (Zhu et al., 2014). Briefly, using the lab data, a process model is developed in Aspen plus from which mass and energy balances are determined for a potential scaled-up technology. Accordingly, the cost of equipment and materials are estimated employing the known indexes and quotations. Finally, the discounted cash flow analysis is performed by applying a list of reasonable financial assumptions.

Despite the promising results from the valorization of wet waste streams via hydrothermal processing in lab-scale, the development of a commercialized technology for hydrothermal treatment of wet wastes has slowed down mainly due to the difficulties of treating fibrous lignocellulosic biomass in high-pressure (Elliott et al., 2017), pumpability of feedstock slurry (Sintamarean et al., 2017) and high capital investment (Medina-Martos et al., 2020). HTC has attracted more attention for commercialization compared to HTL and SCWG, probably due to its milder operating conditions. Saqib et al. listed the information about small enterprises with HTC technology at industrial scale such as SunCoal, TerraNova Energy and Ingelia S.L with a capacity of 8000–50,000 tonnes wet biomass per year (Saqib et al., 2019). Long processing time of 4–12 h for one treatment cycle seems to be a downside of these technologies because it dramatically increases the size of their continuous reactor and the capital investment. Ingelia developed a HTC pilot plant, which can be employed as a decentral biorefinery concept for wet biomass conversion (Hitzl et al., 2015). Later in 2017, a full scale plant of HTC of non-segregated organic-rich MSW in a batch-type horizontal reactor was started in Indonesia and operated for one year with the capacity of 50 tonnes per day (Safri et al., 2017). The economic viability of this plant was not evaluated; however, it was claimed that the plant can utilize 10–15% of the produced hydrochar as a fuel of boiler at the rate of 2 tonnes per hour and the rest can be sold as coal substitute. Biomass HTL system has not been fully commercialized yet and only a few TEAs have been conducted, which were initiated by Pacific Northwest National Laboratory (PNNL) (Jones et al., 2013, 2014; Snowden-Swan et al., 2016, 2017) and National Renewable Energy Laboratory (NREL) (Knorr et al., 2013). In order to develop a more inclusive and cost-effective hydrothermal treatment technology, extensive techno-economic assessments should be done to provide detailed and sufficient technical data. Some of TEA studies reported in the literature are outlined in Table 6.

Most of the works have defined their own arbitrary technical and economic assumptions for process design and cost estimation, hindering the efforts for comparison of the results. Therefore, the idea of Nth-Plant strategy was presented by The US Department of Energy's BioEnergy Technologies Office (BETO) to unify the key assumptions, so that the results from different studies could be compared (Dutta et al., 2011). These assumptions are based on the fact that several plants with similar technology have already been operating, hence all unplanned issues and costs are technically ignored. The internal rate of return of 10%, equity of 40% for capital investment, plant life of 30 years, 7-year MACRS schedule for depreciation and construction period of 3 years are some of the key assumptions.

According to TEA calculations, the minimum fuel selling price from hydrothermal treatment are often high compared to conventional fuel prices due to the high investment and operating cost. Hydrochar is superior to biochar in terms of alkali and alkaline earth metals, heavy metal content, ash content and HHV value at similar operating conditions (Kambo and Dutta, 2015; Zhang et al., 2019). However, the market for hydrochar is not developed enough

when compared to that of biochar, obtained from other thermochemical processes due to the developed technology (Boateng et al., 2015) and regulated applications (Van Laer et al., 2015) of latter one. Also, bio-oil derived from hydrothermal treatment has a higher HHV and less oxygen content compared to pyrolysis, as discussed in section 2.2.1; however, it often has an acidic nature, high viscosity, relatively high oxygen and nitrogen content, therefore requires further upgrading using heterogeneous catalysts (Shakya et al., 2018; Leng et al., 2020). Progress in hydrothermal treatment technology and lowering the processing costs can warrant a secure market for the products. Especially, utilizing the wet wastes for hydrothermal treatment, as they are free of charge or even sometimes bring additional credit for avoiding the management cost. The management cost of sewage sludge is around 80–140 €/tonne (Prestigiacomo et al., 2019), accounting for 50–60% of operating cost in a typical wastewater treatment plant (Medina-Martos et al., 2020). Given the huge amount of wet wastes, the scale of the plant increases and the bio-oil price becomes comparable to that of traditional transportation fuels. The price of hydrochar derived from wet biomass in a pelletized form also competes the wood pellets (Lucian and Fiori, 2017). Additionally, the reduction of waste going to landfill, and its potential contamination of air, land and water might be considered advantageous by many governments and councils in the longer run.

Briefly, hydrothermal processing of wet wastes may not be directly economically viable given the current pre-matured development of technology. The following thoughts can be suggested to improve commercial viability:

- Operating at larger scale in order to achieve economy of scale.
- Reduction in process condition severity by catalyst or by blending.
- Functionalization of products (aim for improved or high-value products).

Given the ongoing more stringent legislation on waste management as well as depletion of reservoirs of conventional fuels, it is expected to see a commercialized plant on hydrothermal processing of wet wastes in the near future.

6. Selecting the best hydrothermal treatment for wet waste management

The contradictory conclusions from studies reported in the literature and diversity of wet wastes hinder definition of a general strategy for managing wet waste through a typical hydrothermal treatment. Depending on the type, composition, moisture content, amount, accessibility, current managing cost, biological hazard and local regulatory requisites of wet waste streams, the management strategy can be different. Several studies performed a comparative study through statistical approaches employing Multi-Criteria Decision Making (MCDM) methods for waste management (Garfi et al., 2009; Achillas et al., 2013; Shahba et al., 2017). For example, Aghajani et al. applied Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) method to different strategies including anaerobic digestion, recycling, sanitary landfill, refuse-derived fuel (RDF) conversion and composting for managing municipal solid waste (Aghajani Mir et al., 2016). However, thermochemical processes such as pyrolysis, gasification and hydrothermal treatment were not included in their study, which are assumed to have better environmental and cost ratings. There is a recent study published which assessed various hydrothermal processes for handling a wet biogenic waste via TOPSIS, and SCWG was found to be the most favourable technique for the criteria and parameters considered (Reißmann et al., 2018). Given the intermixed

Table 6

List of techno-economic studies performed for hydrothermal processes.

No	Feed	Product	Scale	Initial Investment	Operation cost	Profitability assessment	Reference
1	woody biomass	Liquid fuel	2000 dry tonnes per day	\$512 million	100 \$million/year	- 42.9 million gallon gasoline per year. - Production cost of HTL liquid fuel is not competitive to that of commercial product. - Average return on investment is \$45.4 million.	Zhu et al. (2014)
2	defatted microalgae	Transportation fuels	2000 dry tonnes per day	\$504 million	158 \$million/year	- 61.5 million gallon of liquid fuel per year. - Price of produced HTL-fuel is economically competitive with that of conventional fuels. - Average return on investment is \$37 million.	Ou et al. (2015)
3	Microalgae	Bio-oil	200 kg dry per day	\$0.242 million	0.043 \$million/year	- 70 tonnes of bio-oil per year. - 69% of capital investment belongs to HTL reactor and the solar collectors. - Positive cash flow was shown.	Pearce et al. (2016)
4	Dairy effluent	Bio-diesel	1 million gallon per day	\$1.5/gallon	\$2.25/gallon	- Minimum fuel sales price of \$1.23/kg bio-oil. - Minimum fuel selling price of \$4.78 per gallon, compared to \$3.42 per gallon of conventional diesel price in US. - Higher GHG emissions compared to conventional fuel.	Summers et al. (2015)
5	moist biomass (off-specification compost)	Pelletized dry hydrochar	20,000 tonnes per year	\$2.04 million	\$0.957 million/year	- 5300 tonnes of hydrochar per year. - Pelletized hydrochar is produced by \$180/ton. - Considering repayment period of 10 years, hydrochar value is competitive to wood pellets.	Lucian and Fiori (2017)
6	wastewater sludge	Electricity production from air-blown gasification	2.1 million gallon per day	\$1.1 million	NR	- Decreases WWT plant operating costs. - Lowers carbon emissions. - Reduces the land required for waste management.	Lumley et al. (2014)

* NR: not reported.

benefits and drawbacks of each of the hydrothermal technologies, it is not generally always possible to choose one of them without considering a holistic approach, and the final decision must be made according to operational, cost, emission and management objectives. Table 7 compares three hydrothermal processes for their applicability in treating a wet poultry waste in terms of economic, technology, efficiency and environmental aspects (Bora et al., 2020). SCWG delivers a higher conversion and thus generates significantly higher revenue, however at the expense of increased capital and operating costs. Hydrothermal reactor contributes to about 74% of total capital investment mainly due high pressure (i.e. puts them as pressure vessel) and moderate temperature requirement as well as special chemical resistant material of construction to avoid any potential corrosion issues, as reported in the literature (Snowden-Swan et al., 2017). In terms of technology readiness level (TRL) index, the literature suggests the following order: HTC > HTL > SCWG. HTL is challenged by high heteroatom content in bio-oil (Huang et al., 2018), while HTC suffers from an immature market for its main product, i.e. hydrochar. SCWG is yet to be demonstrated at pilot-plant scale. From environmental point of

view, CO₂ emissions in all three processes are more or less the same. More importantly, for wet waste conversion to liquid fuel, HTL requires lesser energy and therefore has lower emission footprints than pyrolysis (Chan et al., 2016).

7. Conclusions and future perspectives

Hydrothermal processing has a great potential to reduce the volume of wet wastes by converting them into value-added products, thus offering an attractive solution to wet waste management. All three hydrothermal processes, namely, hydrothermal carbonization, liquefaction and gasification, demonstrates their ability to covert wet waste into hydrochar, bio-oil and synthesis gas and remove biological contamination. The radical changes in water properties at elevated temperatures in a sealed reactor provide a good medium for treating wet waste materials where water is inherently present and by default needs a treatment (or at least sterilization) before reuse or recycle. Hydrothermal treatment requires a huge capital investment on equipment and infrastructure and therefore the process can be techno-commercially feasible only

Table 7

Benchmarking different hydrothermal processes for treating a wet waste, based on a case studied in (Bora et al., 2020).

Indicators	HTC	HTL	SCWG
Common assumptions	-Capacity: 1000 kg wet poultry litter, with a 25% w/w moisture content. -Data are from experimental results and literature, not process modelling. -The aqueous phase sent to anaerobic digestion coupled with a combined heat and power (CHP) station to recover energy and nutrients. -Emissions linked to feed production was not included in the CO ₂ emission data.		
Individual assumptions	-Hydrochar applied to soil.	-Hydrochar applied to soil. -Biocrude upgraded to produce diesel and gasoline.	-Gas sent to a combined heat and power (CHP) Station.
Capital investment (US\$/tonne)	152	89	230
Operating cost (US\$/tonne)	32	98	105
Revenue generation (US\$/tonne)	92	143	230
TRL	6.5 (Reißmann et al., 2018)	5–6 (Biller and Roth, 2018)	4 (Biller and Roth, 2018)
Conversion efficiency (%) (Ekpo et al., 2016a)	40–65	67–83	79–88
CO ₂ emission (kg-e/tonne)	1170	1192	1079

at a large scale which limits its commercial deployment currently. The wet waste is generally produced in a decentralised manner and accounts for high transport cost and emissions for getting them to a centralised location. There is a need to:

1. Provide government subsidies for deploying decentralised hydrothermal treatment plants for wet waste at the generation site.
2. Encourage councils and waste management industries to avoid landfilling and use such technology that can eliminate biological contaminant risk and convert their wet waste into recyclable water and high-value products
3. Organise public lectures or community engagement activities to demonstrate the benefits of such processing to the environment and health and largely to a nation's economy
4. Encourage government investments into the research and development (including demonstration and improvement) into hydrothermal technologies
5. Lower down the capital and operating cost for hydrothermal processing by process innovation

Some of the recent reviews published in this field have highlighted few areas of improvement such as designing continuous hydrothermal processing reactor with improved heat transfer and developing new designs for slurry feed pumps for efficient pumping of wet waste with high viscosity and high solids concentration. This paper further adds few new recommendations which has the potential either to reduce capital and operating cost or to produce improved products that can outweigh the initial requirement of higher capital and operating cost and help improving the overall techno-commercial viability of the hydrothermal process for wet waste conversion.

7.1. Identifying optimum solids concentration for the hydrothermal processing

It is well known that water plays an important role in the hydrothermal treatment of waste. The advantage with wet waste is that water is inherently present. However, higher (than required) amount of water and lower solids content would require higher energy and larger reactor volume and therefore incur a higher operating and capital cost. Therefore, it is important that through systematic lab investigations, optimum water to solid ratio is identified for different wet waste streams and proper dewatering technique (if required) is employed as a pre-treatment in hydrothermal processing.

7.2. Minerals use in hydrothermal treatment

The addition of natural minerals (e.g., quick lime or zeolite) in the hydrothermal treatment of waste has been proposed in the literature (Alper et al., 2019a). Some of the wet waste such as MSW is expected to have higher heavy metal content (Flyhammar, 1997). Therefore, hydrochar produced from them is also expected to have higher heavy metal content which may limit their application in agricultural land. Addition of minerals might reduce the heavy metal content in the resultant hydrochar. Minerals can be added to hydrochar post hydrothermal treatment. However, it is expected that minerals may introduce catalytic effect and increase the conversion of waste if introduced during the hydrothermal treatment. Alkali salts can enhance the hydrolysis of cellulose and hemicellulose (Kinata et al., 2014). The use of natural calcium borate mineral has been shown to enhance the total bio-oil yield for beech wood (Tekin et al., 2012). Zeolite was also found to improve the degree of carbonization of digestate (solids obtained from

anaerobic digestion of biodegradable materials) (Mumme et al., 2015). In other words, zeolite was found to assist in obtaining hydrochar with improved properties but at lower HTC temperature. Natural minerals are usually low-cost materials. They can positively change the cost-economics of the hydrothermal treatment as they can produce improved quality hydrochar or lower the operating cost through several catalytic and synergetic effects. While there are a few works with minerals, extensive exploration is required on mapping the effects of various minerals on hydrothermal processing as well as for understanding the detailed mechanism.

7.3. Blending with other biomass feedstock

Blending various biomasses prior to hydro-processing can help in shifting the product distribution as well as product characteristics. While this is not a new idea and has been employed for a few studies (Lu and Berge, 2014; Zhang et al., 2017), there is a large spectrum of organic wet and dry waste combinations still unexplored in hydrothermal systems. The blending of organic wastes can be beneficial for many industries. For example, the heavy metal concentration of sewage sludge is high. Therefore, the blending of agricultural/paunch wastes with sewage sludge can produce hydrochar of relatively low heavy metal concentration. Hydrothermal co-carbonization of sewage sludge and pinewood sawdust could enhance the nitrogen and phosphorous contents in hydrochar and further, surface functional groups and aromaticity (Zhang et al., 2017).

7.4. Development of cost-effective phase separation scheme

Hydrothermal process produces between three to five product streams, namely hydrochar, heavy bio-oil/chemicals, light bio-oil/chemicals, aqueous phase and gas. Efficient and cost-effective separation of these products is extremely important in realising the full potential of the hydrothermal processing. Recently, researchers have started exploring the potential of aqueous phase application as a fertilizer due to its richness in several important nutrients (Azzaz et al., 2020). Also, heavy and light bio-oil/chemicals may be used differently and require different upgrading treatments. Hydrochar should be free from oil/chemicals or any other impurities if they are planned to be applied to agriculture land or used as an adsorbent in remediation. The future works should focus on developing new and cost-effective separation schemes for hydrothermal treatment processes and demonstrate their feasibility at a reasonable scale.

7.5. Development of new catalysts for hydrothermal processes

From techno-economic studies, it is found out that biomass-derived products can be economically competitive with those obtained from conventional feedstock (for example bio-oil in comparison to petroleum oil) if the production cost is lowered or high-value products are formed.

Future research on HTC should focus on developing a low-cost catalyst which can be used to reduce the operating temperature/pressure requirement. At the same time help transforming the residual hydrochar product into a high-value material (which has the catalyst material embedded in the structure) that can have a higher sale price. For HTL, catalysts should increase the conversion of wet waste into high-value bio-oil or chemicals while at the same time produce high-quality high-value catalyst embedded hydrochar. For supercritical gasification, the focus should be to develop a catalyst that yields higher hydrogen over other gaseous products and produce high-value catalyst embedded hydrochar.

Declaration of competing interest

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

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