

Hydrochar

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Recently, due to the escalating usage of non-renewable fossil fuels such as coal, natural gas and petroleum coke in electricity and power generation, and associated issues with pollution and global warming, more attention is being paid to finding alternative renewable fuel sources. Thermochemical and hydrothermal conversion processes have been used to produce biochar and hydrochar, respectively, from waste renewable biomass. Char produced from the thermochemical and hydrothermal decomposition of biomass is considered an environmentally friendly replacement for solid hydrocarbon materials such as coal and petroleum coke. Unlike thermochemically derived biochar, hydrochar has received little attention due to the lack of literature on its production technologies, physicochemical characterization, and applications.

Keywords: hydrochar ; biochar ; hydrothermal carbonization ; bioenergy ; carbon

1. Introduction

In recent decades, many researchers have focused on finding sustainable sources for fuel production due to the incremental worldwide energy demand, environmental concerns related to greenhouse gas emissions, and the finite supply of energy from non-renewable fossil fuels ^{[1][2][3]}. Biomass, which is considered a sustainable energy source, is one of the most abundant sources of renewable energy. Biomass can be classified as wet with the moisture content of >30 wt.% and dry with the moisture content of <30 wt.%. The selection of conversion technologies would depend on this classification. The examples of dry biomasses are woody, herbaceous, and agricultural biomass, whereas wet biomasses include algae, sewage sludge, cattle manure, and industrial effluents ^{[4][5]}.

Biomass can be converted to biofuels (liquid and/or solid), through thermochemical and biological processes. Biomass undergoes different and complicated chemical reactions such as dehydration, decarboxylation, decarbonylation and depolymerization to produce biofuels. Reaction temperature has significant impacts on which reactions dominate and, generally, some of these reactions are carried out simultaneously during the process ^[6]. Pyrolysis and hydrothermal carbonization (HTC) are two routes of thermochemical conversion technology for the production of bio/hydrochar as the main products (**Figure 1**). These thermochemical processes are employed to convert the biomass containing the organic compounds to carbon-rich materials. Compared to slow pyrolysis, the hydrothermal carbonization process is considered a promising technology due to the elimination of the drying step. Moreover, HTC is mostly considered economically viable for wet biomass ^{[7][8]}.

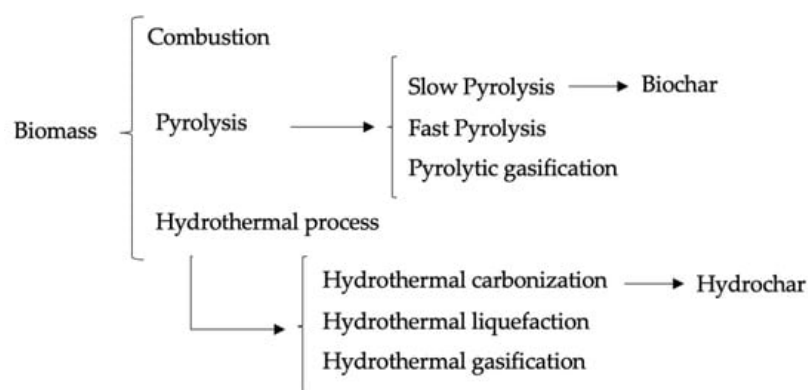


Figure 1. Conversion pathways from biomass to bio/hydrochar.

Hydrothermal carbonization is usually carried out at temperatures ranging from 180 °C to 240 °C for 5–240 min under subcritical water pressures ^{[9][10]}. Pyrolysis is performed at a reaction temperature of 300–650 °C in the absence of oxygen. The products are divided into biochar, which is not fully carbonized, liquid phase, and gas phase. Moreover, depending on the reaction time and heating rate, the pyrolysis process is divided into different categories such as fast,

intermediate, and slow. Slow-pyrolysis is performed with a low heating rate and long residence time, resulting in a higher solid product yield ^{[11][12]}.

The carbon materials include carbon fibers, structural graphite, carbon nanotubes, graphene, and carbon foams, which can be employed in different sectors such as aerospace, electronics, automotive, and construction. Recently, the demand for carbon materials has incrementally increased. Moreover, the high cost of production of carbon materials such as activated carbon using non-renewable petroleum precursors has been considered as one of the environmental concerns. Therefore, the global demand to produce carbon materials using renewable sources has increased with an annual rate of 10% ^{[13][14]}. Bio/hydrochar has received much attention as its feedstocks are abundantly available, renewable and inexpensive ^{[7][15]}.

As was mentioned previously, due to the incremental human population and industrialization, there is a concern related to the greenhouse gas emission by burning fossil fuels as a source of energy to produce value-added products as well as to improve food availability. Thus, the other advantages of utilizing bio/hydrochar for the production of the carbon materials or their application as a soil amendment can be related to global concerns, such as CO₂ emission reduction, pollution control, sustainable land use, and energy storage ^[16].

A lot of researches have focused on biochar utilization as adsorbents or catalysts/catalyst support, carbon sequestration agent, wastewater treatment, soil amendment, and electrode materials ^{[17][18][19]}. Recently, there has been an incremental interest in hydrochar production and utilization. However, a comprehensive study of the physicochemical properties of hydrochar, and the recent advances in the production of hydrochar from biomass, have not yet been reviewed. This review is mainly focused on the following aspects:

- (i) Physical and chemical properties of hydrochar compared with that of biochar
- (ii) Hydrochar production techniques (hydrothermal carbonization, liquefaction, and gasification)
- (iii) Production of highly porous activated carbons through modification of hydrochar or physical and chemical activation methods
- (iv) Applications of activated hydrochar in pollutant adsorption, catalysts support, carbon sequestration, wastewater treatment, and pharmaceutical and cosmetic applications.

2. Hydrochar Production Technologies

Hydrothermal technologies are considered to be promising technologies to produce valuable products from wet biomasses through the elimination of the high energy-consuming drying step, which can be categorized into three technologies (carbonization, liquefaction and gasification) based on their operating conditions ^{[20][21]}. Moreover, hydrothermal technologies, which can be considered theoretically carbon-neutral, play a critical role due to their increasing demand as well as growing environmental concerns.

As shown in **Figure 1**, in addition to hydrothermal carbonization, which is used to produce hydrochar as the main solid product, there are two more processes such as hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG) used to produce hydrochar as a by-product or co-product alongside bio-crude oil and syngas. The objective of the production of hydrochar as a suitable sustainable adsorbent or catalysts/catalyst support through HTL and HTG is to reduce waste materials and provide energy ^{[22][23]}. **Figure 2** shows the mechanism of formation of hydrochar from biomass, which consists of cellulose, hemicellulose, and lignin. These components undergo a series of hydrolysis, isomerization, and dehydration to produce intermediates such as furfural and finally polymerization to produce hydrochar ^[24].

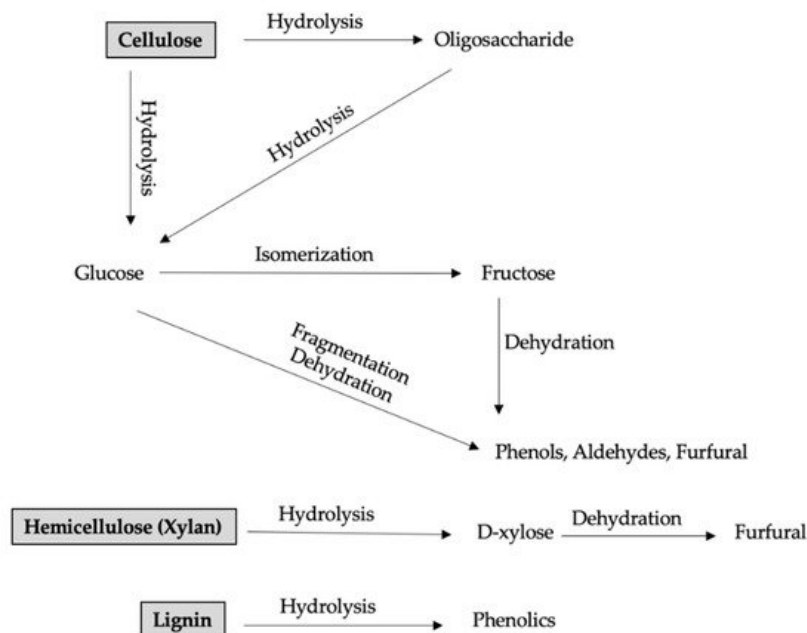


Figure 2. Proposed reaction network for hydrochar production.

The hydrothermal liquefaction (HTL) process is performed at moderate temperature (200–400°C) and high pressure (10–25 MPa) in water media to produce liquid fuel (bio-crude oil) as the main product. In addition, the solid (hydrochar), aqueous, and gas phases are produced as co-products of the process. The suitable utilization of hydrochar, which could be used as a source of heat for the process, could improve the economic feasibility, thus hydrochar characterization is important [25][26][27].

Some researchers have focused on the HTL of biomasses in water-alcohol co-solvent. As alcohols have a lower critical temperature and pressure compared to water, their addition would reduce the pressure and temperature of the HTL process. It has been shown that the addition of alcohols into the system could improve the yield and physicochemical properties of hydrochar [28][29][30][31]. For example, Masoumi et al. [28] studied the HTL of microalgae in a methanol-water system to produce and characterize bio-crude oil and hydrochar in sub-super critical conditions. All produced hydrochar revealed low porous characteristics showing a low specific surface area of 4 m²/g and a pore volume of less than 0.02 cm³/g. FT-IR results showed that supercritical conditions using water or a methanol-water co-solvent system resulted in a reduction of hydroxyl functionalities. The addition of methanol along with water for the HTL process resulted in the presence of more carboxylic acid/ester groups. Regarding the thermal stability of the produced hydrochar, higher reaction temperatures resulted in hydrochar production with higher stability, since the amount of fixed carbon in hydrochar increased, and its volatile compounds decreased because of the increasing temperature.

Hydrothermal gasification is a promising thermochemical technology used to convert carbon-rich biomass into hydrogen, methane, CO₂, CO, and small amounts of higher hydrocarbons as the main products using pressurized hot water. The produced gas can be employed as a heat resource, or it can be further processed to produce more hydrogen-rich gas products. Supercritical water conditions increased the rate of decomposition of biomass, resulting in a lower yield of hydrochar [32][33][34].

In **Table 2** and **Table 3**, different biomasses and reaction conditions are summarized for hydrochar production through hydrothermal carbonization and liquefaction. The hydrochar yield through hydrothermal gasification is not significant enough to consider it a source of solid fuel. The reaction condition required for this process is above the supercritical point of water. This severe condition is suitable to produce biogas composition. Hydrothermal carbonization has been considered as the main process used for hydrochar production, in which the yield of the produced hydrochar is higher than two other hydrothermal technologies for hydrochar production. In addition, according to the data mentioned in **Table 2** and **Table 3**, the hydrochar properties such as yield, carbon content, and HHV are highly dependent on feedstock and the reaction conditions of the hydrothermal process. Increasing the reaction temperature and time results in a decrease in the yield of produced hydrochar. On the other hand, increasing the temperature and time results in higher removal of volatile compounds, therefore the carbon content of hydrochar increases and the oxygen content decreases. Moreover, the temperature had more significant effects on the hydrochar yield and its characteristics as compared to the time.

Table 2. Hydrothermal carbonization process to produce hydrochar from different feedstocks.

| Feedstock | Temperature (°C) | Time (h) | Hydrochar Yield (wt.%) | Carbon Content (wt.%) | Atomic H/C Ratio | Higher Heating Value (MJ/kg) | References |
|--------------------|------------------|----------|------------------------|-----------------------|------------------|------------------------------|------------|
| Chinese fan palm | 180 | 1 | 61 | 55.9 | 1.64 | 24.2 | [35] |
| | 210 | 1 | 57 | 58.1 | 1.6 | 25.3 | |
| | 240 | 1 | 50 | 64.1 | 1.5 | 28.1 | |
| Chinese fan palm | 210 | 0.5 | 60 | 57.3 | 1.62 | 24.9 | [35] |
| | 210 | 1 | 57 | 58.1 | 1.60 | 25.3 | |
| | 210 | 1.6 | 57 | 59.6 | 1.62 | 26.4 | |
| Apple chip pomace | 190 | - | - | 55.9 | 0.13 | - | [36] |
| Grape pomace | 190 | | | 55.7 | 0.1 | | |
| Rotten apple | 190 | | | 62.5 | 0.09 | | |
| Apple juice pomace | 190 | | | 53.9 | 0.11 | | |
| Bamboo shoot shell | 210 | 0.5 | 56.4 | 51.3 | - | - | [37] |
| | 270 | 0.5 | 31.9 | >52 | | | |
| Corn cob residue | 250 | 0.55 | 46.6 | 61.7 | 0.08 | 24.3 | [38] |
| | 250 | | 45.7 | 63.6 | 0.07 | 24.9 | |
| Cotton stalk | 180 | 4 | 60 | 51.2 | 1.2 | - | [39] |
| | 200 | | 55 | 53.2 | 1.3 | | |
| | 220 | | 40 | 59 | 1.1 | | |
| | 240 | | 35 | 69 | 0.91 | | |
| | 260 | | 32 | 70.4 | 0.94 | | |
| Cotton stalk | 240 | 1 | 240 | 61.9 | 0.92 | - | [39] |
| | | 2 | | 64.8 | 1.03 | | |
| | | 4 | | 69 | 0.91 | | |
| | | 6 | | 69.6 | 0.94 | | |
| | | 8 | | 70.6 | 0.92 | | |
| Green waste | 190 | 1 | 80 | 48.8 | 1.2 | 19.2 | [40] |
| Moso bamboo | 220 | 1 | 51.8 | - | - | 19.8 | [41] |
| | 260 | | 40.5 | | | 28.3 | |
| | 300 | | 35.6 | | | 29.3 | |
| Rice husk | 200 | 6 | 66 | 40.8 | 1.27 | 15.7 | [42] |
| | 300 | 6 | 43 | 45.6 | 0.84 | 17.8 | |

Table 3. Hydrothermal liquefaction process to produce hydrochar from different feedstocks.

| Feedstock | Hydrochar Yield | Temperature (°C) | Time (h) | Carbon (wt.%) | Atomic H/C Ratio | Higher Heating Value (MJ/kg) | References |
|------------------------|-----------------|------------------|----------|---------------|------------------|------------------------------|------------|
| Apple pomace | 17 | 250 | 0.08 | 63.2 | 0.1 | 26 | [43] |
| | 16 | | 60 | 69.8 | 0.02 | 28 | |
| Apple pomace | 17 | 250 | 0.08 | 63.2 | 0.1 | 26 | [43] |
| | 12 | 300 | | 73 | 0.06 | 32 | |
| Microalgae | 19.5 | 222 | 0.16 | 52.1 | 0.14 | - | [28] |
| | 12.1 | 272 | | 54.3 | 0.12 | | |
| Microalgae | 19.5 | 222 | 0.16 | 52.1 | 0.14 | - | [44] |
| | 15.4 | | 0.58 | 55.6 | 0.12 | | |
| Microalgae | 28.6 | 210 | 1 | 54.89 | 0.11 | - | [45] |
| | 22.7 | 250 | | 27.33 | 0.12 | | |
| Sewage sludge | 56 | 220 | 0.5 | 7.9 | 0.16 | 3.6 | [29] |
| Wastewater-grown algae | - | 350 | 0.5 | 27 | 0.06 | 20.3 | [46] |

3. Applications of Activated Hydrochar

3.1. Agriculture and Crop Improvement

The adoption of the hydrochar for the application of crop improvement in agricultural sectors depends on the nature of the hydrochar used, the type of feedstock used, the type of the production process and process conditions, the morphological properties, and the nature of the soil, i.e., loamy clay, fertile, sandy, and infertile [47]. However, by applying the hydrochar in the soil, crop yield response could be either productive or counterproductive. The higher surface area and porosity of the hydrochar enhance the soil activity via sufficient aeration to the soil organisms through a supply of water and minerals that protect against infectious diseases [48]. In general, freshly produced hydrochar shows a hydrophobic nature owing to the presence of a low quantity of polar functionality on the surface of the hydrochar. However, when the hydrochar is mixed in the soil, over a period, it becomes oxidized by interacting with atmospheric oxygen and creates a more hydrophilic nature by creating phenolic and carboxylic functional groups on the surface of the hydrochar [49]. Due to the presence of these functionalities on the surface, the water holding capacity, cation exchange capacity, and nutrient retention capacity would increase significantly [50][51].

A vast literature is available on the application of biochar for soil improvement; however, little information is available on the application of hydrochar for this application. Rillig et al. (2010) noticed the positive outcomes on the colonization of arbuscular mycorrhiza fungi and pore germination at 20% loading of hydrochar derived from beetroot chips in soil [50]. On the other hand, anything beyond a 10% increment of the hydrochar in soil deteriorates the plant growth of *Taraxacum*. Schimmelpfennig et al. (2014) reported on a growth experiment via a laboratory incubation study with *Lolium perenne* using 16% hydrochar derived from silver grass as a feedstock [52]. During incubation, hydrochar was found to be degraded but did not show a significant impact on the ecosystem's respiration during the field experiments. Further, Bargmann et al. (2013) noticed the unavailability of nitrogen to the plants due to the absence of nitrogen migration in the first week of hydrochar addition. Nevertheless, a slow release of the nitrogen was noticed with time [53]. This behavior suggests that the hydrochar needs to be mixed into the soil for several weeks before planting. Therefore, in-depth research needs to be carried out to evaluate the ecotoxicological properties of the hydrochar and their impact on the soils to lower the negative effects of the hydrochar in soil improvement for agricultural applications.

3.2. Pollutant Adsorption (from Wastewater and Flue Gases)

As reported previously, hydrochar has a lower surface area relative to the biochars. However, due to the abundance of the oxygen-rich functionality and the presence of the chemically active functional groups such as ketones, COOH groups, and hydroxyl on the surface, the adsorption capability of the hydrochar is higher than biochar [54]. Therefore, several studies have been reported on the utilization of hydrochar for mineral and organic pollutants for aqueous solutions. The adsorption efficiency of the hydrochars depends on the physicochemical properties, experimental conditions, and pollutant properties for removal. With an increase in the hydrochar concentration, surface functional groups increase, which are responsible for adsorbing targeted pollutants. Along with higher hydrochar loading, adsorption efficiency increases with solution temperature [55][56]. Coffee husk-derived hydrochar was produced by Ronix et al. (2017) to remove the methylene blue dye from the aqueous solution. The maximum adsorption efficiency was found to be 34.9 mg/g of hydrochar at 210 °C for 4 h of reaction time [57]. Li et al. (2016) also produced a bamboo-derived hydrochar to adsorb Congo red dye and the maximum adsorption capacity was found to be 97 mg/g of hydrochar [58]. Regmi et al. (2012) prepared the hydrochar and activated hydrochar via the HTC process, using switchgrass to remove copper and cadmium from the aqueous solution [59]. The outcomes of their investigation revealed that KOH-activated hydrochar showed 100 % adsorption for copper and cadmium in 24 h relative to the hydrochar and commercially activated carbon. Pinewood and rice husk-derived hydrochars were produced via the HTL technique and applied in the removal of lead from the aqueous solution by Liu and Zhang (2009) [60]. The thermodynamics of the adsorption study revealed that high temperatures favored the adsorption of lead as it is a physical endothermic process.

Further, Fagnani et al. (2019) prepared hydrochar and activated hydrochar from sugarcane bagasse via the hydrocarbonization technique to adsorb CO₂ from a simulated flue gas [61]. Activated hydrochar showed a higher affinity for N₂ and CO₂ at 50 °C, and the maximum selectivity was found to be in the range of 12–50 °C for N₂ and CO₂, as per the law of ideal adsorbed solution. Silver fir sawdust-derived hydrochar and activated hydrochar were prepared via the HTC technique by Gallucci et al. (2020) [62]. CO₂ capture studies were assayed via pressure swing adsorption and 6.57 mmol/g of CO₂ was adsorbed at 5 bar with hydrochar. This study concluded that hydrochar showed higher adsorption compared to the activated hydrochar and other traditional sorbents. Spataru et al. (2016) attempted to remove orthophosphate (anions) and copper (cations) from wastewater using the hydrochar and activated (enhanced) hydrochar derived from waste sludge from the water treatment plant [63]. Adsorption studies revealed that 97 % of orthophosphates were removed via the enhanced hydrochar at 6 g/L, which showed a higher adsorption capacity for enhanced hydrochar than raw hydrochar.

3.3. Catalyst Support

Hydrochar can alter its physicochemical properties, which leads to the addition of charged surface functionalities to enhance the sorption potential. This section explored the application of hydrochars and activated hydrochars as catalyst materials for enzymatic and heterogeneous catalytic reactions. The schematic representation of the formation of hydrochar, and its adsorption mechanism and enhancement method, is shown in **Figure 3** (Fernandez-Sanroman et al., 2021) [64]. Moreover, the utilization of hydrochar in biotechnological processes such as enzyme immobilization would enhance the economic feasibility of industrial applications. Castro et al. (2017) used hydrochar as a scaffold for the immobilization of lectin proteins through a non-covalent technique, i.e., via electrostatic interaction among COO^- groups on the surface of the hydrochar and NH_2 and NH_3^+ groups of the protein [65]. However, hydrophobic interactions were noticed in the electrostatic interactions, and this binding did not change the protein structure or adhering biological activity. During this study, glucose-derived hydrochar was produced via the HTC technique. Further, cellulase from *Trichoderma* sp. was immobilized on the hydrochar derived via the low-temperature HTC technique by Primozić et al. (2019) [66]. Enzyme activity was evaluated via adsorption and covalent bonding through a cross-linking reagent from olive oil waste and cellulose-derived hydrochar. Hydrochar derived from cellulose was found to be a suitable carrier for immobilization relative to the olive oil-derived hydrochar, owing to the higher residual activity. Kang et al. (2013) prepared the lignin-, cellulose-, wood meal-, and D-xylose-derived hydrochar via the HTC technique and functionalized it with sulfur for the production of 5-HMF from inulin in ionic liquids using carbon-based sulfonated catalysts in a single step [67]. During the reaction, 47–55% of 5-HMF yield was received at 100 °C for 60 min of the reaction time; hydrochar-based sulfonated catalysts showed higher catalytic activity relative to conventional solid acid catalysts. However, when the sulfonated hydrochar-based catalysts were used in ionic liquids, it was challenging to recover the ionic liquid for reuse from the hydrochar-based catalysts. The utilization of hydrochar for catalytic applications would lead to a circular economy and a reduction in the price of biocatalysts and sustainable production. Further, Norouzi et al. (2020) developed a cranberry pomace-derived composite for deoxygenation reactions [68]. Cranberry pomace hydrochar (CPH) and zeolite were introduced to make a composite via the hydrothermal liquefaction technique. Experimental outcomes revealed that cranberry pomace hydrochar was found to be more active relative to zeolite in the conversion of cellulosic sugars into hydrocarbons. However, the presence of the corrosive amino and aliphatic acids hindered the CPH catalytic activity; nevertheless, the addition of zeolite would overcome these challenges. Therefore, composites of zeolite and CPH could solve the challenges in biofuel production and assist with the development and commercialization of advanced biofuels from cranberry pomace. Moreover, Norouzi et al. (2021) reported on the preparation of 2D and 3D recyclable zeolite-based composites via the hydrothermal liquefaction of algae [69]. The composites were developed by loading magnetite and commercial zeolite onto/into the algal hydrochar with meso/macro structures. Prepared 2D and 3D catalyst composites were used for the production of heavy gasoline ($\text{C}_7\text{--C}_{12}$) and biodiesel ($\text{C}_8\text{--C}_{21}$). The 2D architecture of the composites was responsible for the transformation of alkenes into oligomers and ketones, undergoing a series of aldol condensation reactions, whereas the 3D structure enhanced the local pressure and expelled monomers in the form of gasoline from the catalyst pores. Relative to the 2D structure, the 3D structure is more effective, owing to the presence of $\text{Zn}_{4.00}\text{Fe}_{16.00}\text{Ni}_{4.00}\text{O}_{32.00}$ inside the composite. Converting sewage sludge into hydrogen-rich syngas via hydrochar-derived composites was studied by Gai et al. (2017) [70]. Sewage sludge-derived hydrochar supported with Ni nanoparticles was prepared via one-step hydrothermal carbonization of Ni preloaded sewage sludge. Uniformly dispersed NiO nanoparticles were generated in situ during the catalytic gasification process and provided the active sites for the adsorption of tar molecules for catalytic conversion. Owing to the strong interactions among the metal cations and carbon support, $\text{Ni}_{0.1}\text{@HC}$ exhibited the highest catalytic activity in promoting hydrogen production and the reduction of tar under mild conditions. Prepared catalyst composites showed 72.5% of selectivity for hydrogen, and little or no tar was formed, even at low temperatures i.e., 700–800 °C.

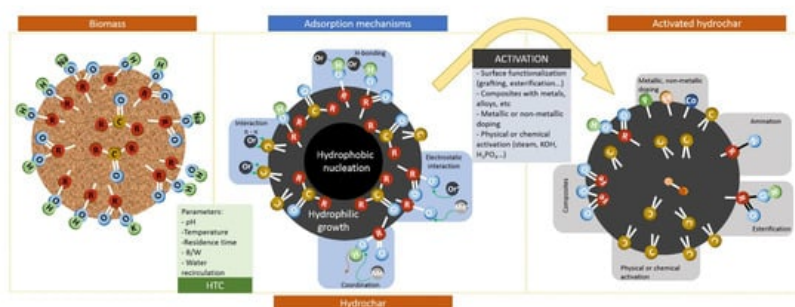


Figure 3. Schematic representation of the formation of hydrochar, its adsorption mechanism, and enhancement method. Reproduced with permission from Fernandez-Sanroman et al. (2021) [64]. Copyright 2021 Elsevier.

3.4. Energy Production

The hydrothermal carbonization of raw biomass produces solid residue that can complement coal for energy production. While treating the biomass in the HTC, depolymerization, decomposition, and degradation of polymeric compounds from the biomass takes place. Typical higher heating values for polymeric materials in biomass is as follows: lignin > cellulose > hemicellulose > extractives > ash [71][72]. Due to the removal of cellulose and hemicellulose during HTC, lignin content increases, which aids as a natural binder in the densification of the HTC residue for coal-like applications. Likewise, during HTC, the C/O ratio also increases, which leads to an increase in the higher heating value of the end-product, i.e., the HTC residue. Due to the increase in the lignin or decrease in the hemicellulose content, the hydrophobicity of the HTC residue increases, thereby the shelf life of the HTC residue would be increased without any biodegradation [51][73]. Moreover, when hydrochar is used as a solid fuel, it should satisfy several requirements such as combustion behavior, hydrophobicity, energy density, thermal stability, and grindability [74]. Sadish et al. (2019) prepared hydrochar from effluent treatment plant sludge via HTC technique to use hydrochar for the creating of energy as a supplement to coal [75]. Among all the experimental studies, HTC char produced at 200 °C for 4 h showed the highest energy densification (1.24), heating value (15.25 MJ/Kg), and energy recovery efficiency (69.8%). Hydrochar was prepared from the effluent treatment plant sludge from a paper mill under optimized HTC process conditions by Oumabady et al. (2020) [76]. HTC char exhibited 15.6% of fixed carbon and 18.4 MJ/Kg heating value; further, reduced O/C (43.7%) and H/C (35.05%) ratios confirmed the coalification of the sludge. Blends of the sludge-derived HTC coal and conventional coal (1:1) revealed an HHV of 22.3 MJ/Kg, making it a suitable candidate for heat energy production in paper mills. Wang et al. (2018) used the co-HTC technique to produce hydrochar with increased higher heating value using sludge and food waste [77]. The carbonization temperature was varied to identify the desired HTC temperature for maximum heating value. The addition of the food waste increased the heating value of the hydrochar from 9.6 to 19 and 23 MJ/Kg at 230 °C with a 50 and 70% addition of food waste. Moreover, there was an increment in the heating value, carbon content increased, and ash content decreased with the co-HTC technique.

3.5. Carbon Sequestration

The process of storing the biomass-derived hydrochar into the soil is known as carbon capture and storage or carbon sequestration. When the carbon is stored in the soil, it is identical to the net removal of anthropogenic CO₂ from the atmosphere. When the carbon sequestration was carried out on purpose, it would lead to a carbon-negative/neutral environment, thereby compensating for the anthropogenic CO₂ emissions. The concept of carbon sequestration gained huge interest around the globe due to the encouraging strategy for CO₂ mitigation [78][79]. Corn-derived hydrochar was prepared via pyrolysis and the HTC technique by Malghani et al. (2013) for soil amendment as a result of their impact on greenhouse gas emissions and carbon sequestration [80]. The addition of 1 wt.% hydrochar to the soils resulted in CH₄ and CO₂ emissions and reduced N₂O emissions. The increased emissions were due to the rapid decomposition of hydrochar within 100 days after the addition of 50 wt.% hydrochar. Kammann et al. (2012) and Schimmelpfennig et al. (2014) noticed identical outcomes, i.e., the emission of CO₂ and CH₄ during their carbon sequestration study using hydrochars derived from ryegrass and peanut hulls and *Miscanthus giganteus* as feedstocks [52][81]. Relative to the biochar, hydrochar degraded at a faster rate due to the easy biodegradability of the carbon present in the hydrochar. However, in-depth research needs to be carried out to include the applicability of the hydrochar in the soil with a positive impact on agricultural productivity and improved stability.

3.6. Electrochemical Devices

Supercapacitors and batteries are some of the products that could utilize the hydrochars for electrochemical devices. Hydrochar has gained attention for these applications due to its lower surface area, polarity, porosity, aromaticity, and stability. This section describes the utilization of hydrochar for the preparation of symmetric supercapacitors. In general, hydrochar-derived supercapacitors exhibit higher cycle stability and power density, whereas rechargeable batteries show lower cycle stability, discharge/charge rate, and a higher energy density [82]. Li and Liu (2014) prepared a walnut shell-derived hydrochar, activated hydrochar, and prepared activated hydrochar on ZnO composites for the making of supercapacitors [24]. The specific surface area of the activated hydrochar on ZnO and activated hydrochar exhibited 819 and 1073 m²/g, respectively. Compared to the activated hydrochar, activated hydrochar on ZnO composite showed 117.4 F/g of specific capacitance at a current density of 0.5 A/g in KOH aqueous solution, and it was found to be stable for 1000 cycles. Corn straw-derived hydrochar was activated via microwave-assisted hydrothermal activation technique by Liu et al. (2020) [83]. During the activation time from 40 to 100 min, hydrochar structure was changed to hierarchical pores from micropore structures, i.e., a change of structure from amorphous to graphene-like sheets. Relative to the corn-derived pyro chars, hydrochars showed higher capacitance (98 F/g), power, the energy density of 340 W/kg, 96 W h/kg at 20 A/g current density, and electrochemical performance, with a higher specific surface area of 1781 m²/g. In another study by Ding et al. (2012), rice husk-derived hydrochar was prepared with a sulfuric acid hydrolysis technique [84]. The addition of the hydrochar on Ni significantly improved the specific capacity by 149%, with a specific capacitance of 174.5 F/g, which was higher than the activated carbon on Ni. Outcomes of the experimental investigations showed that the rice husk-

derived hydrochar could be a promising electrode material for the electrochemical supercapacitor. Aside from the super capacitor's applications, hydrochars can also be used as an electrochemical storage device with high surface area, electrical conductivity, easy accessibility, tunable pore structure and size, and excellent mechanical properties. Biomass-derived hydrochars with a well-defined pore structure were found to be ideal hosts for sulfur [85]. Guo et al. (2015) prepared a porous hydrochar with a high surface area using corncobs [86]. Sulfur loaded on hydrochar showed 1600 mAh/g of discharge capacity, a reversible capacity of 554 mAh/g after 50 cycles. The unique 2D structure of the hydrochars and the highly specific surface area of the hydrochars resulted in the higher utilization of sulfur that is appropriate for cathode material in lithium-sulfur batteries. Furthermore, Norouzi et al. (2021) reported on the preparation of 3D symmetric and asymmetric types of supercapacitors using algal biomass [87]. The three-dimensional interconnected mesoporous network (3DFAB) of the biochar was prepared through pyrolysis of algae in the presence of the NaOH. During the pyrolysis of microalgae, NaOH reacted with ester, carboxyl, carbonyl, ether, and hydroxyl functional groups to generate free radicals and various vacant sites. Vacant sites were created owing to the NaOH reaction with C-C, C-H groups; further oxygen functional groups were formed by penetration of OH and NaOH into the vacant sites. Moreover, 3DFAB was strengthened by introducing the tile-like architecture of cobalt oxide (CoTLM) via a one-pot hydrothermal technique under mild process conditions. In the case of symmetric supercapacitors, the maximum specific capacitance of the raw algal biomass, 3DFAB, and CoTLM was found to be 158, 296, and 445 F/g at 1 A/g current density. On the other hand, the asymmetric supercapacitor retained 100.9% of the initial capacitance after 4000 cycles at 4 A/g of current density.

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