Technological advancements in valorisation of industrial effluents employing hydrothermal liquefaction of biomass: Strategic innovations, barriers and perspectives.

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Technological advancements in valorisation of industrial effluents employing hydrothermal liquefaction of biomass: Strategic Innovations, barriers and Perspectives

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Abstract

Population explosion mediated global energy demand has laid emphasis on the quest for alternate sources of energy. Waste biomass is a widespread renewable resource and can be valorised using thermochemical conversion processes. Hydrothermal liquefaction (HTL) is identified as a promising thermochemical technique to recover biofuels and bioenergy from waste biomass containing low energy and high moisture content. The wastewater generated during HTL process (HTWW) are rich in nutrients and organics. The release of the nutrients and organics enriched HTWW would not only contaminate the water bodies but also lead to the loss of valued bioenergy sources, especially in the present time of the energy crisis. Thus, biotechnological as well physicochemical treatment of HTWW for simultaneous extraction of valuable resources along with reduction in polluting substances has gained significant attention in recent times. Therefore, the treatment of wastewater generated during the HTL of biomass for reduced environmental emission and possible bioenergy recovery is highlighted in this paper. Various technologies for treatment and valorisation of HTWW are reviewed, including anaerobic digestion, microbial fuel cells (MFC), microbial electrolysis cell (MEC), and supercritical water gasification (SCWG). This review paper illustrates that the characteristics of biomass plays a pivotal role in selection process of appropriate technology for the treatment of HTWW. Several HTWW treatment technologies are weighed in terms of their benefits and drawbacks and are thoroughly examined. The integration of these technologies is also discussed. Overall, this study suggests that integrating different methods, techno-economic analysis, and nutrient recovery approaches would be advantageous in maximising HTWW valorisation along with reduced environmental pollution.

Keywords: Biomass, Hydrothermal liquefaction, Supercritical water gasification, Waste valorisation, Industrial rejects

1. Introduction

The increasing world population with its energy-intensive lifestyle has put a serious strain on natural resources like fossil fuels (coal, oil and gas), the main driver of economic development. In developing countries like India, where ensuring an economically affordable energy supply is critical, it can play a vital role for poverty alleviation and economic development. Although, the economy of most of the developing nations depends on fossil derived fuels (coal, oil and gas) moreover, it leads to higher carbon emissions (Varjani, 2017). In addition, the excessive dependence on non-renewable resources like fossil fuel is unsustainable and comes at the cost of environmental degradation by greater greenhouse gases emissions. The 3Rs (Reuse, Recycle, Reduce) of sustainability requires us to constantly search for new technologies and advancements of the existing ones for optimum resource utilisation. The quest for renewable energy has unlocked the enormous potential of biomass as feedstock to produce biofuels *e.g.*, biohydrogen, biodiesel, bioethanol, bioelectricity etc. (Varjani et al., 2021). Traditional lignocellulosic biomass like woods, non-food crops and agricultural residues suffers from the drawback of sustainable supply. In this regard, replacing conventional biomass with organic waste which includes industrial waste, manures, waste water sewage sludge, etc., and microorganisms like microalgae have vast economic potential. A study by the World Bank "What a Waste2.0" predicts that by 2025, the world would be producing 3.40 billion tonnes of waste. It is currently 2.01 billion per annum (per person per day averages 0.74 kilogram but ranges widely, from 0.11 to 4.54 kilograms). The "Waste to Wealth" mantra has been at the forefront of scientific development for the last few decades. Various thermochemical and biochemical technologies have been developed to convert waste biomass into energy (Vyaset al., 2022). Apart from the traditional thermochemical technologies (pyrolysis, gasification, and combustion) for biofuels from biomass, newer hydrothermal technologies such as hydrothermal liquefaction (HTL) are very promising for dealing with biomass having higher moisture content such as sewage sludge and microalgae.

HTL is a wet thermochemical conversion process in which the macromolecules of biomass/feedstock undergo dehydration and decarboxylation reactions to produce the liquid product of bio-oil, solid residue and gas products (Caoet al., 2017) (Figure 1). HTL occurs in the presence of water at slightly elevated temperatures (200-400°C) and pressures (5-20 MPa), and the average residence time varies between from 10 to 60min to produce biochemicals or bio-oils (Elliottet al., 2015;Huang and Yuan, 2015;Leng and Zhou, 2018; Zhouet al., 2013). In general, the hydrothermal procedures are looked upon as sustainable solutions for producing various valued goods from lignocellulosic biomass and black liquor like wet renewable feedstock while addressing to the environmental and societal issues. Hydrothermal technologies can be categorised based on temperature and pressure into three categories. Hydrothermal carbonization (HTC) which carried out at mild temperatures (180-260°C) and low pressures (2-5 MPa), to produce carbon rich solid fuel called hydrochar (Ghanim et al.,2016; Toufiq Reza et al.,2016), HTL and SCWG. SCWG or hydrothermal gasification produces syngas (blend of CO_2, CO, H_2, CH_4 and small fractions of C_{2+} compounds) under further extreme operating conditions, such as temperature and pressures more than 374°C and 22.1MPa, respectively (Hu & Bassi., 2020).

HTL derived wastewater has been characterised from various feedstocks and it was found that organic acids and nitrogen containing compounds dominated in the aqueous phase (Sundararajan al., 2021). Gai et al (2014) reported that protein and carbohydrate compounds showed high propensity to liquefy in the aqueous phase which led to the formation of amine derivatives, organic acids and N/O heterocyclic compounds (Gai et al., 2014). However, hydrothermal processes generate huge amount of HTWW as a result of using water as the reaction medium (Leng et al., 2020b). Though HTWW composition varies according to the input biomass it was found to be rich in nutrient and organic compounds (Leng & Zhou, 2018).

****Insert Figure 1 ****

Direct discharge of HTWW would result in the wastage of its nutrients. Due to various chemicals, it is potentially toxic to different living organisms including microorganisms. Safe utilisation and disposal of HTWW have been identified as one of the major bottlenecks in the industrialisation of hydrothermal technologies. Due to presence of high organic matter (up to 45%) along with nutrients like N-P-K (up to 80%) in HTWW, its valorisation process has attracted increasing interest worldwide. HTWW valorisation for growing microalgae (Elliottet al., 2015; Godwin et al., 2017), production of biofuels, bioelectricity, biochar, biooils etc. via anaerobic digestion (Zhouet al., 2015; Fernandezet al., 2018), microbial electrolysis cell (Liu et al., 2015), microbial fuel cell (Watson et al., 2020; Rout et al., 2020) and super critical water gasification (SCWG) (Leng et al., 2020; Rout et al., 2022) technologies are currently being explored but yet to find the application on a commercial scale.

On subjecting HTWW to anaerobic digestion a maximum methane yield reported was 314mL methane/g COD. A power density of 680 mW/m^3 was achieved by feeding HTWW to MFC maintaining an organic loading rate of 2.41 g/(L/d). A catalytic reaction of HTWW under SCWG maximises the hydrogen production. Combined AD and physico-chemical approach (struvite precipitation) resulted in nearly 100% phosphorous removal and 50% nitrogen removal. The focus is on optimising the aforementioned technologies and developing newer ones that can process a large amount of HTWW for resource recovery and meet environmental regulations. A report by the US Department of Energy highlighted that valorisation of HTWW can make HTL derived oil economically more viable and help compete with fossil fuels (Schwab, 2016). Though HTL is one of the most investigated AP valorisation techniques in last few years, it has not found application on a commercial scale yet. Therefore, the existing AP valorisation technologies needs to be critically reviewed to determine the best suited alternative from economic benefit point of view. This work focused on systematic and critical evaluation of various HTWW processes and put-forward an integrated approach including techno-economic-environmental analysis.

2. Characteristics of wastewatergenerated from hydrothermal process

Characteristics of HTWW is useful for selecting a suitable process to valorise the HTWW (Watson et al., 2018). Table 1 details the important attributes of the wastewater coming from various HTL processes. Box plots of these parameters are projected in Figure 2. Important parameters that define its valorising potential are pH, chemical oxygen demand (COD), total ammoniacal nitrogen (TAN), total nitrogen (TN), total organic carbon (TOC)/COD ratio, total phosphorous (TP), etc., (Li et a., 2019; Martinez-Fernandez et al., 2017; Stemann et al., 2013). pH variation is mostly between neutral to mild alkaline, however acidic to neutral is also reported. The standard range indicated in the literature is from pH 4.5 to 8.5, based on the type of biomass (Li et al., 2019; Leng et al., 2018). The biomass contains varieties of proteins. All the proteins are rich in ammonia and nitrogenous compounds. The biomass breakdown leads to the release of these compounds, consequently keeping the pH in 7-9.5 range. However, the presence of sugars and/or carbohydrates would release organics acids upon their degradation. This results in acidic pH. Lignocellulose biomass, therefore, yields acidic wastewater when subjected to HTL. On the other hand, HTWW from manure and sewage sludge yield mostly neutral wastewater, whereas HTWW from algae was found to be more alkaline. Therefore, pH of HTWW is a very crucial parameter as it indicates the future application of wastewater (Naidu et al., 2016). Another critical parameter, COD, varies from 9.4 g/L for HTWW obtained from swine manure (Yang et al., 2018) to 185 g/L in case of the wastewater generated from hydrothermal treatment of algal biomass (Si et al., 2018). The COD of HTL sludge wastewater was reported to be 84 g/L. The general variation of COD reported in the literature was found to be 50 to 90 g/L. Lignocellulosic biomass has yielded lower COD compared to other biomass (Si et al., 2018). These COD values are reported to be undoubtedly high in various biological valorisation methods. AD process can deal with COD up to 50 g/L but works better at intermediate COD until 20 g/L. MEC process is more efficient at lower COD (6 g/L) (Tassakka et al., 2019). Similarly, the TOC distribution was from 5.2- 76 g/L, but the general range reported is 10-30 g/L (Leng and Zhou, 2018). TOC, in general, closely follows the C percentage in the HTWW. The biochemical constituents of biomass such as protein, carbohydrates and lipids determine the TOC of HTWW. Protein plays the primary role in determining the TOC concentration. The order is generally found to be protein > carbohydrate > lipid (Madsen et al., 2016). Nurdiawati et al. (2018) reported a high TOC of 104.2 g/L from HTWW obtained from chicken feather. High TOC was also observed from HTWW of algae and human faeces (Leng and Zhou, 2018). A COD/TOC ratio of 3 is reasonable for most of the HTWW, although there might be variations (Watson et al., 2020). Both the TOC and COD are primarily governed by the biomass type but is also affected by various operating conditions such as reaction time, solid loading of the reactor, and the recirculation of the wastewater (Barreiro et al., 2015). Moreover, it is imperative to mention that higher COD and TOC values signify the high energy recovery capacity from the HTWW.

****Insert Table 1****

****Insert Figure2****

Concerning nitrogenous compounds, both the TN and TAN are reported in the literature. TN is comprised of mostly organic and ammoniacal nitrogen and some limited nitrate nitrogen (Varjani et al., 2020). TN is found to vary from 0.24 to 52 g/L, whereas TAN variation was in the range, 0.23 to 13.62 g/L (Gai et al., 2015; Lu et al., 2017). The hydrolysis and deamination of proteinaceous substances is the primary factor behind both the TN and TAN (Biller et al., 2012). Expectedly, algae with high protein concentration produces high TN wastewater. The hydrophilicity of nitrogenous compounds leads to their build up at these high proportions in the HTWW. HTWW from lignocellulose biomass had TN concentration as low as 0.8 g/L. The TP in HTWW also found to be dependent on the biomass type. The HTWW from algae produces TP up to 15 g/L (could be due to greater compositions of DNA, phospholipids, etc), but HTWW of various other biomass had TP in the range 0.1-2 g/L. TP is also affected by feeding rate and reaction severity (Leng and Zhou, 2018).

The HTWW usually contains various organic compounds for example, organic acids (acetic acid, formic acid and propionic acid), many types of sugars, hydrocarbons, and multiple phenols. These organic compounds could be considerable obstacles in valorisation (Watson et al., 2020). Madsen et al. (2016) have extensively characterised various organic compounds present in the wastewater from hydrothermal liquefaction of the biomass. They authors have reported several carboxylic acids, cyclic oxygenates, dicarboxylic acids, fatty acids, nitrogenated compounds, and oxygenated aromatics, as well as tricarboxylic acids. The organic compounds were varied depending on the biomass source and the operating conditions (Madsenetal., 2016). Lignocellulosic biomass yielded a higher concentration of organic acids and phenols in wastewater. On the other hand, food waste produced acetic acids and ethanol (Maddi et al., 2017). Nitrogenous organics were common in HTWW from the sludge and algae (Watson et al., 2020). Mursito et al. (2010) characterised various organics from the tropical peat HTWW. The wastewater was found to contain a large number of organic acids and phenols. Methanol and acetic acids were reported at all the process conditions, but decomposition of phenolic compounds took place at high temperature (Mursito et al., 2010). Similarly, Weiner et al. (2014) observed the predominance of acetic acid and lactic in the paper HTWW (Weiner et al., 2014).

The wastewater also results in numerous inorganic species such as ammonia, sodium, potassium, phosphate, etc. and have been reported in the HTWW (Toufiq Reza et al., 2016). The concentration of alkaline metals (Na, K) was found to be very high. Other metals such as Fe, Cu, Zn, Pb, etc., are also witnessed, albeit at low concentrations. The biomass origin plays a significant role in the inorganics' composition. The protein-rich feedstock yields high ammonia, whereas animal manure returns significantly high concentration of zinc in the wastewater. Similarly, freshwater algae result in less alkaline metals than the algae grown in saline water (Elliott et al., 2013). High concentrations of anions are also present in the HTWW, which could result from the presence of high concentrations of cations (Onwudili et al., 2013).

3. Anaerobic digestion of HTWW

Anaerobic digestion (AD) is a biochemical process performed under anoxic (absence of free oxygen) condition, which comprises of several mutually dependent sequential steps, such as hydrolysis, acidogenesis, acetogenesis and methanogenesis to convert organic substrate into energy rich biogas and nutrient rich digestate slurry (Bora et al., 2020). AD is carried out by a complex microbial ecosystem involving diverse synergistic microbial trophic groups like hydrolytic bacteria, fermentative bacteria, acetogens and methanogens exhibiting “process catabolism” in which a product from one microbial group serve as a substrate for the other microbial group (Gumisiriza et al., 2017; Verma et al., 2016). The insoluble biopolymers present in organic wastes including polysaccharides, proteins and lipids are too complex/large for microbial uptake and subsequent intracellular biotransformation processes, therefore, necessitate hydrolysis. Hydrolytic enzymes (amylases, proteases, lipases, etc.) secreted by hydrolytic bacteria (*Clostridium*, *Fibrobacter*, *Ruminococcus*, *Streptococcus*, etc.) hydrolyze the biopolymers into small soluble monomeric and oligomeric units (sugars, amino acids, fatty acids, etc.) to enable membrane mediated microbial uptake and further metabolic transformation as depicted in previous research (Gumisiriza et al., 2017). The fermentative microbes (*Clostridium*, *Lactobacillus*, etc.) degrade the soluble monomers and oligomers to produce short-chain organic acids or volatile fatty acids (acetate, propionate, etc.), alcohols, H_2, and CO_2 through acidogenesis or acid fermentation. The acidogens have a short doubling time and they constitute up to 90% of the total anaerobic microbial populations (Pereira et al., 2003). Acetogenesis is the third phase in the AD, where short-chain organic acids and alcohols are further processed by acetate-forming bacteria to yield mainly CH_3COOH, H_2, and CO_2. Acetogenesis can be accomplished by hydrogen-producing acetogenic bacteria (H_2 producing acetogens) and hydrogen-utilising homoacetogens (Liu et al., 2011). But the acetogenic reaction by H_2 producing acetogens (*Syntrophomonas*, *Fusobacterium*, etc.) is endothermic in nature and is not thermodynamically favourable under standard conditions. So, these acetogens necessitate a low hydrogen partial pressure to yield energy needed for the acetogenic reaction. Hydrogen-consuming microorganisms like methanogens can quickly scavenge hydrogen, thereby, keeping a low partial pressure of hydrogen. Therefore, in the AD system, a syntrophic microbial interdependency (dependency between producer and consumer) among the hydrogen-producing acetogens and hydrogenotrophic methanogens (hydrogen-consuming bacteria) for interspecies hydrogen transfer is essential for the reactions to proceed (Gumisiriza et al., 2017; Liu et al., 2011). However, the homoacetogens (*Acetobacterium woodii*, *Clostridium thermoautotrophicu-m*, etc.) can use H_2 and CO_2 for the production of acetic acid thereby, ensuring low partial pressure of hydrogen in the anaerobic system. The final step of AD is methanogenesis in which a specialised group of microbes (archaea) called methanogens transforms the products of acetogenesis (mixture of acetate, CO_2 and H_2) into methane. Methane is produced by archaea through two key pathways like acetotrophic or acetoclastic and hydrogenotrophic pathways. Methane production by *Methanosaeta* and *Methanosarcina* genera via acetotrophic pathway is more common (70%) than that of hydrogenotrophic pathways (Lalman and Bagley, 2021). However, hydrogenotrophic methanogenic reactions are thermodynamically more favorable and more energy yielding than that of acetotrophic reactions. Therefore, hydrogenotrophic methanogenesis is vitally important in keeping the low partial pressure of hydrogen, letting syntrophic acetogenesis to proceed (Gumisiriza et al., 2017).

AD is receiving considerable interests in recent years as energy efficient and cost-effective process compared to aerobic processes. The key advantages of AD include its simple operation, minimal dewatering needed prior to AD, ability to process a diverse substrates like agricultural residues, manures, energy crops, etc., low sludge production, nutrient rich bio slurry generation, and most importantly renewable energy recovery in the form of biogas (Molino et al., 2019; Lee et al., 2021; Zhou et al., 2015; Lee et al., 2020; Shahid et al., 2020). This makes AD as one of the best waste-to-energy conversion alternatives with minimal energy requirement (Gumisiriza et al., 2017). It is believed that the AD of aqueous phase generated during HTL can maximise the energy production of the system. Some of the significant studies pertaining to AD of diversified HTWW are summarised in Table 2. The HTWW also contains potential toxic organics like phenols, ammonia, furans, etc., and high molecular weight organics. The conversion efficiency of organics in the HTWW to methane can be up to 300 mL/g, based on feedstock properties, HTL experimental parameters, AD operational conditions, etc., whereas approximately 33-64% of organics in the HTWW persisted in the anaerobic slurry (Leng et al., 2020; Si et al., 2019).

****Insert Table 2****

During AD of HTWW, acidogenesis and acetoclastic methanogenesis are the predominant processes since the hydrolysis steps have been completed during HTL process. Higher hydrothermal treatment temperature leads to production inhibitory components which intern further reduces the production of methane. Chen et al. (2017) reported a decrease in the methane yield to 217 mL/g from 314 mL/g on increasing the temperature from 200 to 320 °C. As per the report of Posmanik et al. (2017), biochemical composition of biomass, in particular a lesser lignin content (higher biodegradability) in biomass resulted in better methane yield. Likewise, increasing the AD duration to overcome the existing lag phase and maintaining higher organic loading rates to avoid possible nutrient limitation conditions (in case of diluted HTWW) are helpful in achieving enhanced methane yield (Shanmugam et al., 2017a). However, higher HTWW loading can deter methane production due to higher inhibitory components content in the HTWW (Si et al., 2016). For example, at an aqueous phase content of 33.3% (from HTL of

Spirulina), observed AD inhibition was 100%, and at a content of 6% inhibition was 50% (Zhou et al., 2015; Zheng et al., 2017). Major inhibitory compounds observed in AD of HTWW including 5-hydroxymethyl-furfural (5-HMF), phenols, N-heterocyclic compounds, furfurals, pyridines, pyrrolidines, etc., are presented in Table 2. High concentration of ammonia and accumulated chloride salts may also be inhibitory to AD processes (Fernandez et al., 2018). The level of inhibition effect on the AD of HTWW is dependent on the recalcitrant nature of the inhibitors (Leng et al., 2020). However, some inhibitors might be degraded completely or partially resulting in detoxication and biogas production if resistant microbial variants are used. Figure 3 depicts the anaerobic degradation mechanism of phenol, a potential AD inhibitor. Apart from biological degradation, pretreatment of HTWW by methods like adsorption, solvent extraction, struvite precipitation, etc., are helpful in minimizing the inhibitor's effect on AD (Sudarsan et al., 2015). The inhibitors can be removed from the HTWW partially or fully by these pretreatment methods along with the significant removal of COD (Table 2) (Chen et al., 2016). Among the strategies mentioned above, adsorbents are the most widely practised one. Using powdered activated carbon (PAC), granular activated carbon (GAC), zeolite, biochar, etc., to adsorb inhibitors resulted in improved methane production, reduced the lag phase, and played a role as a microbial carrier in retaining the microbial biomass in the system by preventing their loss through the effluent (Kwak et al., 2020; Leng et al., 2020; Lee et al., 2019; Si et al., 2018). Using biochar in AD, Shanmugam et al. (2018) achieved higher methane yields of 212-296 mL/g against 24-135 mL/g from AD minus pre-treatment (Shanmugam et al., 2018). Ozonation of HTTW, is a potential method to improve the AD since the oxidative properties of ozone make it possible to convert aromatic and N-heterocyclic compounds into acids and amidic compounds like more biodegradable organics, though ozonation may lead to generation of recalcitrant components (Si et al., 2018; Leng et al., 2020). Co-digestion of mixed substrates are also being adopted extensively as a common strategy to dilute the toxic components, optimize feed C/N ratio and facilitate co-metabolism of mixed substrates in order to realize improved AD (Mata-Alvarez et al., 2014). Fernandez et al. (2018) not only successfully mitigated the effects of inhibitors like salt and organic compounds by the co-digestion of HTWW with manure but also achieved high methane yield in the range of 243.9-313.2 mL/g. Additionally, detrimental effects of the inhibitors on AD can be lessened through appropriate design of AD systems and by developing genetically engineered microbial strains with enhanced resistance to inhibitors. For instance, UASB is a favoured configuration for AD systems as it can allow high organic loading while maintaining high performance efficiency (Si et al., 2016). Similarly, a genetically engineered *Pseudomonas putida* exhibited improved tolerance to aldehyde inhibitors by overexpressing the chaperone genes (Jayakody et al., 2018).

****Insert Figure 3****

4. Treatment and Valorisation of HTWW through Bio Electrochemical Systems (BESs)

Bio electrochemical systems (BESs) are developing technologies to generate energy from wastewaters using microbial methods, leading to the production of electricity or biofuels like, hydrogen and methane (Wilberforce et al., 2021; Olabi et al., 2020). Anaerobic digestion also produces these chemicals; however, process needs high COD or organic loading rate (OLR), and is usually performed at a high temperature of 37°C. BESs instead, can work with low COD wastewater and at low temperature. It is thus, more economical and even has the potential to replace the ubiquitous activated sludge process, further decreasing the energy consumption in wastewater treatment (Sadykov et al. 2020; Sayed et al., 2020).

It is a biological form of the conventional electrochemical cell. It contains an anode, cathode and electrolyte. At anode oxidation results in electron liberation, which streams to the cathode producing reduction reactions. What differentiates BESs from a conventional electrochemical cell is that biocatalysts facilitate any of the oxidation or reduction or both. The biocatalysts could be enzymes or whole microorganisms. Two kinds of BESs have been identified; one is an energy-producing device called microbial fuel cell (MFC). In contrast, the other is an energy-consuming device, microbial electrolysis cell (MEC) to facilitate non-thermodynamically spontaneous reactions (Yang et al., 2020). In MFC, overall ΔG is negative, while MEC yields overall ΔG positive. Of course, MEC returns the preferred products or processes. Both the MFCs and MECs have become an indispensable part of novel technologies for wastewater treatment (Kaku et al., 2008).

4.1. Valorisation of HTWW through MFC

Utilisation of HTWW to produce renewable energy has been emerging by exploiting appropriate electroactive microbes for sustainable and efficient demand of power. In this context, MFC technology has attracted significant interest since it does not involve an external energy supply and can resolve the entire problems on waste effluents discharge into electricity. In MFC, bioelectricity can be extracted by a BES using waste disposals containing organic matter as a substrate. Figure 4 shows a schematic representation of MFC system. In the anodic chamber, aqueous phase containing organic substance acted as electron donors [Eq. 1] that can be biologically catalysed by specific microbes such as exoelectrogens to release electrons.

Bioelectricity is generated through capturing these electrons by the anode followed by flow of electrons from the anode to the cathode through an external electrical device with a resistor (Zhen et al., 2017; Jadhav et al., 2017). On other hand, cathodic chamber consumes electrons, simultaneously, proton exchange membrane (PEM) allows protons to transform from the anodic chamber. Consequently, clean water results as a by-product with externally provided oxygen (Eq. 2). Eq.3 represents the overall reaction for bioelectricity production in MFC. Further, the developed biomass due to photosynthesis exits to the atmosphere.

Reaction at anode:

$C_6H_{12}O_6 + 6H_2O \rightarrow 24e^- + 24H^+ + 6CO_2$ ……… (1)

Reaction at cathode:

$24e^- + 24H^+ + 6O_2 \rightarrow 12\ H_2O$ ……… (2)

Overall reaction for bioelectricity production:

$C_6H_{12}O_6 + 6O_2 \rightarrow \text{Bioelectricity} + 6CO_2 + 6H_2O$ ……... (3)

Platinum is commonly used as an electron mediator or a catalyst to speed up the rate of oxidation-reduction on electrodes. In addition, organic loading rate (OLR) is one of the most influenceable factors for ameliorating the performances of MFC. Different studies showed that the appropriate rate of organic loading favours the maximised performance. The low rate of loading will not be adequate substrate for microbe diversity results in lowered power intensity, but an overloaded rate may produce substrate inhibition for microbial growth that hinders the generation of electricity. Liu et al. (2015) witnessed an achievement of 680 mW/m^3 power density at 2.41 g/(L/d) of OLR. In this case, MFC was operated with organic waste from HTL of cornstalk as the feed (Liu et al., 2015). Previous studies showed that the generated power densities differ with respect to types of organic feeds from industrial or domestic sources (Pandey et al., 2016).

****Insert Figure 4****

Due to the occurrence of microbial inhibitors in the waste waters such as furans and phenolic compounds the performance of MFC may be restricted. However, it was reported elsewhere, a reasonable performance was acquired with degradation of indoles, phenols, furfurals or pyridines alone (Pandey et al., 2016). Even though the waste water obtained from the processing of HTL of wood had significant composition of different inhibitors, Toczyłowska-Mamińska et al. (2018) observed that the degradability was increased by adding an appropriate level of municipal wastewater. On this point, the authors recognised that the power density was improved from 71 to 360 mW/m^2 because of inhibitors were controlled significantly due to the case of dilution effect. Liu et al. (2015) perceived that the circuit atmospheres such as closed or open circuit also influences the output of MFC systems. They found that a closed-circuit system favors for ameliorated output from MFC (Liu et al., 2015). However, during degradation process, the removal of COD did not show great influence by the circuit conditions and organic load because of the HTL derived aqueous phases has low biodegradability (BOD/COD = 0.16). Due to the presence of inhibitors in the waste wasters from the HTL of wood, removal of COD was also declined while increasing the rate of loading (Toczyłowska-Mamińska et al., 2018). Nevertheless, the rate of COD removal showed a substantial increment up to 87% when municipal wastewater was supplemented with the waste wasters from wood HTL (Toczyłowska-Mamińska et al., 2018).

4.2. Valorisation of HTWW through MEC

In microbial electrolysis process, organic matter is degraded using microbes in the presence of electricity. In this case, biohydrogen is generated as a value-added product using electrochemically active bacteria that degrade the organic waste with voltage supplementation (Logan et al., 2008; Pandian et al., 2021). During the microbial activity in the anodic compartment, organic molecules are broken down into electrons, protons, and carbon dioxide [Eq. 4]. These protons are migrated to cathodic compartment through the PEM and act as electron acceptor to engender the biohydrogen with electron consumption [Eq. 5]. The overall reaction for MEC process can be represented as Eq. 6. Hydrogen peroxide, methane, and ethanol can also be obtained while using different appropriate electron acceptors (Gude., 2016). Han et al. (2018) have observed that 80% of the COD present in the organic phase can be reduced even the feed with considerable quantity of furan derivatives and intractable complexes such as diethyl phthalate and dimethyl phthalate to produce the rate of biohydrogen at 3.92 mL/(L·d) (Han et al., 2018). Recently, they also found that the productivity of biohydrogen improved significantly up to 168.01 mL/(L·d) when the ameliorated configuration of MEC system and electrode materials was used (Shen et al., 2018). Commonly, strict anaerobes are favoring the production biohydrogen in anoxic MEC. Since there is a lack of oxygen hydrogenotrophic methanogenesis will take place, then the recovery of hydrogen would be reduced (Logan et al., 2008). In this circumstance, methane can be a dominant output from the MEC (Shen et al., 2017).

Reaction at anode:

$C_6H_{12}O$ (organic substrate) + $6H_2O \rightarrow 24H^+ + 24\ e^- + 6CO_2$ ………… (4)

Reaction at cathode:

$24H^+ + 24\ e^- \rightarrow 12H_2$ ……………… (5)

Over all reaction in MEC:

$C_6H_{12}O_6$(organic substrate) + Electricity + $6H_2O$ + $\rightarrow$ $6CO_2$ + $12H_2$ ……. (6)

The voltage supplied for electrolysis is also another aspect that accounted for generation of biohydrogen. Shen et al. (2018) reported that an increase in voltage to 1.2 V from 0.4 V resulted in an upsurge in biohydrogen production to 168.01 mL/(L·d) from 13.27 mL/(L·d) with enhanced removal of COD from 90% to 95%. In addition, they found that loading of organic phase and rate of flow showed a limited impact on biohydrogen production. The study reported that the total nitrogen can be removed significantly up to 93% by MEC with appropriate use of degradation, denitrification, diffusion, and assimilation. Table 3 provides a brief summary of energy valorisation of HTL-WW by bioelectrochemical systems, MFC and MEC.

****Insert Table 3****

5. Super Critical Water Gasification (SCWG) of HTWW

Wastewater from hydrothermal processes has been subjected to SGWG to produce hydrogen rich syngas from organic matter at a higher pressure and temperature at the critical point of water (374.3°C and 22.1 MPa). SCWG process has been proposed as a preferred method to valorise the wastewater as it converts the total organic carbon (with conversion rate over 99%) into gaseous product, COD and other pollutants while yielding high concentration of H_2 in the syngas produced even without the use of catalyst (Lee and Ihm., 2010; Watson et al., 2021; Xie et al., 2019). Zhiyong and Xiuyi (2015) reported that initially the concentration of hydrogen in the syngas increased from 21% to 38% with an upsurge in gasification temperature from 250 °C to

520 °C but the hydrogen content was dropped to 32% at the temperature of 700 °C (Zhiyong and Xiuyi., 2015). Despite the fact that higher gasification temperature favoured the endothermic reactions, it is recommended that the temperature of the gasifier should be carefully controlled because it could increase the CO_2/H_2O ratio compared to the desired CO/H_2 ratio.

Secondly, the residence time play a vital role specifically on the evolved syngas composition and yield during SCWG (Byrd et al., 2008; Reddy et al., 2014; Nanda et al., 2015). Gong et al. (2017) reported an increased in product gas yield from 1.2 to 1.7 mol/kg when the residence time improved from 30 min to 90 min (Gong et al., 2017). These studies reflected that in order to optimise the process it is imperative to ensure a minimum residence is provided. Since higher temperature favours endothermic reactions and higher residence time allows evolved product gases to react amongst themselves leading to a higher concentration of methane via hydrogenation and methanation reactions (Kruse., 2008). In SCWG, water is an influencing factor behind the hydrogen concentration in the product gas mainly due to improved water-gas shift reaction. Byrd et al. (2008) estimated that an increase in the feedstock concentration during glycerol gasification (5 to 40 wt. %) had adversely impacted the concentration of hydrogen (6.5 to 2 mol/g) whereas the methane concentration increased (0.3 to 1.0 mol/g) (Byrd et al., 2008). It was evident that the feed concentration could result in the reduction of product gas quality and the product gas distribution of CO_2, H_2, CH_4, and CO. Therefore, the feed concentration must be decided based on the desired product needed in the product gas, i.e., hydrogen or methane rich product gas and its potential application.

Despite the fact of higher conversion efficiency of catalytic gasification methods, it is a preferred conversion route only when either the complete degradation of feedstock or the syngas with lower tar content is needed due to the associated cost of catalyst. The utilisation of catalyst can significantly improve gasification efficiency and hydrogen production because catalyst use favours the water gas shift and steam methane reforming reaction while reducing the formation of CO_2 due to improved Boudouard reaction (Onwudili and Williams., 2009). The aqueous phase (wastewater) from HTL was subjected to catalytic (NaOH) hydrothermal upgrading process under supercritical water conditions and aimed to maximise the hydrogen production. The addition of catalyst (1.5 M NaOH) doubled the hydrogen yield at the same organic loading clearly indicating the role of catalyst favouring the water-gas shift reaction. The authors have analysed the aqueous phase and demonstrated that the integration of HTL and SCWG produces excess hydrogen while retaining necessary nutrients in the water for algal growth (Cherad et al., 2016).

Although, it is obvious that usage of catalyst increases hydrogen production without affecting the nutrient recovery, but it might not be economically viable to operate. Si et al. (2019) reported that the catalytic hydrothermal gasification accounts for 44% of the total operating cost excluding the feedstock (Si et al., 2019a). Homogeneous (NaOH) and heterogeneous (Raney Ni) catalytic hydrothermal gasification of wastewater originated from HTL of human excretayielded46.9 and 41.2% of hydrogen, respectively. In contrast, Ru/AC reduced the liquid COD by 97.7% (Watson et al., 2017). A similar finding was reported by Cherad et al. (2016) while catalytically gasifying wastewater originating from HTL of *Chlorella* with high organic load (11 g/L). The catalytic gasification process of wastewater yielded 2.25 times higher hydrogen compared to non-catalytic gasification. Zhiyong and Xiuyi (2015) reported that catalyst usage improved carbon conversion efficiency in the range of (8–98%) and found that the hydrogen conversion efficiency was increased to 108% when KOH was used as a catalyst (Zhiyong and Xiuyi., 2015). In conclusion, although catalytic gasification process can be used in small to medium plants but considering the cost of the catalyst, commercially the HTWW cannot be processed via catalytic hydrothermal gasification. The performance analysis of super critical water gasification for HTWW of different feedstock is presented in Table 4.

****Insert Table 4****

5.1. Recycling of HTWW for the enhanced hydrothermal liquefaction process

Lately, studies have proposed to recycle the HTL derived wastewater back into the HTL system to improve the bio-oil production due to the dilution effect on the original biomass. Recycling of the HTL wastewater requires simpler installation, easy to operate, economically cheaper and can easily be scaled-up. In addition, the HTL wastewater can offset the freshwater requirement for the HTL process (Watson et al., 2020). The economic viability of commercial HTL recycling system has been summarised by SundarRajan et al. (2021). Ramos-Tercero et al. (2015) investigated the effect of recycling the HTL wastewater to the HTL reactor to recover carbon and develop an innovative solvent-free process. The authors have observed a significant upturn in bio-oil yield over all the tested range of temperatures (220 to 265 °C) and reached stationary level after sixth recycling process. The study also identified that the nitrogen and oxygen content in bio-oil increased with the increase in recycling number and consequently reduced the higher heating value, so the quality of the bio-oil produced (Kruse et al., 2007; Paterson et al., 2010). Therefore, a minor drop can be witnessed in the solid residues due to inhibition of the bio-oil degradation, after the third recycle (Deniel et al., 2016; Hu et al., 2017). The fuel bound nitrogen at low temperature transformed into ammonia (Pandey et al., 2016) which is an inhibiting compound and is produced by melanoidins (Maillard polymers) and water-soluble nitrogenous molecules (Pandey et al., 2016a; Minowa et al., 2004). Shakya et al. (2015) found that the nitrogen content in bio-oil produced even from catalytic HTL process was still higher compared to that of fossil derived oil and additional treatment was required to make it fit for use in combustion engines (0-0.8 wt%) (Shakya et al., 2015).

A stable upsurge in bio-oil yield from 34.6% to 48.7% was reported by Biller et al. (2016) up to eighth run before dropping to 43.1% at the night run. Furthermore, the carbon content increase from 67.9% to 74.5% whereas the oxygen content declined to 8.8% from 38.8%. Although, recycling the HTL wastewater offers promising potential by yielding higher quantity of the bio-oil nevertheless it could simply not be possible to treat the total amount of wastewater generated from the HTL. It has been observed that the total organic carbon loading increased after several round of recycling run from 12 to 35 g/L, 25–92 g/L and 51.37–110.4 g/L by Deniel et al. (2016), Biller et al. (2016) and Sundarrajan et al. (2019) respectively. It was also reported the HTL generated wastewater could potentially be used in anaerobic digestion.

6. Integrated systems for HTWW valorisation

The presence of resistant organic material in HTWW required the development of cost-effective and novel degradation and valorisation technologies. Each of the systems discussed in the following sections have their advantages and drawbacks. Figure 5 shows the advantages and disadvantages of each strategy. Integration of different HTWW valorisation systems would complement each other because the valorisation process includes multi-dimensional objectives such as nutrient recycling, biofuel generation, chemical separation etc. The advantages of individual techniques can be integrated in the combined systems, resulting in better vaporisation efficiency and effluent quality. This integration of a biological system with physicochemical processes is discussed in the next section followed by two or more biological system. The combination of biological and thermochemical processes in HTWW valorisation is then discussed in a separate section.

Insert Figure 5

6.1. Integrated Bio-Physicochemical Systems

Integration of chemical and biological treatment methods have shown good results for wastewater treatment and valorisation (Raphael et al.,2009). Shanmugam et al. (2017a) observed that a high concentration of nitrogenous compounds ensued in only 12% COD conversion in an AD process. A chemical process of struvite precipitation was used to mitigate this low efficiency by combining AD with struvite precipitation to reduce ammonium nitrogen. This resulted in almost 100% phosphorous removal and more than 50% of nitrogen removal. In addition, the integrated system produced biogas with 3.5 times higher CH_4 yield (182 ± 39 mL/g COD) compared to AD process alone. The X-ray diffraction analysis validated the presence of struvite, and it has the potential to be applied as a slow-release fertilizer. These results indicate both struvite and methane can be produced by integrating AD and struvite precipitation and its feasibility in valorising HTWW. The study projected that around 69.5 kg of struvite could be generated by processing a ton of HTL of dry algae (Shanmugam et al., 2017b).

Similarly, integration of advanced oxidation process (AOPs) with AD has produced greater biogas than AD alone. Both the process is complementary to each other. Chemical treatment has the advantage of using OH radicals, which can oxidise all organic compounds, while the biological system does not work effectively with refractory organics. OH radicals are highly reactive, while AD is a slow process. Si et al. (2018) reported that the ozone pretreatment substantially enhanced the methane production by 109% by converting the inhibitors. The process also necessitates techno-economic analysis as the ozone dosage would increase the cost substantially (Si et al., 2018). In another study, Quispe-Arpasi et al. (2018) reported a greater COD reduction in combining H_2O_2 oxidation and AD. Maximum energy recovery of 66.7% was accomplished by bringing in H_2O_2. This could be due to the decrease in the N-heterocyclic compounds (Siddique et al., 2014). However, a limit on the maximum dosage of H_2O_2 was observed. The increased concentration of H_2O_2 act as a radical scavenger interfering in methanogenesis (Siciliano et al., 2016).

Si et al. (2019) also investigated adsorption pre-treatment of HTWW using granule activated carbon (GAC). It was found that GAC addition improved the methane yield by 298% at a 2X dilution rate of the HTWW. GAC addition led to the formation of biofilms, enriching cleansing bacteria. It also enhances syntrophic acetogens. Even the methanogens showed a notable increase. GAC was likewise able to adsorb inhibitors. GAC also resulted in up to 96.8% of organics removal by adsorbing non-biodegradable organics. Several other studies were conducted on integrating adsorption and AD process to improve the valorisation efficiency (Tommaso et al., 2015; Zhou et al., 2015; Chen et al., 2017).

Zhou et al. (2017) noted that high concentrations of organics (> 13.3%) in HTWW impeded AD with no biogas production. The integration with adsorption using activated carbon greatly improved the anaerobic biodegradability. HTWW with 33.33% organics yielded 49% net energy recovery efficiency for recycled activated carbon, whereas it was 0% without activated carbon.

Even the virgin activated carbon also resulted in 40% net energy recovery efficiency. The activated carbon was also successful in reducing the lag phase for biogas production by 34%. On the other hand, the produced biogas has higher methane concentration compared to biogas without pre-treatment with adsorption (Zhou et al., 2017). Similarly, Zheng et al. (2017) improved anaerobic biodegradability by using zeolite and polyurethane matrices by combining adsorption and AD process. The HTWW was obtained from HTL of cyanobacteria and even at 6% HTWW, anaerobes were 50% inhibited. The use of adsorbents increased the methane yields from HTWW for all the adsorbents. The methane yields were 11% higher for zeolite, 37% higher for GAC and 36% higher for polyurethane matrix than control (Zheng et al., 2017). The adsorbents were noted for their buffering capacity as they could temporarily store the organic compounds and gradually deliver them to the microorganisms. Polyurethane foam and activated carbon also presented an excellent environment for biofilm formation, returning improved conditions for inhibition recovery in contrast with the control. GAC was deemed favourable due to its maximum methane yield of 124 mL/g COD at the second feeding. The lower increase for zeolite adsorbent was due to its inability to eliminate ammonium. However, Li et al. (2019) reported that integrated zeolite adsorption with AD was effective in removing ammonium from HTWW. Zeolite was also able to remove sulfate in HTWW successfully. The key finding was that zeolite adsorption of nitrogenous compounds significantly improved methane production (Li et al., 2019).

6.2. Integrated Biological systems

6.2.1. Dark fermentation-Anaerobic Digestion

Dark fermentation is gradually emerging as a promising alternative for H_2 generation. It occurs in the absence of light and is considered the most straightforward process of obtaining biohydrogen with the most likely scale-up capabilities (due to the size, space and simplicity of the bioreactor required) (Xia et al., 2013). The reaction is exergonic hence a net release of free energy, by 216 kcal/mol. Numerous organic carbon compound sources can be used as substrates which are often abundant in nature, renewable and cheap. Si et al. (2016) combined dark fermentation and AD process using cornstalk HTWW as a substrate for biohythane (mixture of biohydrogen and biomethane) generation. The energy and carbon recovery of the integrated dark fermentation and the AD process was observed to be 79.0 and 67.7%, respectively (Si et al., 2016). The dark fermentation process was also successful in degrading 5-HMF and furfural. These chemicals are potential inhibitors in methane production (Liu et al., 2015). The two-stage process thus revealed efficient methane production rate, acetogenesis, and COD removal.

The microbial distribution study amply confirmed the results. Si et al. (2016) noted that biohydrogen production resulted in the greater circulation of the detoxification bacteria such as *Clostridiaceae*, *Bacillaceae and Pseudomonadaceae*. Besides that, it also increased the higher distribution of acetate-oxidising bacteria (*Spirochaetaceae*), favourable for biomethane production (Si et al., 2016). The two-stage biological process is thus more beneficial in valorising HTWW. In another study, the combined fermentation and AD process yielded 29 mL of hydrogen/g COD and 254 mL methane/g COD (Si et al., 2019). The authors observed a shorter lag phase during the methane production step (<2.9 d) compared to the hydrogen production period. This could be due to the possible detoxification effect in the hydrogen production step. However, hydrogen production had to be optimised and maximum hydrogen production rate and maximum hydrogen yield could be accomplished only at 7 g COD/L. This is one of the key challenges in the integration process and needs to be addressed. Moreover, it was further argued that combining another anaerobic high-rate reactor with the two-stage process can compete with the petroleum products in terms of higher net energy return.

6.2.2. Integrated Biological-Thermochemical process

Li et al. (2018) integrated HTL with catalytic hydrothermal gasification (CHG) for algal biomass and could offset 98.2% of the COD and 97.2% of the TOC. The gas obtained had a high concentration of H_2 (53.4%) and 24.4 % of CH_4. Further downstream process of HTWW using electrochemical stripping and acid extraction was able to recover 91% of nitrogen and phosphorus. The filtrate from the process had practically no phosphorous (Li et al., 2018). In a technical report, Jones et al. (2014) found that H_2 from the CHG process could be exploited in the refining of crude bio-oil, one of the products of the HTL process. The complimentary process can compensate 18% of the total biomass carbon (Jones et al., 2014). Li et al. (2018) also proposed Sankey diagrams for C, N and P flows. The authors contended that the integrated treatment of HTWW could counteract approx. 10% of total carbon and around 63% of the nitrogen, significantly reducing the environmental discharge (Li et al., 2018).

From an economic and environmental standpoint, integrated systems are consequently considered to be the most appropriate. However, integrated systems employ only two processes in general, and there may be more lucrative ways of integration. It can be seen that integration offers hordes of possibilities, and with proper techno-economic and environmental analysis, different options can be suited for various HTWW.

7. Strategic innovations

7.1. Techno-economic analysis (TEA)

The techno-economic assessment (TEA) provides in-depth knowledge about the technical performance such as energy input, efficiency, yield and emissions of a technology/process under consideration and the cost associated to achieve a desired objective from that technology. TEA can be performed using simulation models (often developed using experimentally derived inputs) and is considered as a very cost-effective tool for understanding the overall performance of an emerging technology and its commercial feasibility.

The TEA of HTL process has been widely performed for various feedstocks and is well documented in existing literature. For instance, an investigation carried out by Jiang et al. studied the impact of different algae feedstocks on the biocrude production cost from HTL process revealed that the cost of biocrude could vary between $5-16/GGE and is majorly dependent of the feedstock cost, which was $400 to $1800/dry ton (Jiang et al., 2019). The study also concluded that the economic uncertainties for algae conversion via HTL for biocrude production were due to algae composition (high or low lipid content) and capital investment. Another study on sensitivity analysis of algae to biofuels via HTL showed that the ash content and biomass cost has significant influence on the techno-economic viability of the HTL process (DeRose et al., 2019). The study reported a minimum selling price of $10.41/GGE and suggests system improvements to achieve $3.85/GGE. Aierzhati et al. (2021) used pilot-scale experiments to demonstrate the commercial feasibility of a mobile HTL unit for converting food waste into biocrude oil (Aierzhati et al., 2021). The TEA of the process showed a least selling rate of $3.48/GGE. Li et al. (2021) obtained a minimum selling price of $2.65/GGE for HTL of wet waste. The experiments obtained higher yield for a continuous process as compared to batch process. Their work also indicated that controlling the feed moisture and reaction yield can reduce the uncertainties in the minimum selling price by roughly 50% (Li et al., 2021). To summarise, the reported studies indicated that the feedstock quality, feedstock cost and reactor yield are the primary causes for the economic uncertainties or for the fluctuations observed in the biocrude oil cost. Therefore, a greater control over these factors must be emphasised in future studies. Overall, the TEA outcomes in all these studies support the commercial viability of HTL process for variety of feedstock.

The treatment and valorisation of HTWW is believed to have an important effect on the overall techno-economic performance of biofuel production. For instance, a sensitivity analysis of renewable diesel production from algae via HTL by Juneja and Murthy (2017) showed that for every 10 Mgal/day rise in wastewater production can increase the renewable diesel cost by approximately $3-5/GGE (Juneja & Murthy., 2017). The study reported the cost of renewable diesel to be $6.62/GGE with algae culturing and harvesting contributing to 56% of this cost. A techno-economic investigation of two-stage fermentation and catalytic hydrothermal gasification (CHG) to produce biohythane using HTWW by Si et al., indicated that two stage fermentation (TF) can deliver a lower minimum selling price compared to conventional fossil fuels (Si et al., 2019). Zhu et al. (2019) conducted economic assessment of three HTWW treatment methods (i) recycle to algae farm, (ii) CHG and (iii) AD for algae HTL to biocrude oil (Zhu et al., 2019). The findings indicate 11% and 2.9% increase in minimum selling price for CHG and AD, respectively. This rise was due to higher capital and operating cost for both CHG and AD methods. The authors proposed that HTWW treatment methods are critical to the commercial viability of the HTL technology and needs more research, particularly on its TEA.

7.2. Life-cycle analysis (LCA)

LCAstarted in early 1970s and is increasingly becoming an inevitable tool for upscaling any industrial process. It is considered as the most comprehensive approach for assessing environmental impact. There are various studies on the LCA of hydrothermal liquefaction of biomass (Bennion et al., 2015; Sun et al., 2019; DeRose et al., 2019; Frank et al., 2011). Connelly et al. (2015) performed a thorough LCA on biofuels production from HTL of algae. They observed that under specific circumstances, biofuels generated using HTL could lead to 50% decline in LC-GHG emissions in contrast with the petroleum-based fuels. It has therefore potential to be eligible for an advanced biofuel and biodiesel. Nevertheless, the outcomes are vulnerable to a number of upstream and downstream dynamics, particularly the CO_2 supply chains. However, Frank et al (2013) noted that renewable diesel based on HTL of algae releases 31,000 gCO_{2eq} in comparison to 21,500 gCO_{2eq} for lipid extraction-based diesel. In another study, it was found that HTL affords an energetically achievable conversion route to biofuel. The lee side of the process is the low yield of biofuel. It was also reported that HTL-derived algae fuels resulted in lower GHG releases than corn ethanol and petroleum fuels (Liu et al., 2013). However, a very few studies have conducted the LCA of HTL process taking HTWW valorisationinto consideration. Juneja and Murthy (2017) studied the LCA of renewable diesel obtained from algae based on HTWW. Their findings indicate that the GHG emissions were only 15% of those generated for traditional diesel. Lower GHG emissions could also be achieved if HTWW can be used for algae cultivation (Fortier et al., 2014). The LCA of HTWW process is much more complex due to uncertainties associated with the presence of many parameters. Nevertheless, the commercialisation of HTL process necessitates both the TEA and LCA of wastewater valorisation produced during HTL process. Fig 6 depicts schematic representation of valorisation of HTWW for a future circular bioeconomy.

****Insert Figure 6****

8. Bottlenecks and Perspectives

8.1. Analysis of HTWW compositions and end product

HTWW is generally composed of organic components such as sugars, hydrocarbons, phenols, alcohols, carboxylic acids, and other organic compounds, while the composition varies depending on the input biomass. Characterisation of HTWW is often overlooked by researchers due its complex nature. Therefore, new analytical technologies for comprehensive compositional profiling of HTWW are required to determine the energy production as well as inhibitory activities of the components of HTWW. Furthermore, most of the technologies in use have limited performance efficiency since the HTL mechanism is not fully understood due to the complex nature of the products and its inputs. Characterisation technologies of the desired product as well as the contaminants are thus required for subsequent separation, recovery and purification of HTWW-derived value products.

8.2. Pre-treatment of HTWW for detoxification

For facilitating the cultivation of microalgae, some of the HTWW's persistent growth-inhibiting chemicals can be effectively removed using pre-treatment methods including adding adsorbents like activated charcoal to remove the toxic compounds. Further, the cost-effectiveness and efficacy of existing detoxification procedures might be investigated in the future with a concurrent recovery system of valuable products.

8.3. Co-cultivation of microorganism using HTWW

Since mixed microbial co-culture supports each other in metabolic and growth requirements, substituting pure or monoculture of microbes with consortia can increase resistance to harmful substances. Due to complex nature of HTWW containing varied amount of inhibitors, use of mixed consortia consisting of diverse microorganisms which also builds a symbiotic relationship among them, can make energy valorisation of HTWW feasible.

8.4. Large scale commercial study of HTWW valorisation

Inconsistent composition of HTWW having different properties, may lead to operational inconsistencies of valorisation processes during scaling-up. So far, majority of valorisation methods investigated/proposed are at the lab size, with no commercial scale implementation feasibility data. Additionally, the performance uncertainty also has substantial impact on the techno-economic and environmental sustainability of the HTWW utilization process. Large scale commercial studies of HTWW valorisation are limited, and therefore more investigation is necessary to advance their search of HTWW valorisation.

8.5. Extensive TEA and LCA

Despite advancements in HTWW valorisation technologies, substantial constraints continue to persist, requiring additional exploration in order to achieve a holistic HTWW valorisation approach. Hence, it is critical to conduct a systematic TEA of HTWW valorisation approaches in order to determine the technological and economic viability of the valorising procedures, as well as measuring carbon footprint of the process using LCA tools.

9. Conclusions

Anaerobic digestion, microalgal cultivation, microbial electrolysis cell, microbial fuel cell, and supercritical water gasification technologies are discussed for valorising wastewater produced during biomass hydrothermal processes. The review indicates that, it is challenging to achieve efficient HTWW valorisation using a single conversion technique. For effective HTWW valuation, the use of integrated systems that can overcome the limitations of individual technologies appears to be realistic solutions. There is also a risk of toxicity to numerous life forms, including microbes, due to the presence of these compounds in HTWW. As a result, before discharging HTWW to the environment, a proper valorisation technique is needed to reap the twin benefits of resource recovery and decrease of hazardous impacts of HTWW. The valorisation and treatment of HTWW has a considerable impact on the commercialisation of hydrothermal treatment processes. HTWW is not only processbyproduct of HTL but also produces a valuable resource (energy and nutrient). This review looked into efficient hydrothermal wastewater valorisation pathways, using a variety of conventional and sophisticated technologies which includes recirculation, anaerobic digestion, super critical water gasification, BESs, microalgae culturing, and integration of these approaches. Hydrothermal wastewater was found to be significantly rich in organic acids, nitrogen and carbon. Diverse microalgal species can be cultivated in HTWW using the available nutrients and the cultured algal biomass can further be used to produce biofuels. Re-utilisation of HTWW as diluents in HTL increased the overall energy efficiency ofthe process due to addition of additional carbon content in the bio-crude. However, increased number of recirculation process led to higher accumulation of nitrogen content in bio-oil. To address this limitation, HTWW was processed for renewable fuel (bio-methane) production using anaerobic digestion approach. Anaerobic digestion lowers the amount of inhibitory chemicals in the HTWW. The rejected water from anaerobic digestion process can again be utilised for algal cultivation. Finally, integration of different valorisation approaches provided the chance for an enhanced energy recovery and pollutant removal. Therefore, this review has the potential to have a larger impact on the advancement of simultaneous valorisation and waste water utilisation process from HTL, promoting sustainable developmental process.

Acknowledgements

The authors are thankful to the Thapar Institute of Engineering and Technology (TIET) and Sheffield Hallam University for supporting this work.

References

1. Aida, T. M., Nonaka, T., Fukuda, S., Kujiraoka, H., Kumagai, Y., Maruta, R., Ota, M., Suzuki, I., Watanabe, M. M., Inomata, H. et al. (2016). Nutrient recovery from municipal sludge for microalgae cultivation with two-step hydrothermal liquefaction. Algal research, 18, 61–68.

2. Aierzhati, A., Watson, J., Si, B., Stablein, M., Wang, T., & Zhang, Y. (2021). Development of a mobile, pilot scale hydrothermal liquefaction reactor: Food waste conversion product analysis and techno-economic assessment. Energy Conversion and Management: X, 10, 100076.

3. Barreiro, D. L., Bauer, M., Hornung, U., Posten, C., Kruse, A., &Prins, W. (2015). Cultivation of microalgae with recovered nutrients after hydrothermal liquefaction. Algal research, 9, 99–106.

4. Bennion, E. P., Ginosar, D. M., Moses, J., Agblevor, F., & Quinn, J. C. (2015). Lifecycle assessment of microalgae to biofuel: comparison of thermochemical processing pathways. Applied Energy, 154, 1062–1071.

5. Biller, P., Madsen, R. B., Klemmer, M., Becker, J., Iversen, B. B., & Glasius, M. (2016). Effect of hydrothermal liquefaction aqueous phase recycling on bio-crude yields and composition. Bioresource technology, 220, 190–199.

6. Biller, P., Ross, A. B., Skill, S., Lea-Langton, A., Balasundaram, B., Hall, C., Riley, R., & Llewellyn, C. (2012). Nutrient recycling of aqueous phase for microalgae cultivation from the hydrothermal liquefaction process. Algal Research, 1, 70–76.

7. Bora, R. R., Richardson, R. E., & You, F. (2020). Resource recovery and waste to energy

from wastewater sludge via thermochemical conversion technologies in support of circular economy: a comprehensive review. BMC Chemical Engineering, 2 , 1–16.

8. Byrd, A. J., Pant, K., & Gupta, R. B. (2008). Hydrogen production from glycerol by reforming in supercritical water over Ru/Al_2CO_3 catalyst. Fuel, 87, 2956–2960.

9. Cao, L., Iris, K., Cho, D.-W., Wang, D., Tsang, D. C., Zhang, S., Ding, S., Wang, L., & Ok, Y. S. (2019). Microwave-assisted low-temperature hydrothermal treatment of red seaweed (G*racilaria lemaneiformis*) for production of levulinic acid and algae hydrochar. Bioresource technology, 273, 251–258.

10. Cao, L., Zhang, C., Chen, H., Tsang, D. C., Luo, G., Zhang, S., & Chen, J. (2017). Hydrothermal liquefaction of agricultural and forestry wastes: state-of the-art review and future prospects. Bioresource Technology, 245, 1184–1193.DOI:10.1016/j.biortech.2017.08.196.

11. Chen, H., Rao, Y., Cao, L., Shi, Y., Hao, S., Luo, G., & Zhang, S. (2019). Hydrothermal conversion of sewage sludge: focusing on the characterization of liquid products and their methane yields. Chemical Engineering Journal, 357, 367–375.

12. Chen, H., Wan, J., Chen, K., Luo, G., Fan, J., Clark, J., & Zhang, S. (2016). Biogas production from hydrothermal liquefaction wastewater (HTLWW): Focusing on the microbial communities as revealed by high-throughput sequencing of full-length16s rRNA genes. Water research, 106, 98–107.

13. Chen, H., Zhang, C., Rao, Y., Jing, Y., Luo, G., & Zhang, S. (2017). Methane potentials of wastewater generated from hydrothermal liquefaction of rice straw: focusing on the wastewater characteristics and microbial community compositions. Biotechnology for biofuels, 10, 1–16.

14. Cherad, R., Onwudili, J., Biller, P., Williams, P., & Ross, A. (2016). Hydrogen production from the catalytic supercritical water gasification of process water generated from hydrothermal liquefaction of microalgae. Fuel, 166, 24–28.

15. Deniel, M., Haarlemmer, G., Roubaud, A., Weiss-Hortala, E., & Fages, J. (2016). Bio-oil production from food processing residues: Improving the bio-oil yield and quality by aqueous phase recycle in hydrothermal liquefaction of black currant(*Ribes nigrum l.*) pomace. Energy & Fuels, 30, 4895–4904.

16. D´eniel, M., Haarlemmer, G., Roubaud, A., Weiss-Hortala, E., &Fages, J. (2016). Energy

valorisation of food processing residues and model compounds by hydrothermal liquefaction. Renewable and Sustainable Energy Reviews, 54, 1632–1652.

17. DeRose, K., DeMill, C., Davis, R. W., & Quinn, J. C. (2019). Integrated techno-economic and life cycle assessment of the conversion of high productivity, low lipid algae to renewable fuels. Algal Research, 38, 101412.

18. Dutta, S., Iris, K., Tsang, D. C., Ng, Y. H., Ok, Y. S., Sherwood, J., & Clark, J. H.(2019). Green synthesis of gamma-valerolactone (GVL) through hydrogenation of biomass-derived levulinic acid using non-noble metal catalysts: A critical review. Chemical Engineering Journal, 372, 992–1006.

19. Elliott, D. C., Biller, P., Ross, A. B., Schmidt, A. J., & Jones, S. B. (2015). Hydrothermal liquefaction of biomass: developments from batch to continuous process. Bioresource technology, 178, 147–156.

20. Elliott, D. C., Hart, T. R., Schmidt, A. J., Neuenschwander, G. G., Rotness, L. J.,Olarte, M. V., Zacher, A. H., Albrecht, K. O., Hallen, R. T., & Holladay, J. E.(2013). Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor. Algal Research, 2, 445–454.

21. Erdogan, E., Atila, B., Mumme, J., Reza, M. T., Toptas, A., Elibol, M., & Yanik, J.(2015). Characterization of products from hydrothermal carbonization of orange pomace including anaerobic digestibility of process liquor. Bioresource technology,196, 35–42.

22. Fernandez, S., Srinivas, K., Schmidt, A. J., Swita, M. S., & Ahring, B. K. (2018). Anaerobic digestion of organic fraction from hydrothermal liquefied algae wastewater by product. Bioresource technology, 247, 250–258.

23. Fortier, M.-O. P., Roberts, G. W., Stagg-Williams, S. M., & Sturm, B. S. (2014). Life cycle assessment of bio-jet fuel from hydrothermal liquefaction of microalgae. Applied Energy, 122 , 73–82.

24. Frank, E. D., Han, J., Palou-Rivera, I., Elgowainy, A., & Wang, M. (2011). Lifecycle analysis of algal lipid fuels with the greet model. Center for Transportation Research, Energy Systems Division, Argonne National Laboratory, Oak Ridge,(pp. 11–5).

25. Gai, C., Zhang, Y., Chen, W.-T., Zhang, P., & Dong, Y. (2014). Energy and nutrient recovery efficiencies in biocrude oil produced via hydrothermal liquefaction of *Chlorella*

pyrenoidosa. RSC advances, 4, 16958–16967.

26. Gai, C., Zhang, Y., Chen, W.-T., Zhou, Y., Schideman, L., Zhang, P., Tommaso, G., Kuo, C.-T., & Dong, Y. (2015). Characterization of aqueous phase from the hydrothermal liquefaction of *Chlorella pyrenoidosa*. Bioresource technology, 184,328–335.

27. Ghanim, B. M., Pandey, D. S., Kwapinski, W., & Leahy, J. J. (2016). Hydrothermal carbonisation of poultry litter: effects of treatment temperature and residence time on yields and chemical properties of hydrochars. Bioresource Technology,216, 373–380.

28. Godwin, C. M., Hietala, D. C., Lashaway, A. R., Narwani, A., Savage, P. E., & Cardinale, B. J. (2017). Algal polycultures enhance co-product recycling from hydrothermal liquefaction. Bioresource technology, 224, 630–638.

29. Gong, M., Nanda, S., Romero, M. J., Zhu, W., & Kozinski, J. A. (2017). Subcritical and supercritical water gasification of humic acid as a model compound of humic substances in sewage sludge. The Journal of Supercritical Fluids, 119, 130–138.

30. Gude, V. G. (2016). Wastewater treatment in microbial fuel cells–an overview. Journal of Cleaner Production, 122, 287–307.

31. Gumisiriza, R., Hawumba, J. F., Okure, M., & Hensel, O. (2017). Biomass waste-to energy valorisation technologies: a review case for banana processing in Uganda. Biotechnology for biofuels, 10, 1–29.

32. Han, X., Qu, Y., Dong, Y., Zhao, J., Jia, L., Yu, Y., Zhang, P., Li, D., Ren, N., &Feng, Y. (2018). Microbial electrolysis cell powered by an aluminum-air battery for hydrogen generation, in-situ coagulant production and wastewater treatment. International Journal of Hydrogen Energy, 43, 7764–7772.

33. Hu, Y., & Bassi, A. (2020). Extraction of biomolecules from microalgae. Handbook of Microalgae-Based Processes and Products, (pp. 283–308).

34. Hu, Y., Feng, S., Yuan, Z., Xu, C. C., & Bassi, A. (2017). Investigation of aqueous phase recycling for improving bio-crude oil yield in hydrothermal liquefaction of algae. Bioresource technology, 239, 151–159.

35. Huang, H.-j., & Yuan, X.-z. (2015). Recent progress in the direct liquefaction of typical

biomass. Progress in Energy and Combustion Science, 49, 59–80.

36. Jadhav, D. A., Ray, S. G., & Ghangrekar, M. M. (2017). Third generation in bio-electrochemical system research–a systematic review on mechanisms for recovery of valuable by-products from wastewater. Renewable and Sustainable Energy Reviews, 76, 1022–1031.

37. Jiang, Y., Jones, S. B., Zhu, Y., Snowden-Swan, L., Schmidt, A. J., Billing, J. M., & Anderson, D. (2019). Techno-economic uncertainty quantification of algal-derived biocrude via hydrothermal liquefaction. Algal Research, 39, 101450.

38. Jones, S. B., Zhu, Y., Anderson, D. B., Hallen, R. T., Elliott, D. C., Schmidt, A. J., Albrecht, K. O., Hart, T. R., Butcher, M. G., Drennan, C. et al. (2014).Process design and economics for the conversion of algal biomass to hydrocarbons: whole algae hydrothermal liquefaction and upgrading. Technical Report Pacific Northwest National Lab.(PNNL), Richland, WA (United States).

39. Juneja, A., & Murthy, G. S. (2017). Evaluating the potential of renewable diesel production from algae cultured on wastewater: techno-economic analysis and lifecycle assessment. Aims Energy, 5, 239–257.

40. Kaku, N., Yonezawa, N., Kodama, Y., & Watanabe, K. (2008). Plant/microbe cooperation for electricity generation in a rice paddy field. Applied microbiology and biotechnology, 79, 43–49.

41. Kruse, A. (2008). Supercritical water gasification. Biofuels, Bioproducts and Biorefining: Innovation for a sustainable economy, 2 , 415–437.

42. Kruse, A., Maniam, P., & Spieler, F. (2007). Influence of proteins on the hydrothermal gasification and liquefaction of biomass. 2. model compounds. Industrial & Engineering Chemistry Research, 46, 87–96.

43. Kruse, A., Meier, D., Rimbrecht, P., & Schacht, M. (2000). Gasification of pyrocatecholin supercritical water in the presence of potassium hydroxide. Industrial & Engineering Chemistry Research, 39, 4842–4848.

44. Kwak, W., Rout, P. R., Lee, E., & Bae, J. (2020). Influence of hydraulic retention time and temperature on the performance of an anaerobic ammonium oxidation fluidized bed membrane bioreactor for low-strength ammonia wastewater treatment. Chemical Engineering Journal, 386, 123992.

45. Lalman, J. A., & Bagley, D. M. (2001). Anaerobic degradation and methanogenic inhibitory effects of oleic and stearic acids. Water research, 35, 2975–2983.

46. Lee, E., Rout, P. R., & Bae, J. (2021). The applicability of anaerobically treated domestic wastewater as a nutrient medium in hydroponic lettuce cultivation: Nitrogen toxicity and health risk assessment. Science of The Total Environment, 780, 146482.

47. Lee, E., Rout, P. R., Kyun, Y., & Bae, J. (2020). Process optimization and energy analysis of vacuum degasifier systems for the simultaneous removal of dissolved methane and hydrogen sulfide from anaerobically treated wastewater. Water Research, 182, 115965.

48. Lee, E., Rout, P. R., Shin, C., & Bae, J. (2019). Effects of sodium hypochlorite concentration on the methanogenic activity in an anaerobic fluidized membrane bioreactor. Science of The Total Environment, 678, 85–93.

49. Lee, I.-G., & Ihm, S.-K. (2010). Hydrogen production by SCWG treatment of wastewater from amino acid production process. Industrial & engineering chemistry research, 49, 10974–10980.

50. Leng, L., Li, J., Wen, Z., & Zhou, W. (2018). Use of microalgae to recycle nutrients in aqueous phase derived from hydrothermal liquefaction process. Bioresource technology, 256, 529–542.

51. Leng, L., Yang, L., Chen, J., Leng, S., Li, H., Li, H., Yuan, X., Zhou, W., &Huang, H. (2020a). A review on pyrolysis of protein-rich biomass: Nitrogen transformation. Bioresource Technology, 315, 123801.

52. Leng, L., Zhang, W., Leng, S., Chen, J., Yang, L., Li, H., Jiang, S., & Huang, H. (2020b). Bioenergy recovery from wastewater produced by hydrothermal processing biomass: Progress, challenges, and opportunities. Science of the Total Environment, (p. 142383).

53. Leng, L., & Zhou, W. (2018). Chemical compositions and wastewater properties of aqueous phase (wastewater) produced from the hydrothermal treatment of wet biomass: A review. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 40, 2648–2659.

54. Li, M., Si, B., Zhang, Y., Watson, J., & Aierzhati, A. (2019a). Reduce recalcitrance of

cornstalk using post-hydrothermal liquefaction wastewater pretreatment. Bioresource technology, 279, 57–66.

55. Li, R., Liu, D., Zhang, Y., Zhou, J., Tsang, Y. F., Liu, Z., Duan, N., & Zhang, Y.(2019b). Improved methane production and energy recovery of post-hydrothermal liquefaction waste water via integration of zeolite adsorption and anaerobic digestion. Science of The Total Environment, 651, 61–69.

56. Li, S., Jiang, Y., Snowden-Swan, L. J., Askander, J. A., Schmidt, A. J., & Billing, J. M. (2021). Techno-economic uncertainty analysis of wet waste-to-biocrude via hydrothermal liquefaction. Applied Energy, 283, 116340.

57. Li, Y., Tarpeh, W. A., Nelson, K. L., & Strathmann, T. J. (2018). Quantitative evaluation of an integrated system for valorization of wastewater algae as biooil, fuel gas, and fertilizer products. Environmental science & technology, 52,12717–12727.

58. Liu, X., Saydah, B., Eranki, P., Colosi, L. M., Mitchell, B. G., Rhodes, J., & Clarens, A. F. (2013). Pilot-scale data provide enhanced estimates of the lifecycle energy and emissions profile of algae biofuels produced via hydrothermal liquefaction. Bioresource technology, 148, 163–171.

59. Liu, X., Yan, Z., & Yue, Z.-B. (2011). Biogas, Liu, Z., He, Y., Shen, R., Zhu, Z., Xing, X.-H., Li, B., & Zhang, Y. (2015a). Performance and microbial community of carbon nanotube fixed-bed microbial fuel cell continuously fed with hydrothermal liquefied cornstalk biomass. Bioresource technology, 185, 294–301.

60. Liu, Z., Zhang, C., Wang, L., He, J., Li, B., Zhang, Y., & Xing, X.-H. (2015b). Effects of furan derivatives on biohydrogen fermentation from wet steam-exploded cornstalk and its microbial community. Bioresource technology, 175, 152–159.

61. Logan, B. E., Call, D., Cheng, S., Hamelers, H. V., Sleutels, T. H., Jeremiasse, A. W., & Rozendal, R. A. (2008). Microbial electrolysis cells for high yield hydrogen gas production from organic matter. Environmental science & technology, 42, 8630–8640.

62. Lu, J., Zhang, J., Zhu, Z., Zhang, Y., Zhao, Y., Li, R., Watson, J., Li, B., & Liu, Z. (2017). Simultaneous production of biocrude oil and recovery of nutrients and metals from human feces via hydrothermal liquefaction. Energy Conversion and Management, 134, 340–346.

63. Maddi, B., Panisko, E., Wietsma, T., Lemmon, T., Swita, M., Albrecht, K., &Howe, D.

(2017). Quantitative characterization of aqueous byproducts from hydrothermal liquefaction of municipal wastes, food industry wastes, and biomass grown on waste. ACS Sustainable Chemistry & Engineering, 5, 2205–2214.

64. Madsen, R. B., Biller, P., Jensen, M. M., Becker, J., Iversen, B. B., & Glasius, M.(2016). Predicting the chemical composition of aqueous phase from hydrothermal liquefaction of model compounds and biomasses. Energy & Fuels, 30, 10470–10483.

65. Martinez-Fernandez, J. S., & Chen, S. (2017). Sequential hydrothermal liquefaction characterization and nutrient recovery assessment. Algal research, 25, 274–284.

66. Mata-Alvarez, J., Dosta, J., Romero-G¨uiza, M., Fonoll, X., Peces, M., & Astals, S.(2014). A critical review on anaerobic co-digestion achievements between 2010 and 2013. Renewable and sustainable energy reviews, 36, 412–427.

67. Mau, V., Quance, J., Posmanik, R., & Gross, A. (2016). Phases' characteristics of poultry litter hydrothermal carbonization under a range of process parameters. Bioresource technology, 219, 632–642.

68. Minowa, T., Inoue, S., Hanaoka, T., & MATSUMURA, Y. (2004). Hydrothermal reaction of glucose and glycine as model compounds of biomass. Journal of the Japan Institute of Energy, 83, 794–798.

69. Mohanty, A., Rout, P. R., Dubey, B., Meena, S. S., Pal, P., & Goel, M. (2021). A critical review on biogas production from edible and non-edible oil cakes. Biomass Conversion and Biorefinery, (pp. 1–18).

70. Molino, A., De Gisi, S., Petta, L., Franzese, A., Casella, P., Marino, T., & Notarnicola, M. (2019). Experimental and theoretical investigation on the recovery of green chemicals and energy from mixed agricultural wastes by coupling anaerobic digestion and supercritical water gasification. Chemical Engineering Journal,370, 1101–1110.

71. Mursito, A. T., Hirajima, T., Sasaki, K., & Kumagai, S. (2010). The effect of hydrothermal dewatering of pontianak tropical peat on organics in wastewater and gaseous products. Fuel, 89, 3934–3942.

72. Naidu, L., Saravanan, S., Goel, M., Periasamy, S., & Stroeve, P. (2016). A novel technique for detoxification of phenol from wastewater: Nanoparticle assisted nano filtration (nanf). Journal of Environmental Health Science and Engineering,14, 1–12.

73. Nanda, S., Reddy, S. N., Hunter, H. N., Butler, I. S., & Kozinski, J. A. (2015). Supercritical water gasification of lactose as a model compound for valorization of dairy industry effluents. Industrial & Engineering Chemistry Research, 54,9296–9306.

74. Nazari, L., Yuan, Z., Ray, M. B., & Xu, C. C. (2017). Co-conversion of waste activated sludge and sawdust through hydrothermal liquefaction: optimization of reaction parameters using response surface methodology. Applied Energy, 203 ,1–10.

75. Nurdiawati, A., Nakhshiniev, B., Zaini, I. N., Saidov, N., Takahashi, F., &Yoshikawa, K. (2018). Characterization of potential liquid fertilizers obtained by hydrothermal treatment of chicken feathers. Environmental Progress & Sustainable Energy, 37, 375–382.

76. Olabi, A., Wilberforce, T., Sayed, E. T., Elsaid, K., Rezk, H., & Abdelkareem, M. A. (2020). Recent progress of graphene based nanomaterials in bioelectrochemical systems. Science of The Total Environment, 749, 141225.

77. Onwudili, J. A., Lea-Langton, A. R., Ross, A. B., & Williams, P. T. (2013). Catalytic hydrothermal gasification of algae for hydrogen production: composition of reaction products and potential for nutrient recycling. Bioresource technology,127, 72–80.

78. Onwudili, J. A., & Williams, P. T. (2009). Role of sodium hydroxide in the production of hydrogen gas from the hydrothermal gasification of biomass. International journal of hydrogen energy, 34 , 5645–5656.

79. Pandey, D. S., Kwapinska, M., G´omez-Barea, A., Horvat, A., Fryda, L. E., Rabou,L. P., Leahy, J. J., & Kwapinski, W. (2016a). Poultry litter gasification in a fluidized bed reactor: effects of gasifying agent and limestone addition. Energy& Fuels, 30, 3085–3096.

80. Pandey, P., Shinde, V. N., Deopurkar, R. L., Kale, S. P., Patil, S. A., & Pant, D.(2016b). Recent advances in the use of different substrates in microbial fuel cells toward wastewater treatment and simultaneous energy recovery. Applied Energy, 168, 706–723.

81. Pandian, A. M. K., Rajasimman, M., Rajamohan, N., Varjani, S., &Karthikeyan,C. (2021). Anaerobic mixed consortium (AMC) mediated enhanced biosynthesis of silver nano particles (AGNPS) and its application for the removal of phenol. Journal of Hazardous Materials, 416, 125717.

82. Pereira, M. (2003). Anaerobic biodegradation of long chain fatty acids: biomethanisation of biomass-associated LCFA as a challenge for the anaerobic treatment of effluents with high lipid/lcfa content.

83. Peterson, A. A., Lachance, R. P., & Tester, J. W. (2010). Kinetic evidence of the maillard reaction in hydrothermal biomass processing: glucose-glycine interactions in high-temperature, high-pressure water. Industrial & engineering chemistry research, 49 , 2107–2117.

84. Posmanik, R., Labatut, R. A., Kim, A. H., Usack, J. G., Tester, J. W., &Angenent,L. T. (2017). Coupling hydrothermal liquefaction and anaerobic digestion for energy valorization from model biomass feedstocks. Bioresource Technology, 233 ,134–143.

85. Ramos-Tercero, E. A., Bertucco, A., &Brilman, D. W. F. (2015). Process water recycle in hydrothermal liquefaction of microalgae to enhance bio-oil yield. Energy& fuels, 29, 2422–2430.

86. Reddy, S. N., Nanda, S., Dalai, A. K., & Kozinski, J. A. (2014). Super critical water gasification of biomass for hydrogen production. International Journal of Hydrogen Energy, 39 , 6912–6926.

87. Rout, P. R., Bhunia, P., Lee, E., & Bae, J. (2020). Microbial Electrochemical Systems (MESs): Promising Alternatives for Energy Sustainability. In *Alternative Energy Resources* (pp. 223-251). Springer, Cham.

88. Rout, P. R., Goel, M., Mohanty, A., Pandey, D. S., Halder, N., Mukherjee, S., & Varjani, S. (2022). Recent Advancements in Microalgal Mediated Valorisation of Wastewater from Hydrothermal Liquefaction of Biomass. *BioEnergy Research*, 1-16.

89. Sadykov, V. A., Sadovskaya, E. M., Eremeev, N. F., Pikalova, E. Y., Bogdanovich, N. M., Filonova, E. A., Krieger, T. A., Fedorova, Y. E., Krasnov, A. V., Skriabin, P. I. et al. (2020). Novel materials for solid oxide fuel cells cathodes and oxygen separation membranes: Fundamentals of oxygen transport and performance. Carbon Resources Conversion, 3, 112–121.

90. Sayed, E. T., Abdelkareem, M. A., Obaidin, K., Elsaid, K., Wilberforce, T., Maghrabie, H. M., & Olabi, A. (2021). Progress in plant-based bioelectro-chemical systems and their connection with sustainable development goals. Carbon Resources Conversion.

91. Schwab, A. (2016). Bioenergy Technologies Office Multi-Year Program Plan. March 2016. Technical Report Bioenergy Technologies Office.

92. Shahid, M. K., Kashif, A., Rout, P. R., Aslam, M., Fuwad, A., Choi, Y., Park, J. H., Kumar, G. et al. (2020). A brief review of anaerobic membrane bioreactors emphasizing recent advancements, fouling issues and future perspectives. Journal of Environmental Management, 270 , 110909.

93. Shakya, R., Whelen, J., Adhikari, S., Mahadevan, R., & Neupane, S. (2015). Effect of temperature and Na_2CO_3 catalyst on hydrothermal liquefaction of algae. Algal Research, 12, 80–90.

94. Shanmugam, S. R., Adhikari, S., Nam, H., &Sajib, S. K. (2018). Effect of biochar on methane generation from glucose and aqueous phase of algae liquefaction using mixed anaerobic cultures. Biomass and Bioenergy, 108, 479–486.

95. Shanmugam, S. R., Adhikari, S., & Shakya, R. (2017a). Nutrient removal and energy production from aqueous phase of bio-oil generated via hydrothermal liquefaction of algae. Bioresource technology, 230, 43–48.

96. Shanmugam, S. R., Adhikari, S., Wang, Z., & Shakya, R. (2017b). Treatment of aqueous phase of bio-oil by granular activated carbon and evaluation of biogas production. Bioresource technology, 223, 115–120.

97. Shen, R., Jiang, Y., Ge, Z., Lu, J., Zhang, Y., Liu, Z., & Ren, Z. J. (2018). Microbial electrolysis treatment of post-hydrothermal liquefaction wastewater with hydrogen generation. Applied energy, 212, 509–515.

98. Shen, R., Liu, Z., He, Y., Zhang, Y., Lu, J., Zhu, Z., Si, B., Zhang, C., & Xing, X.-H. (2017). Microbial electrolysis cell to treat hydrothermal liquefied wastewater from cornstalk and recover hydrogen: Degradation of organic compounds and characterization of microbial community. International journal of hydrogen energy, 41, 4132–4142.

99. Si, B., Li, J., Zhu, Z., Shen, M., Lu, J., Duan, N., Zhang, Y., Liao, Q., Huang, Y., &Liu, Z. (2018). Inhibitors degradation and microbial response during continuous anaerobic conversion of hydrothermal liquefaction wastewater. Science of the total environment, 630, 1124–1132.

100. Si, B., Watson, J., Aierzhati, A., Yang, L., Liu, Z., & Zhang, Y. (2019a). Biohythane production of post-hydrothermal liquefaction wastewater: a comparison of two-stage fermentation and catalytic hydrothermal gasification. Bioresource technology, 274, 335–342.

101. Si, B., Yang, L., Zhou, X., Watson, J., Tommaso, G., Chen, W.-T., Liao, Q., Duan, N., Liu, Z., & Zhang, Y. (2019b). Anaerobic conversion of the hydrothermal liquefaction aqueous phase: fate of organics and intensification with granule activated carbon/ozone pretreatment. Green Chemistry, 21, 1305–1318.

102. Si, B.-C., Li, J.-M., Zhu, Z.-B., Zhang, Y.-H., Lu, J.-W., Shen, R.-X., Zhang, C., Xing, X.-H., & Liu, Z. (2016). Continuous production of biohythane from hydrothermal liquefied cornstalk biomass via two-stage high-rate anaerobic reactors. Biotechnology for biofuels, 9, 1–15.

103. Siciliano, A., Stillitano, M., & De Rosa, S. (2016). Biogas production from wet olive mill wastes pretreated with hydrogen peroxide in alkaline conditions. Renewable Energy, 85, 903–916.

104. Siddique, M. N. I., Abd Munaim, M. S., & Zularisam, A. (2014). Mesophilic and thermophilic biomethane production by co-digesting pretreated petrochemical wastewater with beef and dairy cattle manure. Journal of Industrial and Engineering Chemistry, 20, 331–337.

105. Stemann, J., Putschew, A., & Ziegler, F. (2013). Hydrothermal carbonization: Process water characterization and effects of water recirculation. Bioresource technology, 143, 139–146.

106. Sudarsan, J., Deeptha, V., Maurya, D., Goel, M., Kumar, K. R., & Das, A. (2015).Study on treatment of electroplating wastewater using constructed wetland. Nature environment and pollution technology, 14, 95.

107. Sun, C.-H., Fu, Q., Liao, Q., Xia, A., Huang, Y., Zhu, X., Reungsang, A., & Chang, H.-X. (2019). Life-cycle assessment of biofuel production from microalgae via various bioenergy conversion systems. Energy, 171, 1033–1045.

108. SundarRajan, P., Gopinath, K., Arun, J., GracePavithra, K., Joseph, A. A., & Manasa, S. (2021). Insights into valuing the aqueous phase derived from hydrothermal liquefaction. Renewable and Sustainable Energy Reviews, 144, 111019.

109. Tassakka, M. I. S., Islami, B. B., Saragih, F. N. A., & Priadi, C. R. (2019). Optimum organic loading rates (OLR) for food waste anaerobic digestion: Study case universitas Indonesia. Civil Engineering, 10.

110. Toczylowska-Mami´nska, R., Szymona, K., & Kloch, M. (2018). Bioelectricity production from wood hydrothermal-treatment wastewater: Enhanced power generation in MFC-

fed mixed wastewaters. Science of The Total Environment, 634,586–594.

111. Tommaso, G., Chen, W.-T., Li, P., Schideman, L., & Zhang, Y. (2015). Chemical characterization and anaerobic biodegradability of hydrothermal liquefaction aqueous products from mixed-culture wastewater algae. Bioresource technology, 178, 139–146.

112. Toufiq Reza, M., Freitas, A., Yang, X., Hiibel, S., Lin, H., & Coronella, C. J. (2016). Hydrothermal carbonization (HTC) of cow manure: carbon and nitrogen distributions in HTC products. Environmental Progress & Sustainable Energy, 35 ,1002–1011.

113. Varjani, S., Joshi, R., Srivastava, V. K., Ngo, H. H., & Guo, W. (2020). Treatment of wastewater from petroleum industry: current practices and perspectives. Environmental Science and Pollution Research, 27, 27172–27180.

114. Varjani, S., Shah, A. V., Vyas, S., & Srivastava, V. K. (2021). Processes and prospects on valorizing solid waste for the production of valuable products employing bio-routes: A systematic review. Chemosphere, (p. 130954). Varjani, S. J. (2017). Microbial degradation of petroleum hydrocarbons. Bioresource technology, 223, 277–286.

115. Villamil, J. A., Mohedano, A. F., Rodriguez, J. J., & de la Rubia, M. A. (2018).Valorisation of the liquid fraction from hydrothermal carbonisation of sewage sludge by anaerobic digestion. Journal of Chemical Technology & Biotechnology, 93, 450–456.

116. Vyas, S., Prajapati, P., Shah, A. V., Srivastava, V. K., & Varjani, S. (2022). Opportunities and knowledge gaps in biochemical interventions for mining of resources from solid waste: A special focus on anaerobic digestion. Fuel, 311, 122625.URL: https://doi.org/10.1016/j.fuel.2021.122625. doi:10.1016/j.fuel.2021.122625.

117. Watson, J., Si, B., Li, H., Liu, Z., & Zhang, Y. (2017). Influence of catalysts on hydrogen production from wastewater generated from the HTL of human feces via catalytic hydrothermal gasification. international journal of hydrogen energy, 42 ,20503–20511.

118. Watson, J., Wang, T., Si, B., Chen, W.-T., Aierzhati, A., & Zhang, Y. (2020). Valorization of hydrothermal liquefaction aqueous phase: pathways towards commercial viability. Progress in Energy and Combustion Science, 77, 100819.

119. Watson, J., Zhang, Y., Si, B., Chen, W.-T., & de Souza, R. (2018). Gasification of biowaste: A critical review and outlooks. Renewable and Sustainable Energy Reviews, 83, 1–17.

120. Weiner, B., Poerschmann, J., Wedwitschka, H., Koehler, R., & Kopinke, F.-D. (2014). Influence of process water reuse on the hydrothermal carbonization of paper. ACS Sustainable Chemistry & Engineering, 2, 2165–2171.

121. Wilberforce, T., Sayed, E. T., Abdelkareem, M. A., Elsaid, K., & Olabi, A. (2021).Value added products from wastewater using bioelectrochemical systems: Current trends and perspectives. Journal of Water Process Engineering, 39, 101737.

122. Wirth, B., & Reza, M. T. (2016). Continuous anaerobic degradation of liquid condensate from steam-derived hydrothermal carbonization of sewage sludge. ACS Sustainable Chemistry & Engineering, 4, 1673–1678.

123. Xia, A., Cheng, J., Lin, R., Liu, J., Zhou, J., & Cen, K. (2013). Sequential generation of hydrogen and methane from glutamic acid through combined photofermentation and methanogenesis. Bioresource technology, 131, 146–151.

124. Xie, L.-F., Duan, P.-G., Jiao, J.-L., & Xu, Y.-P. (2019). Hydrothermal gasification of microalgae over nickel catalysts for production of hydrogen-rich fuel gas: effect of zeolite supports. International Journal of Hydrogen Energy, 44, 5114–5124.

125. Yang, E., Mohamed, H. O., Park, S.-G., Obaid, M., Al-Qaradawi, S. Y., Casta˜no, P., Chon, K., & Chae, K.-J. (2020). A review on self-sustainable microbial electrolysis cells for electro-biohydrogen production via coupling with carbon-neutral renewable energy technologies. Bioresource technology, (p. 124363).

126. Yang, L., Si, B., Tan, X., Chu, H., Zhou, X., Zhang, Y., Zhang, Y., & Zhao, F.(2018). Integrated anaerobic digestion and algae cultivation for energy recovery and nutrient supply from post-hydrothermal liquefaction wastewater. Bioresource technology, 266, 349–356.

127. Zhang, L., Champagne, P., & Xu, C. C. (2011). Supercritical water gasification of an aqueous by-product from biomass hydrothermal liquefaction with novel Ru modified Ni catalysts. Bioresource technology, 102, 8279–8287.

128. Zhao, K., Li, Y., Zhou, Y., Guo, W., Jiang, H., & Xu, Q. (2018). Characterization of hydrothermal carbonization products (hydrochars and spent liquor) and their biomethane production performance. Bioresource technology, 267, 9–16.

129. Zhen, G., Lu, X., Kumar, G., Bakonyi, P., Xu, K., & Zhao, Y. (2017). Microbial electrolysis cell platform for simultaneous waste biorefinery and clean electrofuels generation: Current situation, challenges and future perspectives. Progress in Energy and Combustion Science, 63, 119–145.

130. Zheng, M., Schideman, L. C., Tommaso, G., Chen, W.-T., Zhou, Y., Nair, K., Qian, W., Zhang, Y., & Wang, K. (2017). Anaerobic digestion of wastewater generated from the hydrothermal liquefaction of Spirulina: Toxicity assessment and minimization. Energy conversion and management, 141, 420–428.

131. Zhiyong, Y., & Xiuyi, T. (2015). Hydrogen generation from oily wastewater via supercritical water gasification (SCWG). Journal of Industrial and Engineering Chemistry, 23, 44–49.

132. Zhou, W., Wang, J., Chen, P., Ji, C., Kang, Q., Lu, B., Li, K., Liu, J., & Ruan, R. (2017). Bio-mitigation of carbon dioxide using microalgal systems: advances and perspectives. Renewable and Sustainable Energy Reviews, 76, 1163–1175.

133. Zhou, Y., Schideman, L., Yu, G., & Zhang, Y. (2013). A synergistic combination of algal wastewater treatment and hydrothermal biofuel production maximized by nutrient and carbon recycling. Energy & Environmental Science, 6, 3765–3779.

134. Zhou, Y., Schideman, L., Zheng, M., Martin-Ryals, A., Li, P., Tommaso, G., &Zhang, Y. (2015). Anaerobic digestion of post-hydrothermal liquefaction wastewater for improved energy efficiency of hydrothermal bioenergy processes. Water science and technology, 72, 2139–2147.

135. Zhu, Y., Jones, S. B., Schmidt, A. J., Albrecht, K. O., Edmundson, S. J., & Anderson, D. B. (2019). Techno-economic analysis of alternative aqueous phase treatment methods for microalgae hydrothermal liquefaction and biocrude upgrading system. Algal Research, 39, 101467.

Table 1: Conventional characteristics of HTWW obtained from several biomass

Table 2: Summary of AD mediated valorization of diverse HTWW

Table 3: A brief summary of HTL waste valorization using bio-electrochemical approach

Table 4: A brief summary of SCWG mediated utilization of HTWW of various biomass feedstocks

Table 1: Conventional characteristics of HTWW obtained from several biomass

Feedstock	Process condition	pH	COD (g/L)	TOC (g/L)	TN (g/L)	TP (g/L)	Reference
Swine manure	-	6.7		80.8	15.8	0.8	
Rice straw	170-320°C, 0.5-4 h, 10%, -	3.68-5.56	11.35-29.02	3.92-10.27	-	-	Chen et al. (2017)
Cornstalk	260°C, 0 h, 20%, -	-	76.19	28.6	-	-	Si et al. (2016)
Swine manure	-	5.6	104.1	-	5.36	1.00	Zhou et al. (2015)
Human faeces	280°C, 1 h, 20%, -	-	52.6	-	1.16	-	Watson et al. (2017)
Tropical Peat	380^{0}C, 25.1 MPa	2.8-4.5		7.5			Mursito et al., (2010)
Dairy Manure	300^{0}C, 10%,	4.4	32.3	-	1.05	0.48	Bauer et al. (2018)
Corn stover	300^{0}C, 9.6-14.5.5 %	4.4	54-74	-			
Pine		4.5-5.4	40-55				
Municipal Sludge	225 – 275^{0}C, 15-60 min	-	-	-	47-66 (%)*		Aida et al. (2016)
Extracted Grain		6.2	55.9			0.46	
Primary Sludge		6.4	40.8			0.02	
Poultry Litter	180-250^{0}C, 5-60 min	5.1-6.5			1.14-2.9	0.29-2.59	Mau et al. (2016
Corn Stover	350^{0}C, 20.7 MPa	4.4-5.4	41-77			<0.8-3.5	
Food industry waste	331-349°C, 2.1-8 L/L-h, -	4.7-7.5	55.9-110.4	-	-	-	Maddi et al. (2017)
Pine forest product residual		4.4-5.4	41-77			<0.8	
Model Food waste	200-350°C, 2.5-20 MPa		2.5- 4				Posmaknik et al. (2017)
Paper	-	2.7	24.8-47.9				Weiner et al. (2014)

Table 2: Summary of AD mediated valorization of diverse HTWW

Source of wastewater	COD content of wastewater	Anaerobic digestion conditions	Methane production (mL/gCOD)	COD removal efficiency	Possible inhibitors	Remarks	References
HTC, digestate, 220 °C, 4 h (>180 °C)	----	Batch, 38 °C, >15 d	16.3 mL/g biomass	----	----	----	(Oliveira et al., 2013)
HTC, maize silage, 220 °C, 6 h	1 g/(L/d)	Continuous, CSTR, 37 °C, 42 d	236	75%	----	----	(Wirth and Mumme, 2014)
HTL, rice straw, 280 °C, 30 min	0.75 g/L	Batch, 37 °C, 27 d	184	----	----	----	(Chen et al., 2016)
HTL, rice straw, 200–320 °C, 0.5–4 h	0.75 g/L	Batch, 37 °C, 31 d	217–314	----	Phenols furan, and 5-HMF.	Long lag phase, high HTL temperature, and long residence time result in aqueous phase with high inhibitors.	(Chen et al., 2017)
HTL, cornstalk, 260 °C, 0 mi	0–8 g/L	Two stage continuous, PBR/UASB, 37 °C, HRT 0.5 d	H_2, 0–147; CH_4, 158–302		Furfural, 5-HMF	Furfural, 5-HMF can be degraded via two-stage fermentation process.	(Si et al., 2016)
HTL, modelled biomass, 200–350 °C, 20 min	4 g/L	Batch, 37 °C, 30 d	41–314	31.4–52.8%	5-hydroxymethyl-furfural (5-HMF) and levulinic acid.	Inhibition can be minimized by lowering lignin content and at low HTL temperature.	(Posmanik et al., 2017)
HTC, food waste, 260	----	Batch, 37 °C, 45 d	57.5	----	----	----	(Zhao et al., 2018)

°C, 4 h							
HTL, swine manure, 270 °C, 60 min	10 g/L	Batch, 37 °C, 50 d	135	43.7	N-heterocyclic compounds and Phenols	Ozonation mediated fully translation of phenols and partial conversion of N-heterocyclic compounds to acids.	(Yang et al., 2018)
HTC, dry sludge, 208 °C, 60 min	5–12.5 g/L	Batch, 35 °C, 45 d	166–237	----	Ammonia nitrogen and volatile fatty acids (VFA)	AD efficiency can be affected by inoculum to substrate ratios and inoculum concentrations	(Villamil et al., 2018)
HTC, dewatered sewage sludge, 170 °C, 30 min	0.75 g/L	Batch, 37 °C, 9.5 d	286	----	----	----	(Chen et al., 2019)
HTL, swine manure, 270 °C, 60 min	20 g/L	Batch, 37 °C, 98 d	111*	44%*	----	----	(Si et al., 2019a)
HTL, human feces, 280 °C, 60 min	1–10 g/L	Two-stage batch, 37 °C, HRT 6 d (H_2)/20 d (CH_4)	H_2, 13–29; CH_4, 228–274	----	----	----	(Si et al., 2019b)

***- Pretreatment, AP- aqueous phase, AD- anaerobic digestion, COD- chemical oxygen demand, HRT- hydraulic retention time, HTC- hydrothermal carbonization, HTL- hydrothermal liquefaction, VS- volatile solids.**

Table 3: A brief summary of HTL waste valorisation using bio electrochemical approach

Organic Source with COD rate	Anode/cathode	Portrayal of MFC/MEC Reactor	Operating condition and output	Reference
Organic phase from HTL of cornstalk at 312 °C with 2.41 g/(L/d) of COD	Carbon fiber felt and multi-walled carbon nanotubes/carbon fiber felt	Fixed-bed MFC with two-chambers	Rates of organic loading: 2.41 g/L/d, Electricity production: 680 mW/m^3	Liu et al., 2015
The mixture of HTL waste from wood and municipal wastewater with COD 2.5 g/L	Carbon- fiber brush/carbon paper with four Polytetrafluoroethylene diffusion layers and a Pt catalyst layer	Air-cathode MFC with Single-chamber	2.5 g COD/L of Organic loading, Electricity production: 360 mW/m^2	Toczyłowska- Mamińska et al., 2018
Waste from wood HTL With COD 3.34 g/L	The same as above	MFC with Single-chamber	3.34 g COD/L of Organic loading Electricity Production: 71 mW/m2	Toczyłowska- Mamińska et al., 2018
Organic waste from HTL of swine manure with 3 g/L of COD	Carbon fiber felt with granules of activated carbon /nickel foam	Fixed-bed MEC with Two-chamber	Organic loading 3 g/L/d, Voltage: 1.2 V H_2 Production: 168.01 mL/L/d	Shen et al., 2018
Organic phases from cornstalk HTL at 312 °C with COD 2 g/(L/d)	CNTs/carbon fibre felt	fixed-bed MEC with two-chamber	2 g/L/d of Organic loading rates, Voltage: 1.0 V, H_2 Production:	Shen et al., 2017

Organic phases from cornstalk HTL at 312 °C with COD 10 g/(L/d)	CNTs/carbon fibre felt	fixed-bed MEC with two-chamber	3.92 mL/L/d 2 g/L/d of Organic loading rates, Voltage: 1.0 V, 826.87 mL/L·d of CH_4 production (at TOC 10 g/L/d)	Shen et al., 2017

Table 4: A brief summary of SCWG mediated utilization of HTWW of various biomassfeedstocks

Source of wastewater	Process conditions	Catalyst	H_2 (%v/v)	CH_4 (%v/v)	CO_2 (%v/v)	CO (%v/v)	Carbon conversion efficiency (%)	References
Pyrocatechol	300–700 °C, 20-40 MPa, 0.25–4 min	KOH	5-47	9-10	18-40	45-0	-	Kruse et al. (2000)
Polyvinyl alcohol-contaminated wastewater	500–600 °C, 20–36 MPa 20–60 s	KOH	30-49	11-37.25	12.91-27.51	40-1	95.92	Yan et al. (2007)
Sewage sludge	700°C, 24 MPa, Weight hourly space velocity ~ 2.5/hour	None RuNi/γ-Al2O3 RuNi/AC	44.7 48.5 54.9	15.8 14.6 12.1	35.0 32.3 30.2	0.7 1.6 0.4	90.1 96.6 92.4	Zhang et al. (2011)
Oily wastewater	500–700 °C, 30 MPa, 180–220 s	KOH	34-78.3	9-38	12-30	0.0	8-98	Zhiyong and Xiuyi (2015)
Black Liquor Wastewater	550 °C, 25 MPa, 0.2 min, No	None	34-45	15-16	28-35	20.14-0.14	15–77	Cao et al. (2015)
Human feces	400–600 °C, 3 MPa, 30 min	Raney Ni/Ru	28-57	4-20	37-55	1.6-5	24-58	Watson et al. (2017)
Human feces	350-500 °C, 3 MPa, 15 to 90 min	Ni-Ru/AC	24.2-38.6	10.2-32.1	-	-	-	Si et al. (2019)

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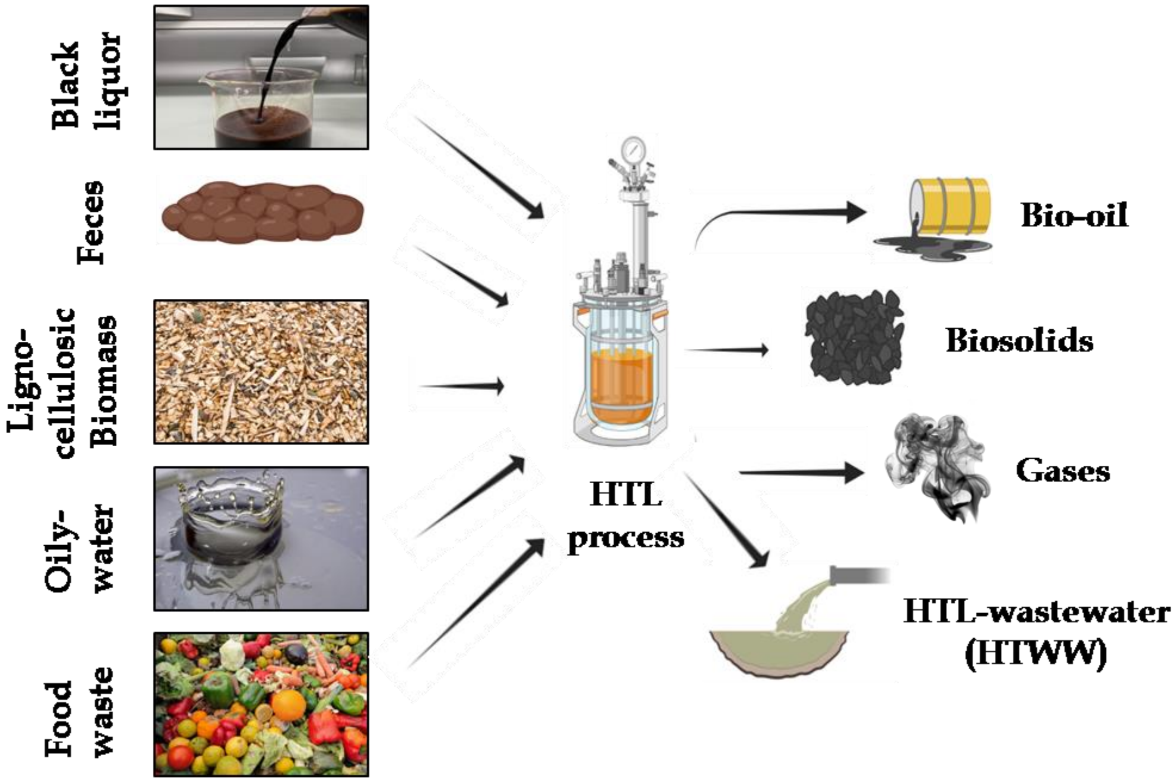

Figure 1: Overview of hydrothermal liquefaction of biomass and other wastes

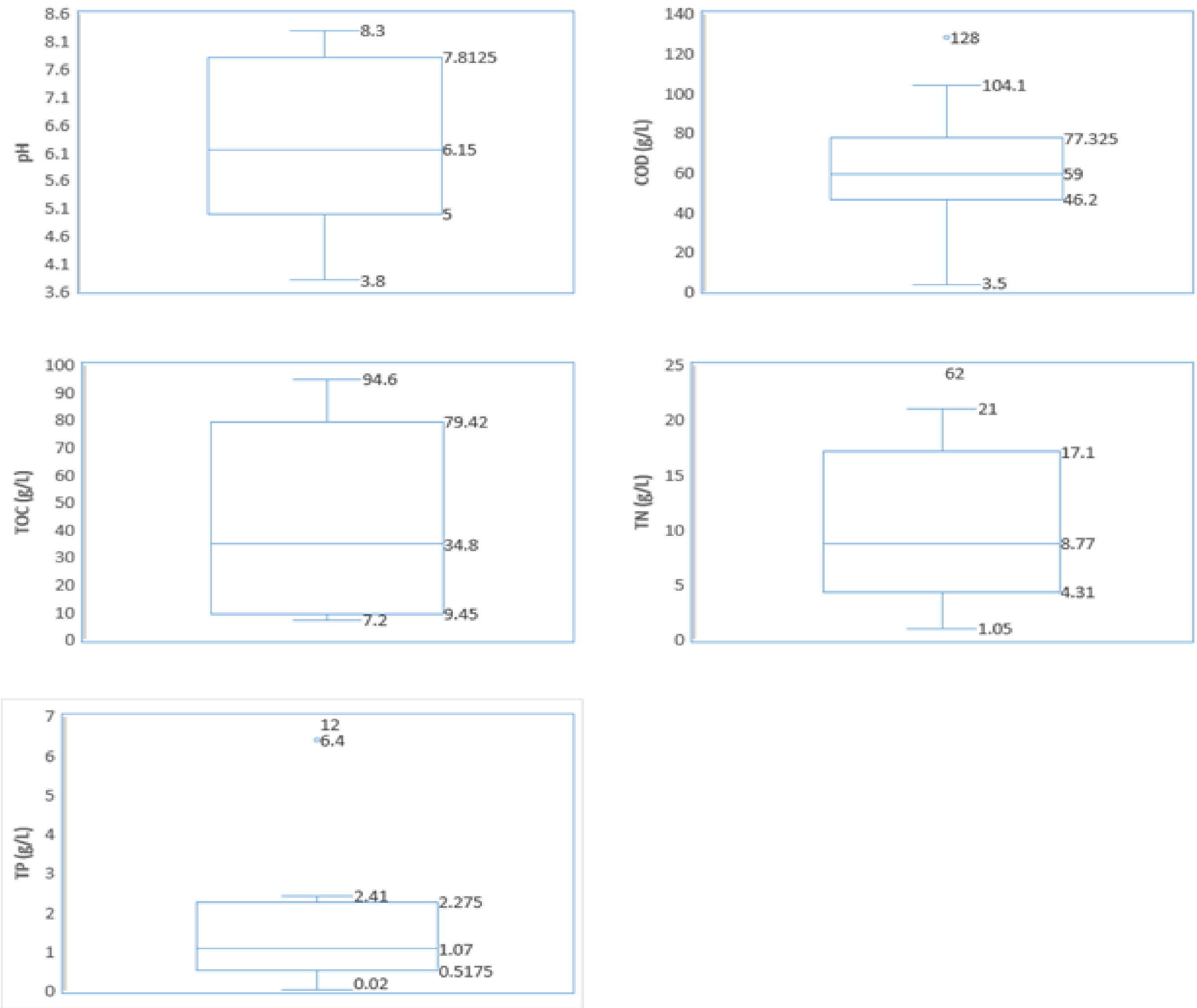

Figure 2: Variations of HTWW parameters (**a**) pH, (**b**) COD, (**c**) TOC, (**d**) TN, (**e**) TP (Summarized from Li et al., 2019; Nazari et al., 2017; Erdogan et al., 2015; Martinez-Fernandez et al., 2017; Stemann et al., 2013; Leng et al., 2018; Leng and Zhou, 2018; Barreiro et al., 2015; Gai et al., 2015; Lu et al., 2017; Watson et al., 2020)

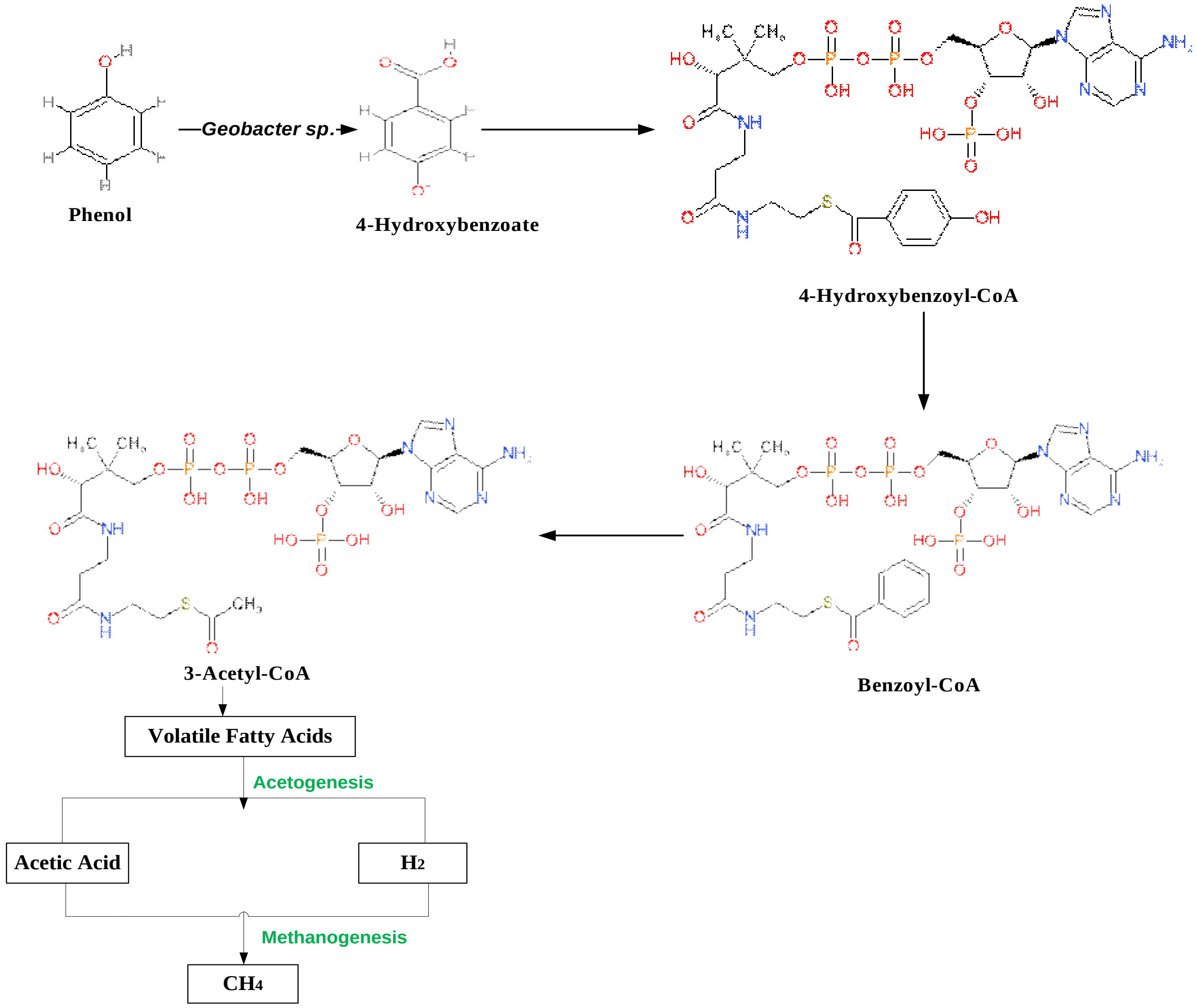

Figure 3: Degradation metabolisms of phenol during anaerobic digestion

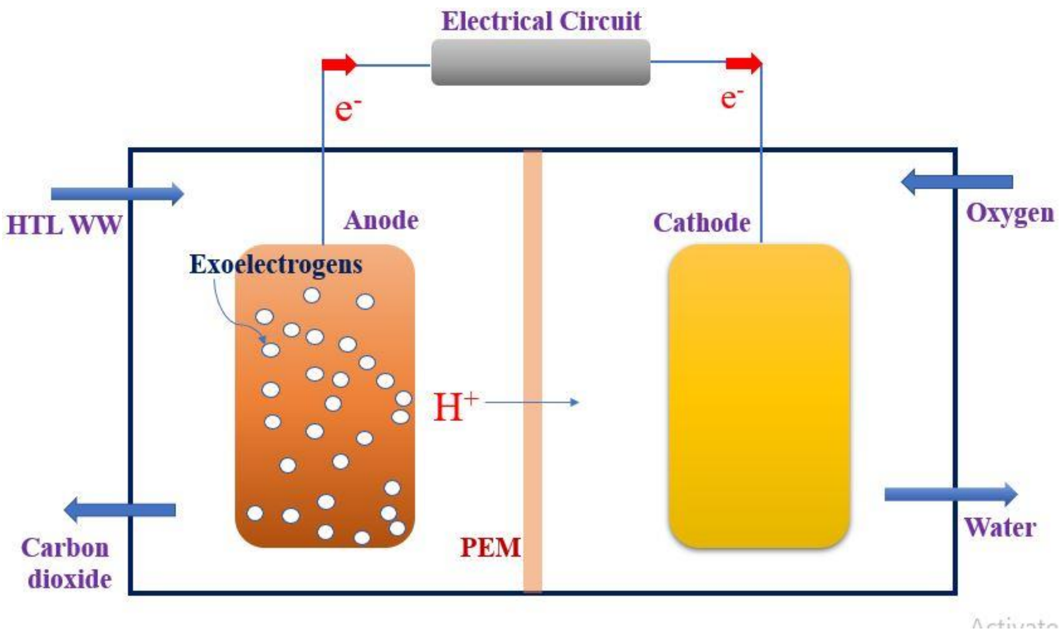

Figure 4: Schematic representation of the MFC system

Valorisation Techniques	Merits	Demerits
HTWW Recycle ~HTWW is recycled to the reactor to act as reactant and solvent. The process can increase biocrude and char production.	- Economical. - No additional reactors required. - High oil yield.	- Economic evaluation of the process lacking; - Accumulation of nutrients.
Microalgal cultivation ~microalgae is grown using the nutrients and carbon present in the HTWW.	- Potent utilization of nutrients; - Potential for a working biorefinery.	- Needs high dilution. - High land area. - Products of relatively low value.
Fermentation/ Anaerobic digestion (AD) ~AD/fermentation of organics in the HTWW lead to production of methane and hydrogen.	- Economical. - Versatile application of HTWW. - Low sludge production. - Bioenergy generation.	- Slow process. - Needs dilution. - Low nutrient removal rate.
Bioelectrochemical systems (BESs) ~HTWW is used as a substrate to generate bioelectricity/biohydrogen.	- Can work with low COD wastewater. - Bioenergy generation. - Employment of nutrients.	- Low energy density; - Uneconomical due to the reactor cost; - Insubstantial nutrients removal.
Supercritical water gasification (SCWG) ~HTWW can be used in SGWG to produce hydrogen rich syngas at an elevated temperature and pressure.	- Effective techniques for decarbonization and hydrogen economy. - Rapid reaction and highly efficient organic conversion.	- Extreme reaction conditions; - Uneconomical due to the reactor cost; - Precipitation of the salt.

Figure 5: Merits and demerits of various HTWW valorisation techniques (modified from Leng et al., 2020; Watson et al., 2020).

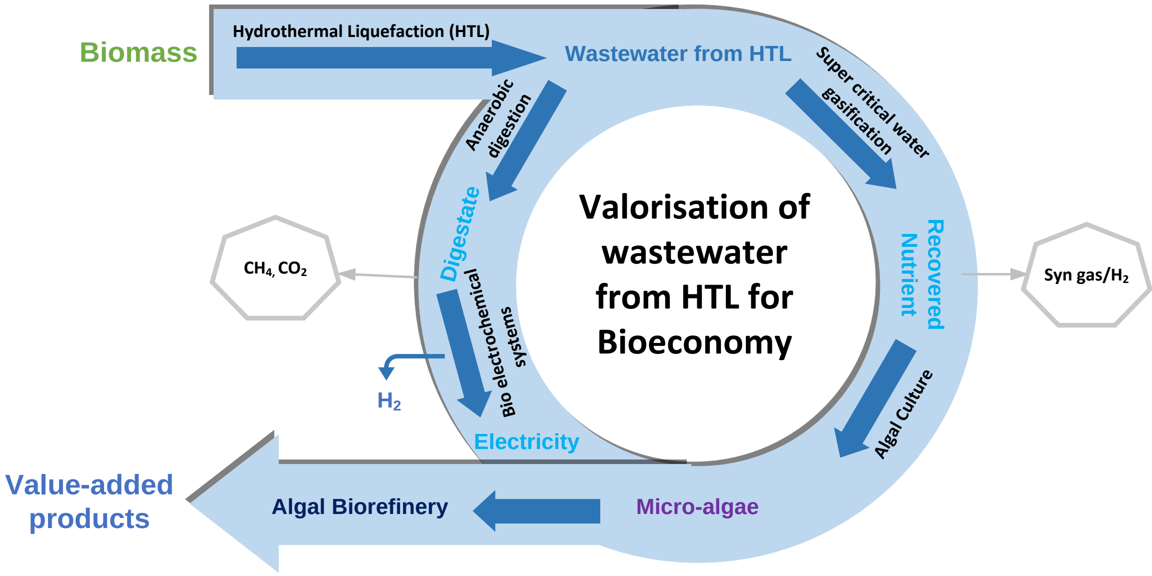

Figure 6: Schematic representation of possible valorisation of HTWW for a future circular bioeconomy