Review

A review on hydrothermal carbonization of biomass and plastic wastes to energy products

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ABSTRACT

Hydrothermal carbonization (HTC) as a promising thermochemical process can convert organic solid wastes (e. g., biomass, plastics) into valuable products (i.e., hydrochar) at relatively low temperatures (180–250 °C) and saturated pressures (2–10 MPa). Hydrothermal conversion generally occurs via dehydration, polymerization and finally carbonization reactions. The carbon materials derived from hydrochar have high potential in various applications such as solid fuel, supercapacitor, fuel cell, and sorbent. Although the energy densification of hydrochar was increased at higher temperatures, most of the benefit was achieved at modest temperatures. Chemical structures of hydrochars include crosslinks of aromatic polymer, surface porosity, organic functional groups and ultimate components. All of these characteristics can be changed significantly by HTC, influencing the reactivity and fuel properties of hydrochars. The reaction pathways including negative and positive effects during (co)-HTC of biomass and plastic wastes are thoroughly concluded. In particular, the co-HTC of chlorinated plastic (e.g., PVC) and biomass can enhance the dechlorination and inorganics removal from hydrochar.

1. Introduction

Increasing population has led to the increase of organic wastes production, the increase of energy demands and rapid depletion of traditional fossil fuels. Polymeric wastes are regarded as one of the largest groups of organic solid wastes produced world-wide and the rate of generation is increasing steadily. It is critical to consider disposing and transforming polymeric wastes into valuable resources such as energy, alternative fuels, nutrients and other chemicals [1]. Polymeric wastes mainly include natural polymers (e.g., lignocellulose) and synthetic polymers (e.g., plastics) [2]. Natural biomass residues (or bio-wastes) are primarily derived from agro-forestry wastes (e.g., livestock manures, lignocellulosic wastes), industrial wastes (e.g., food processing wastes, fermentation wastes) and municipal wastes (e.g., food wastes, waste papers, woods, sewage sludge). Synthetic polymeric wastes are contributed by industrial wastes and the organic fractions of municipal wastes (e.g., plastics, rubber). For instance, plastics have become a basic support for the modern living style due to their low production cost and wide range of suitable properties (e.g., low density, durability and resistance to corrosion) [3,4]. Plastic wastes management has a great challenge to be addressed because of their low degradability, which causes serious environmental issues [5]. Plastic wastes contain different

polymers with low- and high-density materials, such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS), polycarbonate (PC), etc. [6] Although each of these polymers has different monomer composition with different carbon, oxygen and ash content, the typical feature among them is high volatile content, high viscosity along with low melting points and high energy density due to very low moisture and ash content [7].

It is urgently to develop a generalized, robust, and flexible process for recycling energy and resources to deal with the very large amounts of polymeric wastes. In general, the routes for energy recovery from biomass wastes include biochemical technologies (e.g., anaerobic digestion) for wet substrates [8] and thermochemical technologies (e.g., pyrolysis, gasification) for dry substrates [9,10]. However, plastic wastes are commonly treated by thermochemical technologies [11,12]. Among them, hydrothermal processing (HTP) offers a sustainable and cost-effective solution for disposal and creation of revenue streams from both dry and wet substrates through resource recovery. This process involves the utilization of elevated temperatures and pressures with/-without an oxidizing agent to destroy or solubilize organic wastes [13]. Under these conditions, complex organic wastes (e.g., lignocellulosic biomass) are broken down into simpler organic compounds such as
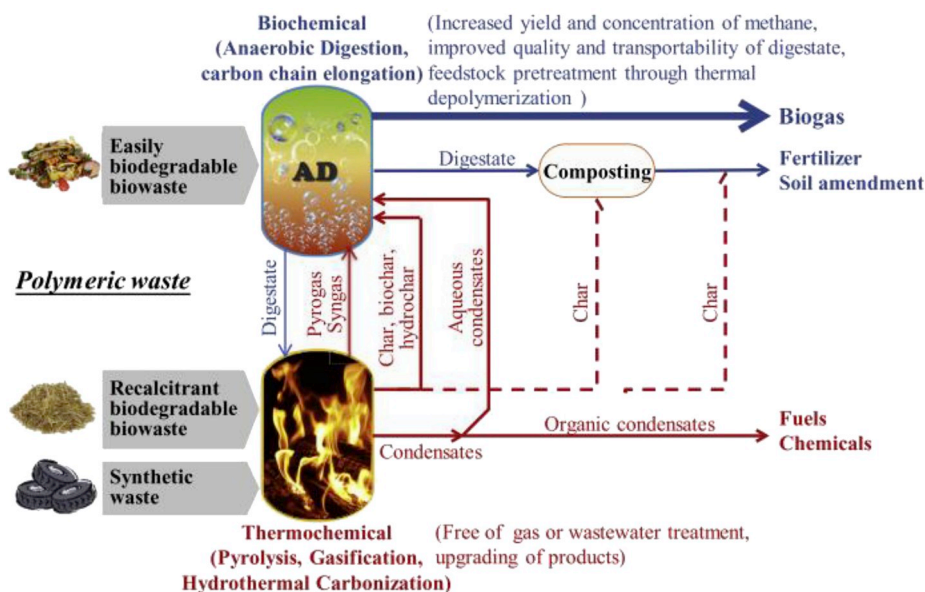
Fig. 1. Flow diagram of the integrated strategy of biochemical and thermochemical process (Copyright with the permission from Ref. [2]).

acetic acids, carboxylic acids, biochar, bio-crude, carbon dioxide and water. In recent decades, HTP has been also used to deal with the very complex municipal solid wastes (MSW) [14–16]. An integrated technology by combining biochemical (e.g., anaerobic digestion, gas fermentation, carbon chain elongation) with thermochemical processes (e.g., HTP, pyrolysis, gasification) has been proposed to enhance the efficiency and stability of biochemical conversion, thus controlling the gas and liquid pollution produced from thermochemical conversion, and sequester carbon (Fig. 1) [2].

HTP can dispose, deconstruct and transform of organic solid wastes into valuable products (e.g., fuels), substantial solid content reduction for more environmentally friendly disposal, and harmful heavy metals removal [15]. The significant advantage of HTP is processing wet wastes without the requirement for an energy-intensive dewatering step [17–19]. Nevertheless, the field of HTP is lack of fundamental data in reaction kinetics and mass transfer. Despite being a scientifically established and known technology, HTP remains predominantly within academia at laboratory or demonstration scales [20]. This process is mostly limited to bench-scale batch systems and needs expensive and complex reactors [21]. Furthermore, industrial HTP is energy intensive. The process modelling and simulation of HTP, especially using commercial process simulators, has lagged behind other processes. The

separation procedures required at the industrial scale are difficult to manage [22].

During HTP, various reactions such as oxidation, hydrolysis, thermal decomposition, and dehydration take place. Here hot compressed water acting as a green reaction medium can convert complex organic compounds into simple-molecular products. Thus far, the HTP of wet biowastes has gained much attention. However, the HTP of plastic wastes has been rarely considered, since the synthetic polymers in absence of water can be treated by the efficient thermochemical technologies such as pyrolysis or gasification. HTP also favors the pretreatment of halogenated plastics, normally co-existing with biomass in municipal solid wastes [23]. The synergistic effects have been found during the co-HTP of biomass and plastics, but the relevant mechanism is required to investigate in depth. Therefore, the review aims at analyzing the existing studies on (co-)HTP of biomass and plastics. It is challenging to establish the research findings due to the variations that arise from different feedstocks and conditions. Main hydrothermal processes with reaction parameters need to be fully understood. section 2 summarizes different HTP depending on the processing temperature and pressure, such as hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), hydrothermal vaporization (HTV), hydrothermal gasification (HTG) and supercritical water gasification (SCWG). section 3 focuses on the
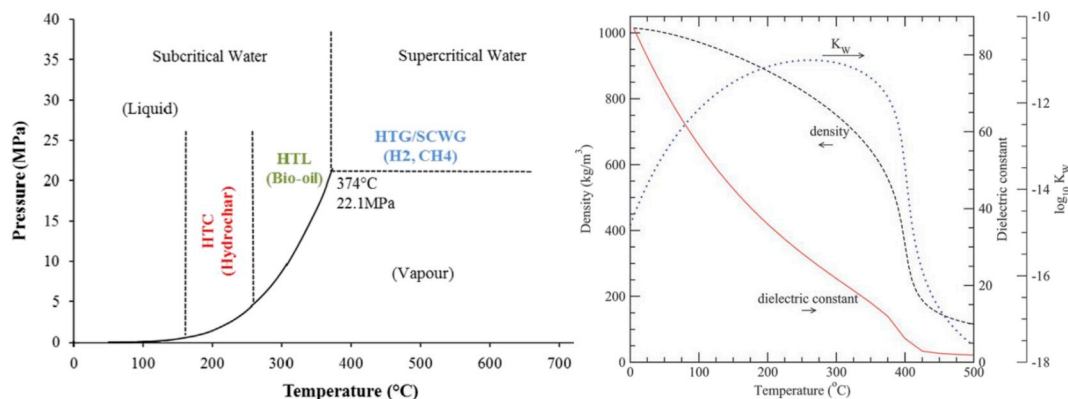

Fig. 2. Classification of HTP of biomass with reference to the pressure-temperature phase diagram of water (**left**) (Copyright with the permission from Ref. [25]); Density, static dielectric constant and ion dissociation constant (K_w) of water at 30 MPa as a function of temperature. The dielectric constant of water drops drastically as it is heated, and approaches that of a (room-temperature) non-polar solvent at supercritical conditions (**right**) (Copyright with the permission from Ref. [24]).

Table 1
Main HTP and different operating conditions for obtaining highly valued products.

Processes	Temperature (T, °C)	Pressure (MPa)	Reaction time	Catalyst	Main products	Ref.
HTC						
Low T	250	2	Several hours	Not essential	Char	[30–32]
High T	250–800	2	Several hours	Optional	Char	[33]
HTL						
Low T	280–370	10–25	Few seconds	Optional	Oil	[34]
High T	300–600	10–25	Few seconds	Alkaline salts: Na_2CO_3, KCl, KOH; Heterogeneous catalysts under high pressure H_2	Increasing oil yield; Improved to transport fuel by increasing C/H ratio	[35]
HTG						
Near-critical	300–500	Various	Few seconds	Metal catalyst and alkaline salts	CH_4	[36]
Supercritical	500–800	Various	Few seconds	Metal catalyst and alkaline salts	Syngas H_2 with minor CO_2, C1–C4 gases	[37,38]
Aqueous phase reforming	220–250	1.5–5	Several hours	Pt/Al_2O_3, Pt/ZrO_2, Rh, Ni and on SiO_2, etc.	H_2 and CO_2 with minor C1–C6 alkanes	[39,40]

fundamentals of HTC using relatively low pressure and temperature. section 4 summarizes the HTC for wastes (biomass wastes in section 4.1 and plastic waste in section 4.2) valorization. And section 5 overviews the challenges of HTC for wastes valorization, including recycling of by-products (section 5.1) and improvement of HTC system (section 5.2).

2. Hydrothermal processes

HTP can be classified into three main regions as shown in Fig. 2 (left): HTC, HTL, and HTV or HTG, or SCWG depending on the processing temperature and pressure [24,25]. HTC (also denoted as wet torre-faction) can convert organic feedstock into a carbon-rich solid product. HTC is conducted at 180–260 °C during which biomass is submerged in water and is heated in a confined system under 2–6 MPa for 5–240 min [26–28]. In usual, the reaction pressure is autogenic with the saturation vapor pressure of subcritical-water corresponding to the reaction temperature. Hydrothermal conversion via the liquefaction pathways occurs generally at 200–370 °C under 4–20 MPa to keep water in a liquid state. At near-critical temperatures (up to 500 °C), effective reforming and gasification requires catalytic enhancement to achieve reasonable rates

and selectivity. At higher temperatures (>500 °C), homogeneous gasification and thermolysis often take place [24]. Three regions take advantage of substantial changes in water properties that occur in the vicinity of its critical point at 374 °C (T_c) and 22 MPa (P_c). From subcritical to supercritical temperatures at pressures above P_c, both the rate of hydrolysis and the solubility of components can be controlled for releasing more chemically and energetically favorable pathways to biofuels (e.g., gas, liquid). In the region near the critical point, water is highly compressible.

The three hydrothermal processes (i.e., HTC, HTL, and HTG) of biomass conversion to desired energy products and different operating parameters [29] are shown Table 1. Generally, HTC is performed at mild temperatures (usually up to 524 K). Carbon-rich solid products obtained have high energy contents. HTL is typically carried out at temperatures between 524 K and 648 K. The product is highly viscous liquid (i.e., oil) used as a pure chemical or an additive of diesel fuels. Additionally, SCWG is performed at highest temperatures (>648 K) for production of syngas (H_2 and CO). The physicochemical properties of target products are affected by hydrothermal temperature and residence time [41]. Compared with traditional biomass gasification technologies, SCWG has
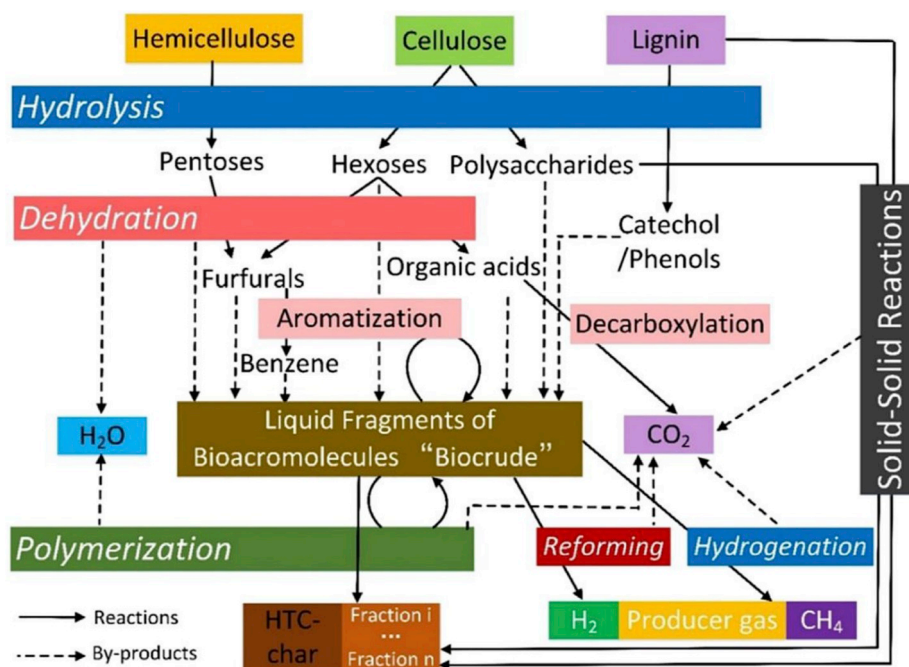

Fig. 3. Principle reaction pathways during HTC of lignocellulosic biomass (Copyright with the permission from Ref. [30]).
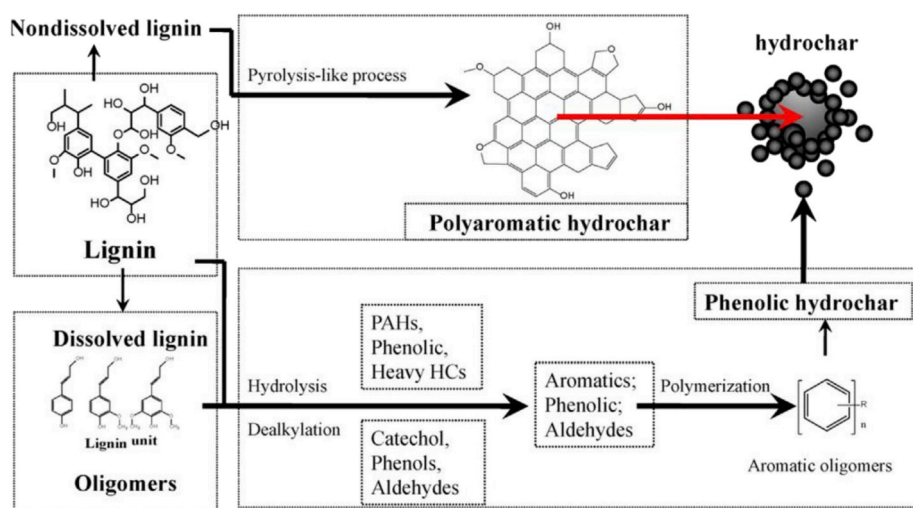
Fig. 4. Formation mechanism of hydrochar from lignin during HTC (Copyright with the permission from Refs. [51,52]).

a number of features due to the unique thermodynamic and fluid dynamic properties of water in supercritical state. Dielectric constant of water is a function of temperature and a strong function of pressure. At normal temperature and pressure, dielectric constant of water is relatively high (>80) due to the strong effect of hydrogen bond in water. With the increase of temperature and pressure, it decreases to 5 at critical point (Fig. 2, right).

HTP has been studied by researchers in three main areas: (i) reaction kinetics and mechanisms, (ii) process understanding, and (iii) new applications. So far, reaction kinetics and process understanding have received most attention. Information about reaction mechanism/kinetics and mass transfer limitations can play significant roles in hydrothermal reactor design and process scale-up. However, there is a distinct lack of information and fundamental data on operating conditions, especially at the beginning of reactions during HTP. The reaction mechanisms of HTP for organic solid wastes are complex. The reaction pathways and kinetics, even for pure materials, are not fully understood due to the formation of various intermediates via parallel and consecutive reactions. The reactor design is typically based on empirical laboratory studies and global rate expressions. However, these empirical techniques provide only a limited insight into the function and nature of reaction chemistry, thus leading to difficulties for reactor/process scale-up. In the following sections, the possible reaction pathways during HTC of polymeric wastes (e.g., lignocellulosic biomass, plastics) will be thoroughly presented.

3. HTC fundamentals

Of the hydrothermal processes, HTC could convert cellulose into coal like materials, similar to mimic the natural process of coal formation [41]. This artificial coalification process has been widely referred to as hot compressed water treatment, subcritical water treatment, wet torrefaction, and hydrothermal treatment. During HTC of organic wastes (e.g., biomass), hydrothermal conversion occurs through dehydration, polymerization and finally carbonization reactions [42]. The first step of HTC reaction is hydrolysis, where water reacts with extractives, hemicellulose, or cellulose and breaks ester and ether bonds (mainly β-(1–4)-glycosidic bonds), resulting in a wide range of products, including soluble oligomers like (oligo-) saccharides from cellulose and hemicelluloses [43]. Fig. 3 illustrates the reaction pathways during HTC of lignocellulosic biomass [30]. The blend of phenols, organic acids, and ketones make up bio-crude via HTL. At critical conditions of water, reactions pertaining to free radicals become prevalent and gasification becomes favored, thus leading to the formation of CH_4 and H_2 [44]. To

facilitate the formation of a char, the temperature is controlled to avoid liquefaction and gasification. The glucose dehydration to form 2, 5-hydroxy-methylfurfuraldehyde followed by aldol condensation outlines the formation of substances like carbon spheres [45–47]. The reactions such as oxidation, esterification and etherification on the hydroxylmethyl group and reactions such as oxidation, reduction and aldol on the formyl group have been reported [48]. Besides, solid-solid interactions (as in torrefaction) are proved [49]. HTC is generally supported through liquid and solid state to form coke and char, respectively [46,50].

HTC generally proceeds two pathways: (i) the dissolution of intermediate products via polymerization and (ii) pyrolysis-like decomposition depending on hydrothermal severity. Hemicellulose present in the biomass can hydrolyze at a lower temperature, so polymerization mainly occurs in the homogenous reaction. The first pathway is the dissolved part of cellulose and lignin since the amorphous cellulose is easily collapsed under subcritical conditions. The second pathway is a pyrolysis-like process for the undissolved biomass. The crystalline regions of cellulose and lignin need to treat at high intensity. The char from the pyrolysis-like process has a relatively high aromatic structure derived from lignin. The whole process can form two types of carbon including phenolic char and polyaromatic char (Fig. 4). In a homogeneous process, various carbons go through automatic integration such as molecule rearrangement and dehydration, and unified HTC products are formed when high temperatures or residence time is used [53].

A comparison of lignin decomposition mechanisms during pyrolysis and HTC processes has been concluded [54]. Compared to hemicellulose and cellulose, the pyrolysis of lignin is more complex and occurs in a wider range of temperatures. During the pyrolysis process, the lignin decomposition starts with the breaking of weaker bonds (e.g., hydrogen bond, C–OH bond) at low temperatures and proceeds via cleavage of stronger bonds (e.g., β-O-4 linkages) with the increasing temperature. The small-molecular aldehydes, toluols, styrenes, and guaiacyl hydroxyls, are the primary products of lignin decomposition in the first stage, while p-hydroxy-phenols, catechols, and cresols are products of further decomposition [55]. Free radicals from the breaking of the β-O-4 linkage is known as the first step of the depolymerization of the lignin chain [56,57]. The radicals can capture the protons to form the products such as vanillin and 2-methoxy-4-methylphenol, while the radicals are passed to other species for further reactions, leading to chain propagations. The reactions are not terminated until two radicals collide with each other to form stable compounds, and the polyaromatic biochar forms via random repolymerisation of the radicals at >350 °C (Fig. 5a) [56]. Hydrothermal treatment of lignin can increase the solubility,
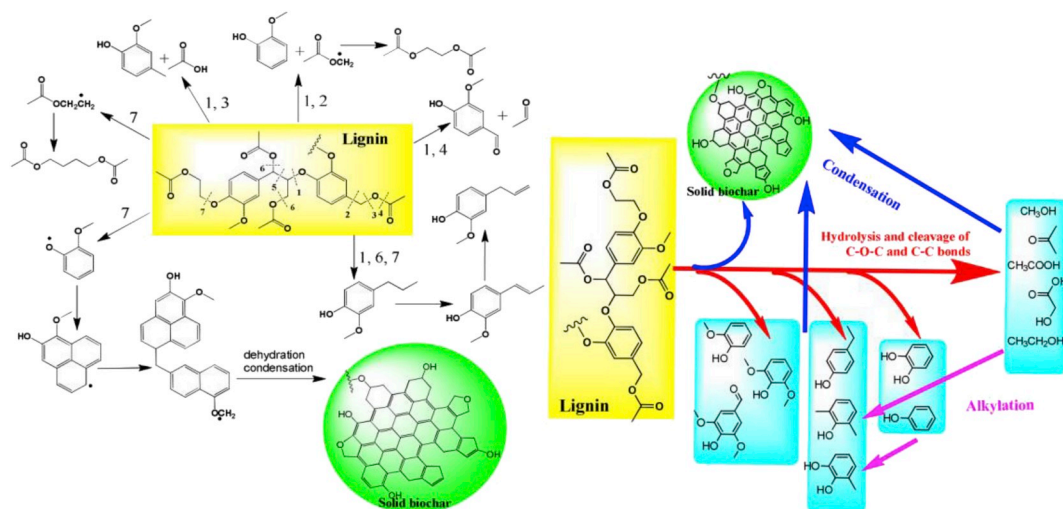
Fig. 5. Mechanisms for the decomposition of lignin during pyrolysis (left) and HTC (right) (Copyright with the permission from Ref. [54]).

accelerate the physical and chemical interaction between lignin and water, and finally lead to the formation of the carbonaceous structures. During HTC, hydrolysis and cleavage of the C–O–C and C–C bonds, demethoxylation, alkylation, and condensation were the main reactions in competition with each other [52,58]. The cleavage of the β-O-4 ether bonds and $^{\alpha}$C-$^{\beta}$C bonds had the precedence during HTC of lignin [59], while the bonds in aromatic rings remain unaffected [60]. Shorter reaction time and lower temperature are favorable for producing phenolic monomers and dimers from lignin via preliminary hydrolysis and cleavage of C–O–C bonds and aliphatic C–C bonds [61]. With increasing reaction temperature and time, demethoxylation and alkylation of phenolic compounds may occur for producing more alkyl phenols (Fig. 5b) [52]. By investigating the changes of the structure of char during HTC of lignin, it was found that the decomposition of lignin was enhanced with the increase of temperature. The char produced at higher temperature usually had rough surface and few vesicle, and high-ordered crystalline structure. Also, most of functional groups (except for the OH group) in char were eliminated above 350 °C [62].

Lignocellulosic biomass represents a non-food resource, mainly composed of cellulose, hemicellulose, lignin and others (e.g., inorganics, extractives) [63]. The formation mechanisms of hydrochars from three components (i.e., cellulose, hemicellulose, and lignin) were concluded in Ref. [53]. Alvarez-Murillo et al. [64] studied the kinetics of cellulose HTC over different reaction time and temperature, developing a first-order-reaction model, where chemical and heat transfer processes were connected and resolved simultaneously. The model indicated that the reaction temperature could play a significant role on the HTC of cellulose, influencing both pre-exponential and exponential factors of the kinetic constant. The model can also describe the changes in H/C, O/C and higher heating value (HHV) during HTC of cellulose, allowing the chemical composition and energy densification to be forecasted. In addition, the kinetics and mechanism of the HTC of lignin model compounds were investigated [65,66].

Lignocellulose is highly complex and its composition influences the various reaction pathways. Three components act as precursors for the hydrochar, so it is essential to elucidate interactions during the decomposition process and the mechanisms involve in solid formation. In recent years, considerable research and industrial applications have focused on lignocellulose pretreatment techniques, such as chemical [67], biological [68], and thermal or an integrated treatment [69,70] to achieve more easily processed materials, which can be further transformed into different chemicals with different purposes. The primary purpose of these applications is to destroy the biomass structure by altering or breaking the lignin seal and disrupting the crystal structure of

cellulose [71]. HTC of lignocellulose follows the same way by breaking up the structure for favorable degradation. The hydrolysis process is crucial to destroy the structure of the biomass components and to reduce the polymerization degree of the biomass. Lignin works as a template for the orientations of polysaccharides, since it is necessary to destroy the covalent bonding between lignin and xylan or cellulose and the internal hydrogen bond in cellulose for further degradation [72].

The fracture of biomass is different to the decomposition of single components due to the strong covalent bonds and hydrogen bonds between components. Conversion of rye straw to hydrochar, the HTC temperature started at higher values compared to pure cellulose [45]. The original lignocellulose requires a higher activation energy to destroy the structure of individual components. The production of hydrochar depends on both the lignocellulose composition and the hydrothermal conditions. The degradation level of lignocellulose follows the order of lignin < cellulose < hemicellulose at a same hydrothermal severity. The phenolic structure of lignin was the main reason for the stability, favoring the condensation reaction [52]. Compared to cellulose with a crystal structure, hemicellulose has a lower molecular weight with a lower polymerization degree (approximately 50–200), and its amorphous properties suggest that it is more easily vulnerable to attack in the critical HTC condition [73].

The feedstocks with complex components usually require longer residence times to obtain stable hydrochars due to the interaction between components [74]. Lignin has a positive effect on carbohydrates in the biomass because it serves as a plant wall support; stabilizing the cellulose by preventing disruption in the crystal structure at low temperatures. By enclosing cellulose and hemicellulose, lignin can slow down the release of monosaccharide, thus hindering the formation of intermediate products. Lignin migrated out of the wood cell wall and was finally deposited on the cellulose surface during HTC [75]. This negative effect was attributed to the insoluble lignin retarding hydrolysis [76]. The surface blockage of cellulose by lignin inhibited further degradation. Thus, HTC has negligible effects on lignin, but its presence has a positive effect on the decomposition of lignocellulose during the hydrochar formation [64].

4. Wastes valorization by HTC

4.1. HTC of biomass wastes

HTC can convert organic solid wastes into value-added products (i.e., hydrochar) at a comparatively low temperature (180–250 °C) and saturated pressure (2–10 MPa) [45,77–79]. The resulting product has
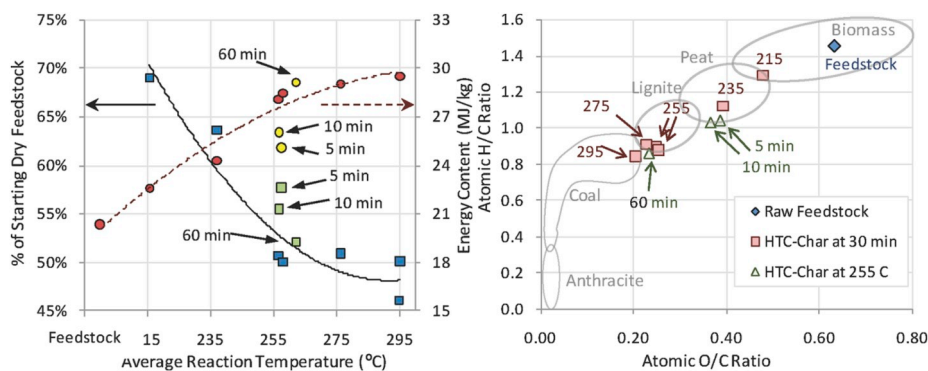
Fig. 6. Effects of temperature and holding time on mass recovery and energy content of HTC-char (time = 30 min). The mass is represented by squares, and the energy content is represented by circles (**left**); Van Krevelen diagram of HTC-biochar (time = 30 min). The temperature was 255 °C for indicated hold times (**right**) (Copyright with the permission from Ref. [85]).

carbon content similar to lignite with mass yields varying from 35% to 60% [46,80–83]. The aqueous phase has most of the dissolved organics in the form of carbon with a small amount of gas [46,84,85]. The process is mostly influenced by the feedstocks and process conditions [20,86]. Although the energy densification of hydrochar was increased at higher process temperatures, most of the benefit was achieved at modest temperatures (Fig. 6, left). Also, higher temperature entails higher process pressure, thus requiring more complex and costly equipment and increase handling difficulties in a commercial application. Under the optimal conditions (e.g., 255 °C, 5 MPa), a hydrochar was most

effectively produced with high energy density and coal-like properties (Fig. 6, right), exhibiting favorable behavior with respect to thermal processes (e.g., gasification, combustion) [85]. Thus, the carbonization process improves the heating value and dewatering capability of the feedstocks [15]. Process efficiency and dewatering capacity are improved by boosting the solid yield and recycling, respectively [15]. Solid loading has a positive effect on the products distribution [81,83]. Moreover, internal heat recovery has a positive effect on the process design [87,88] as the HTC reaction heat is low [89]. Carbon materials from hydrochar have a high potential in various applications (e.g., solid
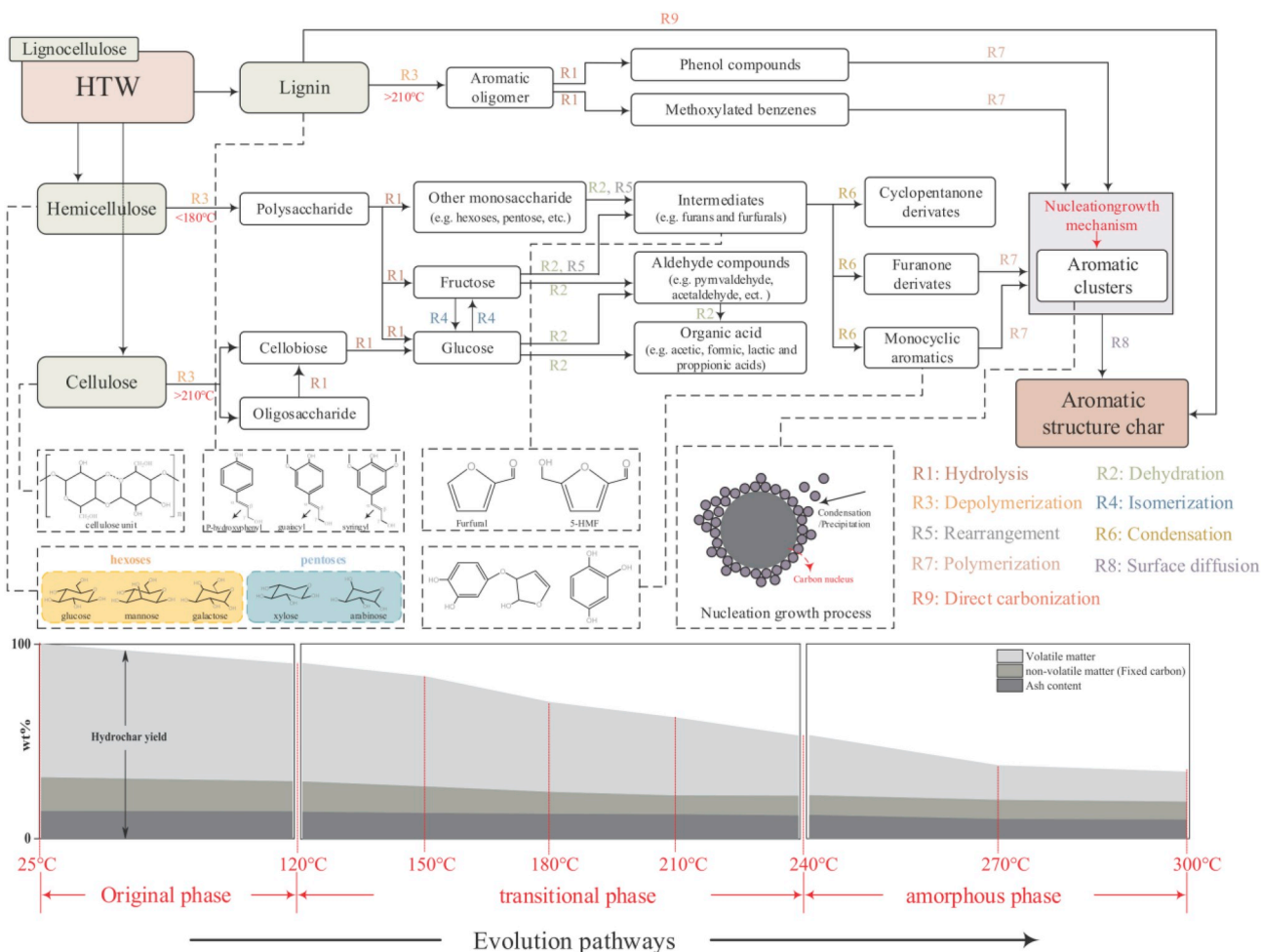

Fig. 7. The evolution pathways of lignocellulose biowastes (herbal tea waste - HTW) during HTC (Copyright with the permission from Ref. [115]).
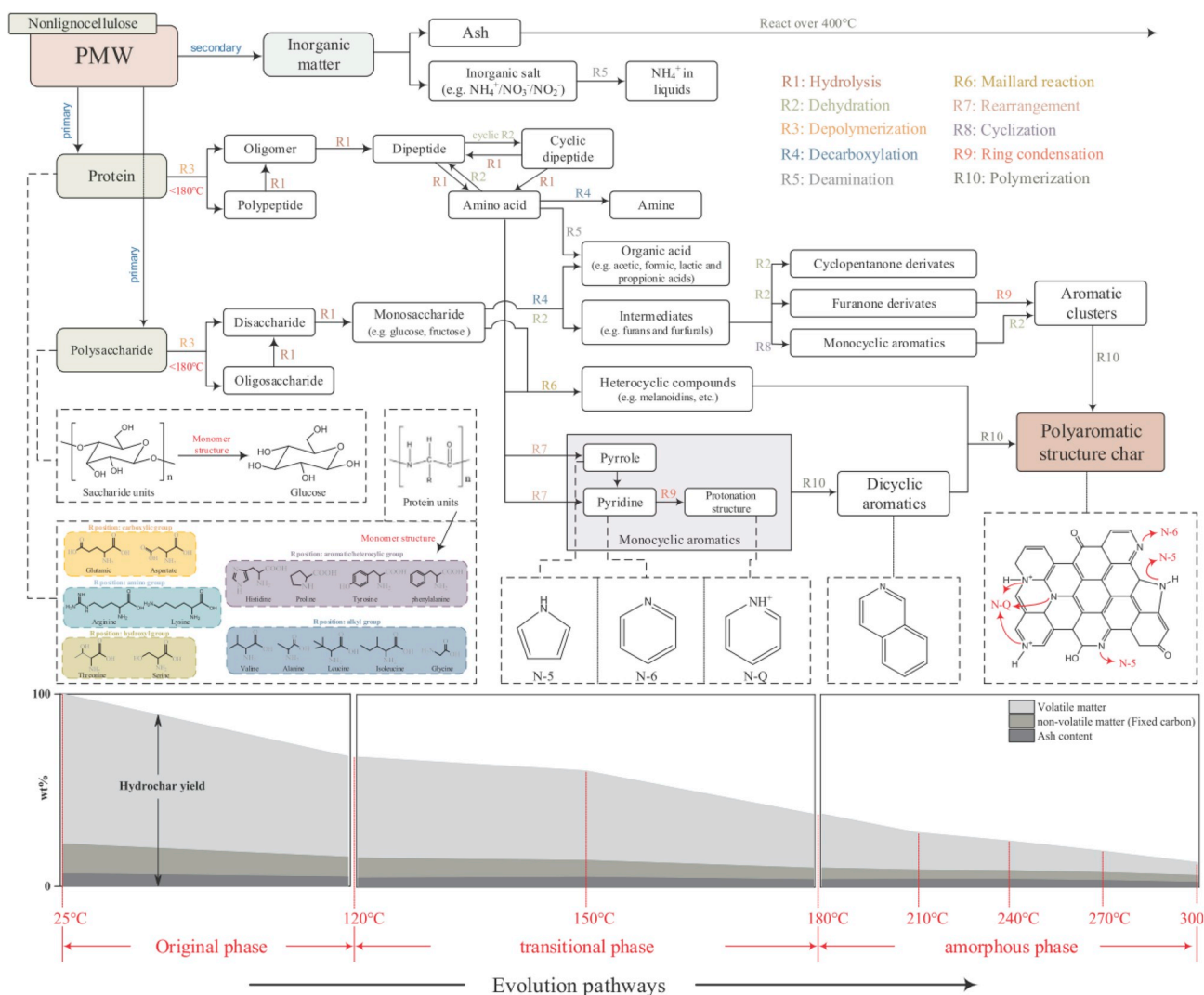
Fig. 8. The evolution pathways of non-lignocellulose biowastes (penicillin mycelial waste - PMW) during HTC (Copyright with the permission from Ref. [115]).

fuel, supercapacitor, fuel cell, and sorbent) [15,30,90–92].

In terms of organic waste streams treatment by HTC, most of works have focused on the production of hydrochars for solid fuels. Indeed, the HTC process can lead to the hydrochar with high energy density and less dusty, thus improving pelletization characteristics [93,94]. The commercialization of HTC is mostly influenced by the requirement of high temperature and pressure. Pellet quality measured in terms of mechanical durability represents its ability to remain intact during handling or storage [95]. Pellet durability can improve when the HTC temperature increased [96]. Hydrochar can produce highly stable, water-resistant pellets [94]. Additionally, the durability and combustion characteristics of the hydrochar/lignite pellets were studied [97]. Hydrochar blended with lignite can improve the tensile strength of pellets (especially with a hydrochar fraction above 50%). However, logistic problems exist associated with the large-scale utilization of the hydrochar pellets. From an economical point of view, the transportation, handling and storage of pellets impacting its mechanical durability are significant [98]. Pellet crumbling causes the reduction of combustion efficiency and the increase of gas emissions [98]. Another logistic problem originates from the hydrochar hydrophobicity impacting the pellets mechanical durability. To make the HTC technology more environmental friendly, the spent liquor can be treated by anaerobic digestion [99–104] and by recirculation [105–108], which contributes to increase the mass and energy yields of hydrochar.

HTC is served as a key intermediate step in optimizing the chemical structures of solid fuels that is subject to thermal processing [109–111]. The relationship between HTC conditions and chemical structures of hydrochars is a long-term hot research topic. A comprehensive knowledge of mechanisms controlling the evolution of biomass wastes structures and subsequent structure-reactivity is crucial for the terminal application of hydrochars. Chemical structures of hydrochars include but not limit to carbon skeleton, crosslinks of aromatic polymer, surface porosity, functional groups and ultimate components [112–114]. All of these characteristics can be significantly changed via HTC, thus influencing the reactivity and fuel properties of hydrochars. However, fundamental understandings for the evolution pathways of chemical structures in relation to various biomass waste-derived hydrochars are still necessary.

To fill up this knowledge gap, Zhuang et al. [115] recently studied the hydrothermal process of lignocellulose (Herbal tea waste, HTW) and non-lignocellulose (Penicillin mycelial waste, PMW). Fig. 7 illustrated the evolution pathways of lignocellulose during HTC. Initially, hemicellulose was rapidly depolymerized to polysaccharides (e.g., glucuronoxylan, galactoglucomannan and xylanglucose) at 180 °C [116,117]. Then, various monosaccharide units including hexoses (glucose, mannose and galactose), pentoses (xylose and arabinose) and other saccharides (rhamnose and fructose) were generated from the continuing hydrolysis of polysaccharides [116]. A mutual conversion

Table 2

HTC of various biowastes to hydrochars in energy applications.

Feedstock	Processing condition	Reactor	Application	Ref.
Lignocellulose				
Cellulose	HTC: 200 °C, 16 bar, 8–48 h	Stainless steel autoclave	Solid fuel	[122]
Holocellulose	HTC: 220 °C, 4–20 h	Stainless steel autoclave	Solid fuel	[123]
Lignin	HTC: 300–390 °C, 1 h KOH activation: 600–900 °C, 1 h	Stainless steel autoclave	highly microporous carbons/CO_2 and H_2 storage	[124]
Loblooy pine	HTC: 180–240 °C, 2–6 h	Parr reactor	Solid fuel	[125]
Eucalyptus bark	HTC: 220–300 °C, 2–10 h	Stainless steel autoclave	Solid fuel	[126]
Chinese fan palm	HTC: 180–240 °C, 30–100 min	Stainless steel autoclave	Solid fuel	[127]
Hazelnut shells	HTC: 200 °C, 8 h; Activation: 700 °C, 2 h	Stainless steel autoclave	Supercapacitor	[128]
Empty fruit bunch	HTC: 150–350 °C, 20 min	Parr reactor	Solid fuel	[129]
Palm shell	HTC: 180–260 °C, 0.5–2 h	Stainless steel batch reactor	Solid fuel	[130]
Bamboo shoot shell	HTC: 200 °C, 24 h; KOH activation: 600–800 °C, 1 h	Stainless steel autoclave	Porous carbon/Supercapacitor	[131]
Cornstalk	HTC: 190–240 °C, 0.5 h	Stainless steel autoclave	Solid fuel	[132]
Corn Stover	HTC: 180–260 °C, 1–24 h	Stainless steel autoclave	Solid fuel	[133]
	HTC: 175–250 °C, 4 h, biomass/H_2O of 1:10	Pilot-scale reactor	Solid fuel	[134]
Rice husk	HTC: 230 °C, 48.0 h; Activation: 900 °C	Teflon autoclave	Porous carbon/battery material	[135]
Tobacco stalk	HTC: 180–260 °C, 1–12 h	Teflon autoclave	Solid fuel	[136]
Peanut shell	HTC: 200 °C, 6 h; KOH/H_3PO_4 activation	Teflon autoclave	Porous carbon/sorbent	[137]
Non-lignocellulose				
Microalgae	HTC: 203 °C, 2 h, 1.65 MPa	Parr reactor	Solid fuel	[138]
Lipid-extracted algae	HTC: 180–240 °C, 0.5 h	Teflon autoclave	Solid fuel	[139]
Macroalgae	HTC: 180–210 °C, 2–16 h	Teflon-lined stainless steel autoclave	Solid fuel	[140]
	HTC: 180 °C, 24 h; KOH activation: 600–800 °C, 1 h	Autoclave	N-doped porous carbon/Supercapacitor	[141]
Paper sludge	HTC: 180–260 °C, 0.5–5 h	Non-stirred pressure reactor	Solid fuel	[142]
	HTC: 180–240 °C, 0.5 h	Autoclave	Solid fuel	[143]
Sewage sludge	HTC: 180–300 °C, 0.5–8 h	Stainless steel autoclave	Solid fuel	[144]
	HTC: 160–240 °C, 1–4 MPa, 1 h		Fertilizer/Solid fuel	[145]

Table 2 (*continued*)

Feedstock	Processing condition	Reactor	Application	Ref.
Anaerobic granular sludge		Stainless steel autoclave		
Pig manure	HTC: 180–300 °C, 1.5 h	Stainless steel autoclave	Soil amendment	[146]
Human excreta	HTC: 180–240 °C, 0.5–2 h	Stainless steel reactor	Fertilizer/solid fuel	[147]
Poultry litter	HTC: 150–300 °C, 5–480 min	Stainless steel autoclave	Fertilizer/solid fuel	[148]
Food waste	HTC: 200–300 °C, 1 h	High-pressure batch reactor	Solid fuel	[149]
Sweet potato waste	HTC: 180–300 °C, 0–4 h	Autoclave reactor	Solid fuel	[150]
Sugarcane bagasse	HTC: 140–180 °C, 0–4 h	Teflon-lined autoclave	Sugar/Graphene quantum dots/porous carbon	[151]
Chitosan	HTC: 200 °C, 12 h, 10 bar; Carbonization: 1000 °C, 2 h	stainless-steel autoclave	N-Doped carbons/Electrocatalysis	[152]
	HTC: 250 °C, 4–14 h; KOH activation	autoclave	N-Doped carbons/Supercapacitor	[153]

between two major monosaccharides (glucose and fructose) was found, namely isomerization [117,118]. The reactions with increasing temperature led to the diversification of hydrothermal products [45,112, 117,119]: (i) retro-aldol condensation broke C–C bonds to produce aldehyde compounds (e.g., pyrnvaldehyde and acetaldehyde); and (ii) acid-catalyzed dehydration produced organic acids and soluble intermediates (e.g., furans and furfurals). Likewise, the only monosaccharide derived from cellulose went through a similar pathway to that of hemicellulose, albeit the hydrolysis temperature of cellulose was higher [117]. The predominant reactions can shift from hydrolysis toward condensation and polymerization as the temperature >240 °C. A large number of intermediates with significant reactivity began to form cyclopentanone, furanone derivatives or even monocyclic aromatics via ring condensation and intermolecular dehydration [118]. Under hydrothermal conditions, (hemi-)cellulose comprised of carbohydrates can also build aromatic structures [45] with higher stability, which was an important reason for the formation of aromatic clusters via polymerization [52,112]. As the concentration of aromatics in aqueous phase reached its threshold value, a burst of nucleation process took place and considerable number of aromatic clusters were concurrently accumulated by the LaMer model [52]. Finally, hydrochars with abundant aromatic structures were steady formed via the surface diffusion of aromatic clusters as reaction time went on. Compared to HTW, PMW as a type of non-lignocellulose consisted of proteins and polysaccharides. The HTC of polysaccharides followed the pathway in line with that of hemicellulose in HTW; nevertheless, proteins complicated the evolution pathways by two important mechanisms: the self-rearrangement of amino acids and the synergistic reaction with reduced sugar [117,120] (as illustrated in Fig. 8). The formation mechanisms of hydrochars during HTC of two typical biomass sources (N-free lignocellulose and N-rich sludge) were also concluded in Refs. [53,115,121].

Table 2 presents the HTC of various biowastes to hydrochars in energy application. It is found that two reactors of pressurized Parr reactor and autoclave (e.g., Teflon-lined, stainless steel) have been widely used in the HTC process in batch or semi-continuous modes. So far, commercial application of HTC has been hindered by the operational requirements of high temperature and pressure, limiting deployment of continuous process units and increase capital expenditure costs.
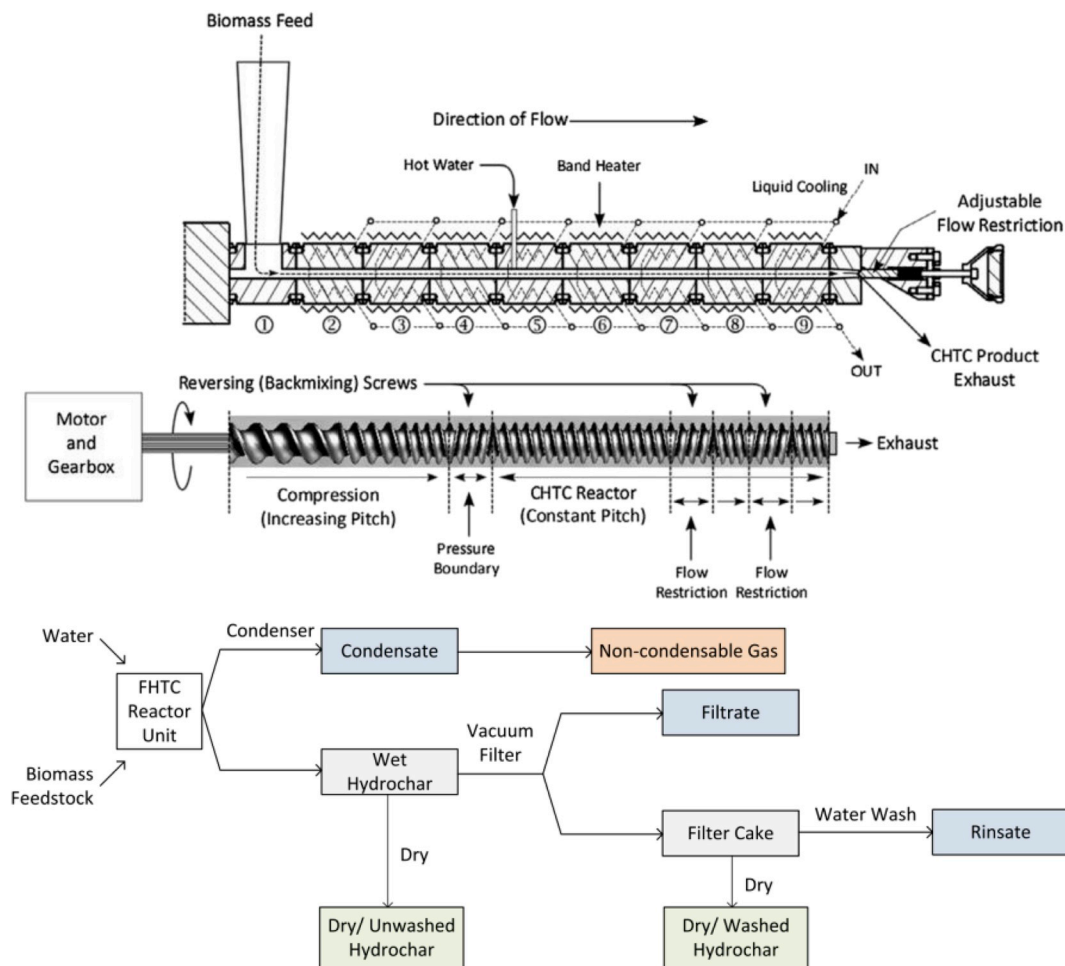
Fig. 9. (a) Schematic cross-section drawing of the BC-21 TSE (**top**) and detailed configuration of one of two intermeshing screws showing barrels inserted onto splined shaft (**bottom**); (b) Fow chart of TSE-based FHTC system (Copyright with the permission from Ref. [154]).

Hoekman et al. [154] developed a reactive twin-screw extrusion (TSE)-based fast hydrothermal carbonization (FHTC) to produce hydrochar from loblolly pine by a continuous process as shown in Fig. 9. Compared to batch reactors, the FHTC reactor had a very short reaction time (20–30 s) and a higher yield of hydrochar. In particular, FHTC of loblolly pine at 290 °C produced hydrochar with a yield of 85%. Condensation of the flashed vapor products provided a relatively clean

water stream containing only 1.2% organics (i.e., primarily furfural, acetic acid). Recovery of these organics and recycling of the condensed water will further improve the economic effectiveness of FHTC.

From the reported works, hydrochars can be used as solid fuels. Due to low surface areas, hydrochars should be further modified (e.g., activation) into porous carbons that can be considered in advanced energy applications such as supercapacitor, battery materials and
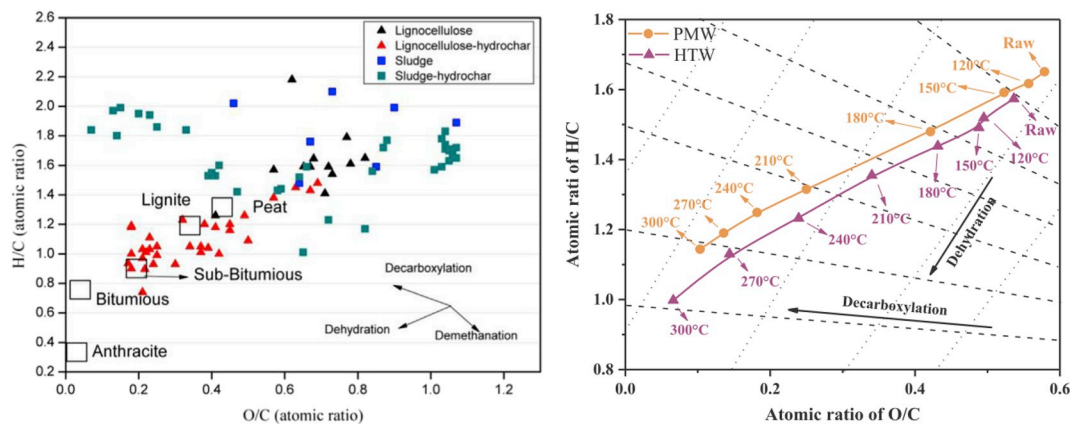

Fig. 10. Van Krevelen diagrams of (a) lignocelluloses/sewage sludge and the corresponding hydrochars (Copyright with the permission from Ref. [53]); (b) hydrochars from lignocellulose (Herbal tea waste, HTW) and non-lignocellulose (Penicillin mycelial waste, PMW) at different temperatures (Copyright with the permission from Ref. [115]).
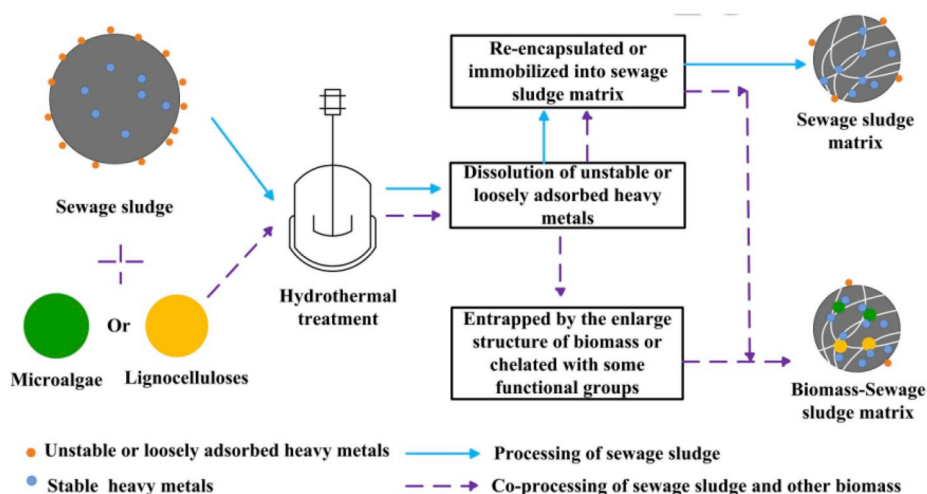
Fig. 11. Mechanism on the heavy metals immobilization during co-HTC of sewage sludge and biomass (e.g., lignocelluloses, microalgae) (Copyright with the permission from Ref. [163]).

electrocatalysts [155]. Generally, HTC of lignocellulosic biomass needs relatively high temperature and time compared to non-lignocellulosic biomass. The H/C and O/C ratios are significant criteria to assess the degree of deoxygenation, and the aromatic content during HTC of biomass [156]. A higher H/C ratio indicates that the aromatic content of hydrochar is lower [156]. In usual, the H/C and O/C atomic ratios can be analyzed by a Van Krevelen diagram to compare biomass with hydrochar [93,157]. The H/C and O/C ratios decreased when the temperature or retention time increased for all hydrochars. The ratio shift delineated the reaction pathways; the dehydration (production of H_2O) and decarboxylation (production of CO_2 or carbonyls including carboxylic acids) reaction during HTC [82,158]. Hydrochar from lignocellulose (e.g, HTW) in Fig. 10 had a high degree of coalification compared to hydrochar from sludge (e.g., PMW).

Some organic wastes contains toxic substances. In particular, sludge contains heavy metals, and MSW contains halogenated-plastic (e.g., PVC) wastes. Disposal of these wastes without removal of toxic substances has a highly risk to the environment and human/animal health [23]. For instance, many works have been recently performed on evolution of organic-N during HTC of sludge, because the subsequent thermal processing (e.g., combustion) of sludge hydrochar (as solid fuel) can produce the harmful nitrogen oxides (e.g., NO), causing the environmental pollution [159,160]. Generally, the HTC process can transform parts of organic-N from the solid phase to the liquid phase [159]. HTC can also deal with heavy metals in organic wastes. Most of heavy metals are concentrated in the hydrochar, which is easy to treat compared with dispersed heavy metals in raw organic wastes [161,162]. There is lack of a full understanding about the evolution of heavy metals during HTC. Huang et al. [163] concluded a synergetic mechanism on the immobilization of heavy metals during co-hydrothermal carbonization (co-HTC) of sewage sludge and biomass (Fig. 11). The unstable heavy metals are initially dissolved under hydrothermal conditions, and then re-encapsulated or immobilized into the processed sludge matrix. The acid soluble/exchangeable fraction is easily released to the liquid phase, which is subsequent transformed into more stable fractions via complexation, precipitation, adsorption or other procedures. The released heavy metals are entrapped by the enlarged structure of biomass or chelated with specific organic functional groups and fixed in the stable biomass-sludge matrix during HTC. In addition, co-HTC of sludge with biomass has attracted much attention, contributing to the improvement of fuel properties of hydrochars [164–169]. It was reported that co-HTC of fallen leaves with iron sludge can prepare magnetic iron product and solid fuel at the same time [169].
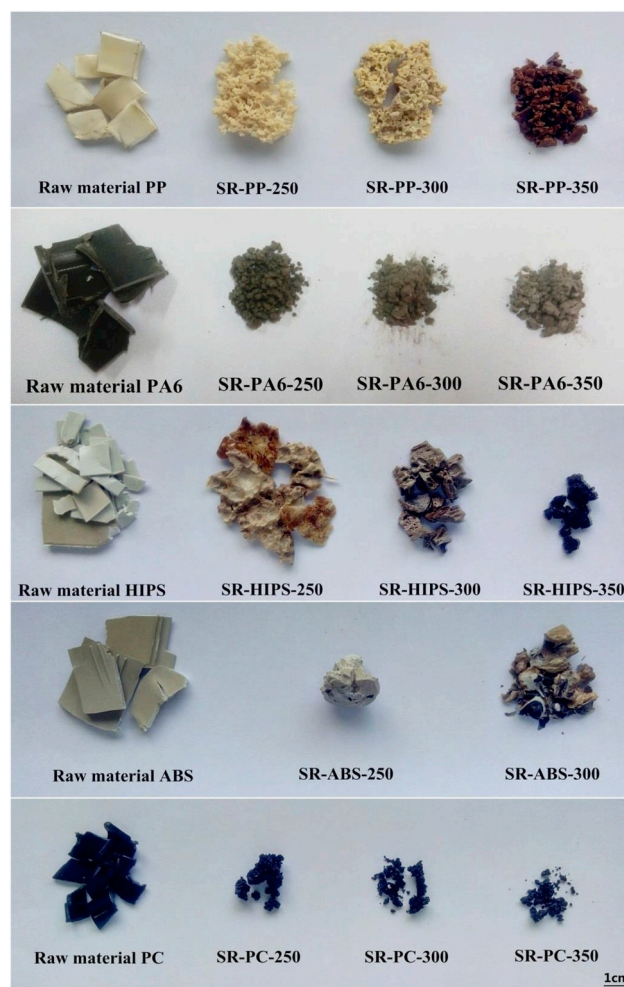

Fig. 12. Different kinds of plastic wastes (PP - polypropylene, PA 6 - polyamide 6, HIPS - high impact polystyrene, ABS - acrylonitrile butadiene styrene, PC - polycarbonate) and their corresponding hydrochars derived from HTP at different temperature (Copyright with the permission from Ref. [176]).
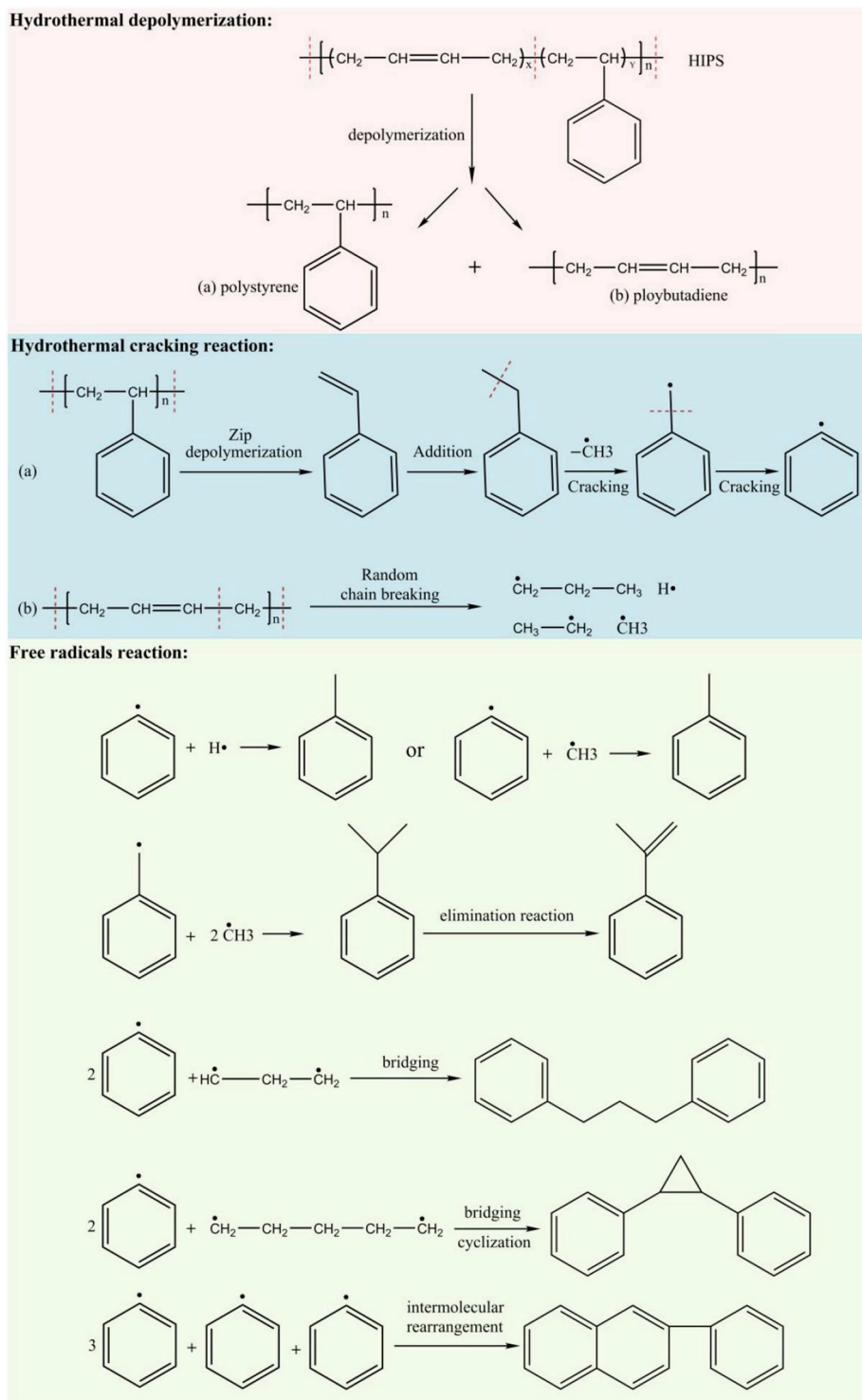
Fig. 13. Hydrothermal decomposition mechanism of HIPS in subcritical water (Copyright with the permission from Ref. [177]).

4.2. HTC of plastic wastes

Plastic wastes with low moisture and oxygen contents have been commonly treated by thermochemical processing (e.g., liquefaction, gasification) at higher temperatures for reovery of fuels (e.g., oil, gas) with higher heating values [170,171]. However, a number of works have been conducted on HTC of MSW [172–178] typically including organic fraction (e.g., foods, plastics, papers), which can be hydrothermally converted into solid fuels [179]. Directly combustion of brominated/chlorinated plastics will produce brominated/chlorinated

compounds, which impact the oil quality and cause environmental pollution (e.g., toxic halogenated dibenzodioxins and dibenzofurans from the PVC combustion). Dehalogenation (e.g., debromination, dechlorination) of these plastics can be achieved under hydrothermal conditions [23]. Zhao et al. [176] studied the HTP of five typical plastics (PC, HIPS, ABS, PP and PA6) from e-wastes and end-of-life vehicles. Different kinds of plastics and their corresponding hydrochars were shown in Fig. 12. HTP improved the energy density and facilitated effective combustion. The oil can be used as chemical feedstock, whilst the hydrochar is used as solid fuels. Furthermore, Zhao et al. [177]
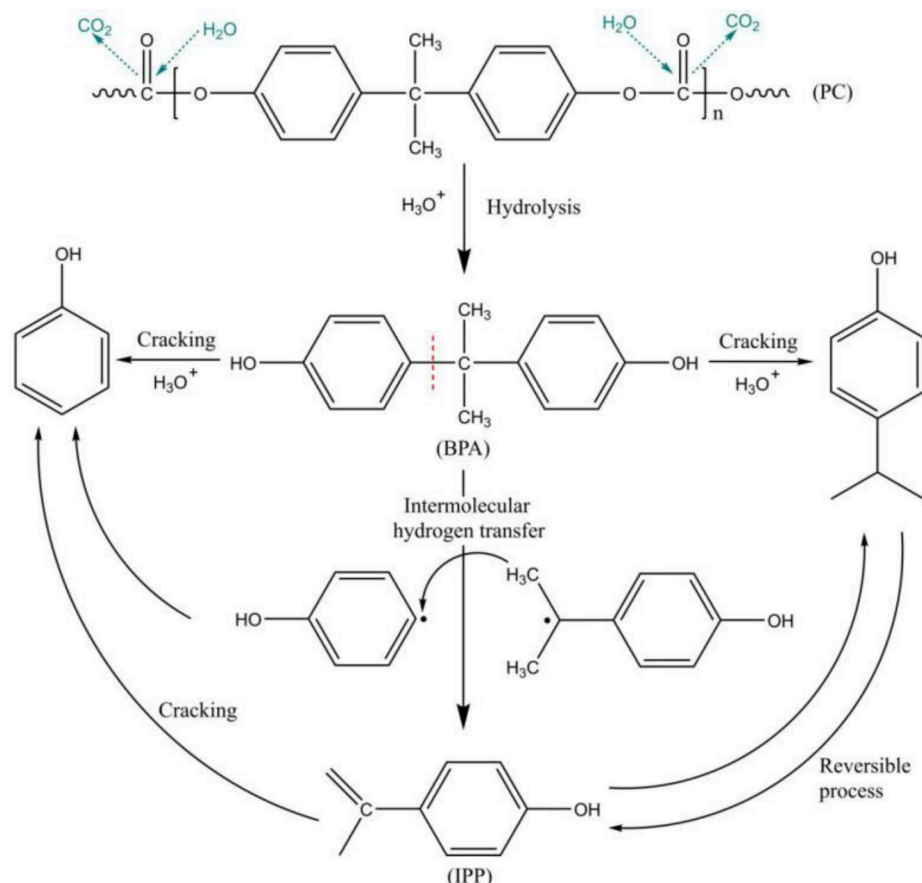
Fig. 14. Hydrothermal decomposition mechanism of PC in subcritical water (Copyright with the permission from Ref. [177]).

stuided the HTP of e-waste plastics at higher temperatures (250–350 °C) to oils. The optimal HTP temperatures were in the range of 250–300 °C for PC and PA 6 and at 350 °C for HIPS and ABS.

HIPS is a copolymer by blending two monomers of butadiene and styrene through conjunct polymerization. HTP of HIPS is the mixed decomposition of polystyrene and polybutadiene phases. The decomposition of HIPS includes zip depolymerization and random chain breaking (as illustrated in Fig. 13). Firstly, the resin is depolymerized into two different polymers. The polystyrene is cracked into the monomer of styrene via zip depolymerization. A part of styrene eliminates double bonds by addition reaction, and then hydrothermal energy breaks the C–C bond to produce phenyl radicals, phenylmethyl radicals and alkyl radicals. Meanwhile, the energy provided by the subcritical water could break the C–C bonds dissociation energy [174] of the polybutadiene phase via random chain fracture to form linear alkyl radicals with different carbon atoms. Generally, the decomposition of polymers involves three processes including the chain initiation, free radicals reaction and termination reaction. Organic products such as the diphenyl compounds with lengthened carbon chain between phenyl radicals are profited from the combined reactions of different free radicals [177]. Similar to HIPS, ABS is the co-polymer synthesized from three polymerized monomers of polyacrylontrile, polybutadiene and polystyrene. Due to the existence of the same polystyrene and polybutadiene phases, the product slate has high similarity. Depolymerization, cracking and free radical reactions involve the whole HTP of ABS. Styrene, toluene and other styrene derivatives are intermediate products derived from a continuous decomposition of polystyrene and free radicals combination. The free radicals produced by cracking polystyrene and polybutadiene combine with each other via end-to-end reaction to scavenge the reaction space, thus forming the diphenyl compounds with alkyl bridging. These mechanisms are in full accordance with the decomposition mechanisms of HIPS.

During HTP of PC, the organic compounds with hydroxyl terminal groups are the main products. The hydrolysis of carbonic ester bonds is the decomposition pathway in the early stage. As increasing the temperature, the cracking reaction is involved. The decomposition pathway is presented in Fig. 14. Firstly, the depolymerization of PC is accomplished by hydrolysis. Water attacks the carbonic ester bond and reacts with them to release CO_2. As a liquid above 200 °C, the native hydronium and hydroxyl ion concentrations in water are higher than room temperature. Thus, a large number of hydrated protons participate in the reaction and combine with the groups of missing electrons to form bisphenol A (BPA). Based on the bond-energy theory, the bond energy of C–C, C═C, C–H and O–H are 332 kJ/mol, 837 kJ/mol, 414 kJ/mol and 464 kJ/mol, respectively. The C–C bond on the main chain of BPA is broken by the energy from the reaction system, and the intermediate product is combined with hydrogen proton to form phenol. 3-(1-methylethyl)-phenol is produced by the same cleavage mechanism of BPA. Meanwhile, the intermediate products of cracking the BPA can generate phenol and p-isopropenylphenol (IPP) via intermolecular hydrogen transfer. The hydrogenation and cracking of IPP extends the pathway to generate 3-(1-methylethyl)-phenol and phenol. Deep and intense cracking will reduce hydroxyl groups to generate phenyl substances. The formation of 4-Methyl-2-phenylphenol is derived from the combination of phenols and phenyl.

The hydrothermal decompostion mechanism of PA6 is illustrated in Fig. 15. Firstly, the hydrogen bonds in the cross-linked polymers are broken by the superheated water and transformed into the linear polymers. Subsequently, the hydrolysis of the linear polymers occur in subcritical water to form aminocaproic acid. Water acts as a nucleophile and substituted for the carbonyl groups via the nucleophilic substitution reaction. Followed by the dehydration and cyclization reactions, the
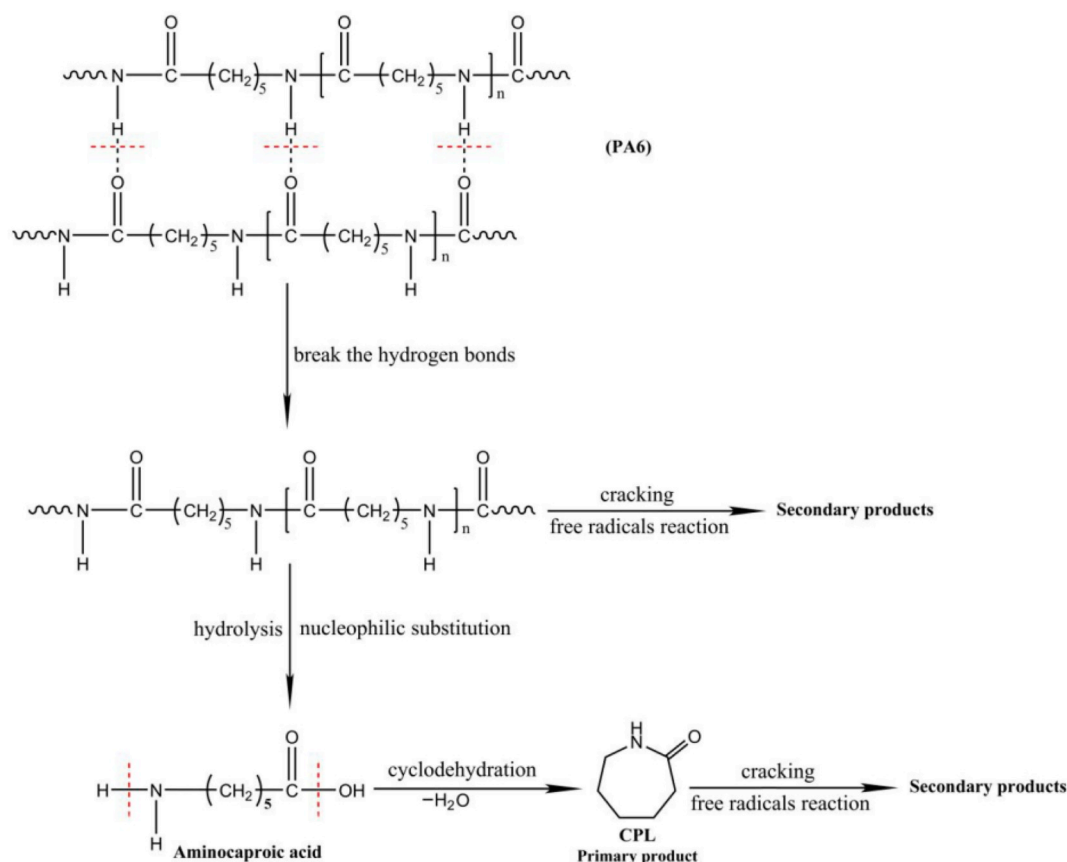
Fig. 15. Hydrothermal decomposition mechanism of PA6 in subcritical water (Copyright with the permission from Ref. [177]).
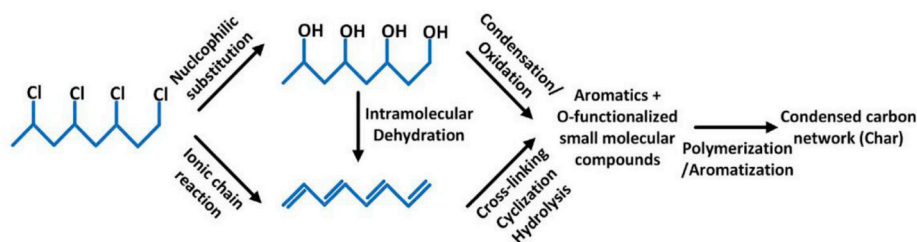

Fig. 16. Reaction pathway of PVC decomposition in the HTC process (Copyright with the permission from Ref. [175]).

aminocaproic acid is converted into the caprolactam (CPL), which are the primary products in oils. Additionally, the structures of PA6 are vulnerable to the effects of temperature. As the thermal energy is higher than the activation energy, the chemical bonds of some intermediates would be destroyed. For instance, the heteroatoms connecting to the carbon atoms (e.g., N–C) are first interrupted and followed by the irregular C–C bonds broken in the monomer. Therefore, many free radicals fragments form by cracking and re-cracking of the intermediate products. These free radicals bind together and being secondary products like 4-Hexanolide, 3-methyl-N-allyl-But-2-enoic-acid-amide, 1-cyclohexyl-1-propanone via possible elimination reaction and cyclization reactions.

The co-HTC of PVC (e.g., medical wastes) and biomass has been widely studied [180,181]. Generally, dechlorination of PVC accords with a free radical mechanism [182]. The reaction can start with the generation of free radicals and chloroallylic structures characterized by low thermal stabilities. A subsequent HCl elimination leads to the formation of polyene (i.e., a non-free radical reaction mechanism) [183]. Remarkably, conjugated double bonds are created by a "zipper" mechanism [184]: once a double bond is formed, the allylic Cl-atom on

the C-atom adjacent to the double bond will split off HCl forming two double bonds during HTC, which in turn activates adjacent Cl to propagate the dehydrochlorination process. In aqueous suspensions, the PVC decomposition is concluded by ionic chain reactions and cracking. The nucleophilic substitution with water as the nucleophile proceeds to generate alcohols, diols, and polyols. Reactive polyenes with the diol/polyol structures, are regarded as the precursors of aromatics and oxygen-functionalized low molecular weight compounds. Temperatures below 450 °C and high water densities are favour of OH-nucleophilic substitution with water acting as a role of nucleophilic agent (Fig. 16) [175].

The presence of lignin can significantly inhibit the particles agglomeration of hydrochars during HTC of PVC; that is, lignin-rich biomass has a positive effect for hydrothermal dechlorination of PVC. The fine particle hydrochars will be beneficial for thermal processing. Additionally, the co-HTC of medical wastes and woodchips was performed in a pilot-scale system, including hydrothermal reactor, steam boiler, condenser, dehydrator, and screening machine. Noteworthy, the condensed water could be recycled for the washing process. The addition of woodchips improved the dechlorination efficiency of PVC wastes.
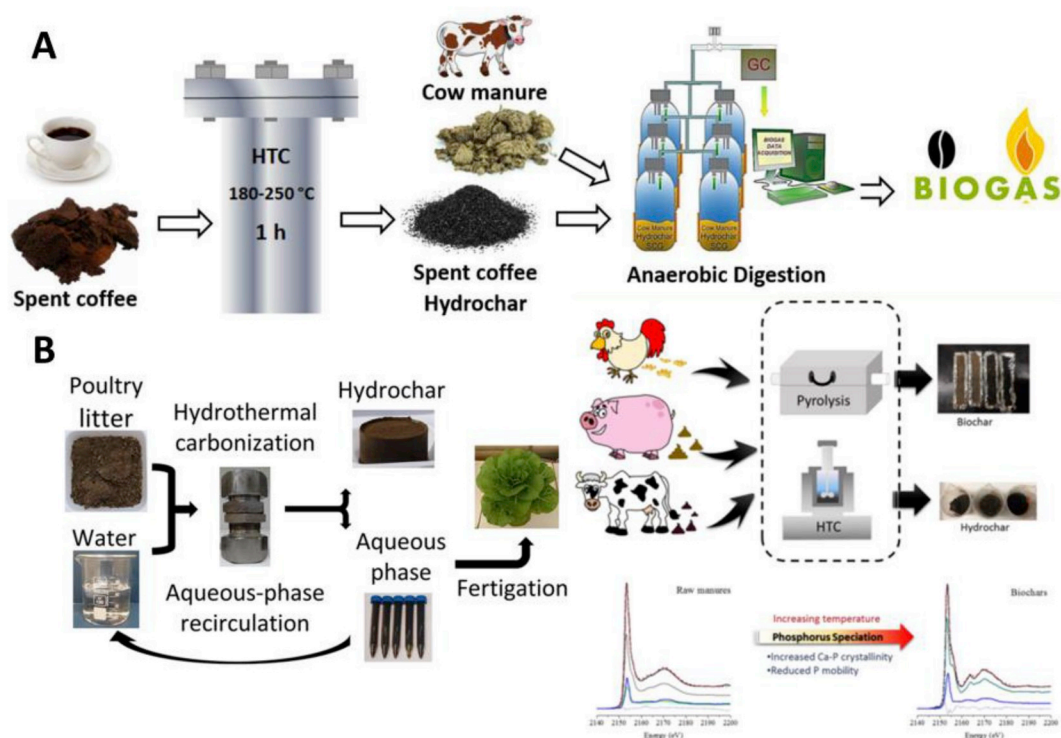
Fig. 17. Recovery of liquid product from HTC of biomass wastes for production of (a) biogas via anerobic digestion [188] and (b) fertilier (Copyright with the permission from Refs. [189,190]).

The hydrochars with low-chlorine content, higher heating value and small particle size could be used as a clean solid fuel [181]. Furthermore, it was confirmed that co-HTC of PVC and moist biomass under the alkaline condition enhanced the removal of chlorine and inorganics [185].

5. Challenges

5.1. By-products recycling

In terms of HTC, most of studies have focused on the hydrochar, but the liquid and gas products receive limited concern. These by-products with intermediate products need more detail analysis for better understanding the whole hydrothermal process in relation to the hydrochar formation. The liquid products can be generally treated by wet oxidation [186] or recovered for production of biogas (methane) [187,188] and fertilizer [189,190] (as illustrated in Fig. 17). In particular, the post-treatment process is essential to the wastewater and hydrochar for recovery of nutrients (e.g., N, P). Qualitatively and quantitatively works should be promoted for the distribution, transformation mechanism and recovery, and future efforts should take relevant analysis and treatment into more account. The fertilization potential of HTC products mainly depends on a variety of factors, such as nutrient speciation in the products, properties of soil and HTC products, plant type and growth stage, local weather, and microbial activity. Among these factors, nutrient elements (e.g., P) speciation plays a key role in P mobility, bioavailability, and overall recyclability. Hence, HTC will enable the production of fertilizers with improved P efficiency (compared to raw manures and inorganic fertilizers) via P speciation modulation during HTC, in addition to other waste management benefits such as decontamination and volume reduction. In addition to P speciation, more studies are required to correlate elemental speciation and matrix properties of the products as fertilizers and soil amendments, in order to effectively synchronize the biomass waste management and agricultural practice systems for efficient nutrient recycling. It is noted that nutrients

Fig. 18. Potential challenges of the HTC process of wastes.

in the liquid phase cannot be completely utilized, mostly depending on the form of elements and types of soil and plants. More studies are needed to determine the effect on other plants and the effect on soil over prolonged fertigation periods. The combination of aqueous-phase recirculation and use as a fertilizer can be an appropriate method to reuse the liquid phase and return nutrients to support plant growth, thus increasing the HTC efficiency and economic feasibility.

5.2. Improvement of the HTC system

The challenge also includes the improvement of the HTC process (as shown in Fig. 18) One of the most significant benefits of HTC is that they do not necessitate drying, which reduces the overall process expenditures and energy requirement. However, conventional HTC has drawbacks of heat loss, non-selective heating, uncontrolled side reactions leading to lower yield and longer residence times, therefore, researchers start to develop the microwave-assisted HTC (MHTC) process [191]. Research regarding MHTC of biomass has been rarely reported. The MHTC process combines the capability of carbonizing wet biomass with the advantages of dielectric heating by microwave irradiation. Particularly, the heat is generated within the reactant through direct molecular interactions initiated by electromagnetic waves during MHTC. The main strength of using microwave heating lies in its high selectivity, fast reaction kinetics, and homogeneous heat distribution, which significantly decreases the processing time, energy input, and capital cost [192,193].

Kang et al. [192] studied the MHTC of corn stalk for solid biofuel production by optimization of process parameters. It showed that the MHTC process can produce hydrochar with satisfactory properties as a direct solid fuel or auxiliary fuel. However, more studies on techno-economic and life-cycle assessments between MHTC and HTC are required to assess their benefits, limitations and sustainability in terms of process efficiency, energy consumption, product quality and carbon balance. In addition, research regarding the HTC of wastes in the continuous process is significant less compared to the batch process. Due to the complex operational barriers of the continuous HTC process, more improvements are required to make it a commercial technology. Furthermore, the challenges faced in attempts to improve the process have been identified as lack of valid kinetic and heat transfer models and insufficient data on continuous and large-scale reactors [194–196].

6. Conclusions

HTC as a promising thermochemical process can convert organic solid wastes (e.g., biomass, plastics) into value-added products (i.e., hydrochar) at a comparatively low temperature (180–250 °C) and saturated pressure (2–10 MPa). The hydrochar with high energy density and low dusty can be directly used as solid fuel. Moreover, the hydrochar can be activated to porous carbon that has a high potential in emerging energy applications (e.g., battery materials, supercapacitor, and fuel cell). HTC is mostly influenced by the feedstock types as well as loading and processing conditions. As increasing the HTC reaction severity, the extent of energy densification increased. Most of the benefit was realized at modest temperatures, since higher temperature and pressure require more complex and costly equipment and increase handling difficulties. Under the optimal conditions, the hydrochar with coal-like properties exhibited favorable behavior with respect to thermal processes (e.g., combustion). The carbonization improved the heating value and dewatering capability of the feedstocks. Process efficiency and dewatering capacity were improved by boosting the solid yield and recycling, respectively. In addition, solid loading had a positive effect on product distribution, and the process design was positively affected by internal heat recovery as the HTC reaction heat was low.

HTC is served as a key intermediate step in optimizing the chemical structures of solid fuels. The relationship between hydrothermal conditions and chemical structures of hydrochars is a long-term hot research field. A comprehensive knowledge of mechanisms controlling the evolution of organic waste structures and subsequent structure-reactivity is crucial for the terminal application of hydrochars. Chemical structures of hydrochars include but not limit to carbon skeleton, crosslinks of aromatic polymer, surface porosity, functional groups and ultimate components. All of these characteristics can be changed significantly by HTC, influencing the reactivity and fuel properties of hydrochars. However, fundamental understandings for the evolution pathways of chemical structures in relation to various hydrochars are still necessary. The reaction mechanisms of HTC for organic wastes are very complex. The reaction pathways and kinetics, even for pure materials, are not fully understood due to the formation of many intermediates via parallel and consecutive reactions. In this review, the reaction pathways including negative and positive effects during (co)-HTC of polymeric wastes (e.g., biomass, plastics) are thoroughly concluded. Significantly, the co-HTC of halogenated plastics (e.g., PVC) and biomass can enhance the removal of chlorine and inorganics from hydrochar, thereby improving its fuel properties.

Acknowledgements

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