Hydrothermal liquefaction of sewage sludge for biofuel application: A review on fundamentals, current challenges and strategies

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ABSTRACT

Scientific studies have demonstrated that hydrothermal liquefaction (HTL) can be suggested as a cost-effective and eco-friendly solution for the valorization of sewage sludge in the fields of waste management and renewable energy production. On-going efforts are continued extensively to improve conversion efficiency in order to transform this technology into industrial application. The present review focuses on state-of-the-art of HTL of sewage sludge, systematically, the HTL fundamentals, the influences of the essential operation parameters, main existing challenges and integrated upgrading are evaluated in detail. Opportunities and strategies including pretreatment, co-liquefaction, post-application of aqueous and solid phases are addressed. Additionally, some available results regarding the continuous-flow tests of sewage sludge are summarized. Finally, further considerations and recommendations are made for improving or completing the economic feasibility of HTL process.

1. Introduction

Sewage sludge (SS) is the by-product of wastewater treatment plant, and generated in large quantities during waste water treatment. With the rapidly rising urban population and demand for better treatment of sewage, there is a drastic increase in SS generation. Recently, the annual SS production has been estimated at 20 million Mg (dry matter) and 10 million Mg in China and Europe, respectively [1,2]. The ever-increasing amount of SS has intensified environmental challenges, including waste management and environmental pollution issues. A development in sustainable treatment of SS has become an urgent concern globally. Previous reports show that landfilling, composting, and combustion do not only create environmental problems but also waste renewable materials. This creates a need to substitute traditional ways of disposal, for which a multitude of technologies have been proposed. Besides, initiatives for the reduction of CO_2 emissions are driving society to find alternative sources to supply an ever-growing demand for fuel products, providing an opportunity to view SS as a source of carbon and energy.

In recent decades, hydrothermal conversion process is considered one of the most promising technologies to produce renewable energy and value-added products from waste residue. In hydrothermal conversion, water is an important reactant and catalyst, and thus the organic components can be directly converted without a drying step, which can be observed in competing thermal technologies such as pyrolysis and incineration. hydrothermal liquefaction (HTL) has been suggested an effective approach for the valorization of SS. HTL is the process where biomass undergoes thermochemical decomposition in an inert atmosphere, and produce liquid bio-crude at elevated temperatures and heating rates, with relatively short reaction times [3,4]. Moreover, HTL enables efficient energy recovery from the waste SS, avoiding competition between bioenergy production from farmland and food supply.

With increasing attentions paid to the emerging valorization of SS, some reviews on the waste-to energy conversion and HTL process are available in the current literatures, as listed in Table 1. Toor et al. [5] reviewed the HTL of biomass, with focus on the model compounds and catalysts, pointing out rare information related to SS. Jing et al. [6], Manara et al. [7] and Syed-Hassan et al. [8] successively reviewed the direct thermochemical liquefaction of SS for oil production, providing deeper understanding to the comparison between pyrolysis, liquefaction and gasification. The published reviews emphasized more on the processing concepts, in-depth process descriptions, fundamental reaction pathways, and effects on the reaction conditions [1,9–11]. Regarding the overviews on HTL of biomass or the related processing include co-liquefaction and upgrading, many papers can be found in the field of model compounds, woody biomass and algae [12–15], less information

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Table 1
Reported review literature on HTL of biomass for bio-crude production.

| Subjects	Focused of review	Ref.
Model compounds and biomass	Woody biomass and algae, catalyst effects, nutrients recovery	[5,15, 22]
Thermochemical liquefaction of SS	Comparison between pyrolysis and liquefaction or gasification, focus on fundamental principles and operating conditions	[1,7,8, 11]
hydrothermal treatments of municipal SS	Comparison chemical reactions pathways and the effect of reaction parameters between HTC, HTL and HTG	[2,16]
Co-HTL of biomass	Influence of parameters, interaction pathways for the blending biomasses	[12, 13,23]

can be found with the focus on SS (see Table 2).

Although, Zhang et al. [16] and Djandja et al. [2] systematically reviewed the findings emerged from hydrothermal treatments of municipal SS. It revealed the focus on the related chemical reactions pathways and the effect of reaction parameters from hydrothermal carbonization (HTC), HTL and hydrothermal gasification (HTG). However, a review with an emphasis on the challenges and developed strategies in HTL of SS is still not available. Recently, significant progresses have been made on pre-treatment [17,18], integrated process [3,19], post-treatment including upgrading [20] and the applications of side products [21], which can provide valuable information and useful tools to investigate the whole-chain process with the aim to maximize the bioenergy from SS. Unfortunately, no review article on these topics is provided.

This paper therefore aims to provide an in-depth overview on HTL of SS based on existing knowledge and recent development in the field. The integration of pre-processing step such as physical-chemical treatment, as well as alternative post-treatment of end products, are also discussed. The review begins with a brief introduction of SS production, conventional disposal practices. Then, the paper focuses on the dedicated details related to HTL of SS. Finally, this paper provides insights into the future of HTL of SS and new development strategies. This paper, however, does not provide detailed economic evaluation of this technology.

2. A brief review on the production and treatment of sewage sludge

2.1. Sewage sludge production

SS is the semisolid, or slurry residual material that commonly classified as primary and secondary sludge. The production of SS from waste water treatment plant (WWTP) is shown in Fig. 1. Primary sludge is generated from chemical precipitation, sedimentation, while secondary sludge is the activated waste from biological treatment process.
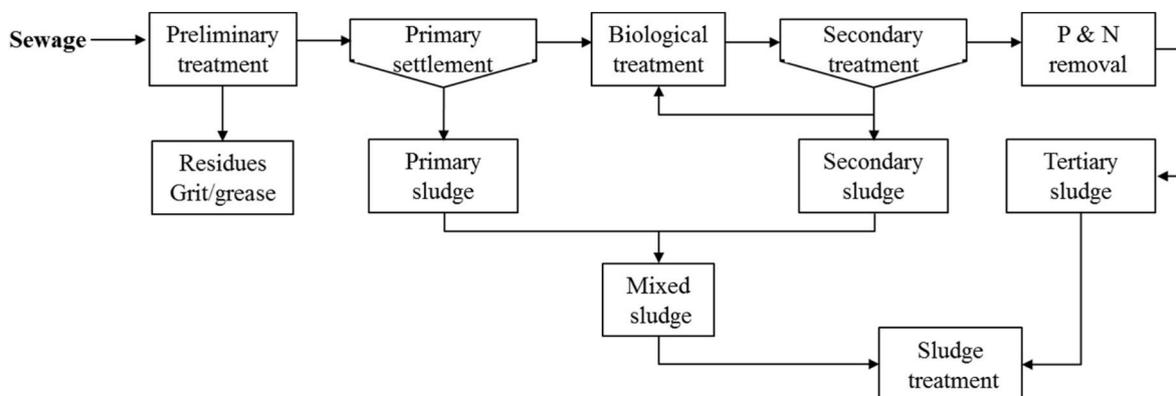
Reducing its volume to decrease the storage cost and stabilizing its organic materials to decrease harmful risks are the two basic goals of treating sludge before final disposal. In most cases, dewatered sludge contains as much as 80% water [24]. SS is composed of inorganic compounds, a large amount of nutrients, organic chemicals, as well as pathogens. It is extremely important to properly treat such sludge in order to minimize its environmental and social impacts.

2.2. Treatment of sewage sludge

A review of different approaches applied for SS treatment is classified in the term of valorization waste into resource and energy recovery. An overall potential route of various treatments of SS is summarized and displayed in Fig. 2.

The use of wastewater sludge as a source for resource recovery is a good alternative for its management considering the circular economy principles. Landfilling and composting are the traditional ways to treat SS. This is because the nitrogen (N) phosphorus (P) and potassium (K) contents of sludge provide high fertilizer value and the organic matter acts as useful organic amendment in the remediation of contaminated sites [25]. However, when compost is used as fertilizer, the pollutants such as heavy metals, microplastics and toxic chemicals can accumulate in the soil and enter the food chain via crop plants. Moreover, dewatering of sludge is an important consideration since composting of any material generally requires a moisture content of less than 60% (wet weight basis) [26].

SS is the potential resource to recover P (typical 1.4% P). According a study for the European Commission around 41% of P in municipal SS is currently recovered and reused in agriculture, so the potential for P recovery of sewage sludge would be 297 kt/a of P for the EU27. In China, the total P concentration in municipal sewage sludge varies significantly, from a 2.2–51.3 g/kg, which is estimated to 167.6 kt/a [27]. P may be efficiently recovered through the precipitation of struvite crystals (ammonium magnesium phosphate) that can be applied directly to farm fields [28].

In addition, due to the carbonaceous structure of SS, it has been considered a potential feedstock to produce activated carbon by chemical activation and carbonization of the dried sludge. Thus, they can be used as low-cost adsorbents to remove heavy metals and organic pollutants from water and soil [29]. However, carbonization and physical activation did not yield high surface areas as a consequence of the high inorganic content of sludge.

In order to meet the globally growing energy demand and support climate mitigation strategies, the attention to make energy recovery from widespread waste has been increasingly paid to the disposal of SS. The energy content of dried SS reported varies between 11 and 22 MJ/kg, which indicates comparable calorific values in comparison to various biomass samples [1]. The energy conversion technologies include lipids
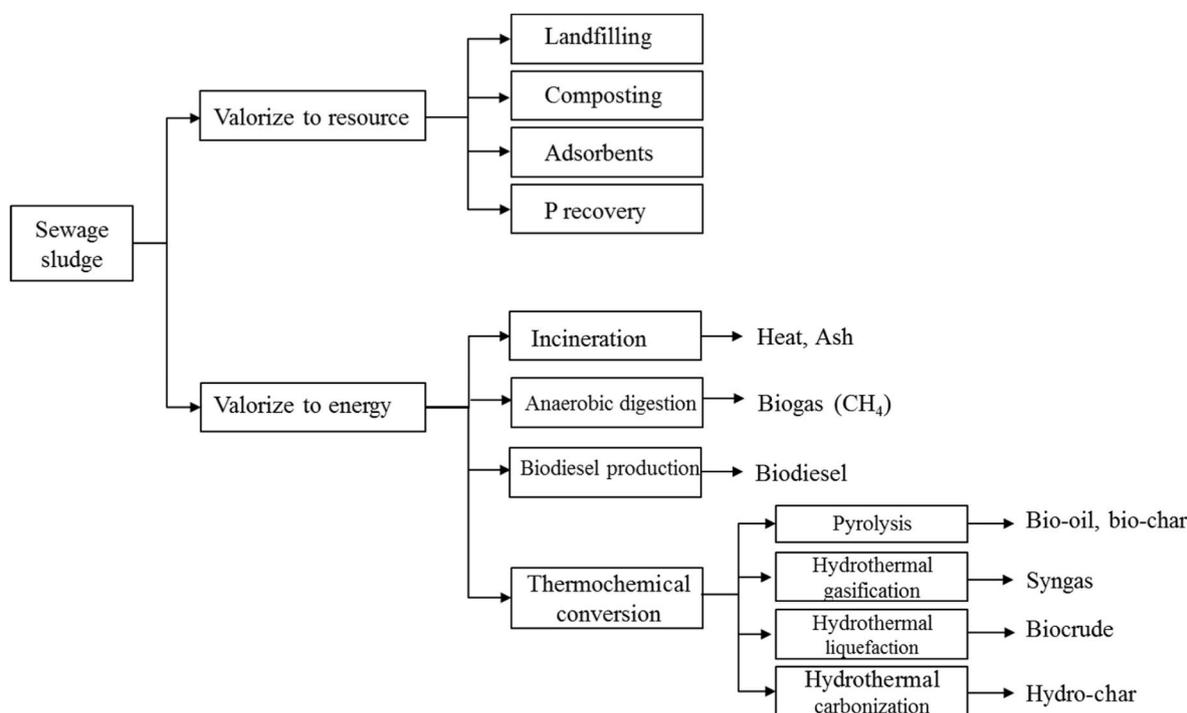

Fig. 1. Flow chart of wastewater treatment and sludge generation, adapted from [7,8].

Fig. 2. Potential sewage sludge to resource and energy recovery routes [1,8].

extraction, incineration, anaerobic digestion (AD), as well as thermo-chemical conversion.

SS is considered a cost-effective alternative for raw biodiesel materials because it contains an abundant amount of lipids, typically in the range of 20% (daf.). The average yield of methyl esters from the SS lipids is 24%, the total average of saturated fatty acids reaches as high as 55% [30–32]. However, lipid extraction from sludge is also expensive and requires large volume of organic solvent and acid catalysts, the exploration to achievable solvent reuse and promising catalyst can significantly improve the economic efficiency. The incineration is the most popular sludge disposal method in Europe, USA and Japan, allowing to reduce its volume and make disposal more economical [33]. However, high content of water in SS limited its combustion, which requires further drying of the dewatered sludge. SS typically must be at least 28–33% solids to burn without external heat to maintain the incineration process. Unlike incineration, anaerobic digestion can avoid drying procedure for valorization of SS. AD, which is a biological conversion method, widely used due to its ability to utilize organic matter for the production of biogas, The methane (CH_4) yield obtained from sludge varies between 80 and 377 mL/g. However, the digestion time is quite long with 7 days to 5 weeks of fermentation time. With the standard digestion process, the conversion efficiency is usually low, only approximately 20–30% of the organic matter is converted [1,34].

Pyrolysis is thermal decomposition of biomass in an inert atmosphere, the operating temperature ranges from 300 to 900 °C, degrading the biomass chemical molecules into bio-oil, fixed carbon, ash and gases [35]. However, pyro-oil has high viscosity and rich in oxygen content, the improvement of pyro-oil quality is necessary. Gasification is the thermochemical process through which carbonaceous content of the fuel is converted to combustible gas, normally hydrogen (H_2). This process involves at temperature ranges from 400 to 1400 °C, with pressure up to 40 MPa [24,36]. However, HTG is getting less attention, the high temperature and heat recovery make the choice of reactor material challenging, and high ash content conversely inhibit complete HTG. In contrast, hydrothermal carbonization (HTC) and HTL processes at temperatures and pressures near and below the critical point (374.2 °C and 22.1 MPa) provide an excellent opportunity for processing SS that contain high water contents. Water is utilized as a reaction medium, acting as solvent and catalytic reagent [2,16]. HTC is a process to convert wet sludge to a carbon-rich material with a heating value like that of lignite. Typical reaction conditions are in the range of 180–220 °C with reaction times from 30 min and several hours. Challenges are that the hydro-char is not stable in soil, fresh material is phytotoxic and fossil coal is too cheap compared to the HTC production costs. However, currently, a drastic increase of research in this field given the no-fuel application of hydro-char as new materials, being applied as super-capacitors or electrode materials for e-mobility [37].

At elevated temperature, HTL therefore stands out as a promising technology as it can convert high-moisture SS to an energy-dense biocrude which could be further refined into transportation fuels. This technology will be reviewed in the following section.

3. Hydrothermal liquefaction of sewage sludge

3.1. Fundamentals of hydrothermal liquefaction

HTL is a thermochemical process in which biomass is decomposed and transformed to liquid, solid and gas fractions in sub- or super-critical water, and sometimes in the presence of organic solvents and/or catalysts. The typical processing medium temperature ranges from 250 °C to 370 °C, while the operating pressure is between 4 and 22 MPa. The wet feedstocks and a supplementary amount of water, in general, are kept in the range 1:10–1:5 (biomass: water weight ratio) [16,38]. When the temperature and pressure are close to the critical point (374 °C, 22 MPa), the physical-chemical properties of water change significantly, including density, dielectric constant, and permittivity, etc. Water, being highly compressed, is still maintained into a liquid state but has a relatively higher ionic product and lower relative permittivity than that at ambient conditions. It can crack cell structures, destroy the meta-stable systems, and modify the equilibrium of their sedimentation in the feedstocks [2]. The combination of elevated pressure and temperature leads to the decrease of density, the hydrogen bonds of water become weaker, and the solubility of non-polar organic compounds increases. The water ions in such condition can facilitate the decomposition of

biopolymers in biomass to further form liquid (bio-crude oil and water-soluble product), gaseous and solid fractions.

3.1.1. Main reaction pathways

Owing to the complex composition of biomass, it is difficult to identify the reaction pathways for bio-crude production. Some of the bio-crude components could originate from the raw feedstocks, while others could be converted through various reactions, such as hydrolysis (e.g., hydrolysis of esters to form carboxylic acids and alcohols, hydrolysis of nitriles to form the corresponding amides), depolymerization, decomposition and recombination of reactive fragments. In detail, when HTL occurs at lower temperature, the biomass firstly undergoes hydrolysis to convert macromolecular organic content into dissoluble intermediates such as 5-hydroxymethyfurfural (HMF), furfural, amino acids and fatty acids. Hot compressed water breaks the bonds of biomass materials at heteroatom sites and hydrolyzes the fragments. The hydrolysis of polysaccharides and proteins begins to occur around 190 °C, hemicellulose and lignin dissolved into liquid phase at 220 °C, the decomposition of remaining lignocellulose takes place at higher temperature [39,40]. Lipids or fats split at 220 °C to glycerol and fatty acids via cleavage reaction [41]. When temperature increases, the decomposition of the monomers takes place by cleavage, dehydration, reverse-aldol defragmentation, decarboxylation and deamination to reactive intermediates, involving the loss of H_2O, CO_2 and NH_3. Dehydration can remove oxygen heteroatom in the form of H_2O. Decarboxylation is the thermal cracking of long chain carboxylic acids, which releases CO_2 and reduces the chain size. Deamination of free amino acids leads to the production of ammonia. As a result, the macromolecules are hydrolyzed to macro form polar oligomers and monomers. The majority of the degradation products such as polar organic molecules, glycolaldehydes, phenols and organic acids are highly soluble in water. At higher temperature, hydrolyzed and depolymerized reactive fragments and products usually undergo secondary reactions to generate bio-crude, aqueous phase, solid products and gases. Major reactions among these are recombination, rearrangement, cyclization, condensation and repolymerization.

The water-soluble intermediates are playing extremely significant role in the distribution of end products and highly depending on the reaction conditions. At slower heating rate, which means longer reaction time at lower temperature, the polymerization and carbonization occur to generate hydro-char, which is barely converted into oily products. On the other hand, those water-soluble organic compounds, converted to heavy oil via dehydration reaction. With the increasing of temperature, usually higher than 350 °C, bio-oil are levelled off then slightly decreased at the expense of higher-molecular compounds in the solid residue formed by condensation and repolymerization of water-soluble products, as well as the hydrocarbon gases generated by cracking reaction [15,38,42].

3.1.2. Model substances

Aiming to have a deeper understanding of the mechanism reaction pathways, model substances are always carried out for HTL. Teri et al. [43] studied hydrothermal conversion of model compounds (corn-starch, cellulose, soy protein, albumin, sunflower oil and castor oil) in a small scale system, and found in these mixtures, the measured bio-oil yields exceeded the mass-average yields calculated from the pure compound results, providing evidence that interactions induced by proteins/amino acids influence the bio-oil yield. However, less information is reported about the interactions between model compounds. Posmanik et al. [44] performed HTL of model compounds (starch, bovine serum albumin and linoleic acid and their binary and ternary mixtures) into bio-oil under different temperatures and retention times. The authors revealed the influence of interactions that occur between these different model compounds based on the change of yields, elemental compositions and higher heating values (HHVs) of the bio-oil obtained from HTL. Fan et al. [45,46] further determined the possible interactions

between carbohydrates, proteins and lipids. They pointed out that Carbohydrates mainly undergo carbonization to produce hydro-char, HTL of an isolated amino acid led to a higher biocrude yield, with the formation of amines and amides by cyclization and dimerization. Maillard reactions (MRs) happening between proteins and carbohydrates affect the mechanistic reaction of bio-crude formation. When adding lysine to lactose or pure HMF, a drastic decrease of HMF is observed. Titirici et al. [47] reported that HMF is the key intermediate, which finally condenses to hydro-char during HTC of hexose-based sugars. The reduction of solid hydro-char and HMF support the theory that MRs have some inhibition effects on the carbonization of sugars by elimination of HMF, as shown in Fig. 3. Instead of polymerization, HMF reacts with the amino acids, reducing the formation of hydro-char. These findings further indicating that the MRs can enhance the bio-crude yields by the depression of carbonization of carbohydrates alone.

Typical Maillard reactions products are formed at 150 °C during the heating up period of HTL, then reached to maximum at 250 °C before 10 min. The polymerization of these products most likely occurs at higher temperatures and longer reaction times, resulting in the formation of macromolecular chemicals. Peterson et al. [48] determined the degradation kinetics of glucose and glycine during hydrothermal conversion. Results show that Maillard-type reactions strongly affected the kinetics at 250 °C. Regarding the effects of lipids, only higher temperatures seem to increase the conversion of lipids into biocrude through the formation of alkanes and alkenes by decarboxylation, which is favorable reaction to improve the quality. However, amide formation between proteins and lipids is also observed as undesired reaction as it contributes to the N content in the bio-crude and decreases the fatty acid yields [49,50].To some extent, this reaction can compete with MRs to modify the distribution of components along in the bio-crude.

A simplified reaction network is summarized and proposed in Fig. 4. However, among the aforementioned HTL studies using model compounds, relatively limited information is available regarding the reaction kinetics between these interactions.

3.2. Influence of process parameters

SS appears to be suitable feedstock for HTL due to its constituents that mainly comprises of proteins (~40%), lipids (~10–25%), carbohydrates (~14%), and ash (~30–50%) [11,51]. Owing to its volatile organic contents, which reported in past literature varies between 21 and 48%, the energy of dried SS range from 11 to 22 MJ/kg, suggesting the comparable calorific values in comparison to various biomass [1]. In addition, it is reported that compared to dry sludge, exploiting wet sludge able to decrease the consumption of energy by 30% [52,53]. To date, different kinds of SS, such as municipal sludge (digested sludge, activated sludge) [2], high-ash containing SS (40.63%) [4], industrial sludge (paper mill sludge) [54]. The different biochemical compositions were revealed in Table 2, biochemical constituents largely influence the amount of biocrude formed through these cross-linked reactions, as demonstrated in section 3.1.

In HTL process for biofuel production, the common desirable product is bio-crude, which can be used as promising candidate for transportation fuel. The objective of HTL is to obtain high yield bio-crude with good quality. The yields of bio-crude from SS are influenced by operation conditions, type of catalysts and solvents. The bio-crude produced from reported HTL varies from 10 to 48% [55–57]. Different from petroleum, bio-crude is a complex mixture of nitrogenated and oxygenated compounds with a wide range of molar mass. Its quality can be characterized by its HHVs, viscosity, density, acidity, stability, molar mass distribution, O/C or H/C ratios and chemical compositions in bio-crude. A general summary of key research on HTL of SS is thoroughly introduced in Table 2. The parameters that mainly influence this process were revealed to be temperature, residence time, pressure, the addition of catalysts (Table 3), solvents (Table 4), biomass to water ratio and others.

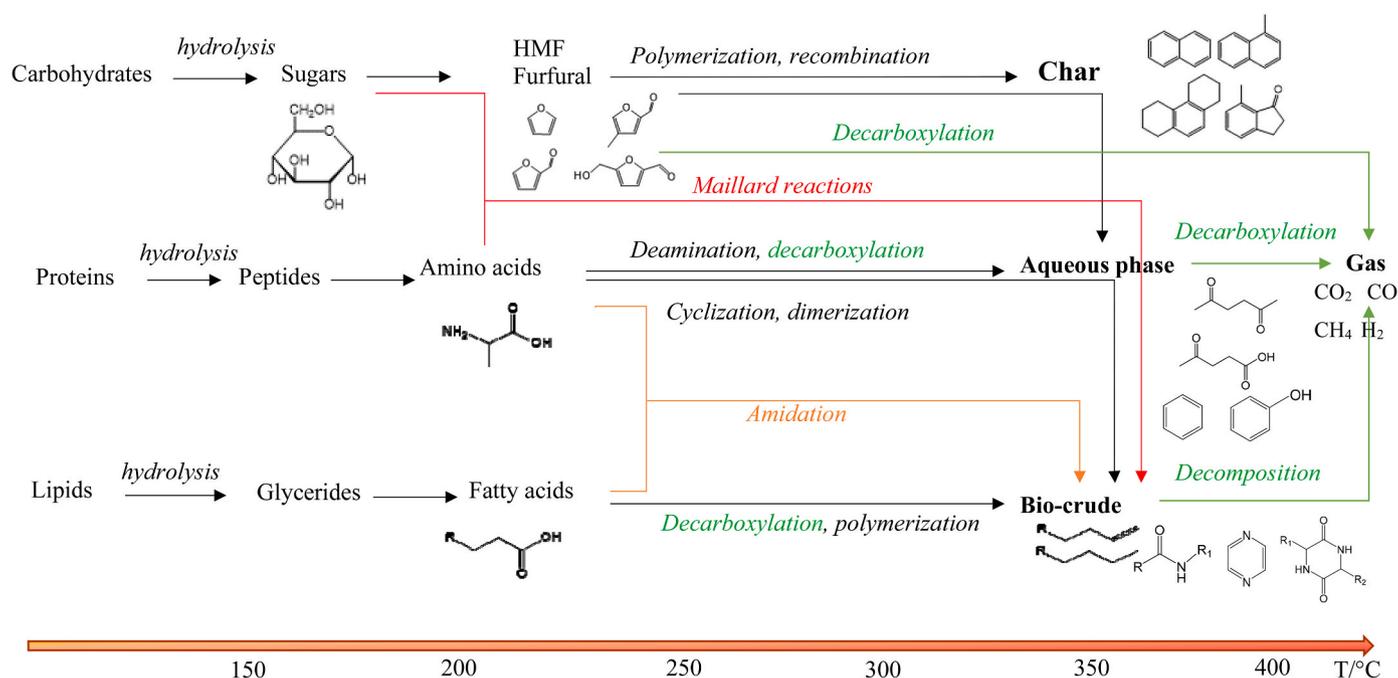**Fig. 3.** Proposed depression of carbonization by adding proteins.

Fig. 4. General reaction network for HTL of sewage sludge, constructed with experimental results and summarized literature resource.

3.2.1. Temperature

Even though many factors can affect the results of the HTL, generally, it is accepted that temperature plays the dominant role in the production of bio-crude. The temperature referred in literatures varies from 200 to 450 °C [38,60,62]. An increase in HTL temperature favors organic compounds hydrolysis and the production of oligomers and monomers through condensation, dehydration, and decarboxylation reactions. At a temperature of 250 °C or higher, proteins, carbohydrates, cellulose, hemicellulose, and lignin degrade, being gradually transformed into bio-crude. While, regarding lipids, which are mostly non-polar compounds with aliphatic characters, chemically, they are referred to as water-insoluble compounds at ambient conditions. Usually higher temperature (>300 °C) are required to obtain cracking reaction [41,63]. Suggestable temperature for hydrothermal liquefaction can be designed higher than 300 °C, when pure water used as reaction medium, lower temperature is favored to produce bio-char, and higher temperature was preferred to gases production. After reaching an optical temperature, the bio-crude yield shows a downward tendency because the liquid intermediates are degraded into smaller fragments, which may be lost during the solvent evaporation process. When the temperature is sufficiently larger than the activation energies for the bond cleavage, the extensive gasification and depolymerization will occur. The secondary decompositions become active, leading to the formation of gases, the occurring of bio-crude cracking reactions to form light gas species. Besides, the repolymerization of oil intermediates into solid residue was also improved at a high temperature, the recombination of free radical reactions results in char formation due to their high concentrations [15].

3.2.2. Residence time

The residence time of HTL process varies between 0 and 480 min [57]. Yokoyama et al. [58,64] firstly investigated the influence of residence time on the bio-crude yields obtained from HTL of several kinds of SS. Results showed that no marked differences in the yields of oils were observed with holding time. Qian et al. [55] compared the influence of heating procedures on the bio-crude compositions using isothermal (673 K, 60 min) and fast (773 K, 1 min) HTL of SS. Bio-crude produced with fast HTL features a lower N/C ratio than that obtained with isothermal HTL, while a longer reaction time results in a higher concentration of N-containing compounds in the bio-crude. Zhuang et al. [61] reported the similar findings that prolonged duration time from 60 to 480 min at 300 °C had slightly effects on the yield of bio-crude. In terms of the products yields and the energy cost, the typical residence times are destined in the range between 5 and 30 min, the increase of residence time leads to higher bio-crude yields. However, beyond a certain threshold, further increase in the time of reaction leads to the opposite results, secondary decomposition and repolymerization of oil fragments result in the decrease of bio-crude. In general, the rate of hydrolysis and decomposition is relatively fast in supercritical processes, the short residence times are expected to degrade organic compounds effectively.

3.2.3. Pressure

Pressure is another parameter to impact the conversion efficiency from HTL of SS. Pressure maintains single-phase media for sub- and supercritical liquefaction, the rate of hydrolysis and biomass dissolution can be controlled. However, once supercritical conditions for liquefaction are achieved, the influence of pressure on the bio-crude yields is

Table 2a

General overview for hydrothermal liquefaction of sewage sludge (Part 1/2).

Categories	Water (%)	Ash (wt%)	Biochemical composition (%) [a]				Temp (°C)	P (MPa)	Time (min)	Reactor	Solvent recovery	Crude yields (%)	HHV$_S$ (MJ/kg)	Energy recovery (%)	Observations	Ref.
			Protein	Fat	CHs[b]	Fiber										
Mixture of primary and waste-activated Sludge	75	16	30	13	24	33	250 – 340	9–18	0–120	autoclave 300 mL	DCM	19.5–50		39.4–82.7	Temperature dominantly effects the biocrude yields, the operating pressure and holding time have no influence on the yield of heavy oils.	[58]
Digested sludge	80.9	43.1	51.1	7.5	35.8	5.6	300	12	0	autoclave 300 mL	DCM	25	>33	–	Raw primary sludge or mixed sludge is the optimum kind of sludge for HTL. The nature of sludge has no significant influence on the elemental compositions and heating values.	[56]
Waste activated sludge	81.9	29.5	59.5	2.7	31.4	6.0						35		–		
Raw primary sludge	79.9	25.9	44.3	16.4	26.5	12.7						44		–		
Raw mixed sludge	74.1	45.5	45.5	14.4	22.7	17.4						42		77.8		
Dewatered sewage sludge	90						350 400			autoclave 300 mL	DCM	14.96–30 9.86–17	37–39	–	350 °C with SSAC-550 favored the oil yield owing to the catalytic effects	[59]
Sewage sludge	80.5	36.68					200 to 350	2–11	10–100	autoclave 500 mL	DCM	38.9–47.8	31.42–35	52.3–67.6	FeSO$_4$ enhances bio-oil production with higher energy recovery at the suitable ratio of SS to water 1/5	[60]
Dewatered sewage sludge	77.87	56.52					150–300		30–480	Tubular reactor 250 mL	DCM			–	Most of N in SS was converted into liquid, gas and oil products; besides, heterocycle-N became dominant in solid phase.	[61]
Secondary sewage sludge	73.39	40.63	43.16	7.79	48.16		350–400	15	autoclave 10 mL	acetone	40.2–45.2	35–36.6	63.4–74.6		The leaching action of citric acid with SS not only removed 40% of ash content but also reduced 38% of the fat content.	[4]

a Dry ash-free basis.

Table 2b
General overview for hydrothermal liquefaction of sewage sludge (Part 1/2).

Categories	Water (%)	Ash (wt%)	Biochemical composition (%)[a]				Temp (°C)	P (MPa)	Time (min)	Reactor	Solvent recovery	Crude yields (%)	HHV$_S$ (MJ/kg)	Energy recovery (%)	Observations	Ref.
			Protein	Fat	CHs[b]	Fiber										
Sewage sludge	85	10.3					400 500	22	60 1	Mini reactor 4.1 mL	DCM Ketone, Hexane, Xylenes, chloroform, Methanol, ethanol, Acetone	12–27	35–40	20–50	Highest bio-crude yield and energy recovery achieved with DCM. Fast HTL produces bio-crude with higher H/C and lower N/C ratio.	[51, 55]
Secondary sewage sludge	84.52	23.01	37.84	8.01	31.14		210–330		0–30	Tubular reactor 600 mL	DCM	17.1–47.5		–	The highest bio-crude yield and HTL conversion was obtained at 270 °C in the present of ethanol as co-solvent.	[57]

[a] Dry ash-free basis.
[b] Carbohydrates.

insignificant. Malins et al. [60] observed that the increase in pressure (2–11 MPa) has negligible influence on the bio-crude yield during HTL of wet SS, energy recovery and total conversion were relatively similar. Qian et al. [55] also found that the bio-crude yield changes very little as the pressure rises from 25 to 40 MPa, which suggests that once the critical pressure of water (22.1 MPa) is reached, the impact of pressure on the properties of water or solvent medium is very small. As a fact, few publications concerning the investigation on pressure can be found in the fields of HTL of either SS or other biomass.

3.2.4. Catalysts

According to the researches summarized above and listed in Table 2, the yields of bio-crude obtained from HTL of SS are relatively low. In order to achieve the higher conversion efficiency of waste into energies, catalysts are often applied into HTL process. The presence of catalysts generally reduces the activation energy and thereby increases oil yields and overall conversion efficiency. Catalysts can reduce the condensation and/or repolymerization reactions of the intermediate products formed by the decomposition of biomass, leading to higher bio-crude and a lower solid residue yield. A summary of catalytic HTL of SS is listed in Table 3.

It is well-known that alkali salts have a positive influence on hydrothermal processes. These were typically water-soluble inorganic compounds, often called, homogeneous catalysts, in the form of alkali salts, such as Na_2CO_3 or KOH. For example, Na_2CO_3 reacts to form sodium formate in the presence of CO, which is generated from organic constituents. A series of subsequent reactions such as dehydration, isomerization, decarbonylation and hydroxylation of organic monomers, result in generation of OH^- and $HCOO^-$ ions that favor further decomposition of hydrocarbon macromolecules. The compounds then rearrange through condensation, cyclization and polymerization leading to complex groups forming the bio-crude. The catalytic effects vary on the chemical components of feedstocks. Shah et al. [4,65] reported that no significant improvement in bio-crude yield was observed after the addition of K_2CO_3, due to the substantial amount of proteins (43%) present in the SS. Similar observations have been illustrated by previous researches. Suzuki et al. [56] and Malins et al. [60] discovered that even 5% loading of Na_2CO_3 could decrease the yield of bio-crude from HTL of SS. Usually, dehydration might result in unsaturated compounds which further polymerize into char. Zhang et al. [54] reported that HCOOH can have higher catalytic effects than KOH and FeS, and that the addition of HCOOH could improve the bio-crude yield from 24.9 to 34.4% at 300 °C. Ross et al. [66] and Prestigiacomo et al. [67] suggested that the decomposition of small chain organic acids can form carbon monoxide and in-situ hydrogen, which further acts as a proton donor to improve bio-crude yield. However, the addition of acetic acid in HTL of SS resulted in a negligible increase (1.5%) in bio-crude yield [66]. Transition metal catalysts, like $CuSO_4$, $ZnSO_4$, $CoSO_4$, and $FeSO_4$ were applied to catalytic HTL of municipal sewage sludge [57,60]. $CuSO_4$ can promote the formation of esters and amides and impede the decarboxylation of fatty acid, leading to a better quality of bio-crude.

Whereas heterogeneous catalysts like Ni-containing catalysts have been so far less frequently utilized in HTL, these are widely used in SCWG of biomass [68]. Previous studies on HTL of biomass in the presence of potential heterogeneous catalysts are rare, mostly applied in algal biomass [69]. Limited information is available on the catalytic liquefaction of SS with the application of heterogeneous catalysts. Qian et al. [55] reported that MoO_3–CoO/c-Al_2O_3 and Ru/C significantly decrease the bio-crude yield when their loadings are 50% of the dried sludge. Recently, Rahman et al. [70] used red mud as catalyst to increase the bio-crude yields by promoting polymerization, the viscosity and heteroatoms was efficiently reduced.

3.2.5. Solvents

During HTL, water was often used as the green solvent and reaction medium. However, the higher critical temperature (373.95 °C) and

Table 3a
Effects of catalysts on HTL of sewage sludge (Part1/2).

Feedstocks	Temp (°C)	Catalyst types	Amount (%)	Yields (%)	Characteristics of bio-crude (%)					HHV (MJ/kg)	Remarks on catalyst effect	Ref.
					C	H	N	O	S			
Digested sludge	300	No catalyst		47	71.4	11	5.3	12.3	–	37.8	Catalyst loading has no significant influence on the properties of heavy oils, owing to some inorganic content in the sludge has a catalytic action.	[56]
		K$_2$CO$_3$	5	43	72.5	11	6.3	10.2	–	38.2		
		K$_2$CO$_3$	20	32	71.9	12.2	4.2	11.7	–	39.7		
Raw mixed sludge	300	No catalyst		40.4	66.03	8.45	6.31	17.9	1.31	31.42	FeSO$_4$ improved the bio-oil yields, however, it also introduced more S-containing compound.	[60]
		Na$_2$CO$_3$	5	38.85	70.24	9.14	5.04	14.43	1.15	33.90		
		Raney nickel	5	42.1	66.17	8.83	6.27	17.51	1.22	31.79		
		FeSO$_4$	5	45.58	71.09	10.29	4.25	12.99	1.38	35.76		
		MoS$_2$	5	40.4	68.12	8.79	4.36	17.20	1.53	32.52		
Raw sludge	300	No catalyst		24.9	70.48	6.82	0.32	22.38	–	29.56	HCOOH shows the most effective effect, due to in situ formation of highly reactive hydrogen atoms or free radicals.	[54]
		HCOOH	5	34.4	69.93	6.85	1.09	22.13	–	29.46		
		KOH	5	31.2	70.15	6.87	0.61	22.37	–	29.52		
		FeS	5	27.7	71.36	6.71	0.56	21.37	–	29.88		
Secondary sludge	270	No catalyst		38.8	69.5	9.4	7.4	9.0	1.4	35.1	CuSO$_4$ promotes the formation of esters and amides and impede the decarboxylation of fatty acid.	[57]
		CuSO$_4$	10	47.5	69.9	9.8	6.3	13.3	0.6	35.2		
		ZnSO$_4$		–	68.0	9.6	7.3	12.5	1	34.4		
		CoSO$_4$		34.1	69.1	9.6	7.2	10.9	0.8	35		
		FeSO$_4$		39.0	69.3	9.2	7.1	13.1	1.3	34.4		

Table 3b
Effects of catalysts on HTL of sewage sludge (Part2/2).

Feedstocks	Temp (°C)	Catalyst types	Amount (%)	Yields (%)	Characteristics of bio-crude (%)					HHV (MJ/kg)	Remarks on catalyst effects	Ref.
					C	H	N	O	S			
Municipal sewage sludge	350	No catalyst		37.1	54.13	6.55	4.26	33.8	1.3	28.3	The reduced red mud lowered acidity and viscosity, but calcined red mud promoted polymerization.	[70]
		Calcined red mud	33		63.32	8.34	4.8	22.64	0.9	29.01		
		Reduced red mud 500	33		54.52	6.95	4.04	33.39	0.95	28.53		
		Reduced red mud 700	33	26.7	53.53	6.98	4.42	33.94	1.18	26.62		
Sewage sludge	400	No catalyst		26.8	-	-	-	-	-	-	The additives examined had little positive effect on the biocrude yield, and thus showed no promise as potential HTL catalysts.	[55]
Sewage sludge	400	K$_2$CO$_3$	10	21.6	-	-	-	-	-	-		
		Na$_2$CO$_3$	10	20.9	-	-	-	-	-	-		
		HCOOH	10	20.7	-	-	-	-	-	-		
		CH$_3$COOH	10	20.8	-	-	-	-	-	-		
		MoO$_3$–CoO/c-Al$_2$O$_3$	10	21.7	-	-	-	-	-	-		
		Ru–C	10	18.9	-	-	-	-	-	-		
Dewatered SS	350	No catalyst		15						37.4	The metallic compounds were the catalytic factor of SSAC obtained at 550 °C (SSAC-550), while carbon was the catalytic factor of SSAC obtained at 650 °C.	[59]
	400			9.9	–	–	–	–	–	–		
	350	SS-based activated carbon (SSAC)	20	15–30	–	–	–	–	–	37.8–37.9		
	400			10–17	–	–	–	–	–	–		

critical pressure (22.06 MPa) of water meant challenging operating conditions and extra energy input [57]. Ethanol and methanol were introduced into the HTL process, this is because that the critical points of ethanol (240.75 °C, 6.14 MPa) and methanol (239.45 °C, 8.09 MPa) are much lower than those of water. Accordingly, they also have a lower dielectric constant compared to water and boiling point [62]. Regarding the additional solvent application, unlike woody or algal biomass [71–75], solely water is often applied during HTL of SS, very few involved alcohol co-solvent, such as ethanol or methanol [57,76,77]. Effects of reaction solvents on HTL of SS has been summarized in Table 4.

Wang et al. [57] employed ethanol mixed with water to liquify SS with catalysts, higher bio-crude yields with better quality were obtained. Optimized operating conditions can reduced N and S content in biocrude by 14.6% and 55.0%, respectively. Adding CuSO$_4$ increased the light-oil like content in biocrude and more than 60% of compounds in biocrude were esters. These can be ascribed to the special advantages of ethanol, on the one hand, as an active hydrogen donor during HTL process, ethanol is a suitable polar protic solvent which favors the unimolecular nucleophilic substitution reaction. On the other hand, ethanol can react with acidic compounds by esterification and provide the biodiesel-like biocrude. Li et al. [77] investigated the influences of mixed solvents, methanol-water and n-hexane-water with SS at 340 °C, and highest bio-crude yield was achieved with methanol-water solvent. Whereas the maximum HHV (36.45 MJ/kg) was detected with n-hexane-water solvent. But these alcohol solvents are mutually soluble with the target product bio-crude, which makes the separation of bio-crude solvent extremely difficult. These organic solvents may cause new types of environmental pollution, besides, the cost of organic solvent itself must be considered.

Table 4
Effects of reaction solvents on bio-crude from HTL of sewage sludge.

Feedstocks	Solvent	Amount	Conditions	Yields (%)	Remarks on the results	Ref.
Secondary sludge	Ethanol-water Ratio (0:10 to 10:0 (v/v))	SS/solvent: 1:3 240 mL	210–330 °C for 0–8 h	17.1–47.5	Ethanol can react with acidic compounds by esterification reaction and provide more esters production (60%).	[57]
secondary sewage sludge	Methanol-water hexane–water (50:50, v/v)	SS/solvent: 1:2.9 200 mL	300–380 °C for 0–60 min	33.2–46.5	Synergic effect of mixed solvents mainly due to the interaction between organic solvents and water during biomass liquefaction. Methanol enhanced the solubility of organic matter and generated free radicals steadily as the hydrogen donor to promote the crude formation.	[77]
municipal sewage	Methanol-water (50:50, v/v)	SS/solvent: 1:4 200 mL	Two-stage First stage: 160–260 °C, 10–40 min Second stage: 340 °C, 40 min	maximum 42.2	Methanol promotes esters production, and extending the residence time under low temperature (first stage) was conducive to the release of organic matter in the extracellular polymer of the sludge.	[78]
dewatered sludge	methanol-water (75:25, v/v)	SS/solvent: 1:2 100 mL	Adding mixed surfactants for pretreatment	23.7–47.6	Subcritical water pretreatment with methanol promotes esterification and deamination, leading to higher biocrude yields and better quality.	[76]

3.2.6. Other parameters

Temperature, residence time, pressure, and catalysts are not the only parameters influencing HTL process, type of feedstocks [79,80], heating rate [81,82], feedstock particle size [9,15] and solvent density [15,55] also have influences on product formation. Heterogeneity in feedstock leads to the modification in bio-crude products in the yields and quality, mostly due to the proportion of different chemical constituents like proteins, carbohydrates and lipids behave differently to hydrothermal temperature variations. In 1988, Suzuki et al. [56] have already compared the HTL efficiency of different kinds of sludge, they observed that raw primary sludge or raw mixed sludge are the optimum feedstocks for liquid oil products in terms of yields, however, the elemental compositions and heating values are independent on the nature of individual sludge. In general, fast heating rates influence the rate of feedstock degradation and devolatilization. Fast heating rates may lead to the formation of highly reactive intermediate species, resulting in the reactive interaction among different produced intermediates at short residence times. Slow heating rates usually lead to char residue formation. Moreover, the liquid oil yield is not very sensitive to large variations in high heating rates. Therefore, the moderate heating rates may be enough to produce high bio-crude yields, meanwhile, to overcome the heat transfer limitations [15].

It is expected that the reduction in particle size can obtain better homogeneity of complex real feedstock, and achieve higher degree of hydrolysis and fragmentation. In terms of HTL of SS, to date, most researches have been performed in a lab scale, the sludge samples were directly treated by a series of pretreatment including drying, mechanical pulverization, screening and then drying again to obtain uniform feedstock. The particles are re-mixed with water to adjust the mixture content based on the designed concentration. The sieved fine particle is usually in a range of 40–150 mesh, with the absolute loading of dry sludge from 0.07 to 50 g [55,59,60]. In some cases, SS was used directly as received raw sludge [39,54]. No comparable research can be found to reveal the influence of the sludge particle size on the bio-crude yields during HTL. One study of Zhang et al. [83] refers to the effect of three different particles sizes (25.4 mm, 2 mm and 0.5 mm) on the liquid oil yield in HTL of grass perennials, and found that particle size reduction did not improve the liquid oil yield at 350 °C, indicating that HTL is relatively insensitive to the size of particle. It is also true that reduction biomass particle size is a costly process to consume additional energy. Hence, an optimum particle size is required to achieve high HTL efficiency at low grinding cost.

The mass ratio of biomass to water is also considered a key parameter in HTL. In general, a high moisture content results in increasing bio-crude yields, most likely, due to the faster SS hydrolysis reaction associated with improved solubility of the organic fragments. At lower water to sludge dry mass ratios, the relative interactions among molecules and water become less active, which can suppress the dissolutions and produce solid residues. However, increasing water content does not always yield high bio-crude amounts, Qian et al. [55] determined the influence of water content ranging from 75 to 97.2% on the HTL products, they observed the maximum bio-crude yields was obtained at 85% water content, the sufficient water content leaded to an decrease of bio-crude with an increase of water-soluble products and gas.

4. Challenges and strategies in HTL of sewage sludge

4.1. Challenges in HTL for biofuel production

Despite all the promising approaches which have been proven to improve the HTL efficiency, some suspending issues still exist within HTL. These need to be resolved before its application on a commercial scale. The relative low quality and heating value of the bio-crude, the management of the aqueous phase and solid residue are the leading challenges related to HTL.

4.1.1. Heteroatoms in bio-crude

In HTL process, the bio-crude should be potentially utilized as drop-in fuel, which is functionally equivalent to petroleum fuels and is fully compatible with existing petroleum infrastructure. This functional equivalence implies that bio-crude must meet existing standards with certain physi-chemical and bulk properties such as miscibility with petroleum fuels, compatibility with fuel performance specifications, good storability, transportability with existing logistics structures and usability within existing engines (vehicles, jet planes, etc.). Chemically, a drop-in biofuel should have low heteroatom content, low water solubility and a high degree of carbon bond saturation. However, the bio-crude itself comes out higher in O, N and S atoms than most refinery streams. The O content in the bio-crude is typically in the range of 8–20%. Excessive amount of O-containing compounds in bio-crude can cause low heating value, instability and high corrosiveness, especially in the presence of high amount of carboxylic acid. These O-containing compounds include organic acids, aldehydes, alcohols, ketones, furans, phenols, guaiacols and other oxygenates [14].

Bio-crude has potentially high N content (0.3–8%) depending on the different feedstocks [61,84]. N in bio-crude is undesirable not only because its lower heating value and the pollution of the atmosphere by NO_X emission during combustion, but also leads to high viscosity and instability of bio-crude [61]. Furthermore, reduction of this N content would increase the cost of downstream processing, since N-containing

heterocycles in the bio-crude are more recalcitrant to hydrotreatment than compounds with aliphatic nitrogen or oxygen heteroatoms. Cyclic nitrogen compounds are particularly problematic during upgrading since they require ring hydrogenation to weaken the C–N bond before cleavage. Additionally, their high basicity can lead to adhesion to acidic active catalyst sites, preventing further hydrotreatment reactions [85]. The high S content in the bio-crude (0.3–1.6%) hampers it as the direct liquid fuel due to the formation and emission of gaseous SO_x and associated acid rain problems. On the other hand, sulfur containing compounds (Benzothiazole, thiophene, 4-methylthiophenol, 4-hydroxythiophenol, and 2-methyl-1-propane-thiol) show a strong tendency either to form particles by nucleation or to attach to existing particles [86,87]. The presence of a sulfur containing compound in the bio-crude may be the significant reason for the deactivation of hydrothermal or upgrading catalysts. Practically, sulfur is known to irreversibly poison the Ru/C catalysts.

4.1.2. Heavy metals in bio-crude

Except the high content of heteroatoms, the high minerals can be problematic. Although some metallic species have positive catalytic effects on HTL, their presence in the SS produces more adverse effects to the HTL process.

As mentioned above, heavy metals (HMs) are a type of inorganic pollutants in SS. After HTL, HMs distributed mainly (>90%) into the solid residue, with less than 10% observed in the biocrude. Leng et al. [88] reported the total concentration of Pb, Zn, Cu and Ni in biocrude were still as high as 6.7, 121.0, 30.6 and 7.9 mg kg-1, respectively, which is undesirably high compared to the regular petro-diesel (0, 0.11–0.14, 0.081–0.097 and 0–0.045 mg kg-1 for Pb, Zn, Cu and Ni, respectively). Shah et al. [4] investigated the migration of HMs during HTL of high ash (40.63%) containing SS, and found that bio-crude contained 3–21% of heavy metals like Cr, Cu, Mn, Pb, Zn, and Ni. Biocrude with high HM contents, if used in the engine, would cause metal emissions into the atmosphere and lead to adverse human effects. The accumulation of metals can lead to slagging, fouling, and corrosion in the combustion boilers [88,89]. Therefore, understanding the migration and transformation of HMs during HTL is significant for the reduction of HMs from bio-crude. The reaction temperature and extraction solvent significantly affected the metal content in the bio-crude. Research reported that liquefaction temperature had a negative effect on the reduction of HM risk in biocrude. Leng et al. [88] found that with the increase of liquefaction temperature (from 280 to 360 °C), the portions of Cu, Pb and Ni distributed in bio-oils increased. The available fraction (acid soluble/exchangeable fraction) of heavy metals in bio-oils will increase with the increase of reaction temperature. In general, high reaction temperature could enhance the extraction effects of heavy metals and thus more portions of heavy metals will be distributed into bio-oils. Huang et al. [90] and Yuan et al. [91] found that the addition of NaOH can enhance the immobilization of heavy metals in solid residue. Yuan et al. [92] investigated the distribution of heavy metals (Pb, Zn, Cu and Ni) in biocrudes obtained from the HTL of SS in different solvents (acetone and ethanol). It has been found that acetone has better performance on the immobilization of HMs compared to ethanol during the liquefaction of SS. The acid soluble/exchangeable fractions of Zn and Ni in bio-oils obtained with acetone as solvent were noticeably lower than those in bio-oils produced in ethanol. Pan et al. [93] also found that pure ethanol facilitates the migration of HMs into biochar products than that from pure water.

4.1.3. Micropollutants and microplastics

Micropollutants and microplastics (MPs) in the SS have been recently become a globe concern to the environment and human health. To date, neither of them has been found in the bio-crude. Thomsen et al. [94] investigated the effect of HTL on bioactive compounds during HTL, the analysis of the HTL products shows no micropollutants found in bio-crude, at least 9 out of 30 pharmaceuticals and 5 out of 7 biocides

are removed with over 98%, indicating HTL is indeed a suitable technology for the destruction of micropollutants. Chand et al. [95] discovered the HTL process of SS led to a microplastics free bio-crude, and reduced the amount of MPs significantly, namely by 76% as particle numbers and 97% as plastic mass. The HTL process was found to decrease the particle size of the more resistant polymers, such as the polyethylene, polypropylene and polyurethane. The HTL process is thus able to not only convert sludge to bio-crude, but also mitigate the issue of the sludge being polluted by MPs, clearly creating residual products with significantly less microplastics. In addition, hydrothermal treatment could block the adsorption of polar microplastics for polar pollutants [96].

Bio-crude is a complex mixture of several hundreds of organic compounds, chiefly containing acids, alcohols, aldehydes, esters, and N-containing compounds. Table 5 shows the physical properties of liquefaction-derived bio-crude from SS as well as heavy petroleum fuel oil [97]. Bio-crude derived from HTL of SS has comparable heating values to petroleum crude, however its undesired properties for fuel applications such as higher water content, O and N content, high viscosity and corrosiveness, making it is commonly considered as the challenge to meet the direct application of transportation fuel. The effects of undesirable characteristics for fuel applications of HTL bio-crude and their possible solutions have been summarized in Table 6.

Therefore, upgrading of bio-crude is inevitable to improve its quality using as liquid fuel. There are varieties of techniques for bio-crude upgrading including physical and chemical methods.

4.2. Post-treatment of bio-crude

4.2.1. Catalytic upgrading

Hydrotreating is an established refinery process to reduce N, O, and S atoms from oil. Catalytic hydrodenitrogenation, hydrodeoxygenation and hydrodesulfurization are required to remove N, O and S in the bio-oil. O is removed as water by catalytic dehydration. N and S are removed as NH_3 and H_2S. The process typically needs hydrogen (35–200 bar H_2) and heterogeneous catalysts (e.g., sulfided Co–Mo, Ni–Mo), to upgrade raw bio-crude at high temperature (300–450 °C) [20].

With hydrotreatment of the sludge derived bio-crude, an increase of the carbon content (77–84%) and hydrogen content (10–15%) in the hydrotreated oils was obtained, a concurrent decrease in nitrogen (4.3 to < 0.05%), oxygen (8.4–1.2%), and sulfur (0.63–23 ppm) content indicate successful upgrading [20]. The moisture content, density, viscosity and ash of the hydrotreated bio-crude are lower than that of the raw bio-crude. Hydrotreating has been already commercialized in oil refineries, however, two disadvantages are still existing. One is the consumption of high-pressure H_2 which needs to develop a sustainable H_2 resource, and high invest of the high-pressure equipment. The other is the coking which reduces the catalyst lifetime by deactivation.

Hydro-cracking is a catalytic cracking thermal process which hydrogenation accompanies cracking in the presence of H_2, which is used to break C–C bonds, aiming to produce lighter products with improved properties. The process takes place at temperatures more than 350 °C and relatively high pressure up to 14 MPa [14]. This process is performed by dual-function catalysts, with at least one acidic function mainly promoting catalytic cracking and a second component promoting hydrogenation. Usually, silica-alumina or zeolite catalysts provide the cracking function, and platinum-tungsten oxide catalyze the reactions, or nickel provides the hydrogenation function. This process might be an effective way to break heavy molecules into large amount of light products, from an economical point of view, it requires higher process cost to reach more severe conditions such as higher temperature and H_2 pressure.

4.2.2. Others kinds of bio-crude conditioning

Some alternative approaches to upgrade bio-crude have been investigated. Polar solvents include methanol, ethanol, ethyl acetate,

Table 5
Comparison of the selected properties of HTL-derived bio-crude and upgrading crude from sewage sludge.

Properties	Heavy petroleum fuel [97,98]	Digested sludge HTL-derived crude [99]	sludge catalytic HTL-derived crude [60]	Primary sludge HTL-derived crude [20,100]	Hydrotreated HTL –derived oil [20,100]
Acid value (mg KOH/g) TAN	N/D	N/D	N/D	65	<0.01
Density (g/cm³)	0.94	0.91 at 50 °C		1 at 40 °C	0.79
Viscosity (cP)	180 at 40 °C	818.3 at 50 °C		571	2.5
HHV (MJ/kg)	40	36.14	31.42–35.76	37.8	N/D
Water content (%)	0.1			13	<0.1
Ash content (%)	0.1	N/D		0.33	N/D
Elemental composition (%)					
C	85	72.51	66.03–71.09	77	84
H	11	9.44	8.45–10.29	10	15
O	1.0	11.09	12.99–17.90	8.4	1.2
N	0.3	6.96	4.25–6.31	4.3	0.05
S		N/D	1.15–1.58	0.63	23 ppm

N/D: Not determined.

Table 6
The main drawbacks of bio-crude with their effects and possible solutions.

Drawback	Effect	Solution
high water content	lowers calorific value, density, stability, and affects catalysts	Phase separation
high viscosity	equipment cost High pumping cost	Solvent addition, blending, Hydro-cracking, Catalytic cracking
high acidity	leading to corrosiveness of pipes and containers	Chemical extraction; Esterification
high O content	lowers calorific value Non-miscibility with hydrocarbons. Low stability	Hydrodeoxygenation
high N content	poisons the catalyst, fuel exhaust contains NOx, foul odor	Hydrotreating Catalytic cracking
high S content	Catalyst poisoning	Hydrotreating
high minerals content	Precipitation, corrosion, Blocking	Demetallization Co-liquefaction
thermal and chemical instability	increased viscosity and stratification	Catalytic cracking

and acetone often used as solvent addition. Reportedly, solvent addition, esterification, emulsification and steam reforming have been investigated as a technique for bio-oil upgrading [101].

The introduction of bio-crude in a refinery distillation unit is still a problematic due to its high inorganic content and acidity. Chiaberge et al. [102] explored the possibility of co-distilling a blend of fossil crude with bio-crude from HTL of SS, and found that reducing the blending ratio or performing specific upgrading pretreatments prior to blending could decreased the recalcitrant compounds in the distilled fractions.

4.3. Integrated processes

It turned out that adjusting these reaction parameters can lead to higher bio-crude yields with better quality. However, these methods are not always economic when a severe reaction environment and expensive catalysts are required. Thus, alternative approaches are highly suggested to improve HTL efficiency and to decrease the severity of reaction conditions. Recently, several studies were conducted in the attempt to improve HTL efficiency of SS by integrating various processes.

4.3.1. Coupling of pre-treatment
Currently, some physical and chemical methods for SS pre-treatment were studied. Kapusta [103] investigated the effects of ultrasound pretreatment on HTL of municipal SS and found that the pretreatment was beneficial for the bio-crude production; a maximum increase of 19% was

achieved at 320 °C compared with un-treated sludge. Chen et al. [104] explored the influence of microwave power (180–900 W) on yield and composition of bio-crude from HTL of SS, where increasing the microwave power can improve the bio-crude yields by between 2 and 10%. These physical pretreatments possibly destroy microbial cell walls and the complex structure of SS effectively. This can increase the concentration of soluble proteins, carbohydrates and lipids to some extent, improving the disintegration.

The effects of inorganic (HCl, HNO$_3$ and H$_2$SO$_4$) and organic acid (HCOOH, CH$_3$COOH and HOOCCOOH) pretreatments on HTL of municipal secondary sludge were also investigated [18,105]. Acids have been proven to have a better performance for HTL efficiency in terms of an increase of bio-crude yields with higher relative content of hydrocarbons. Zimmermann et al. [18] also found the quality evaluating value H/C$_{eff}$ ratio (the effective hydrogen to the carbon ratio) significantly increased to 1.48. To further reduce the content of HMs and immobilize the HMs in biocrude, demetallization was suggested before HTL of SS. Leng et al. [106] implemented demetallization of SS by sequential extraction before HTL. The total concentrations and the acid soluble/exchangeable fraction (F1 fraction, the most toxic heavy metal fraction) of heavy metals (Cu, Cr, Pb, Zn, and Cd) were significantly reduced and the environmental risks of these products were also relived considerably.

Pre-extraction is an integrated process together with HTL, to produce value-added chemicals and biofuel. Each organic fraction accounts less than half of total organic matters, therefore, the residue of SS is still large volume and needs to be utilized to achieve complete utilization. The previous work investigated the possibility of HTL of SS residual after lipid extraction, below 300 °C, similar values are found with and without lipid-extraction, indicating the extracted residue can be further converted into bio-crude [3]. In the fields of algal studies, the interest to HTL of residue from extraction is relatively increasing [107], notable integrated outputs have been achieved. Therefore, it is worthy to investigate the HTL process of residual sludge after extraction.

4.3.2. Co-liquefaction of SS with other feedstocks
Recently, hydrothermal co-liquefaction of various feedstocks has attracted considerable research interest as it aims to increase bio-crude yield with improving quality, to make full use of different kinds of biomass available. One challenge in the production of qualified biocrude using SS is the high moisture content which is usually higher than 85%, co-liquefaction process can reduce water content by introducing dry or less moisture content feedstocks, and by that, also modify the ratios of chemical constituents in the mixed feedstocks.

Many research groups have investigated co-liquefaction SS with other types of feedstocks, about 75% energy recovery can be obtained, as summarized in Table 7. Zhang et al. [54] has determined the

Table 7
Hydrothermal co-liquefaction effect on bio-crude yield from SS mixed with the other biomass.

Mix feedstocks	Conditions	Mixed ratio	yields	Remarks on the effects	Ref.
SS-waste newspaper	250–380 °C for 20 min	0–100%	The highest heavy oil of 26.9% was obtained with the sludge-to-waste newspaper ratio of 1:2.	The synergistic effect on the oil yield owing to the presence of alkali and alkaline earth metals in the sludge.	[54]
SS-biomass filter	340 °C for 20 min	0–100%	At suitable mixing ratio (2:1), The measured yield (47%) was higher than the theoretical yields (36.0%).	Due to the high carbonate and low protein and lipids of SS in the mixture exerted a negative impact on bio-crude production.	[108]
SS-rice straw/ wood sawdust	280–300 °C for 10 min	0–100%	The actual values of bio-oil yield were all slightly lower than the theoretical/calculated values.	The anti-synergistic effects due to the chemical components of SS with high carbohydrate low protein and lipid.	[19]
SS-rice straw/ wood sawdust	300 °C for 20 min	0–100%	The bio-oil yields obtained from co-processing were considerably increased from 22.74% to 26.73%.	The synergistic effects were mainly ascribed to the interactions between lignin and proteins from of the degradation of different components.	[113]
SS- Swine manure (SM)	350 °C for 15 min	0–80%	The highest bio-crude yield (42.38%) via maximum synergistic effect was obtained at ratio SS/SM of 1:1.	Due to the mutual interaction enhanced by the addition of proteins and fat in SS, and the catalytic action of alkali carbonates existed in the form of ash in SS.	[111]
SS-oil tea cake (OTC)	300 °C for 30 min	0–50%	The addition of OTC increased the yield of oil from 37.9% to 86.2%.	The synergistic effect on the oil yield owing to the high free fatty acid in OTC and the catalytic heavy metals enhance bio-crude formation.	[114]
Primary SS-beverage waste	300 °C for 30 min	0–100%	The strongest synergy was obtained with the SS-to- brewery trub ratio of 1:3 and the highest heavy oil was 15.45%.	The high cellulose of beverage waste increased the biocrude yield of their combinations.	[115]

co-liquefaction paper-mill sludge with waste newspaper under different conditions, and found that the optimum heavy oil yield attained was 26.9% at 300 °C. The synergistic effects on bio-crude yield could be attributed to the presence of alkali and alkaline metal ions (Na, K, Ca, etc.) in paper sludge, which could positively catalyze newspaper to produce oily products. Primary sludge was co-liquefied with biomass filter at 340 °C for 20 min by Biller et al. [108], the increased dry matter content of filter cakes (~25%) has been proven to increase the bio-crude yields and energy efficiency of HTL of primary sludge. Fox et al. [109] conducted the hydrothermal co-liquefaction of blended low-value food production waste and low-value municipal sewage sludge at 500 °C after 200 °C pretreatment in supercritical water. This blended waste processing provides recovered gases and liquid fuels containing 37.7 and 40.5 MJ/kg, respectively. Huang et al. [19] investigated the effects of process parameters on the yields/properties of biocrude from co-liquefaction of SS and rice straw/wood sawdust, the bio-crude quality was improved by the reduction of the contents of N and S. Algal biomass was also co-liquefied with sewage sludge [110]. The distillation profile of bio-crude was improved to contain 10.1% and 23.9% of heavy naphtha and kerosene, respectively. Swine manure was also co-liquified with SS under different mixed ratio and temperatures, the highest bio-crude yield (42.38%) via synergistic effect was obtained from HTL at ratio 1:1, owing to the interaction occur between different biochemical compositions [111].

Adedeji et al. [115] investigated SS co-liquefied with beverage waste, a positive synergistic effect in terms of crude yield was observed between co-HTL of brewery trub and SS, leading to a maximum biocrude yield of 15.45%. Co-liquefaction of SS mixed with oil-tea-cake was carried out under the condition of supercritical methanol [114]. Results showed that the addition of oil-tea-cake extraordinarily increased the yields of oil from 37.9% to 86.2%. Furthermore, the bioavailable fraction of Cd and Cu was largely decreased. Leng et al. and Xiao et al. [116, 117] also found that Co-liquefaction SS with lignocellulosic biomass benefited the immobilization of HMs in the biocrude and promoted the distribution of HMs to solid bio-char. The major "immobilization effect" of HMs in MSS may probably result from the dilution effect rather than the synergistic immobilization effect of the mixed biomass. The immobilization of Zn and Cu seems to be from dilution effects, while the adsorption, complexation, and precipitation of Pb, Cd, and Ni during processing may account for part of the synergistic immobilization effects.

Thus, hydrothermal co-liquefaction of SS with other types of biomasses generally improved bio-crude quality by synergistic effects, and the observed additive effects seem to be highly associated with the abundantly available alkaline metals in sludge. The major challenge in the study of co-liquefaction is identified such as understanding of co-liquefaction effect at a molecular level, as well as the remaining undesirable heteroatoms.

4.4. Applications of the side products

4.4.1. Use of the aqueous phase

Despite all the promising approaches which have been proven to improve the HTL efficiency, several issues have limited its development beyond laboratory scale, one of which is the limited energy efficiency. HTL cannot convert and transfer all the organics in the feedstock into bio-crude, leaving abundant amounts of aqueous phase (AQ) products. The aqueous byproduct from HTL of sludge contains significant amounts (20 − 50%) of the biogenic feed carbon, identified compounds include organic acids, alcohols, aldehydes, ketones and nitrogen compounds, and 60–80% of the nutrients from the feedstock are released into aqueous phase [118]. The applications of AQ are summarized in Table 8. Silva et al. [94] has reported chemical oxygen demand (COD) concentrations of the aqueous phase from pilot scale HTL processing range 40000–50000 mg/L, which is two orders of magnitude higher than a typical wastewater treatment influent concentration (typically 200–800 mg/L). The high COD concentrations inhibit the direct streaming back to the WWTP influent. Several studies suggested different technologies for the use of AQ, which includes algae and microbial growth, anaerobic digestion, hydrothermal gasification, electrochemical oxidation and microbial electrolysis [119]. Combined the post-treatment, the AQ may be possible to steam back to the influent of WWTP, making the process more economically feasible. Ovsyannikova and her coworkers creatively recovered the phosphate and ammoniacal nitrogen as struvite from the liquid byproducts from HTL of SS. The obtained struvite has potential for use as a fertilizer based on its elemental composition [21]. Villamil et al. [120] have studied the mesophilic anaerobic co-digestion of the liquid fraction from hydrothermal conversion of dewatered waste activated sludge with primary sewage, methane production decreased as the AQ ratio increased, which can be related to the presence of recalcitrant compounds in water phase, such as alkenes, phenolics, and other oxygen-and nitrogen-bearing aromatics hard-to-degrade through anaerobic digestion. Zhong et al. [121] utilized supercritical water gasification (SCWG) to valorize the AQ from HTL of SS, a simulated aqueous organic waste (composed of glucose, acetic acid and guaiacol) was compared. It found that γ-Al$_2$O$_3$-supported Ni catalyst was effective in catalyzing SCWG of a simulated aqueous phase, but deteriorated rapidly during the SCWG of real waste, this mainly because of the

Table 8
The Summarized treatment of aqueous phase from HTL of SS.

Methods	Aims	Major results	Ref.
Struvite-Producing Unit	Nutrient recovery	The simultaneous recovery of phosphate and ammoniacal nitrogen as struvite was achieved, air-agitated system enhanced the shape and quality of struvite.	[21]
Supercritical water gasification	Syngas	Catalytic SCWG experiments at 700 °C yielded H_2 with 43.1 mol/kg/carbon, γ-Al_2O_3-supported Ni catalyst deteriorated rapidly due to the alkali and nitrogen compounds.	[121]
Hydrothermal liquefaction	Solvents	Energy recovery in the form of bio-crude increased by 50% via aqueous phase recirculation, introducing the N content.	[65]
Electrochemical oxidation	Biohydrogen	The largest chemical oxygen demand removal (99%) and hydrogen production rates were attained at the highest current density.	[122]
Wet oxidation	Chemical oxygen demand reduction and heat production	97.6% of the chemical oxygen demand and 96.1% of the total organic carbon were removed at 350 °C with 180 min.	[123]
Upgrading	Removal phenols and minerals	Hydro-char could remove 100% of guaiacol, phenol and resorcinol present and 61% of vanillyl alcohol in the presence of alkaline metals.	[124]

significant amount of alkali and nitrogen compounds inside deactivated the catalyst activity. The focus on relative energy recovery from aqueous phase has been conducted by Aalborg University [65], obtained results showed that the energy recovery in the form of bio-crude increased by 50% via aqueous phase recirculation into HTL process, however, the N content in the bio-crude was approximately doubled after eight rounds of recycling.

Electro-oxidation was applied to treated the aqueous phase produced from HTL of SS, to simultaneously produce hydrogen and reduce the COD. The largest COD removal (82 and 99%) and hydrogen production rates (2.0 and 1.8 NL/h) were attained at the highest current density [122]. Silva et al. [123] has investigated the non-catalytic wet oxidation for the reduction of organic compounds and heat production in the

aqueous phase from HTL of SS at different temperatures and residence times. the chemical oxygen demand and the total organic carbon can be effectively removed. After an effective utilization and removal of COD, the potential integration of wastewater treatment plant with HTL and other processes can be applied for economic feasibility. A flow chart is displayed in Fig. 5.

In addition, as mentioned before, AQ contains huge amount organic compounds, many are high-value chemicals, including saccharides, monosaccharides, lignin fragments, phenol derivatives, fatty acids, long chain alkanes, esters, ketones and aldehydes. On the one hand, these commonly detected contaminants are pollutants, which make it difficult to recover the recyclable water from AQ. Marx et al. [124] recently upgraded the AQ by adsorption of hydro-char to simultaneously remove minerals and phenolic components. HCl washing of the char removed more alkaline and alkaline earth metals than phenols. On the other hand, if they can be efficiently separated and recovered from the AQ, great economic benefits will achieve while reducing the environmental footprints of the HTL process and the cost of biocrude production. Chromatographic separation with resins have been used to separate phenolic compounds, lignin fragments, furfural and 5-hydroxymethyl-furfural [125], membrane separation used to separate mono-saccharides, acetic acid and aromatic compounds [126]. These methods are barely applied as post-treatment for AQ from HTL of SS, probably due to the complicated composition of water phase and the low concentration of valuable chemicals, resulting in the difficulty to extract pure single component with high efficiency.

4.4.2. Application of solid residue

Solid residue (SR), also called hydro-char, is often overlooked as a side-product although with an organic fraction of char and other nutrient elements. Except bio-crude and AQ obtained from HTL, the SR ranging from 17 to 45% is also a potential end product adding value to the production chain [127]. Sewage sludge has been considered an attractive secondary phosphate source, because the major part of the phosphate obtained from wastewater is transferred to sludge [27]. Ovsyannikova et al. [21,128] have systemically investigated the migration and transformation of P in primary SS by the HTL, half of the phosphorus (46.8%) was distributed in the solid residue, phosphate has been successfully recovered in the form of struvite, which can be further used as fertilizer. The nutrient recovery of N has got more attention recently, since the original SS possesses considerable amounts of N (2.4–9%) after hydrothermal conversion, even most of solid-N was converted into liquid and oil phase during hydrothermal process, still resulting in around 10% of N remained in solid residue, in the form of quaternary-N, pyrrole-N as well as pyridine-N. Thus, the N-rich solid residue may be candidates for the development of slow N-release fertilizers, since the mobilization of their N is expected to be sufficiently low to avoid fast N losses due to leaching or nitrification shortly after fertilizer application [61]. Even though, further studies have to be
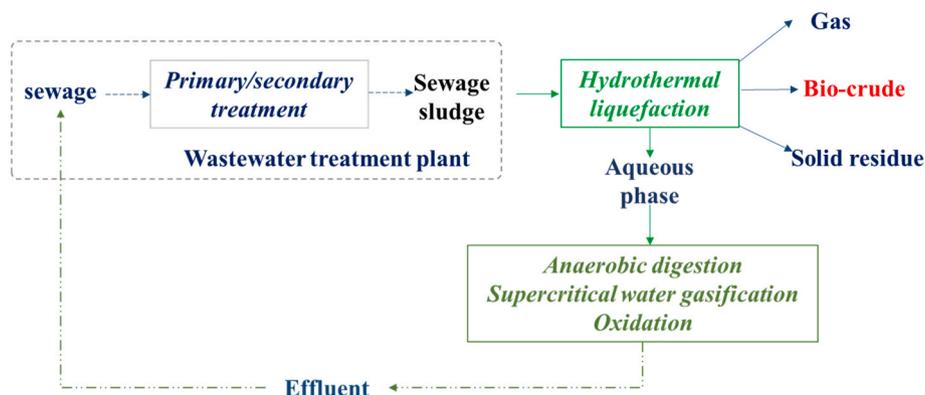
Fig. 5. A proposed flow chart for a potential integration of WWTP with HTL and other processes.

developed to analyze the effects on applying the solid residue as soil amendment/bio-remediation, owning to the toxic heavy metals, as well as the harmful concentrated organic compounds like polycyclic aromatic hydrocarbons [129]. In addition, SR can be used as adsorbent due to its large surface area, porous structure, charged surface, and functional groups including carboxyl, hydroxyl, carbonyl and phenolic hydroxyl groups, to remedy the soils contaminated with organic compounds and heavy metals through adsorption [130].

The gas yields ranged from 2% to 17% for SS based on the HTL operating conditions used. It was mainly affected by the reaction temperature and retention time. Generally, the HTL gas yield significantly increases with an increase in HTL temperature and slightly decreases with an increase in residence time when water is used as the sole solvent. HTL process produces a gas product that can contain both condensable and incondensable gases. More gas is produced from HTL with less condensable gases such as N-heterocyclic components, substituted furans and aromatic compounds [131]. More non-condensable gases reported in the literature mainly contained CO_2, CO, CH_4, and H_2. There were also a few other flammable gases (such as C_2H_4 and C_2H_6) generated in HTL process [89]. CO_2 is the dominant component, which occupied over 90% of the total mass of the gases, suggesting that decomposition and decarboxylation was occurred. The proportion of CO_2 declines, while the percentages of CO, H_2 rise as the temperature increases. This is most likely because the water-shift reactions are enhanced at higher temperatures Furthermore, the formed biocrude and aqueous phase undergo second decomposition and produce more low-molecular-weight hydrocarbons. Among all gaseous products, the produced H_2 can be used to hydrotreating the biocrude, while CO, CO_2, and CH_4 are considered as greenhouse gases and contribute to global warming, a detailed life cycle analysis should be performed to comprehensively evaluate the global warming potential caused by this process. Besides, CO_2 can be used for the microalgae production system.

5. Continuous HTL processing of SS

Although HTL has been widely investigated with promising results, it is still in an early stage of process development. Besides the uncomplete understanding of HTL reaction mechanisms, less competitive, low level biofuel, and exploratory treatment of the side-products, the application of economic, continuous HTL is less demonstrated. The investigation of continuous processing is required for transferring this technology into industrial scale-up (see Table 9). Date back to 1992, Itoh et al. [132] successfully tested the continuous HTL of sewage sludge with a capacity of 500 kg/d, at 270–300 °C, a holding time 0–60 min running more than 700 h without any trouble. Organic maters in the sludge were converted into 40–53% heavy oil. The selection of sludge slurry is needed for further development due to the high concentration and ash content that will largely increase the operation cost and the difficulty for pumping. High-pressure feeding systems for biomass slurries have been recognized as a process development issue. More investment to prepare feedstock like grinding for easier pumping, on the other hand resulting high energy cost penalty. Pacific Northwest National Laboratory (PNNL) has reported 37% yields of bio-crude achieved from 12% dry matter slurries in a continuous stirred stank HTL system [133]. The novel pilot-scale continuous HTL plant incorporated an oscillating flow technology,

developed by Aarhus University in Denmark, has processed algae and sewage sludge with a capacity of up to 100 L/h [134]. Average yields of 25% bio-crude was obtained from HTL of 4% dry primary sludge slurry, at 350 °C for 1 h retention time. However, the low dry content limited the energy recovery to 33%, and around 20% bio-crude was comprised of inorganic solid owing to the separation by gravity. It is accepted that higher dry mater concentration can yield more bio-crude, but pumping and feeding solid suspensions can lead to major plugging issues. Therefore, finding efficient pumping systems is necessary to develop HTL to industrial scales. In addition, the separation between aqueous phase, bio-crude and solid phase is emerging challenge for continuous HTL process. As a fact that the organic acids would catch water into bio-crude phase, while metals like silica and iron would participate into bio-crude, both lead to the lower quality and cause new issues.

Nevertheless, one of the most obvious drawbacks in HTL technology is the high cost in the equipment necessary for industrial scale processes. Corrosion in the subcritical water environment is a critical issue [88]. Despite the current economic and technical concerns, as well as the identified several commercialization bottlenecks, including expensive materials, recycling huge process chemicals, unguaranteed performance, the lack of industry and product standards, a numbers of research groups in corporation with industries are working on the industrial and global commercial developments of HTL.

There are some examples of HTL demonstration plants under developments or in commissioning but limited information on reaction designs, operation conditions and capacities are available. For examples, Genifuel in collaboration with Metro Vancouver and PNNL is developing a pilot HTL plant next to the located WWTP with aim to dispose 2 dry Mg sludge per day [135].

5.1. Future considerations and recommendations

5.1.1. Heteroatoms removal by adsorption

Plenty of studies have shown that the removal of heteroatoms (N, O and S) from bio-crude can be achieved by catalytic hydrotreating, to obtain energy-dense upgraded bio-fuel. However, the need for H_2 consumption at high pressure is still a drawback of this technology. In the case of bio-crude derived from SS, the presence of relatively higher N/S/O-containing compounds would require energy-intensive inputs owing to the frequent deactivation of catalysts. Adsorption would be an alternative option for the removal of problematic heteroatoms both from raw SS and end products. Adsorptive denitrogenation has attracted more attention as an alternative method for the removal of nitrogenous compounds. Adsorptive denitrogenation works on the principle that involves selective adsorption of N-containing compounds onto active adsorbent sites, thus separating them from the remaining oil. Activated carbon shows high adsorptive capacity and selectivity for the removal of nitrogenous compounds (indole and quinolone) from a model diesel fuel, indole and hexadecanamide in the bio-crude derived from pyrolysis of microalgae [136]. The identified specific heterogenous compounds can help to screen cost-effective adsorbents based on their adsorptive selectivity and capacity. However, these atoms removal by reactive absorbent should be accompanied with a simple regeneration process for the adsorbent.

Table 9
Continuous HTL of SS documented in the literature.

Process	Reactor concept	Flow rate (kg/h)	Temp. (°C)	Pressure (bar)	Residence time (min)	Bio-crude yields (%)	Mass balance (%)	Ref.
Organo Co., Japan	Column	15	270–300	60–120	0–60	40–53	–	[132]
PNNL, USA	Stirred + tubular	1.5	300–350	200	18–19	25–37	101–103	[100]
Aarhus University, Denmark	Tubular (pilot), with oscillator	60	350	220	60	25	–	[134]

5.1.2. Renewable nitrogen-heterocycles production

Bio-crude derived from HTL of SS contains considerable amounts of N-containing heterocycles, which are not available from conventional fuel resources. Recently, there has been increasing interest in development of sustainable processes with simple and green approaches to access value-added heteroatom-containing chemicals. Nevertheless, the production of N-containing organic materials could also be a great opportunity for the use of bio-crude. In fact, more attention has been paid to the development of sustainable processes with green approaches to produce value-added N-containing chemicals, especially N-containing heterocycles, such as pyrroles, indoles, and pyrazines which are widely used in the pharmaceutical, agrochemical and polymer industry [137]. However, it must be pointed out that the low concentration of valuable chemicals may result in the difficulty to extract pure functional components with high efficiency. Effective separation and purification should be developed to get bio-based chemicals.

5.1.3. The feasibility of integrated processes

The combination and/or integration of different processes can be considered a valorization route to improve energy recovery. Regarding upgrading, a further focus must be on the direct impact of heteroatom-species and inorganics on the deactivation of catalysts, as well as the design and viability of the upgrading stage. As the implementation of industrial application has already started by some research groups in cooperation with industries, standards of bio-crude and bio-fuel application should be agreed as soon as possible for subsequent research and further development. The side-products must be further utilized. The technical strategies, such as dewatering and stabilizing, should to be effective and economically feasible for high-value applications of hydro-char. In addition, when the integrated process is considered as a new approach to valorize SS into energy and other products, a comprehensive energetic evaluation by energy recovery efficiency, an economical assessment and life cycle analysis is necessary to broadly evaluate its potential industrial application.

5.1.4. Emerging technologies for waste water treatment plant

SS, which traditionally is regarded as end or downstream product from WWTP, appears as suitable feedstock for HTL. Once this technology is commercially applied for bio-fuel or chemical production, at the same time, the WWTP has also been transitioning to prepare for future challenges, such as providing suitable SS with high biochemical property for industrial HTL processing. Many older wastewater treatment facilities require upgrading because of increasingly strict water quality regulations and human health protection, associated technological treatment should be also integrated with emerging technologies for follow-up HTL process.

6. Conclusion

The review provided above reveals the potential of waste SS as a valuable resource and energy carrier. However, the complex composition of SS remains an important limitation due to the high moisture and ash content as well as presence of toxic heavy metals and organic contaminants, which influence the quality of final products, reduce the process efficiency, and increase the overall cost of the applied technology. High water content significantly limits the application in landfilling and composting as the sludge volume requires high capacity; incineration and pyrolysis require energy-intensive pre-drying to improve conversion efficiency. Taking the best advantage of higher water content, hydrothermal conversion is a promising technology to simultaneously achieve disposal and utilization. Compared with HTC and HTG, HTL has been drawing more attention in recent years. Without pre-drying, condensed liquid biocrude can be obtained at relatively low temperatures with reasonable reaction times.

HTL of SS has received increasing attention in the published literature, with considerable amounts of studies being conducted in batch reactors, and more recently, on the development of continuous flow processes. Considerable work can be found to improve the yields and quality of bio-crude by adjusting the reaction parameters. Overall, the initial increase in reaction temperature and time enhanced the formation of bio-crude, whereas beyond a certain point the bio-oil yield tended to be reduced or levelled off. To achieve the highest bio-crude yield, reaction temperature and residence time should be optimized to inhibit the repolymerization and condensation of oily intermediates during HTL. The use of solvents can.

The optimal reaction temperature and time depend on the biomass type and its inherent constituent. Notably, the addition of suitable catalyst with a proper amount can reduce the required reaction temperature and time for bio-oil production. The employing alcohol co-solvent can largely improve biocrude yields and quality under mild conditions compared with pure water system.

The synergic effect of mixed solvents mainly due to the interaction between organic solvents and water during HTL process, alcohol solvent promotes the solubility of organic matter and generates free radicals steadily as the hydrogen donor to promote the bio-crude formation. Ethanol can react with acidic compounds by esterification reaction and provide more esters production, leading to a better bio-crude quality. Considering the high-water content, heavy metals, and low energy density of SS, co-HTL is performed to improve the economic performance of such treatments. The mixing of other materials can supplement the necessary components in the process of producing bio-oil and significantly improve the quality. Co-liquefaction effects, such as simply additive effect, synergistic effect or antagonistic effect, are ascribed on the interaction of intermediates of degraded from biochemical compositions of mixed feedstocks.

Pre-/post treatments are inevitable combined with HTL to improve the bio-crude quality for fuel application. Pre-treatment can facilitate HTL conversion of SS by changing the physical and chemical structures of organic components. Pre-treatment was conducive to the release of organic matter in the extracellular polymer of the sludge, and demetallization can happen during acid leaching. It is preferentially suggested to improve the HTL of SS by a demetallization pretreatment, in ethanol-water mixed solvents by introducing conventional lignocellulosic/algal biomass for co-liquefaction.

Post-treatment like catalytic upgrading for heteroatoms could achieve desirable results, for example, the N content in the upgraded bio-oil can be effectively reduced to 0.1%. however, the cost for sustainable H_2 supply and activated catalysts cannot be ignored. Adsorptive denitrogenation can be considered an alternative method for the removal of nitrogenous compounds. Meanwhile, the side-products, such as nutrient-rich water phase and solid residue, after appropriate treatments, can be achieved as by-products adding value to the production chain, the wastewater may be possible to steam back to the influent of WWTP, thus improving or economic feasibility of HTL process.

It seems apparent that abundant research studies are devoted to fill up the inadequacies of the existing technologies and improve the efficiency, future research still needed to determine technical, environmental, energy and economic feasibility of various possible strategies for HTL process.

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