Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: www.elsevier.com/locate/biombioe

Hydrothermal carbonization of lignocellulosic biomass for carbon rich material preparation: A review

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ARTICLE INFO

Keywords: Lignocellulosic biomass Hydrothermal carbonization Reaction mechanism Process parameters Carbon rich material

ABSTRACT

Hydrothermal carbonization (HTC) is an active area of research in synthesizing carbon-rich materials because of its ability to transform wet biomass into valuable products. Carbon-rich materials have received a great deal of attention because carbon is a raw material for several industrial products and their production from various biomasses is currently an active area of research. In addition, lignocellulosic biomass has been of great interest as precursors for the preparation of carbon-rich materials because of their low cost and due to environmental concerns. This review exhibits the research on the hydrothermal carbonization of lignocellulosic biomass, production of carbon-rich materials or carbon spheres or hydrochar by the HTC process and the role of water and the proposed mechanism in the HTC process. This research on hydrothermal carbonization mostly focused on lignocellulosic biomass materials and the effect of process parameters including the temperature, pressure residence time, pH, heating rate and substrate concentration are also discussed. The reaction mechanisms of hydrolysis, dehydration or decarboxylation and carbonization are elaborated in detail. Solid carbon-rich materials have a wide range of applications as environmental additives, biofuels, catalysts and energy storage and have been covered in detail. At the end of the review, we deliver an outlook on future research prospects and applications of hydrothermal carbon-rich materials.

1. Introduction

Carbon is a raw material for several industrial products and their production from various bio-resources is an active area of research [1]. Environmental disasters, energy scarcity and emerging customer requirements have forced people to discover environmentally friendly, simplistic, low cost and non-toxic methods to produce novel useful materials that can potentially be commercialized in the future [2]. Recently, carbon spheres have received greater research attention due to the porous structures of the spheres [3–5], exceptional chemical stability [6,7] and high electrical conductivity [8] which shows possible applications in adsorbents [9], catalytic support [10], and also in supercapacitors [11,12]. In order to prepare the carbon spheres, numerous methods have been used e.g. templating process [13,14],

pyrolysis of carbon bases [15,16], chemical vapor deposition [17,18], and hydrothermal carbonization (HTC) treatment [19]. Amongst the above-mentioned methods, the hydrothermal carbonization treatment process is more promising due to its mild operational parameters [20] and the manageable carbon sphere size [21,22]. Therefore, the hydrothermal carbonization process offers an effective and practical path to synthesize carbon particles at a low temperature and pressure [23].

Biomass denotes biological materials from plants or animal sources and their derived residue and waste [24]. Due to the potential reduction in greenhouse gas (GHG) emissions, society has recognized the usage of waste biomass as a sustainable resource [25,26]. By balancing the production of plant biomass and its utilization in the future, it is possible that zero GHG emissions can be achieved [27]. For energy recovery, diverse methods of utilization of biomass have been found

https://doi.org/10.1016/j.biombioe.2019.105384

Received 25 October 2018; Received in revised form 21 August 2019; Accepted 18 September 2019 0961-9534/ @ 2019 Published by Elsevier Ltd.



Review



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Table 1

Comparison study of hydrotherm	d carbonization pro	ocess with the other	conventional biomass	processes	[35-37	′].
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	Incineration	Gasification	Pyrolysis	Hydrothermal Carbonization
Primary reaction	Combustion	Combustion	Combustion	Dehydration
Input condition	Dry	Dry	Dry	Wet
Operating condition	800–900 °C	> 700 °C	400–900 °C	180–350 °C
Reaction	$C_6H_{10}O_5$ (s) $+6O_2 \xrightarrow{\Delta} 6CO_2$ (g) $+ 5H_2O$ (l)	C ₆ H ₁₀ O ₅ (s) +3O ₂ \xrightarrow{A} 6CO (g) + 5H ₂ O (l)	$\begin{array}{l}C_{6}H_{10}O_{5}\left(s\right)\overset{\varDelta}{\rightarrow}6C\left(s\right)\ +\ 5H_{2}O\left(l\right)\end{array}$	$C_6H_{10}O_5(s) + H_2O \xrightarrow{\Delta} C_6H_2O + 5H_2O(l)$
Reactant	Air/Oxygen (Excess)	Air/Oxygen (Partial)	None	Water
Initial Process	Chopper dryer	Chopper dryer	Chopper dryer	Chopper
By-Product	Ash	Ash	Char	Volatile liquid + CO_2
Main Product	Gas	Gas	Oil	Char

environmentally friendly and economically viable [28]. Biomass, for instance lignocellulosic waste, municipal solid wastes and sewage sludge are believed to be ample and renewable resources which can be transformed into solids, liquids and gases by utilizing thermo-chemical, bio-chemical and physico-chemical technology [24,29,30]. There are some drawbacks to biomass as a sustainable resource (which immediately needs to be overcome; e.g. its heterogeneity, presence of contaminants, low energy, high moisture content, and low density. In earlier investigations, common approaches of biomass utilization have comprised biological conversion, densification to a solid fuel, pyrolysis, and hydrothermal carbonization processes [31–34]. The HTC process is vastly pioneering in the field of biomass utilization because of a number of advantages. HTC can be performed at low temperatures (180–350 °C) compared to the other conventional biomass processes like incineration, gasification and pyrolysis as listed in Table 1.

Hydrothermal carbonization is an effective technology to carbonize wet biomass to evade the energy concentrated pre-drying step [38]. Normally, in the HTC procedure, the wet biomass remains heated in a high-pressured container at comparatively lower temperatures i.e. 150-350 °C [39]. The HTC process has been introduced successfully and applied practically. The water use here is economical, non-toxic and environment-friendly [40]. The HTC process is directed by hydrothermal parameters like temperature and residence time, which control the reaction severity and degree of coalification of the raw biomass [41,42]. The hydrochar obtained from the HTC procedure exhibits highly hydrophobic and brittle properties, and therefore is easier to separate from the liquid product. Hydrochar has been extensively utilized based on the different kinds of biomass for chemical industry, carbon sequestration, agronomy, bioenergy production, and other uses like the biomedical field etc. Compared to the solid products, the liquid product requires a separation process by means of extraction similar to those used for bio-oil production. Besides this, the investigation has demonstrated that liquid products obtained from HTC treatment are bio-degradable because of their organic substances [43-45]. Hydrothermal carbonization is an exothermal process that lowers both the oxygen and hydrogen content of the feed by mainly dehydration and decarboxylation [46]. The carbon-rich materials have many interesting utilizations. The sustainability advantages of production of hydrochars and their potential applications are summarized in Fig. 1.

Firstly, the lignocellulosic materials like plants and their derived residue and waste goes through the hydrothermal process at an elevated temperature. Hydrochar, bio-oil, and synthesis gases or syngas are produced during the hydrothermal process. During the HTC process, the hydrochar produced can be employed in water treatment, soil amendment, as a solid fuel, biomedical uses etc. The bio-oil comprises many organic compounds e.g. phenolic derivatives, aromatic hydrocarbons, alkanes and some extents of ethers, ketones, amines, alcohols, sugars and esters. Furthermore, the syngas obtained during the process primarily comprises hydrogen, carbon monoxide, and very often contains carbon dioxide. The syngas too remains an intermediary in generating synthetic petroleum to utilize as a fuel or lubricant. Hydrochar or carbon spheres or carbon materials in recent years have received substantial attention because of potential applications and benefits in various fields like energy storage, environmental protection, clean solid fuels etc.

There has been a rapid growth since 2009 in the HTC of biomass research and the number of publications related to the production and application of hydrochars has increased. In 2011, Libra et al. [39] and in 2014 the Reza et al. [47] studied the technical and climatic change aspect of hydrochar production and also discussed detailed applications in soil remediation. The benefits of hydrochars derived from waste biomass by means of a clean solid fuel from the hydrothermal process have been reviewed by researchers such as Zhao et al. [33] and Kambo et al. [48]. Okajima et al. [49] studied the commercial and large scale applications of the hydrothermal process. Jain et al. [50] reviewed the transformation of waste biomass by means of the HTC process into activated carbon by high porosity hydrochar formation mechanisms and acknowledged a functional group of high density oxygenated products. Khan et al. studied nitrogen-phosphorus-potassium (NPK) fertilizer coated with superabsorbent carbonaceous microspheres polymer (SPC) and results showed that NPK coated with SPC has a low release rate with < 50% nutrient release compared with uncoated NPK at the 30th day [51].

So far, a small number of reviews have concentrated on describing the mechanism of hydrochar formations, particularly in terms of available lignocellulosic biomasses. As silviculture and agricultural production continues to rise, the extra biomass to support the bio-based industries will become available. The HTC process needs to be understood in the development of biomass conversion and also to discover the challenges, research progression and prospects of carefully using the advantages of hydrochars. In this review paper, we discuss the research on hydrothermal carbonization of lignocellulosic biomass, production of carbon-rich materials or carbon spheres or hydrochar by the HTC process and the role of water in the HTC process and the proposed reaction mechanism of hydrothermal carbonization (HTC). Carbon-rich materials obtained from the HTC process have potential applications ranging from waste water treatment to soil amendments, biofuels in gasification to combustion processes and low-cost catalysts to energy storage applications have been discussed in detail. Furthermore, we deliver an outlook on future research prospects and applications of hydrothermal carbons.

2. Hydrothermal carbonization process

The chemistry behind HTC in the conversion of biomass into carbon-rich materials are not yet known widely and the reaction rates during the process are also unknown because of limited research work carried out in this field [46]. The hydrothermal process takes place in the subcritical region as seen in Fig. 2.

At various pressure and temperature ranges, Kruse [52] considered the key probability of the HTC process as shown in Fig. 2. Hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG) are the three subcategories of the HTC process. Every process converts the biomasses into different valuable T.A. Khan, et al.



Fig. 1. Graphic diagram of workable models about the carbon rich materials manufacture, applications.

products and offers various benefits.

It is generally realized that under subcritical conditions, water properties change drastically. As the temperature increases above 374 °C, it decreases the dielectric constant, and therefore weakens the hydrogen bonds in water and generates the high ionization constant which in turn increases the alienation of water into the acidic H3 O⁺ (hydronium ions) and basic OH- (hydroxide ions) [53–55]. Moreover, compared to liquid water, the aforementioned subcritical water can brag an adequately higher H⁺ focus which is an exceptional medium for acid catalyzed reactions of organic compounds without further acid [53,56]. The properties of water change intensely under different temperature ranges. Throughout the HTC process, water in the biomass possesses exceptional reactions and also works as a solvent medium [39]. The conditions are measured at moderately low temperatures between 180 and 250 $^{\circ}$ C under autogenous pressure maintained for a fixed residence time [39,46].

The various feedstocks in the recent analyses were chosen for the hydrothermal process extending from ideal materials to the actual feedstock comprising agricultural waste [57], glucose [58], cellulose [58,59], food waste [60,61], municipal solid waste (MSW) [62], sewage sludge (SS) [63,64], algal and aqua culture residues [65], and animal manure [66]. It is evident that the HTC procedure is not confined to conventional lignocellulosic biomasses only; the feedstocks can be more diverse, in addition this sustainable feedstocks translate to substantial amounts of organic matter that requires appropriate handling to prevent environmental pollution. The hydrothermal products mostly comprise three constituents; the solid (carbon-rich materials like hydrochar), the liquid solution (bio-oil) and a small portion of gases (syn



Fig. 2. Hydrothermal conversion process on biomass [52]. HTC: Hydrothermal Carbonization HTL: Hydrothermal Liquefaction

HTG: Hydrothermal Gasification Temperature (°C).

gases like CH4, CO, CO_2) and the properties and dispersal of these types of products are greatly influenced by feedstock and process conditions [67,68]. The solid carbon-rich material is viewed as the primary HTC product and can be effectively isolated from the suspension because of its homogenous and hydrophobic property [69]. Besides, HTC parameters can generate a great variety in the physico-chemical properties of the hydrochar. To completely investigate the exceptional properties and potential uses of the hydrochar, it is important to comprehend the basic procedure parameters representing HTC and the systems of the hydrochar development process.

2.1. Role of water in the HTC process

The amount of water added has an impact on product distribution [70]. Water is easily available and is essential to sustain life. Humans need water to dissolve nutrients and circulate them around the body. Other than washing and cooking, water plays an important role in various industries. For example, in the textile industry, a mixture of water and dye is essential for the process of coloring fabric.

Water exists in three different phases: ice (solid), liquid, and vapor (gas) and is the only natural substance in the world that can take on all three phases. In this research, water in the subcritical region is required to obtain better quality in the HTC process. In the subcritical region, the dehydration process is dominant compared to other processes such as the carboxylation and liquefaction processes. The physical properties of water in the subcritical region are different compared to ambient conditions (Table 2).

As a solvent, water plays an important role as an active transfer medium for ions and move from one bond to another. It also continuously breaks and connects the inactive chemical bonds and randomly connects them from one compound to another [72]. During the HTC process, water is a crucial substance because it acts as a reactant to rearrange the biomass structure. In addition, water in subcritical condition acts differently compared to water at ambient condition. During subcritical condition, organic compounds are easily miscible with the water. Lignocellulosic materials consist of solid and polymeric organic compounds therefore it increases the tendency to break the lower molecular weight organic compounds, such as OH and COOH bonds, which eventually become miscible with water. In the HTC process, the liquid mixture is known as volatile liquids. Another unique characteristic of the subcritical water is the ionization constant. The high range of ionization constant is indicating a high amount of H+ and OH- ions in the subcritical conditions. During this state, the hydrolysis process of lignocellulosic materials can be accelerated due to in-situ acid- or basecatalyzed reaction [52].

Therefore, the reaction between water and polymeric structures at a certain temperature and duration can influence the reaction process and speed up the physical and chemical interactions. As a result, solid carbonaceous materials with a high carbon content are expected to be produced at the end of the process.

3. Hydrothermal carbonization of lignocellulosic biomass

The lignocellulose-based biomasses are mostly derived from forest and agricultural resources mainly composed of cellulosic, hemi-cellulosic, lignin and some polymeric materials with low-molecular weight

Table 2

Properties of ambient and subcritical water [71-74].

Characteristic	Ambient Water	Subcritical Water
Temperature (°C)	25	300
Density (kg/m ³)	1000	713
Dielectric Constant	78	19
Solubility of Organic Compounds	Very low	Miscible
Ionization Constant	10 ¹³	10 ¹¹

materials comprising extractives and some inorganic substances [75]. Instead of primary maiden wood-based materials and vigor crops, second generation feedstocks such as forest and agricultural residues and industrial waste biomasses are cheap, often freely existing, and do not interfere with land needed for food production [76]. Paper and pulp industries produce varieties of biomass deposits that are not affected by seasonal availability or costly logistics. For example, Swedish paper and pulp industries are currently the main energy consumers in the country and make up about 46% of the total manufacturing sector. 65% of energy utilized by these industries are produced from renewable energy sources [77]. Further, industrial utilization of wood residues, waste water treatment and residual sludge streams from recycling fibers suggests further opportunities to expand the usage of renewable energy and at the same time decrease the peripheral sludge management cost. About 2 TW (TW) hour per year of potential energy is generated by Sweden's paper and pulp industries and currently merely half is used in the mill boilers [77].

The HTC process combines raised temperature and pressure and is usually done using water as a solvent [78]. The biomasses can be treated hydrothermally in a series of situations from sub to supercritical conditions separated through critical pressure (22 MPa) and temperature (374 °C) of the water [79]. In order to maximize the solid carbon material produced by the HTC process, the temperature in the reaction can be additionally limited to 180-260 °C approximately. The dielectric constant of the water under these conditions is subsequently reduced enabling properties comparable to the organic solvents at room temperature whereas increased ionization constant helps reactions which are usually catalyzed by acids or bases [79,80]. The first HTC process of biomass was reported in the early 20th century by means of a technique aimed at simulating natural coalification [81]. However, it did not acknowledge subsequent attention for advancement of different biomass and waste feedstocks until 5-10 years ago. The HTC process appears practicable for upgrading wet, low-value fuels by growing corresponding energy density, reducing volatile contents and oxygen and improving hydrophobic property [39,46]. HTC has the potential to convert the biomass into a hydrochar especially from sludge (low cost feedstock), moving toward the qualities of low rank coals thus expanding the potential utilization in the energy production and thus providing subsequent straightforward storage, handling and transportation [33,46,82]. As the HTC process is preferably operated under a saturated steam pressure, the energy required for evaporation can be avoided making the theoretical energy requirement for heating the reaction medium significantly lower compared to active drying [79,83]. Energy is as vital and aimed at post treatment of solid and liquid separation, however, it can be subsequently lower as compared to the orthodox sludge drying because of potential sludge breakage of cells and improved drying features [84]. The majority of literature published in the journals on the hydrothermal carbonization of biomass for solid fuel fabrication has been concentrated mostly on the carbonization of model compounds e.g. cellulose [59,85], original wood materials [86,87], herbaceous materials [69,88] and also varied feedstock's [58,88,89] to clarify the mechanism of carbonization and properties of hydrochars.

The HTC process is a thermo-chemical transformation process aimed at changing biomass into a carbon-rich material product. In recent years, the hydrothermal process has generated some interest as potential applications for biomasses. Research and development have been carried out to measure the possibility and to discover further application possibilities. Research has been conducted on lignocellulosic biomasses and extractives like cellulose, glucose, lactose, xylose etc., to produce carbon-rich materials or carbon spheres or hydrochar by HTC. An assessment of the HTC process for carbon-rich materials formation has been concisely presented in Table 3.

Table 3

Summary of hydrothermal carbonization research with some key results for the carbon rich material formation.

Feedstock	Temperature °C	Time hours	Products	Product Size	Carbon Yield (%)	Reference
Enzymatic hydrolysis lignin	270	7	carbon spheres	3–6 µm		[90]
Oil palm pressed fiber (OPPF)	200	4	Hydro-char		58.8	[91]
Glucose	200	0.45	Hydro-char	1–10 µm	62.32	[92]
Corn Stalk	200	40	Hydro-char microspheres		56.97	[93]
Glucose	180	10	carbonaceous material	1.5 µm	65.3	[94]
Glucose	180	4	Carbon nanospheres	100-200 nm	62.69	[95]
Rice husk	300	16	Biochar		47.32	[96]
Rubber wood fiber	260	7	Carbon microspheres	1.5–5 μm	68.10	[1]
Wood Meal	265	20	Hydro-char	1–5 µm	74.22	[97]
Lignin	265	20	Hydro-char	1–5 µm	68.43	[97]
Cellulose	265	20	Hydro-char	1–5 µm	72.10	[97]
D-Xylose	265	20	Hydro-char	1–5 µm	72.80	[97]
Glucose	180	2	Carbonaceous material		61.03	[98]
Lactose	180	4	Carbonaceous material		40.05	[98]
Olive waste	180	4	Carbonaceous material		58.97	[98]
Hazel Nutshell	180	4	Carbonaceous material		52.98	[98]
Palm oil empty fruit bunch	220	22	Bio-carbon		62.16	[99]
waste corn stalk (CS)	250	4	Carbon microspheres	1–3 µm	71.36	[100]
Tamarix ramosissima (TR)	250	4	Carbon microspheres	1–3 µm	72.08	[100]
Glucose	190	4	Carbon spheres	350 nm	-	[101]
Jeffrey Pine and White Fir (Tahoe Mix)	295	0.3	Solid char	-	73.01	[102]
Cellulose	250	2	Carbonaceous micro-spheres	2–5 µm	71.46	[103]
Glucose	500	12	carbon micro-spheres	1–2 µm	-	[104]
Glucose	160 & 500	6 & 4	disordered carbon spheres	100-200 nm	-	[105]
Kenaf Fiber	225	10	Bio-char		60.2	[106]

4. Effect of process parameters

4.1. Temperature

The rate of reaction in the HTC process is affected by temperature to a substantial degree [46]. In the hydrothermal process, temperature is a vital factor as it is the key factor of water properties which initiates an ionic reaction in the subcritical regions. Beyond the key point, the reaction mechanism shifts from ionic reactions to free radical reactions in the supercritical region [53]. In the ion-led hydrothermal reaction, the increasing temperature changes the viscosity of water, allowing for easy permeation into the porous media, and therefore degrades the biomass further [46].

Temperatures approaching a definite reaction concentration have a conclusive impact on the hydrolysis reaction of biomass, and the higher temperatures can lead to dehydration, decarboxylation, and condensation simultaneously. At higher temperatures, with adequate time, it may prompt a higher degree of intermediary dissolution and consequent transformation via polymerization and secondary char formation which controls the mechanism of hydrochar development [107]. Using temperature modification, the resulting variations can also be validated through the elemental compositions of hydrochar products and Van-Krevelen diagram analysis describing the development of O/C and H/C atomic ratios [108]. An increase in hydrothermal temperature from 230 to 250 $^\circ$ C instigates a reduction in the atomic ratios of H/C and O/C, proposing that an increase in temperature boosts the degree of the condensation reaction of the hydrochar products as reported by Sevilla et al. [103]. Jamari et al. [99] investigated the HTC process on palm oil empty fruit bunches and employed an operating temperature between 180 and 220 °C and the result indicates the H/C and O/C decreases with an increase in temperature. A reduction of 55% of O/C and 38% of H/C atomic ratios was calculated and they also observed a clearer dehydration tendency as compared to a lower operating temperature. A study of empty palm fruit bunches as the lignocellulosic materials by Parshetti et al. [109] employing the temperatures of 150, 250 and 350 °C showed that the atomic ratios of O/C and H/C of the hydrochars decreased gradually with the increase in temperature. A similar trend is also observed for the other biomass materials such as sewage sludge (SS), starch, municipal solid waste (MSW) [110-112].

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Additionally, the rate of polymerization of fragments depends greatly on the temperature but the process isn't yet clearly understood due to lack of research [46].

In general, the product distribution is greatly determined by means of temperature and when the temperature is increased, the hydrochar yield of bio-oil and gas products decreases. However, Ying et al. [59] discovered that once the temperature rises over 200 °C, the solid products of cellulose decreases because of enhanced disintegration by means of the fragmentation of big molecules into the constituents of liquid or incondensable low gas molecules. As the temperature is raised, it leads to secondary disintegration of the solid residues which results in the advanced conversion of the condensable product into incondensable gaseous products. The hydrochar yield in terms of the mass of lignocellulosic biomass is decreased from 69.1% to 50.1% once the temperature is increased from 215 to 255 °C as reported by Hoekman et al. [102] because of the transformation to total organic carbon (TOC) in the liquid products comprising sugars and organic acids. However, temperatures above 295 °C leads to lower TOC by means of lower sugar contents and higher organic acid contents. Once the hydrothermal reaction temperature of SS is increased from 180 to 300 °C, the yield of hydrochar is decreased from 66% to 53% which results in an advanced degree of condensation as a result of increasing the temperature of the hydrothermal process. This lower yield was ascribed to the dehydration, decarboxylation and volatile matter reduction with low hydrogen and oxygen content at higher temperatures [113]. Though the higher temperature leads to a decrease in solid residues, the energy densification of hydrochars has been detected in numerous reviews which reinforces hydrochars as a good source of solid fuels. The hydrothermal reaction temperature affects also the average diameter and size distribution of carbon-rich materials where a higher temperature leads to a more uniform average diameter and uniform size distribution [114]. However, a temperature that is too high carries a risk of forming carbon microspheres that are fused together and larger in size. Romero-Anava et al. [115] studied the change in morphology at different temperatures i.e., 180, 200, 220 and 240 °C by HTC treatment on three carbohydrates (glucose, saccharose and cellulose) with a constant residence time (24 h). The change in morphology as a function of all the three carbohydrates at the various temperatures can be seen in Fig. 3. The study concluded that at 200 °C, all three carbohydrates developed carbon



Fig. 3. Morphology of glucose, saccharose and cellulose before and after HTC treatment at different temperatures (180-240 °C) [115].

spheres with larger sizes.

4.2. Pressure

The hydrothermal reaction pressure impacts the network reaction in accordance with Le Chatelier's principle, also known as the equilibrium law. At a higher reaction pressure, it can be simply determined that both dehydration and decarboxylation as the main general reactions remain depressed. This outcome has been proven by experiment and demonstrated to lowly affect both the HTC process and natural coalification [116–119]. The hydrothermal reaction pressure increases isotropically with the increase in temperature or by adding liquids, therefore, it is vital to differentiate the type of force that is applied. In the course of heating period (in the case of unstirred reactor), the solids are dispersed simply by gravitational force in addition to natural possible convection. Interestingly, a few tests connected guided forces keeping in mind the end goal to simulate lithostatic pressure because of overlying materials [120–122]. It is believed that the removal of extractable material from the biomass materials is possible at higher

pressure. It is presumed that condensed gases are dissolved and compressed in the liquid which permits a wider access of aqueous phase [123]. A century ago, some publications reported the compaction of hydrothermal reaction of coal during HTC increases the carbon content [124,125]. Therefore, compaction mainly influences the physical qualities and may upgrade the reaction rate indirectly by permitting a higher biomass/water ratio.

4.3. Residence time

The residence time of hydrothermal reaction is one of the important factors for carbon-rich materials formation. It is reported that residence time ranges from few hours to several days but the exact time could not be determined except for some published data which varied between 1 and 72 h [46]. Compared to temperature, residence time has a similar but smaller impact on the recovery of solid products. Residence time has a direct influence on hydrochar production; when the residence time is short the solid hydrochar content is high and when the residence time is long, the solid hydrochar content is low. An extended residence

time brought about the polymerization of fragments in the fluid stage that prompted the development of auxiliary hydrochar by means of polyaromatic structures [97,126]. The auxiliary hydrochar development heavily depends on residence time in the case of lignocellulosic biomasses because a wide polymerization is a requisite for dissolved monomers. In contrast, non-dissolved monomers possibly will have a larger dependency on temperature. An increase in residence time from 0.5 to 24 h at 240 °C shows the different hydrochar surface properties of water hyacinth [127]. The results show trenches and cracks on the hydrochar surfaces at a short residence time i.e. at 0.5 h, but at 6 h' residence time, the development of micro-spheres and carbon microspheres with 1 um diameters. An accumulation of micro-spheres on the hydrochar surface developed at 24 h residence time [127]. The degree of decomposition of biomass is controlled by the residence time at a specific temperature by determining the hydrolysis and polymerization of the monomers, resulting in different texture of hydrochar after the micro-sphere formation. This factor not only runs the means of aggregation or dispersion of the micro-spheres, but also influences the diameter of microspheres. A detailed conventional hydrothermal process with residence time is described by Titirici [128]. A constant 10% wt. concentration of glucose for a 2-h residence times showed no solid residue and the glucose was dehydrated and decomposed into small soluble organic molecules. After a 4-h residence time, the solution color became dark indicating that aromatization/polymerization has happened, known as the polymerization stage. Sevilla et al. [111] discovered that hydrothermally carbonized glucose at 170 °C with 4.5 and 15 h residence times exhibited different mean micro-sphere diameters. A comparable outcome was seen in the study of Romero-Anaya et al. [115] where they demonstrated that lengthier residence times i.e. 12-48 h revealed that at 12 h residence time, the carbon spheres do not possess a clear morphology when compared to 24 and 48 h residence time as shown in Fig. 4.

4.4. pH

Several reports have noticed a drop in pH level because of the formation of organic acid during the hydrothermal process. Organic acids act as a crucial transitional throughout the hydrothermal reaction succession to catalyze bio-macromolecule decomposition and development of hydrochar. Therefore, during the HTC process, differences in pH have an impact on hydrochar characteristics. Normally, the hydrothermal procedure is thought to be auto-catalytic for the development of organic acids like lactic acid, levulinic acid and formic acid from the biomass, causing a drop in pH [50,129]. During the hydrothermal reaction process, the addition of acid or alkali can be utilized as a catalyst which leads to a growth in protons or hydroxide-ions that causes a high ionic strength, altering the pathway of reaction or accelerates the rate of reaction to accomplish the anticipated hydrochars [46,50,130]. In the hydrothermal reaction experiments the different acids and bases have been used for various purposes. Ca(OH)2, NaOH, KOH, NaHCO3, Na2CO3, K2CO3 and CH2COOH have been used as catalysts to accelerate the rich hydrogen gas production [131,132]. The effect of the hydrothermal reaction of cellulose in the occurrence of various primary concentrations of acids and bases by using H2SO4, NaOH, Ca(OH)2, and HCl as additives have been studied by Lu et. Al [85] The result shows that these additives accelerate the disbanding of solid cellulose and once the additive concentration is increased, the conversion of glucose is accelerated. The result also shows that the presence of acids improves the dehydration process, which remains a dominating carbonization technique ensuing in a significant decrease in oxygen content in hydrochar. The outcomes also demonstrated that CO₂ production by acidic additives improved the decarboxylation of organic acid decomposition [85]. A similar impact has been found in basic conditions on solid hydrochar although this condition appeared to have a significant impact on 5-hydroxy-methyl-furfural-1-aldehyde (HMF) decomposition which was converted into formic or levulinic acid.

Nevertheless, there was no effect on the dehydration mechanism with the addition of bases [85]. The Reza et al. [133] operated the hydrothermal reaction of wheat straw using feed water with pH of 2-12 prepared by means of potassium hydroxide and acetic acid. The results showed that the hydrochar and liquid products varied according to the pH level. The lower pH condition leads to low sugar content and high furfural byproducts, pore volume, organic acids and high surface area. Compared to cellulose and hemi-cellulose, lignin was discovered to be extra reactive in basic water. Phenolic compounds like guaiacol and catechol were found and their concentration increased marginally in the basic water, which indicated that the lignin had started decomposing to monomers [133]. It is not surprising that based on these results, the catalytic part of high pH level in the hydrothermal process indicates a lower yield of solids through a sped-up hydrolysis process or decomposition during the HTL. The hydrothermal reaction study of husks and nuts at a pH range of 4-13 by Yang [134] showed that pH 13 level reduced the solid yield significantly but there was no change during the 4-10 pH range. Flora et al. [135] studied the effects of alkalinity and acidity of the process water and hydrochar washing on the adsorption of atrazine on hydrothermally produced hydrochar and the result shows that final filtrate pH was different significantly but varies in a small range between 4.98 and 5.21 during the hydrothermal reaction of waste food utilizing NaOH and HCl additives.

All these results emphasize the solid effect of basic and acid additives to the treating water, and by what means the hydrochar structure attached with the process mechanism can be decided through the hydrothermal environment. The adding of acids accelerates the hydrolysis process and also decomposition by means of improving the intermediary products, comprising the production of organic acids and the decarboxylation meant for CO_2 production.

4.5. Heating rate

Another important factor which affects the hydrothermal process is the heating rate. In general, a higher heating rate does not support hydrochar formation. Zhang et al. [136] investigated the impact of heating rates from 5 to 140 °C min-1 on the HTC process of grassland perennials. The result indicated that when the heating rate is increased, the solid hydrochar yield is reduced from 22-23% to 8-9% while the liquid yield is increased significantly from 61-63% to 73-76% of the entire biomass. Zhang et al. [137] in another study clarified that the hydrochar yield of corn stover and wood chips decreases (from 19 to 9%) with the increase in heating rate i.e. from 5 to 140 °C min-1. By utilizing high heating rates, the heat transfer and mass transfer restrictions can be reduced and for the secondary reactions the available time for intermediary products is also minimized during the hydrothermal process [138]. Therefore, the higher heating rates are normally utilized for HTL. Brand [139] examined the impact of heating rate on cellulose and pine sawdust and in his results a similar trend was discovered. The result indicates that an increased heating rate from 2 to 20 °C min-1 was favorable for the conversion of biomass into bio-oil, signifying that a decreasing trend was discovered for solid hydrochar formation. The H/C and O/C atomic ratios are also decreased as the residence time and temperature are increased in the case of low heating rates. Therefore, lower heating rates enhances the degree of carbonization and clarifies the moderately low HHV (Higher Heating Value) of hydrochar acquired at higher heating rates and shows that a proper heating rate can be chosen for the period of hydrothermal process to influence the dispersal of solid hydrochar and liquid products. Table 4 summarizes some important properties of solid hydrochars in relation to heating rate [28].

4.6. Substrate concentration

The higher concentration of substrates utilized in the hydrothermal reaction process are probably to accomplish a high production level but



Fig. 4. Carbon spheres obtained by HTC treatment of glucose and saccharose at different residence times from 12 to 48 h [115].

only a small number of studies have concentrated on the impact of hydrothermal process concentration. Knezevic et al. [140] exhibited that a high primary concentration of glucose delivered the HMF that promptly formed some polymerization reactions. Though increasing the concentration of raw substrates have shown inverse relationship for liquefaction reactions during the hydrothermal reaction process, the products obtained from the raw biomass may partially produce a polymerization reaction due to the incomplete hydrolysis of polymers. An increased concentration of cellulose lead to a decreased yield of hydrochar and the solid product shows comparatively high H/C and O/ C ratios as reported by Sevilla et al. [103]. Their outcomes demonstrate that the inadequate hydrolysis procedure prompt the development of a few monomers, which produces the precursors for condensation or polymerization. Simultaneously, because of an inadequate polymerization reaction of solvable product resulting from the higher concentration of raw biomasses, the solid product may have a lower degree of agglomeration of microspheres, which can be conditional from the micro-sphere diameter. Sevilla [103] reports that an increased concentration of cellulose from 40 to 160 g L^{-1} at 250 °C resulted in smaller micro-sphere development. Therefore, it is concluded that hydrochar properties resulting from various concentrations heavily depends on the type of precursor and HTC condition, particularly the residence time which delivers adequate time aimed at the fabrication of solvable products and polymerization. There is a need for a systematic study to examine the variations of biomass concentrations and single modules of hydrochar properties.

5. Reaction mechanism

Many chemical reactions that might appear during hydrothermal carbonization have been mentioned throughout the literature, but just a few have been the focus of detailed investigations. The rate of reaction

Table -	4
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Effects of the different	process par	rameters of H	ITC on the	physical/chemical	characterization of	of hydro-char	[28].
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-	-	-						
	Increase parameters	Solid yield	BET surface area	Porosity	H/C	O/C	Energy densification	Equilibrium moisture
	Temperature Residence time Feed water pH Substrate concentration Heating rate	- - ND ND -	+ + - ND ND	+ + - ND ND	- - + +	- - + +	+ + ND ND -	- ND ND ND
	e e							

"+": increase effect. "-": decrease effect. ND: not determined.



Aromatic carbon network

Fig. 5. The proposed mechanism of formation of spherical like structure hydrothermal rubber wood (HTRW) carbon from rubber wood by hydrothermal carbonization [1].

which happens during the HTC procedure is not broadly known due to the lack of research work done in this area [8]. So, for the time being, only a separate discussion of general reaction mechanisms that have been identified can provide useful information about the possibilities of manipulating the reaction. These mechanisms include hydrolysis, dehydration, decarboxylation, condensation, polymerization, and aromatization. Fig. 5 represents the proposed mechanism of the hydrothermal carbonization (HTC) process by Khan et al. [1].

They do not represent consecutive reaction steps but rather form a parallel network of different reaction paths. It is understood that the detailed nature of these mechanisms, and their relative significance during the course of reaction, primarily depends on the type of feed. The mechanism seen in Fig. 6 can be summarized as follows:

5.1. Hydrolysis process

The hydrolysis process ensues during the elevated temperature period and short residence time. In this process, water molecules form hydroxyl (-OH) and hydronium (H3O+) ions and depolymerize the polymer bonds that exist in plants into smaller bonds, such as cellulose into glucose substances [19,46].

5.2. Dehydration or decarboxylation process

Dehydration or decarboxylation process occurs as dehydration expels the oxygen (O) and hydrogen (H) particles. Amid the decarboxylation procedure, the oxygen and carbon (C) ions are expelled. Compared with the decarboxylation procedure, the dehydration process is a better process as it upgrades the production of carbon-rich materials. An effective dehydration process requires an abundant amount of water during the process. Moreover, organic materials respond well in subcritical water conditions due to the physical and chemical characteristics of the liquid phase. Accordingly, it is vital to ensure that the



- a) Hydrolysis, dehydration, fragmentation
- b) Polymerization
- c) Solid-Solid conversion

Fig. 6. Mechanism of carbon rich material formation from lignocellulosic biomass [93].

samples are submerged all through the process [19,46] to decrease the production of carbon dioxide (CO₂).

The dehydration process is utilized to dispense water molecules from a material. This procedure is a routine method in alkene and ether development from alcohol. A study using this reaction on carbohydrates has likewise been done. For instance, the splitting process of glucose through dehydration to deliver lighter chemical products, for example alkanes and 5-hydromethylfurfural (5-HMF) has been contemplated [141,142]. Equation (1) underneath is a case of the disposal procedure of water from biomass through a dehydration process.

$$C_6H_{10}O_5(s) \xrightarrow{\Delta} C_6H_2O + 4H_2O(1) \qquad \Delta H_{rxn} = 2.4kJ/Kg$$
(1)

In the HTC process, the event of the decarboxylation procedure should be decreased to guarantee that the polymeric structure of the biomass will experience the dehydration procedure to obtain the solid carbon product. Amid the procedure, the HTC and O/C proportions will be reduced gradually and by implication, carbon is left in the basic strong frame. Hence, a wet biomass is helpful as no pre-drying process is required in the HTC procedure [143]. Heat is applied all through the procedure to decrease the van der Waals and hydrogen bond forces between atoms. Flimsy ions with low energy move from the primary structure and the hydroxyl groups will trap the water molecules when the temperature is reduced. Amid this condition, almost all the hydroxyl group ions are changed into water and a new product is formed. Finally, the carbon structure is assembled in the carbonization phase. In the last stage, cross-linked polymer and aromatization forms are expected to occur [46]. Amid the polymerization, the precipitation procedure improves the arrangement of solid substances, while aromatic compounds, for example benzene can be recognized by spectroscopy examination.

5.3. Carbonization

The HTC reaction is an exothermic process which from an energetic point of view is helpful because energy is produced. Furthermore, the high thermodynamic stability of water amid the condensation process of carbon increases the amount of energy generated. This process, known as the dehydration process (Equation (1)), discharges around 33% of the energy delivered from the biomass ignition process [143]. The premise of HTC originates from the coalification procedure of wood and polysaccharides. The coalification process enhances the burning ability of wood as coal has higher density and heating values [144]. Coalification is a natural process which changes the biomass to a purer type of carbon, for example coal. Although natural coal development converts biomass material, it isn't considered to be a sustainable procedure because it takes a long time. In this way, carbonization of wood to deliver coal has turned into a more prevalent choice since this process is speedier and easier compared to the natural process. The procedure is completed in a closed framework and is ready after less than 20 days of carbonizing. The conventional kiln is known as an earth kiln, where wood is stacked on the ground before being covered with soil.

6. Applications

Carbon is a raw material for several thousand industrial products and the production of carbon-rich materials from various bioresources is an active area of research. The hydrothermal process has been recognized as an effective technique to synthesize a broad range of carbon-rich materials. Here we discuss the outlook of some applications of hydrothermal carbons and future research prospects.

6.1. Environment applications

As the hydrothermal process works on biomass, its chemistry and technology on the basis of its products are essentially supportable, a near to CO_2 -neutral process and acts in the sequestering of atmospheric CO_2 by means of diversion of biomass into the form of carbon products. The hydrothermal process of biomass represents a major conversion into carbon with maximum effectiveness to collect and bind CO_2 away from the air. Any type of carbonization can transfer the biomasses into less degradable coal compounds. Therefore, utilizing the hydrothermal process to convert biomass into coal products rapidly could signify the most effective tool for CO_2 sequestration [36].

Another potential application for the hydrothermal process of carbon material is to generate new sorbents for environmental applications to counteract the undesirable transportation of compounds among environmental section [50]. The feedstocks for hydrothermal carbons that have been examined are aimed at sorption abilities with a

wide range of biomass materials e.g. bamboo sawdust [145], feedstocks (wheat-straw, corn-stalk, saw-dust) [146], switchgrass bio-char (bioenergy crop) [147], agriculture residues [148], animal manure [149], pea-nut hull [150], rice husks, orange waste, olive pomace, compost [151], banana peels [152] etc. Water contamination is currently a universal issue that endangers human health because contaminated water contains heavy metal ions, drug residues, and pesticides. Recently some scientists have started to investigate carbon-rich materials obtained from biomass materials through the hydrothermal process as a precise sorbent. Gwenzi et al. [153] reviewed bio-char as a low-cost and viable technology for water treatment systems for under-developed countries. The usage of progressively severe ecological guidelines in developed countries to shield water bodies from contaminants (organic and inorganic) [154] has made it a necessity to acquire low-cost adsorbents from residual materials for corresponding applications. Numerous adsorption investigations by means of non-actuated pyro-chars have been completed in the most recent decade and have been outlined in recent reviews that are centered around contaminant elimination from soil and water.

Xu et al. [155] fixed glucose-based carbon nanospheres against an activated carbon host (obtained by calcination of the activated carbon at 400 °C) to obtain a novel composite of the alleged nanoarchitecture activated carbon (NAC). Demir-Cakan et al. [156] reports an alternative fascinating technique to make functional rich carbonaceous materials through the hydrothermal process. They hybridized the carbon biomass of up to 10% of acrylic acid into a carbohydrate (glucose) aqueous solution. The carbohydrate (glucose) during the HTC process decomposes into the hydroxy methyl furfural (HMF) which then experiences cyclo-addition by means of acrylic acids and poly-condenses into the derivative carbon nanospheres. When compared with pure glucose products, the resultant products have more carboxylate groups that can bind the metal ions. The results show that the sorption capability of the resulting materials have a great ability to remove Pb and Cd ions. This opens a new door to synthesize carbon-rich materials from biomasses to generate sorption materials in order to remove hazardous materials from drinking water and improve the soil conditions as well. Table 5 summarizes some important comparisons of sorbent characteristics for the heavy metals from the various feedstocks.

6.2. Biofuel

The hydrothermal process has a high potential to produce high energy density solid fuels. Firstly, the high heating values of hydrochars makes them viable to produce other forms of carbon like lignite [158]. Besides the high heating values, the hydrothermal process features other advantages e.g. sulphur or tunable-ash and contents [159], the existence of a natural binder which may encourage advance pelleting [160], and lower slagging and fouling indices that makes it more promising for ignition [47]. The performances of hydrochars in ignition and gasification processes have been studied underneath a variable scale and variable conditions. Most of the studies on ignition behavior of hydrochars have been done on a laboratory scale and that too mostly by TGA (thermo-gravimetrical analysis). Similarly, numerous researchers have investigated the co-ignition process (hydrochar and coal) by means of flexible procedures in order to regulate the fuel properties e.g. peak temperature, heat loss, emission, ignition etc., for the optimum operational condition. The performance of hydrochars from coal, sewage sludge, and their mixtures through the combustion via TGA was reported by He et al. [159]. Despite exhibiting different thermal measures that remained connected to their distinctive composition, they concluded that hydrochars and their mixtures might be proficiently utilized in the prevailing co-firing power plants and the NO_x gas emission has also reduced because of mixing and the development of corrosive sulphuric acid (H₂SO₄).

The combustion behavior should remain studied from an industrial perspective. Attention should also be paid to operational conditions and

Table 5

Comparison of sorbent characteristics for the heavy metals from the various feedstock's.

Feedstock	Temperature (°C)	Time	Sorption Capacity qc (mg/g)		Capacity qc (mg/g)			Reference
			Pb (II)	Cd (II)	Cu (II)	Zn (II)	Sb (II)	
Carbon rich material (hydrochars)								
corn stalk	200	20 h		14.5				[146]
wheat straw	200	20 h		13.9				[146]
sawdust	200	20 h		14.5				[146]
corn stalk (multi-metal)	200	20 h	2.9	1.6	2.7	1.3	-	[146]
Wheat straw (multi-metal)	200	20 h	2.8	1.3	2.2	0.7		[146]
Sawdust (multi-metal)	200	20 h	3.8	1.3	2.2	0.7	-	[146]
Prosopis africana shell	200	20 min (microwave)	45.3	38.3	-	-		[157]
Switch grasses	300	30 min		1.5	4.0			[147]
Peanut hulls	300	5 h	0.88					[157]
Modified carbon rich materials (modified	l hydrochars)							
Corn stalk + KOH	200	20 h		30.4				[146]
Saw dust + KOH	200	20 h		4.78				[146]
Wheat straw + KOH	200	20 h		38.75				[146]
Wheat straw (multi-metal) + KOH	200	20 h	21.8	4.7	11.8	3.6		[146]
Corn stalk (multi-metal) + KOH	200	20 h	18.8	4.6	10.0	3.1		[146]
Sawdust (multi-metal) + KOH	200	20 h	15.6	4.2	8.9	3.8		[146]
Peanut hulls) + H_2O_2	300	5 h	22.82					[150]
Peanut hulls (multi-metal) + H ₂ O ₂	300	5 h	16.45	0.21	1.22			[150]
Switch grass + KOH	300	30 min		34	31			[147]

this comprises the ash performance. The ash contents in a fuel may possibly lead to problems in the boiler such as slagging impact and fouling, and even the ash melting is encountered most commonly. The impact of the hydrothermal process on the combustion features of sludge was studied by Li et al. [158] who discovered that including the hydrothermal process as a pre-treatment improves the combustion and fouling issues drastically. Furthermore, the concentration of chlorine content was reduced which allowed the boiler to operate in a better condition and hence yielded an improved combustion behavior. The incorporation of the hydrothermal process in a usual cogeneration heat and power (CHP) plant has been investigated primarily by Saari et al. [161]. They explained a situation evaluated in terms of energetic and economic and parameters in order to get a profitable scheme for hydrochar production along with a heat of the combustion plant. Despite this focused incorporation, there are a few disadvantages to be considered, for example the utilization of water in a high amount and the liquid sewage treatment which increases the misuse cost. Recently, some researchers have studied this segment regarding the valuable liquids originated from biomass HTC process and signifying a highly commercial rentability [162]. Hydrochars have been examined as a precursor in order to produce synthesis gases (also known as syngas) via the gasification process with steam or air as a gasifying agent. Due to its higher carbon content as compared to the respective precursors, hydrochars can provide a larger proportion of carbon monoxide (CO), hydrogen (H₂) and under certain conditions, methane (CH₄). Furthermore, the gas composition and flow rate are less variable over time, due to the lessor volatile matter of hydrochars.

Similar findings have been identified by Moon et al. [163] and Alvarez-Murillo et al. [164] by utilizing sewage sludge and olive stones, respectively. In contrast, Lin et al. [165] discovered that the hydrothermal process as a pretreatment improves the carbon dioxide (CO_2) gasification of MSW (municipal solid wastes), endorsing the advanced reactivity. Gunarathne et al. [166] also completed an analysis in a constant up-draft gasifier situated in an experimental plant; gasifying hydrochars from spent brewery grains. Even though their results showed potential i.e. a syngas with a calorific value of 7.9 MJ·Nm^{-3} , they discovered certain issues because of ash slagging. It demonstrates that special care must be paid to this phenomenon, as also seen in the case of experimental combustions.

6.3. Catalyst

The necessity for discovery more environmentally supportable routes to synthesize materials or degrading dangerous products has also interested the scientists towards the exploration for green catalysts. Recently, many alternatives have focused on the hydrothermal process of biomass materials and their derivatives. The objective is these materials will be utilized as a catalyst with a tunable surface, high stability properties, and are efficient in many ways. Using hydrochars as a catalyst in the area of hydrogen production have been studied extensively. Safari et al. [167] examined the HTG (hydrothermal gasification) of macro algae for hydrogen (H₂) rich gases production. They discovered that hydrochars acquired high contents of ash and potential catalytic activities from these processes. The catalyst not only catalyzed the production of H₂ gas, but then also improved the formation of phenols in the liquid stage while the acid production was hindered. Shang et al. [168] studied the catalytic production of hydrogen (H₂) from room temperature hydrolysis of ammonia borane. The sodium polyacrylatebacked catalyst via hydrothermal process of glucose at 180 °C for 8 h was pyrolyzed further at 800 °C for 1 h and improved through Ni_x-Pdy nanoparticles. This process allows them to achieve the homogenous biomass centered carbon spheres with a surface area of 1186 m² g⁻¹. The highly dispersed Ni-Pd nanoparticles attached on the carbon spheres have been effectively synthesized via a simple co-reduction path and by utilizing the catalyst efficiently enhanced the hydrogen (H₂) production. The resulting Ni₃-Pd₇/CS catalysts show some exceptional catalytic activities aimed at the hydrolysis of ammonia borane at room temperature by means of an incoming frequency of 182 mol hydrogen (H_2) mol catalyst⁻¹ min⁻¹. These hydrothermal carbon spheres as catalysts have higher values as compared to the commercial activated carbons and also the prepared catalysts will endorse the serviceable applications of ammonia borane in the fuel-cell systems.

The lignocellulosic biomass hydrochars have been used also to improve the degradation of organic compounds in addition to some favorable outcomes that have been obtained so far. For example, Gai et al. [169] arranged pine sawdust hydrochar microspheres by adding iron salts with various concentrations and heated the solution (200 °C for 1 h) in a sealed autoclave and applied them to enhance the degradation of phenol i.e. used as tar model compounds. The result shows that the uniform dispersion of carbon spheres with a Fe precursor tightly embedded in micro- and mesospheres have been obtained by hydrothermal synthesis. These materials were used as catalysts through the phenol degradation and provided larger catalytic activities and also showed resistance to coke deposition. Prasannan and Imae [170] synthesized carbon dots from orange leftover peels by means of the hydrothermal process and then utilized them as successful photo catalysts for naphthol blue black (NBB) azo dye degradation under an ultraviolet (UV) radiation. Excellent photo catalytic activities were exhibited. Lastly, because of their rich and tunable surface functionality mostly the oxygen ones, the biomass of hydrochars have been utilized in a number of carbo-catalyzed reactions in which specific active sites are required, provided that a simpler and environmental friendly paths, without using acids e.g. H_2SO_4 or HNO_3 , to produce such functionalities. Some examples are nitrobenzene reduction and Beckmann reordering reactions, by using glucose hydrochar [171] and glycerol etherification [172].

6.4. Energy storage applications

Carbon materials has been used in the application of energy storage e.g. as electrode material for super capacitors (Electrostatic doublelayer capacitors (EDLCs) or electro-chemical capacitors (ECs)). These types of devices can be utilized in numerous electric vehicles, electronic portable devices or cold start (automotive) assistants, and shows an improved execution over the secondary batteries like lengthier lifecycle and capability rate [173]. There are numerous types of carbon materials used so far such as activated carbon, carbon nanotubes (CNTs), and composite materials etc., but the environmental and cost effect associated with these processes requires the examination of new and more viable synthesis methods [174]. The earlier stated benefits of hydrothermal process in connection to other thermo-chemical processes have inspired the study of this process in order to produce energy storage devices from biomass. The absence of inherent porosity related to the biomass-based hydrothermal process material is a key hindrance in their utilization in energy storage devices. An adequate distribution of pore sizes and high surface area in the small ion diffusion pathway (mostly micro-porous and also with the presence of larger pores) are desired to ensure the effective diffusion and transportation of ions throughout the materials. The hydrothermal process materials typically show a favorable and homogeneous dispersal of nitrogen and oxygen functionalities on hydrochars which can be extremely fascinating when aimed at improving pseudo-capacitance by means of further Faradaic reaction and inherent catalytic activities in the electro-chemical devices. Therefore, low carbohydrate contents and higher protein precursors are extremely fascinating.

Furthermore, prior to the hydrothermal process the additional functionalities can be inserted into the framework of carbon via chemical addition. The other important point of hydrochars in connection to their utilization as a super capacitor are higher mineral contents which can enhance their behavior. The hydrothermal process can be used to increase this characteristic [50]. The literature offer a wide range of work in using pure biomass materials such as polysaccharides, amino acids, monosaccharides, sugars, proteins etc., while mixed biomasses have been studied to a limited degree. Most of the authors acknowledges that the hydrothermal process can't be singularly suitable to produce materials with super conductive properties but many have successfully executed the two-step process coordinating the hydrothermal process and chemical activation in order to obtain carbon materials with a tunable porous arrangement. A number of reviews show that KOH is undoubtedly the most utilized activated agent aimed at better porosity growth in the hydrochars with the aim of enhancing super capacitor execution [175-179] as compared to the other chemical agents such as NaOH or H₃PO₄ [180]. KOH chemical activation has thus far the desired synthetic process to improve the porosity in a hydrothermal-based super capacitor manufacturing. Despite its success, this chemical is still plagued by environmental issues because of its harmful and corrosive characteristics due to its intense alkalinity [180]. Hence, finding efficient and viable synthesis methods to yield high porosity

materials is a work in progress. In recent times, Sevilla et al. [181] investigated the manufacturing of an electrode material derived from a glucose-based hydrochar by utilizing KHCO₃ (potassium bicarbonate) as a chemical activating agent and they succeeded in producing a high surface area of carbon material at 2230 m² g⁻¹.

The recent utilization of biomass-based hydrochars for microbiological bio-electrochemical applications is also discussed in this section. The production of enzyme derived biofuel cells from a saccharide derivative (furfural) and phenolic compound (phloroglucinol) was investigated by Brun et al. [182]. They isolated both compounds from the biomass i.e. they used pure compounds in their study. Flexer et al. [183] fabricated the monolithic carbonaceous materials HIPE (High Internal Phase Emulsion) via a hydrothermal chemical process followed by pyrolysis at 740 °C. HIPE with a high macro-pore volume (9 mL g⁻¹) and high surface area of 1130 m² g⁻¹ were used for testing the anode materials using a microbial bioelectrical technique with the aim of oxidizing the waste water and generating electricity. The result revealed that so prepared HIPE had a great biocompatibility and allowed the long-term activities of microbial groups inside the scaffolds.

7. Conclusion and future perspective

In conclusion, HTC plays an important role in converting biomasses into homogenous carbon-rich materials or carbon spheres or hydrochars. In recent years, the efficiency of HTC as a low-cost or cost-effective and determined approach to transform biomasses to value added products has been recognized. The literature review in this study identified the vital variations in the characteristics of carbon-rich materials under various parameters. Carbon-rich material products differ based on the biomass origin and the variables in the hydrothermal process. An increase in temperature and residence time lead to highly condensed carbon through the removal of oxygen and hydrogen in a process similar to coalification. Apart from temperature and residence time, water also plays an important role in the HTC process. The mechanisms of raw biomasses go across numerous degradation processes during the hydrothermal process but intermediary chemicals derived from the biomass in subcritical water and a combination of solid-solid transformation are viewed as the main carbon-rich material formation mechanisms. The carbon-rich materials can potentially be used for waste water treatment, soil amendments, biofuels in gasification and combustion processes, low-cost catalysts, and energy storage applications. All these applications have been explained in detail in the literature review.

7.1. Future perspective

In accordance with the literature cited in this review, massive development has been made with respect to sympathetic HTC conversions, formation of carbon-rich materials like hydrochars, carbon spheres etc., and their characteristics. The technical and scientific difficulties that have hampered the mechanisms behind the HTC conversion of biomass and carbon-rich material structures are completely understandable given the lack of research done in this area. Most of the research done on HTC conversion is in petroleum by-products. There is a huge number of lignocellulosic biomass materials to convert into economically viable and ecofriendly carbon-rich materials. Temperature has been identified as an important parameter influencing carbon-rich material characteristics. Besides the HTC circumstances reviewed in this literature, other parameters also deserve consideration. There is also a lack of research on the role of water in the HTC process. Therefore, detailed studies are needed in order to progress the model reactions to investigate the other process parameters in order to assess their effect in both laboratory and industrial scale level experiments. Regardless of the large number of research on carbon-rich materials in recent years, gas and liquid products have received limited attention although these by-products contain transitional products and require a more detailed research. This further research is vital to better comprehend the HTC process in connection to the formation of carbon-rich materials.

Acknowledgments

Authors are thankful to Lab. of Adhesion & Bio-Composites, Seoul National University, Seoul, Republic of Korea for necessary funding to complete this research.

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