



# Catalytic Hydrothermal Carbonization Treatment of Biomass for Enhanced Activated Carbon: A Review

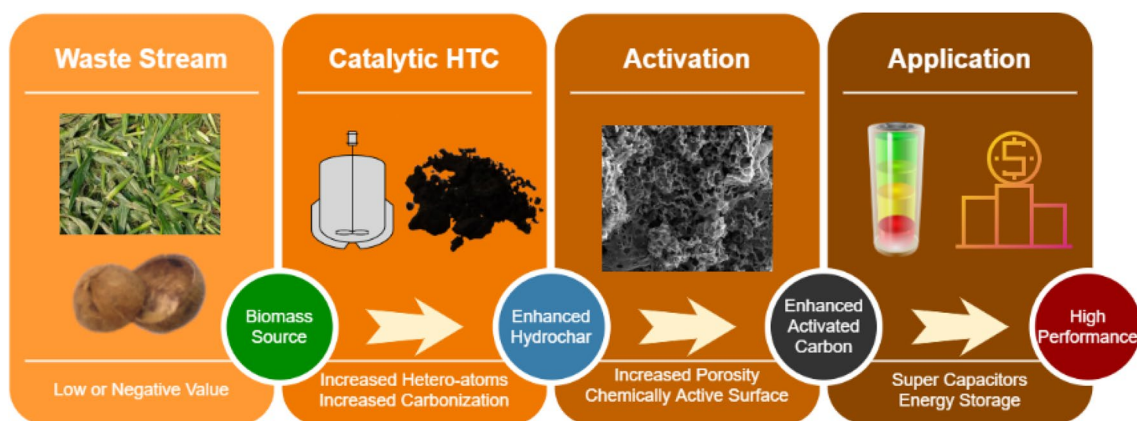
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## Abstract

Biomass for activated carbon production has had been gaining interest in a wide variety of applications such as water filtration, gas adsorption, and electrochemical devices as a renewable carbon source while meeting desired porosity, surface area, conductivity, and stability requirements. Activated carbon production has been extensively investigated, proving to provide high performance in applications including electrochemical devices. Hydrothermal carbonization (HTC) has shown potential as a pretreatment method for activated carbon production, especially when surface functionalization is desired. However, research into catalytic HTC is still limited. In this review, the processing methods used to convert biomass waste products into high value activated carbon are briefly reviewed, with a focus on recent progress in catalytic HTC as a pretreatment method to activated carbon. Areas of interest for catalytic HTC for activated carbon production are identified. Recent studies have found that the use of catalysts enhances the degree of carbonization, surface modification, and introduction of key heteroatoms significantly augmenting the performance of activated carbon. With further development of catalytic HTC technology, more competent carbon material for electrochemical devices can be produced cost-effectively and move towards meeting the ever-increasing demands of activated carbons for high-performance electrochemical devices.

## Graphic Abstract



**Keywords** Activated Carbon · Biochar · Catalyst · Hydrothermal Carbonization · Supercapacitors

## Statement of Novelty

Activated carbon production, hydrothermal carbonization, and the use of hydrothermal carbonization (HTC) for activated carbon have been extensively investigated and reviewed. However, while catalytic HTC and nitrogen/

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sulfur additions for activated carbon has shown significant potential in experimental studies in the literature, a review on the effects of these modifications to HTC on the final activated carbon product, as well as recent progress and summary of studies of interest, is not available. This work may provide an alternative perspective for those new to the area, and allow researchers to see the potential benefits of investigating modified HTC procedures. This will produce higher quality activated carbon material for better performances in supercapacitors, helping to meet the increasingly high demand on electronic devices.

## Introduction

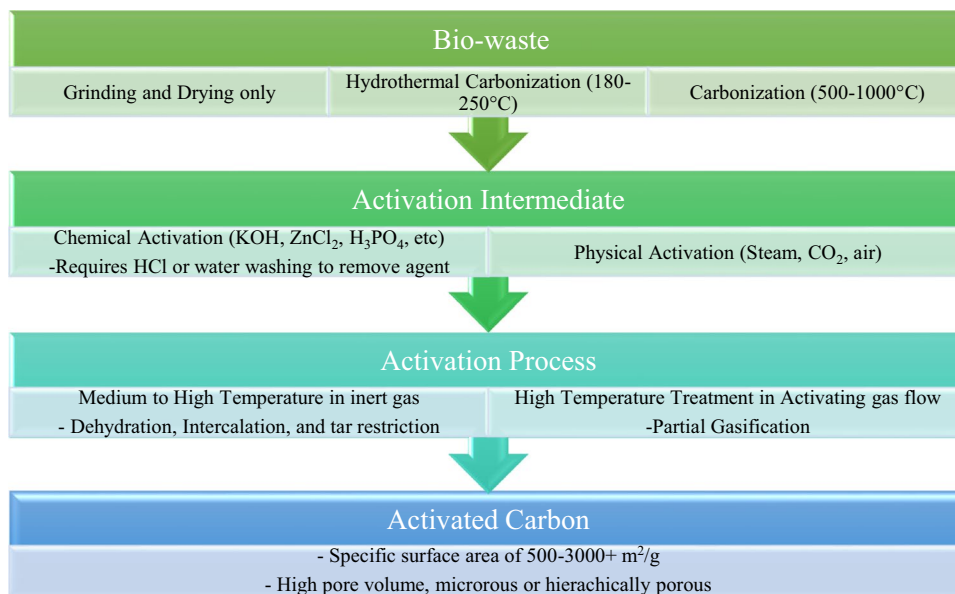
### Activated Carbons Overview

Porous carbon materials have gained significant interest in several fields and applications, including electrochemical energy storage systems such as Li-ion, Li-S batteries, and supercapacitors [1–4]. Activated carbons are carbonaceous materials which have an extremely high specific surface area (SSA), often in the range of 500–3000 m<sup>2</sup>/g [5, 6], with some ratio of micropores (< 2 nanometers (nm)), mesopores (2–50 nm), and macropores (> 50 nm). The production of activated carbons is largely done in one of two ways, physical or chemical activation. The conditions upon which these procedures and the preprocessing treatments (pyrolysis/carbonization, hydrothermal carbonization (HTC), or no pre-treatment) are conducted can be altered to tune the properties and porosity profile. Porous carbons may also be obtained through other less common methods. For example, Deng et al. tested the molten salt carbonization of chitosan in 10

times the weight of ZnCl<sub>2</sub>, at temperatures from 400–700 °C, above the melting temperature and below the boiling temperature of ZnCl<sub>2</sub>. They produced an activated carbon with high specific surface area and nitrogen content, which then performed well as an electrode for a supercapacitor [1]. Yahya et al. provide a summary of different processing methods in the literature, as well as biomass precursors tested [7]. Other reviews have presented a summary of activation methods and their resulting activated carbon properties, including physical activation (carbonization in partially oxidizing atmospheres such as steam or CO<sub>2</sub>), chemical activation (mixed with chemical activating agents and then carbonized in an inert atmosphere), Physicochemical activation (combined physical and chemical activation), and microwave-assisted activation [8, 9]. Figure 1 outlines common pretreatments, activation procedures, and mechanisms by which activated carbons are most often produced. Using grinding or no pre-treatment allows for a one-step activation, whereas HTC or carbonization may provide more desirable properties in the product. Chemical activation provides several quality benefits and lower operating temperatures when compared with physical activation, however the use of large amounts of chemicals and the necessary washing step are major disadvantages. In the case of the one-step process, biomass is directly converted to activated carbon, whereas in the two-step process a hydrochar or biochar is produced and then activated.

The source material is the first parameter which must be considered when creating activated carbon. A wide variety of biomass precursors have been tested in the literature, including coconut shells [10–15], mango leaves [16], bamboo fungus [17], spores [2], rice husk ash [5], fruit peels [18, 19], fruit stones [20–22], nutshells [23–26], coffee husks

**Fig. 1** Flow diagram of typical procedures for activated carbon production



and grounds [27, 28], corn hulls [29], woods and sawdust [30–32], and various straws and grasses [3, 33–35]. Mixing precursors has also been shown to be beneficial [36]. Coconut husks have been widely used due to their inherent microstructure, which helps create porosity, and high lignin content, which can result in higher yields. Woody biomass with course cellular structure is typically less desirable for activated carbon [37], with preference usually going towards waste materials such as fruit stones and shells.

Preprocessing of biomass is a method of enhancing the properties of the precursor to activation. Preprocessing is typically done through pyrolysis/carbonization, HTC, or less conventional methods such as Ionothermal carbonization (ITC) [38], microwave treatment [39], acid soaking [40], and thermo-compression [32]. These processes aim to alter the biomass or create a char material before activation, which allows for a more complete activation and thus higher porosity development [41]. Grinding and sieving of the biomass are also common, as smaller particle sizes have been shown to result in higher quality activated carbons. Şentorun-Shalaby et al. found an increasing surface area when particle size was reduced from 3.35–4 mm to 1.7–3.35 mm and again to 0.85–1.7 mm, however, the solid yield was also reduced [20]. HTC maintains significant surface chemical functionality in the hydrochar, developing oxygen functional groups and maintaining nitrogen due to lower operating temperatures [42]. ITC has the added benefit of lower operating pressure compared to HTC, but the high cost of ionic liquids is a major barrier to their application [38].

In addition to the activation and biomass type, impregnation ratio, activation temperature, activation time, and nitrogen flow rate [43, 44] have been shown to significantly impact the resulting properties of the activated carbon. Figure 2 provides a summary of the factors important to consider when designing a high-performance activated carbon for supercapacitors.

Chemical activation of biomass or char involves a chemical activator which is impregnated into the material, before being carbonized at temperatures typically around 500–800 °C for times between 1 and 24 h under inert gas flow, and then washed in HCl and water to remove the activator. A large number of chemical activators have been tested in the literature, including KOH [3, 4], ZnCl<sub>2</sub> [6, 17], H<sub>3</sub>PO<sub>4</sub> [45, 46], K<sub>2</sub>CO<sub>3</sub> [31, 47], NaOH [19, 48], FeCl<sub>3</sub> [49, 50], Na<sub>2</sub>CO<sub>3</sub> [5], and H<sub>2</sub>SO<sub>4</sub> [51]. Some of the main reactions which are thought to take place during chemical activation are dehydration, aromatization, and intercalation of ions into the carbon matrix [52]. It should be noted that chemical activation often uses a large amount of toxic reagents. For example, Hjalila et al. studied the life-cycle analysis of H<sub>3</sub>PO<sub>4</sub> activated carbon and found that 64% of the human toxicity and over 90% of the land and aquatic toxicity of the total process came from the impregnation of the chemical

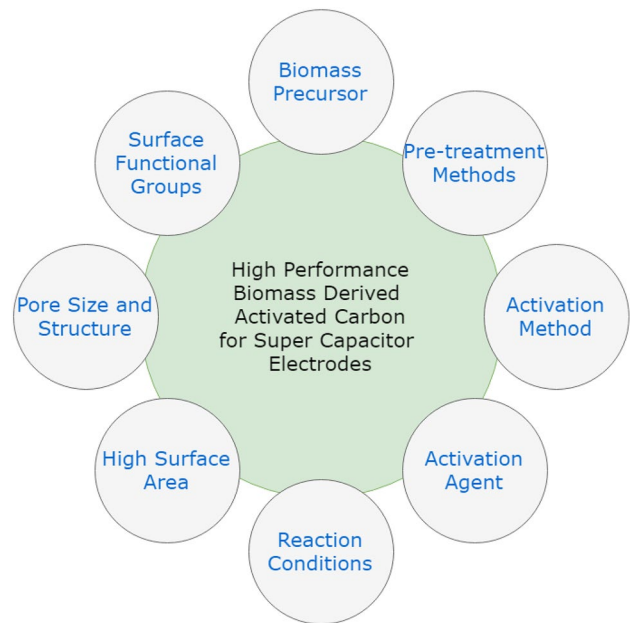
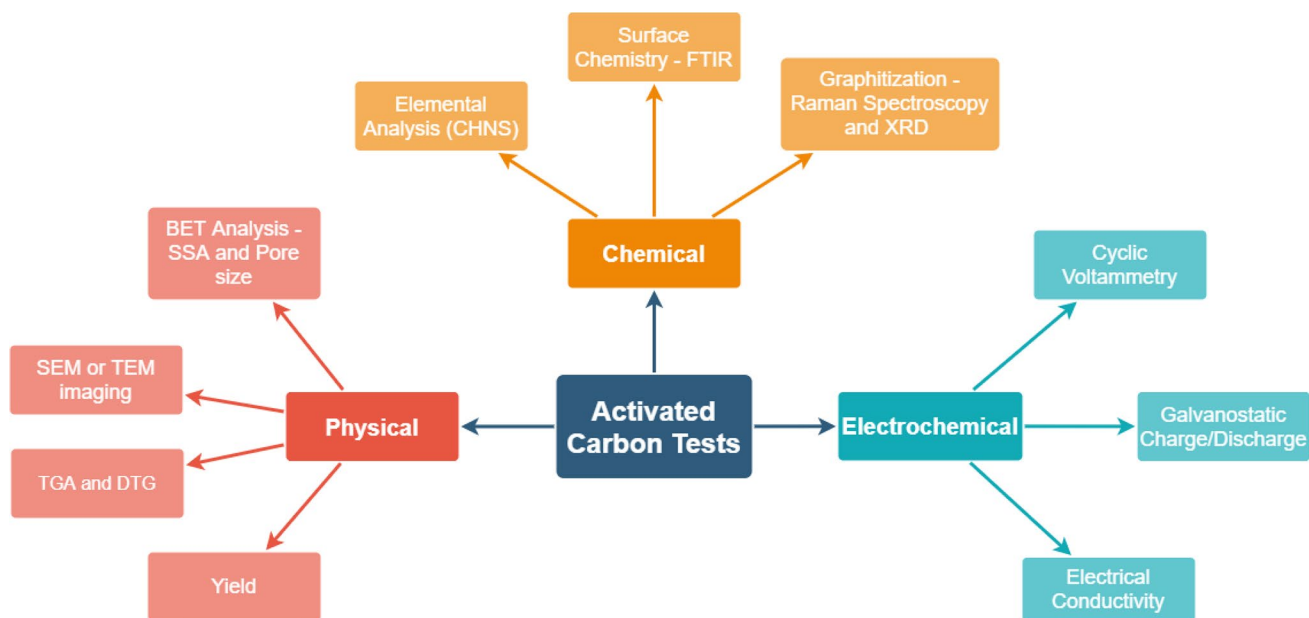


Fig. 2 Factors for consideration for activated carbon production

activator [53]. Some work has been done to attempt to reuse the activating agents to reduce the environmental and cost impact of the chemical agent, with mild success under specific conditions [54]. Alternatively, utilizing more environmentally friendly activating agents such as KHCO<sub>3</sub> may also help [55]. However, significantly more work is needed to increase the sustainability of chemical activation on a larger scale.

Physical activation is a high-temperature treatment under a gas flow for a several hour period, typically using CO<sub>2</sub> [2, 33], steam [11, 12], air [56], a combination of the gas flow types [11], or a combination of these with other gas types such as CO [57] or N<sub>2</sub> [58, 59]. The heating process may be assisted by microwave heating [19, 60]. Wigmans proposed a mechanism for physical activation by partial gasification for CO<sub>2</sub> and steam activation [61].

The performance of activated carbon in electrochemical applications such as supercapacitors is dependent on certain aspects of the material. As per various reviews available on activated carbons [8, 62, 63] and experimental papers [3, 4, 64], the most commonly assessed parameters in the literature are specific surface area, total pore volume, micropore volume, mesopore volume, surface functionalization, elemental composition, and mass yield. Electrical conductivity or degree of graphitization and final test performance are also considered important features in electrochemical applications. Several other tests, such as thermogravimetric analysis (TGA) or derivative thermogravimetry (DTG), may also be performed. Figure 3 provides a visual representation of the characterization strategy used for the main important



**Fig. 3** Overview of main characterization techniques used on activated carbons for supercapacitors

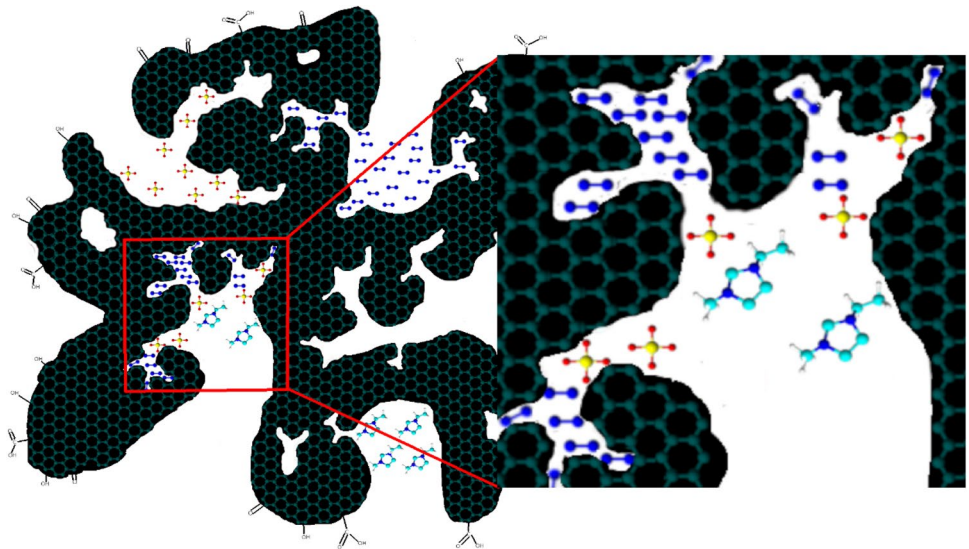
properties. Brunauer–Emmett–Teller (BET) surface area or Density Functional Theorem (DFT) specific surface area (SSA) and pore volumes are the main parameter of interest in most cases, obtained through nitrogen or CO<sub>2</sub> adsorption tests. Several studies have suggested that the BET method may not accurately represent SSA for highly microporous materials, depending on the structure of the solid micropore [65, 66], however, BET SSA is still useful for relative comparisons, and remains the most common method for calculating SSA of activated carbon. A high SSA is beneficial by increasing the available reaction sites. Micropores are the main contributor to the total SSA of the activated carbon, however, mesopores act as fast ion-transportation channels in the carbon matrix, providing short diffusion pathways [67], encouraging fast mass transportation of ions within the electrode. Thus, a hierarchically porous interconnected structure (including micropores, mesopores, and macropores) is typically considered ideal. Liu et al. provide a review of recent advances in engineering techniques to optimize pore distribution, with a focus on maintaining good volumetric performances [68].

While SSA and capacitance are highly related, it is possible for a larger specific surface area activated carbon to have a lower capacitance, due to pseudo-capacitance and pore availability to the electrolyte [69]. Liu et al. compared activated carbon produced by KOH activation of HTC and ITC chars and found that despite the HTC char producing a slightly higher surface area, the ITC char produced a higher capacitance due to its pore distribution and surface functionalization [3]. The plateau of capacitor performance with increasing SSA is often associated with the limited ability of

the electrolyte to access the sub-nanometer pores [70–73]. This effect is illustrated in Fig. 4, where the nitrogen is able to enter the small pores (and thus contribute to the surface area of the activated carbon), the SO<sub>4</sub> electrolyte ion is able to enter some pores, and the EMI ion is able to enter even fewer pores due to its larger size. This illustrates the importance of optimizing the pore size distribution to the electrolyte used to maximize electrochemically active area. Largeot et al. (2008) found that tailoring the pore size of the electric double layer capacitor to match the ionic liquid electrolyte ion size significantly increased gravimetric capacitance. They attributed this to the efficient minimization of unused space. Zuliani et al. isolated the effect of pore size distribution by comparing multiple activated carbon samples of similar SSA and chemical composition. They found that microporous activated carbons had a higher normalized capacitance to mesoporous ones, but only above a certain voltage potential. This indicates that a minimum voltage is required to induce this sub-nanometer ion adsorption [74]. Many other studies have investigated the effects of nanopores and electrolyte ion size on capacitance, with similar findings [71, 73, 75–77].

While pore distribution is important for enabling fast ion transportation, a high electrical conductivity allows for fast electron transport, increasing the power capabilities of the supercapacitor. While activated carbon may not always have extremely high electrical conductivity, the graphitization of porous carbons has been shown to increase electrical conductivity by as much as two orders of magnitude [78]. Sun et al. produced highly conductive and porous graphene-like nanosheets from simultaneous activation and graphitization

**Fig. 4** Illustration of pore distribution in porous carbon material. The electrolyte ions ( $\text{SO}_4$  and EMI) are unable to enter the smaller pores which are still accessible to nitrogen



with  $\text{ZnCl}_2$  and  $\text{FeCl}_3$ , which performed well in supercapacitors, and concluded that the combined effect of fast ion and electron transport capabilities increased supercapacitor performance [15].

Surface functionalization is another way of altering electrochemical performance. Oxygen or nitrogen functional groups are most commonly shown to be beneficial for supercapacitors [79, 80], however, sulfur-doped carbons are used as well [81]. Qu studied activated carbons for double-layer capacitors, taking a detailed look at the workings and effects of surface functionalization on the capacitance. One of the study conclusions was that surface functionalization affects capacitance in two ways, namely the increase in wettability of the electrode by use of hydrophilic functional groups, and through pseudo-capacitance adding to the apparent capacitance [82]. Abioye and Ani discuss surface functionalization in their review of recent advances in activated carbon for supercapacitors, commenting that recently surface functionality has significantly impacted the electrochemical performance of activated carbons [9]. Surface chemistry may be introduced through carryover from the activation precursor [17], or introduced during the activation process [83], and is typically referred to as heteroatom doping. Hu and Dai (2018) provide a review of doping methods for various carbon materials [84].

### Hydrothermal Carbonization Overview

Hydrothermal carbonization (HTC) is the carbonization of biomass in water under autogenous pressures in an autoclave. Temperatures for hydrothermal carbonization are typically within the range of 180–250 °C, however, temperatures up to 300 °C have been investigated as well [85]. Beyond 300 °C, the process produces mostly liquid or gaseous products, and as such is then referred to as hydrothermal liquefaction

(HTL) or hydrothermal gasification (HTG) respectively. The lower temperature (compared to traditional carbonization reactions of around 500–1000 °C) and the water medium which removes the need for drying before treatment, make HTC a very appealing process for biomass conversion, both for energy saving potential and maintaining chemical functional groups [42]. There are several drawbacks limiting HTC's widespread application. The combination of temperature and high-pressure requirements has made the development of a continuous HTC reactor difficult, although some attempts at continuous reactors have been investigated [86–89]. Additionally, the energy required to heat the water used in the reaction may be significant, meaning that HTC becomes more economically viable for high moisture content biomass where the relative energy loss is smaller. As such, the development of a continuous reactor utilizing waste heat or process water recycling would significantly increase practical viability. In addition to potential energy savings, studies on process water recycling have found that it may increase mass yields [90–92]. While the exact mechanisms of HTC are complex, biomass dependent, and not fully understood, the main reactions which occur during HTC are generally considered to be hydrolysis, dehydration, decarboxylation, polymerization, and aromatization [93]. Processing time for HTC can range significantly, with studies ranging from 5-minute residence time [85] to 24 h [17], with higher residence times resulting in a slightly more carbonized product. However, the temperature has a much greater effect on the resulting hydrochar than residence time [85]. A more in-depth review of the existing hydrothermal carbonization knowledge and concerns has been recently published by Heidari et al., with a partial focus on kinetic modeling [94]. Alternatively, Khan et al. also provide a recent in-depth review on HTC with more of a focus on reaction mechanisms [95]. Jain et al. provide a review on HTC with respect

to activated carbon production and mention that research into catalytic HTC for activation is limited, but provides only a very brief look at the subject [62].

### Alternative Thermochemical Conversion Methods

In addition to HTC, several other thermochemical biomass conversion techniques have been studied in the literature. Many of these are not intended or suitable for use as pre-treatment for activated carbon production. For example, torrefaction is a low-temperature process useful for increasing the quality of biomass for fuel applications. Torrefaction increases energy density, hydrophobicity, and reduces energy for grinding [96]. Alternatively, gasification is intended for the conversion of biomass to syngas (CO and H<sub>2</sub>, with some CO<sub>2</sub> and CH<sub>4</sub>) in low oxygen environments [97].

Pyrolysis (also called carbonization) is a common pre-treatment for activated carbon production [98]. Pyrolysis involves heating the biomass to medium or high temperatures (generally from 500 to 1000 °C) under an inert atmosphere. Heating rate and residence time can be varied to change the products, namely that slow pyrolysis maximizes solid char yields and fast or flash pyrolysis maximizes bio-oil production. Slow pyrolysis is then the best option for maximizing solids for activation, while substantially increasing carbon content compared to the raw biomass [99]. However, pyrolysis requires dry biomass, and the high temperatures used can destroy a significant amount of surface chemistry compared to HTC [42].

Ionothermal carbonization (ITC) has many of the benefits of HTC, however, it uses an ionic liquid as the medium instead of water. This has the added benefit of reducing the operating pressure, even operating at ambient pressures [100], however cost of the ionic liquid is a major barrier to its application.

As such, particularly for high moisture biomass sources, HTC offers a relatively cost-effective method of maintaining material chemical activity while pre-processing the biomass to obtain a higher value activated carbon.

### Introduction to Catalytic Hydrothermal Treatment

Hydrothermal carbonization has a focus on solid products, whereas hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG) have a focus on the liquid and gaseous products respectively. As such, different catalysts are used depending on the desired products from the reaction. With respect to HTG, many studies have recently increased H<sub>2</sub> production by catalytic HTG of biomass sources such as glucose [101], microalgae [102], olive pomace [103], human feces [104], and others. With respect to HTL, Chen

et al. provide a study of NH<sub>3</sub>·H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub>, and glycerol as catalysts for HTL of dairy manure to enhance the formation of chemicals and decrease energy requirements [105]. As for HTC, solid products of interest may include sugars or hydrochars. Lu et al. (2014) studied the effects of additives including HCl, H<sub>2</sub>SO<sub>4</sub>, NaOH, Ca(OH)<sub>2</sub>, NaCl, CaCl<sub>2</sub>, and acetic acid on HTC of cellulose. They found that basic catalysts altered 5-hydroxy-methyl-furfural (HMF) decomposition pathways, whereas acidic conditions increased cellulose dissolution and thus decreased solid yields at lower residence times [106]. In contrast, basic conditions also increase the concentration of sugars, formic acid, and lactic acid in the process water [107]. Alternatively, Maleic acid-catalytic HTC at temperatures around 150 °C can increase xylose yields from hemicellulose hydrolysis [108]. Catalytic hydrothermal carbonization focuses on improving char quality and thus may involve an increased level of carbonization for a set reaction temperature, modifying the physical char structure, reducing ash content of the char, or introducing specific chemical properties. Wang et al. provided a brief overview of the effects of HTC process conditions such as pH on products [109] in their in-depth review on HTC. Dapsens et al. provide an in-depth look at catalyst use in the general conversion of biomass into chemicals [110], and reviews on hydrothermal carbonization of biomass, such as the recent review by Krylova et al. [111], typically include a small section on catalyst usage. Also, Kumar et al. provide a detailed review including catalyst usage during HTC, HTL and HTG [112]. However, to the authors' knowledge, a focused review of the recent use of catalysts and additives in HTC for activated carbon production is not available.

### Catalysts for Increased Carbonization and Porosity

One of the most common catalyst types used in HTC is acidic catalysts. Intermediates made during HTC include several acids, such as acetic acid and formic acid, making hydrothermal carbonization often self-catalyzing [113]. Further effects can be introduced by adding additional acids to the reaction. Lu et al. found that acidic catalysts (HCl and H<sub>2</sub>SO<sub>4</sub>) at concentrations as low as 0.0001 N increased hydrolysis and dehydration reactions, increasing carbonization level at certain residence times and reducing the oxygen content of the biomass [106]. In general, catalysts used in HTC help speed up reactions that take place (allowing higher carbonization levels at low residence times), change reaction pathways to favor specific reactions, or reduce a reaction activation energy to allow it to occur at a lower temperature. This enhanced hydrochar may also lead to increased activated carbon quality after subsequent activation. Recently, Susanti et al. used citric acid-catalytic HTC hydrochar to produce activated carbon by KOH activation for use in a lithium-ion capacitor. They

found that the citric acid-catalytic reaction increased the surface area of the hydrochar, as well as the activated carbon and the performance of the resulting supercapacitor [114]. Other acid catalysts that have been used include acetic acid [107], acrylic acid [115], phosphoric acid [116], HCl [117], and solid acid catalysts [115]. Solid acid catalysts have the added benefit of ease of recoverability, increasing feasibility for industrial applications. In addition to traditional acid catalysts, other acid-type catalysts such as Lewis acids are often used including metal-salts such as  $ZnCl_2$  [118],  $LiCl$  [119], and  $FeCl_3$  [120]. In a study on  $FeCl_3$  by Abd Hamid et al. , they found that the catalyst increased the level of carbonization, average pore diameter, and surface area when compared to non-catalytic HTC of cellulose around 200 °C [120]. A study by Fechler et al. on the addition of various eutectic salts to HTC of glucose at 180 °C showed that hygroscopic additives such as  $ZnCl_2$  in high concentrations could produce moderate surface areas directly from HTC. They explain this phenomenon as a result of the hypersaline environment stabilizing the material and reducing Oswald ripening [118]. Molten salt carbonization of biomass also can directly result in high surface area porous carbons [121]. The results of these studies indicate the high potential for various metallic salts when used in high concentrations during hydrothermal treatment. In addition to carbonization and porosity modifications, studies

on metallic compounds have shown they may increase graphitization at higher temperatures for increased conductivity [122–124]. Table 1 provides many example studies that have tested various catalysts during HTC. It can be seen that the use of catalysts increased the carbonization level (as seen by the carbon content) relative to the non-catalytic HTC hydrochar.

Other additives to HTC have been investigated for influencing the structure of the hydrochar. Templating is a common method for introducing porosity, although templating materials may have additional effects as well, and is divided into two groups, soft templating and hard templating. Hard templating involves the introduction of a porous frame material (such as silica spheres [130]) and produces a porous material after carbonization and removal of the template material reverse replica. Soft templating works similarly but uses the self-assembly of an agent to simplify the process [131]. Kubo et al. provide a review of hard templating in HTC [132]. Templating methods have recently been used to introduce specific morphologies into the hydrochar, as can be seen in studies presented in Table 2, although the removal of templating agents often requires an additional treatment step. An interesting example of an additive in HTC for structural modification is seen in the study by Krishnan et al. which investigated the effects of graphene-oxide on HTC. They found that even small amounts of graphene-oxide resulted in the formation of carbon monoliths, with

**Table 1** Summary of Acid Type Catalytic HTC Relative to Traditional HTC Results

Biomass	Temp (°C)	Time (h)	Catalyst	Loading	Catalytic C%	Uncatalytic C%	References
Wheat Straw	200	6	Acetic acid	pH 2	53.5	51.2	[107]
Wheat Straw	260	6	Acetic acid	pH 2	66	64.2	[107]
Microcrystalline Cellulose	215	40	HCl	2M solution	77.2	67.8	[125]
Microcrystalline Cellulose	215	40	HCl	5M solution	81.1	69.7	[125]
Glucose	200	48	$Al(OTf)_3$	4 mmol	68.85	68.47	[126]
Cellulose	200	48	$Al(OTf)_3$	4 mmol	67.61	67.02	[126]
Banana peel	230	2	$H_3PO_4$	50 wt%	69.13	63.02	[116]
Maltose	200	4	HCl	8 mmol	63.5	62.73	[117]
Maltose	200	4	Polyacrylic acid	14g:24 mg	62.62	62.73	[117]
Cellulose	220	24	$FeCl_2$	33 wt%	73.66	70.70	[120]
Cellulose	220	24	$FeCl_3$	33 wt%	73.90	70.70	[120]
D-(+)-Glucose	180	Overnight	$ZnCl_2$	9 to 6 g glucose	70.0	Not reported	[118]
D-(+)-Glucose	180	Overnight	$LiCl/ZnCl_2$ (23 mol% $LiCl$ )	15 to 6 g glucose	68.2	Not reported	[118]
Masson Pine Akali Lignin	240	10	Acrylic acid	10–50 wt%	Not reported	Not reported	[115]
Hornwort	300	0.5	Acetic acid	1 ml of 1M	64.2	60	[127]
Hornwort	300	0.5	KOH	3 wt% of feed	71.1	60	[127]
Hornwort	300	0.5	$Na_2CO_3$	0.5 wt% of feed	68	60	[127]
Glucose	160	3	Metal oxides ( $Fe_3O_4$ , $Ni_2O_3$ , $TiO_2$ )	0.016 g in 25 ml of 1.5M glucose	Not reported	Not reported	[128]
Metasequoia leaves	210	3	Iron sludge	1 g for 5 g biomass	70.74	54.76	[129]

**Table 2** Studies on the Hydrothermal Templating of Biomass for Porous Hydrochar

Biomass	Templating agent	HTC conditions	Post-treatment	SSA (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)	References
D-Fructose and dicyandiamide	Pluronic® F127	130 °C for 3 days	550 °C for 2 h in Ar	730	0.65	Not Reported	[134]
Glucose	P-123	HTC 180 °C for 1 day	4 wt% HF treatment	520	0.40	6.9	[135]
D-(+)-glucosamine hydrochloride	P-123	HTC 180 °C for 20 h	600 °C in N <sub>2</sub>	980	0.78	Not reported	[136]
D-(+)-glucosamine hydrochloride	Ultra-thin tellurium nanowires	HTC 180 °C for 18 h	900 °C for 2 h in Ar	350.59	0.25	23.28	[137]
Chitosan	F127	HTC 220 °C for 5 h	800 °C for 2 h in N <sub>2</sub>	326	0.20	2.29	[138]
Chitosan	1-butyl-3-methylimidazolium chloride	HTC 220 °C for 5 h	800 °C for 2 h in N <sub>2</sub>	363	0.21	2.28	[138]

ratios as low as 1:800 having significant effects on the carbon structure, while simultaneously increasing level of carbonization [133].

### Catalysts for Chemical Modification

In addition to catalysts used to increase the level of carbonization or surface area, catalysts may be added to introduce a specific chemical functionality into the hydrochar. Heteroatom doping is the introduction of certain atoms/functional groups into the carbon matrix, which can affect the physical and chemical properties of the carbon. Heteroatom doping before activation can typically be accomplished by either using biomass high in the desired chemical (such as nitrogen-rich biomass) or by adding a chemical source to the reaction. As an example, Liu et al. used Junjun grass during hydrothermal and ionothermal carbonization to produce a hydrochar rich in nitrogen, which produced an activated carbon showing presence of nitrogen and oxygenated functional groups and exhibiting impressive performance as a supercapacitor [3]. Kruse et al. provide an analysis of what happens to the nitrogen content during HTC, indicating that the nitrogen content in the hydrochar decreases slightly with

increased reaction time, and significantly decreases with increased temperature [139]. Wang et al. studied a variety of nitrogen sources during HTC, finding that both natural nitrogen sources (protein) and chemical additives (such as NH<sub>4</sub>Cl) resulted in significant nitrogen content, up to 9.2% from less than 1% in hydrochar without a doping source [140].

Innate doping using nitrogen-rich biomass sources has been investigated by many studies in the literature. Alternatively, the use of co-hydrothermal carbonization of a nitrogen-rich source with another biomass with other desirable properties (such as better microstructure or yield) is a promising method that has been investigated. As an example, Sevilla et al. (2014) performed co-hydrothermal carbonization on cellulose and nitrogen-rich spirulina micro-algae for high nitrogen content in the resulting hydrochar [141]. More examples of innate doping sources and co-hydrothermal studies can be seen summarized in Table 3. It can be seen that these methods can introduce significant N content into the hydrochar, in the range of 3–7%.

One of the more common catalysts used for HTC is H<sub>2</sub>O<sub>2</sub>, which can be added to introduce increased oxygen functional groups. Jain et al. tested H<sub>2</sub>O<sub>2</sub> enhanced HTC as a

**Table 3** Innate Doping and Co-Hydrothermal for Heteroatom Doping in HTC

Biomass	Temp (°C)	Time (h)	Product composition	References
Rice Husk and <i>Chlorella pyrenoidosa</i> Micro-Algae (40 wt%)	200	1	7.38% N up from 1.28% without	[142]
Black locust seed dregs	180	2	Not reported	[143]
Silkworm Excrement	180	12	Not reported	[144]
<i>Chlorococcum</i> sp. microalgae	200	3	2.94%	[145]
Glucose and isolated soy protein (1:1)	180	2	6.41%	[140]
<i>Scenedesmus</i> Microalgae	260	4	2.57%	[146]
D (+) - glucosamine hydrochloride	180	Overnight	6.7%	[42]



pretreatment for activation, and found that hydrochar from  $H_2O_2$  catalyzed HTC had significantly increased oxygenated functional groups, which was found to be strongly related to the mesopore volume of the resulting activated carbon [147]. For nitrogen doping, chemical additives include urea [83] and ammonia [148]. Sulfur doping, while less studied than nitrogen and oxygen doping, has shown some potential. Sulfur doping through HTC may be done using additives such as sulfuric acid [149] or sublimed sulfur [150]. Kiciński et al. provide a review of sulfur doping methods and effects [81]. Other modifications include phosphorus doping [151] and combination doping, such as N and S co-doping [152]. Examples of studies on doping additives are summarized in Table 4, indicating that a significantly higher proportion of the desired atom can be introduced relative to the main precursor.

### Catalytic HTC Hydrochar for Activated Carbon

Several studies have tested doping or catalytic agents during HTC followed by subsequent activation, with very promising results. Table 5 provides examples of recent studies producing activated carbon from biomass under a variety of process conditions, with a focus on those involving HTC as a pre-treatment method. It should be noted that for the study by Demir et al. on activated carbon produced from Lecithin, while the result reported in Table 5 at 900 °C had the highest SSA, the activated carbon produced at 800 °C had the highest electrochemical performance despite a significantly lower SSA, likely as a larger amount of nitrogen was retained in the final product due to the lower process temperature [69]. Zhao et al. used high nitrogen content hydrochar as a precursor to KOH activation to produce activated carbon with high performance in supercapacitors [42]. Hou et al. produced a high-performance supercapacitor electrode through sulfuric acid-catalyzed hydrothermal carbonization of nitrogen-rich Black-Locust seed dregs, gaining the benefits of both innate nitrogen doping through precursor choice and increased carbonization through acidic catalysts [143]. Liu et al. used sulfur doping during high-temperature HTC of glucose followed by KOH activation to produce sulfur-doped

nanoporous carbon spheres, which resulted in increased specific capacitance relative to the non-doped sample [150]. Susanti et al. used small weight percentages of citric acid in catalytic hydrothermal carbonization, followed by KOH activation to produce activated carbon for supercapacitors. They found that the citric acid-catalyzed hydrochar produced an activated carbon with a significantly higher BET surface area, as well as increased specific capacitance [114]. Each of these examples shows how the addition of a catalyst for heteroatom doping or increased carbonization can result in a more effective activated carbon product. As such, there is a clear benefit to introducing catalysts into hydrothermal carbonization before activation, as well as continued research into new catalysts or alternative treatment methods which may provide better results.

### State of the Literature and Gaps

Catalytic HTC has been shown to have many benefits, such as increasing the degree of carbonization, introducing hetero-atoms into the carbon matrix, and modifying the physical structure of the hydrochar [120, 158]. These changes can result in a better hydrochar or may carry over after activation, resulting in a higher quality activated carbon. Despite these major potential benefits, some catalysts which have shown potential have still not been fully investigated. Metal-based catalysts have been shown to increase the degree of carbonization when used in HTC [120], and develop microstructure and SSA approaching that of activated carbon [159]. However, they have only limited studies investigating their use. As an example,  $ZnCl_2$  and  $FeCl_3$  have shown potential as both a catalyst for HTC and an activation agent, however, studies on metal salts in catalytic HTC for activation have not been investigated thoroughly. Many HTC catalyst studies only cover HTC temperatures in the range of 180–250 °C, likely due to increasing complications with pressure and corrosion, leaving much potential for testing various catalysts with higher temperature HTC. Studies have indicated that mixing multiple catalysts may result in a better product than an individual catalyst alone [118], leaving a wide variety of catalyst mixing options to optimize product

**Table 4** Introduction of heteroatom content by chemical additives in HTC

Biomass	Temp (°C)	Time (h)	Doping source	Product composition	References
Coconut Shell	200	1/3	$H_2O_2$ solution (10% by weight)	1.58 meq/g Oxygen FG	[147]
Glucose	260	2	$(NH_4)_2SO_4$ , (5 to 10 g of biomass)	8.15% N from < 1% without	[140]
Glucose	550	3	Sublimed Sulfur (6 to 20 g glucose)	0.7% S from 0%	[150]
D-(+)-glucose	200	24	Borax and Ammonia solution	9.00% N	[148]
carboxymethylcellulose	220	14	Urea (1 wt%)	5.4% N	[153]

**Table 5** Recent Studies on Activated Carbon Production from Biomass Produced in Various Process Condition

Biomass type	Pretreatment	Activation method	Temp (°C)	Time (h)	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>Pore_Total</sub> (cm <sup>3</sup> /g)	Pore size (nm)	References
Jujun Grass	ITC (180 °C, 10 h)	KOH, 3:1	800	2	2710	1.226	N.R.	[3]
Jujun Grass	HTC (180 °C, 10 h)	KOH, 3:1	900	2	2838	1.231	N.R.	[3]
Enteromorpha algae	None	KOH, 3:1	800	1	2073	0.97	0.85	[154]
Arundo donax	None	ZnCl <sub>2</sub> , 3:1	500	–	3298	1.9	3.5	[6]
L. clavatum spores	Air heated (300 °C, 6 h) and Carbonized (300 °C, 2 h)	CO <sub>2</sub>	900	6	3053	1.43		[2]
Salacca peel	Citric acid catalytic HTC (250 °C, 5 h)	KOH, 4:1	800	1	1635.44	0.881	2.154	[114]
Salacca peel	HTC (225 °C, 5 h)	KOH, 4:1	800	1	908.39	0.156	2.150	[114]
Wheat straw	ZnCl <sub>2</sub> catalytic HTC (200 °C, 24 h)	H <sub>3</sub> PO <sub>4</sub> , 2:1	500	1	1258	0.6867	2.1828	[155]
Lecithin	KOH and Urea catalytic HTC (300 °C, 0.5 h)	KOH, Directly from HTC	900	1	2695	1.2	1.1 to 2.5, 3.2	[69]
Glucose and Sublimed Sulfur	HTC (550 °C, 3 h)	KOH, 3:1	800	2	3357	1.64	1–2	[150]
Glucose and S. Platensis Microalgae	HTC (180 °C, 24 h)	KOH, 2:1	750	–	2190	0.94	1.3	[141]
1,6-hexanediamine And lignin (1:1)	HTC (180 °C, 12 h)	KOH, 3:1	800	2	1867.4	0.997	2.255	[156]
Moso Bamboo Culms	Pre – Carbonization (650 °C) Post – HTC (180 °C, 24 h) in ammonia/ ethylene glycol solution.	KOH, 4:1	800	2	3485	1.67	1.39	[98]
Citric Acid	Catalytic Microwave HTC (800W, 5 min) with Urea, followed by carbonization (700 °C, 2 h) in Ar	KOH, 2:1	800	2	2397	1.07	1.78	[157]

properties. In addition, the study of new catalysts could give rise to further improved performance over that which is currently available. Related overall reaction chemistry and control of reaction path needs to be established to target carbon materials surface characteristics and application dependent properties.

### Areas of Future Research

In terms of future research focus, a wider variety of hydrochars produced by catalytic HTC should be investigated for activated carbon production, at a variety of conditions, to optimize the process and find a combination of biomass, HTC catalyst, and

activation procedure which will result in the highest performance of supercapacitor. In addition to performance, environmental impact and cost should also be considered in the process, which may require testing of novel activating agents and HTC catalysts with lower environmental impact, as well as recycling of HTC process water and the activation agent where possible. Optimization and catalyst choice may be facilitated by a better understanding of catalytic HTC and chemical activation mechanisms, which are still relatively uncertain.

## Conclusions

Hydrothermal carbonization is an effective pretreatment method for activated carbon production, especially for high moisture biomass or for applications that require surface functionalization. To date, a variety of catalysts have been used in the literature to modify the physical properties of the hydrochar or to introduce surface chemistry modifications. These catalysts have successfully enhanced the degree of carbonization, porosity, or presence of functional groups such as oxygen, nitrogen, and sulfur into the hydrochar. In addition, catalytic hydrochars have shown significant improvements in activated carbon production when compared to activated carbon produced without catalytic HTC treatment. In particular, when highly doped activated carbon is used in supercapacitor applications, the performance was significantly improved in most cases. As such, the benefit of using catalysts and additives to modify the physical and chemical properties of the hydrochar is substantial. While these catalytic HTC techniques have shown significant progress, there remain many experimental conditions that have not been tested, such as high-temperature tests of many catalysts, catalyst mixtures, or higher catalyst loadings, and a deeper understanding of reaction chemistry is needed. Overall, catalytic HTC, with a secondary treatment stage if necessary, has the potential to resolve the existing barriers and deliver activated carbon with unique properties that are beyond current standards.

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