

A review of biochar production and its employment in synthesizing carbon-based materials for supercapacitors

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ABSTRACT

Biomass waste treatment via thermochemical processes such as pyrolysis, hydrothermal carbonization, flash carbonization, and gasification results in biochar formation. These various pathways of biochar production provide an eco-friendly basis for obtaining further carbon-based materials. Carbon materials such as porous carbon material, doped biochar, carbon nanotubes, graphene, and carbon quantum dots can be prepared via physical and chemical modification of biochar. Furthermore, the biochar can be treated or processed under varying conditions regarding the physiochemical properties of these carbon-based materials. Their ability to store charge and its utilization as electrode materials for supercapacitors are summarized. The challenges and future perspectives associated with preparing these materials are also discussed in this review.

1. Introduction

Biomass is a plant or animal-based organic substrate commonly considered as waste. According to a study (Dahmen et al., 2019), nearly 181 billion tonnes of organic waste is generated per annum around the world. The majority of which is discarded through burning and makes its way to open fields or manmade landfills leading to air, soil, and water pollution. Biomass is also the only carbon-containing renewable in nature, which can be used for producing green chemicals, fuels, and materials. Various techniques and methods i.e., thermochemical and biological have been investigated for their proper conversion. Thermochemical pathways, including hydrothermal conversion, gasification, and pyrolysis, degrade biomass into products in the form of liquid, solid, and gas (Ong et al., 2019). Biochar is the solid carbon-rich by-product

generated from these techniques, that is formed by thermally degrading biomass in an oxygen-starved environment. It is a kind of low-cost and sustainable biocarbon material as biomass is an abundantly and readily available renewable resource (Guardia et al., 2018).

The process employed to obtain biochar is dependent on the type of biomass substrate. Biomass consisting of lower and higher moisture content are better suited to be processed via pyrolysis and hydrothermal conversion respectively. Characteristics of the obtained biochar vary according to the substrates, thermochemical methods, and operating conditions. Furthermore, lignocellulosic biomass possessing higher amounts of cellulose, hemicellulose, and lignin serves as a better substrate as it has fewer starch-based constituents. The application of biochar mainly depends on its varying physiochemical properties. It is not only constrained to the soil healing (Wang et al., 2020), but also includes

Abbreviations: SC, Supercapacitor; Ha, Hectare; MSW, Municipal solid waste; SS, Sewage sludge; BET, Brunauer, Emmett and Teller; PTEs, Potentially toxic elements; HTC, Hydrothermal carbonization; HTL, Hydrothermal liquefaction; ER, Equivalence ratio; XPS, X-ray photoelectron spectroscopy; HPC, Hierarchical porous carbon; EDL, Electric double-layer; SWCNT, Single-wall carbon nanotube; MWCNT, Multi-wall carbon nanotube; CVD, Chemical vapor deposition; FLG, Few layered graphene; CQD, Carbon quantum dots; EDLCs, Electric double-layer capacitors.

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the CO₂ sequestration (Dissanayake et al., 2020), heavy metals removal (Zhang et al., 2020), and acting as a catalyst or support for the active metals (Kumar et al., 2020a). Biochar can be used to suppress the emissions of CO₂, NO_x, CH₄, and other greenhouse gases from being released into the environment as well (Das et al., 2023).

The recent progress in research regarding biochar-based materials has propelled its application domains towards electrochemical storage and generation in supercapacitors and fuel cells respectively (Liu et al., 2019). Supercapacitors (SCs) are energy storage devices that have a high-power density as compared to batteries and can be charged and discharged providing the required power instantly (Mahmood et al., 2020, 2019). SCs are employed in various electronic gadgets, hybrid vehicles, and medical sector, etc. (Banerjee et al., 2020). More application scenarios and opportunities continue to emerge with the rapid development of the new energy power industry. The fabrication of such energy storage devices from a green substrate is highly necessary for today's technological advancement. Recent articles on biomass processing and obtained carbon materials have proven their applicability in various domains (Ali et al., 2025; B. Li et al., 2023a; Magoua Mbeugang et al., 2025; Mahmood et al., 2021).

Recent review articles have discussed the porosity of activated carbon obtained from biomass (Saini et al., 2021; S. Yang et al., 2019). Alongside porosity, other characteristics regarding the charge storage mechanism in other bio-derived carbon materials should be considered. Whereas other types of carbon-based materials can be prepared which exhibit variable energy storage capacities. This article is a facile try to review the recent progress made in preparing carbon materials derived from various renewable biomass substrates. The processes utilized and properties attributed to the material's ability to store charge have also been discussed. A brief layout of this review is summarized in Fig. 1.

2. Substrates for biochar production

2.1. Agriculture waste

Agricultural-based waste is known as unwanted biomass generated at the end of crop harvesting. It consists of rice husk, rice straw, wheat straw, corn cobs, stover, etc. Since there are no proper disposal protocols in place in developing countries, most farmers burn the residues in open air causing large amounts of particulate matter and CO₂ in the atmosphere which leads to detrimental health and environmental issues (Abdurrahman et al., 2020). Generating by-products and biochar from such waste adds to the value of not only these substrates but also the thermochemical processes. These include techniques such as gasification, pyrolysis, and hydrothermal conversion to transform the residues

into value-added chemicals. Hence, the readily available and cheap agro-based residues can prove to be a sustainable resource for generating biochar and by-products. Some commonly used agro wastes utilized for biochar generation are rice and wheat straw (Gabhane and Vaidya, 2019; K.V. Sarkanen, 1971), sugarcane bagasse (Jeong et al., 2016), corn straw (Ouyang et al., 2015), maize cob and stover (Intani et al., 2016; Yang et al., 2017), cotton stalk (Liao et al., 2016), and biomass from peanuts and switchgrass (srinivasan et al., 2015). Physicochemical properties of biochar can vary when produced from various processing conditions and biomass feedstocks.

2.2. Forest wastes

More than half (i.e., 54 %) of the globe's forests can be accounted for in Brazil, China, Russia, and the United States of America (Food And Agriculture Organization Of The United, 2020). According to the Forest Resources Assessment 2020 (FRA 2020) report, the world has at least 1.11 billion hectares (ha) of forest. Since 1990, approximately 420 million ha has been lost due to deforestation. However, the annual rate of deforestation has decreased from 12 million ha (2010–2015) to 10 million ha (2015–2020) (Food And Agriculture Organization Of The United, 2020). Wood from forests is employed as the main raw material for the craft, paper, furniture, and fuelwood industries. In regard to the quality of biochar produced, wood is considered a valuable feedstock. Wood consists of lignin, pectin, resin, and volatile materials, which can be attributed to a variation in the calorific value of biochar. Forest wastes include herbs, branches, and wood, which have been widely studied for producing different products. Wood has also been successfully utilized for preparing biochar (carnimeo et al., 2023; Gabhi et al., 2020a; Pipiška et al., 2022; Sirico et al., 2021). From reports, wood has proven to be a suitable resource for biochar, but it must be kept in mind that relying too heavily on this resource may lead to deforestation.

2.3. Bio-based industrial waste

Industries relevant to various sectors generate waste that is ample in carbon content and can be used for biochar production. Annually approximately 50 million tons of lignin is generated from the paper and pulp industry as a by-product, 95 % of it is fed in burners as a fuel, and 5 % of it is utilized for commercial purposes (Demuner et al., 2019). Various agriculture-dependent industries may generate wastes such as fruit and vegetable peels etc. Second-generation biorefineries producing bioethanol generate lignin as a waste by-product. The properties of the lignin are dependent on the pre-treatment parameters employed to separate biomass's various components (Rawat et al., 2021).

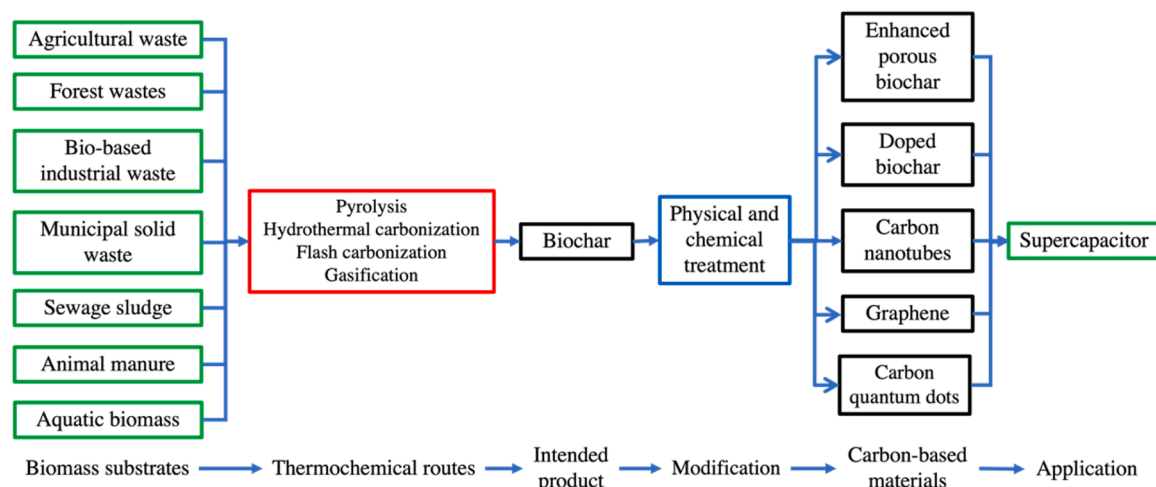


Fig. 1. Various biomass substrates for biochar production that can be modified to obtain different carbon-based materials for the application of supercapacitors.

Carbon-rich waste from industries is desirable as it is generated in large amounts and can be further valorised into biochar and other valuable products.

2.4. Municipal solid waste (MSW)

Due to the increase in population and urbanization, huge urban waste has been an issue in major metropolitan cities around the world. As depicted in Fig. 2, MSW consists of various types of waste. Biodegradable waste normally is decomposed by biological organisms while some organic and inorganic portions of non-biodegradable waste are recyclable.

According to recent studies, nearly 2.01 billion tons of MSW is generated annually and it is estimated that by 2050 this amount will be increased to 3.40 billion tons per annum (Torres et al. 2020; Xiao et al., 2020). This unprecedented growth poses a serious issue to the environment. Most articles have utilized various biomass-based feedstocks as previously mentioned in Sections 2.1 and 2.2. Whereas few studies have been carried out investigating suitable MSW as a substrate for biochar production (Jayawardhana et al., 2019; Rehrah et al., 2016; Taherymoosavi et al., 2017; Yan et al., 2020). Intrinsic properties of the MSW such as its structure and chemical composition affect the physicochemical properties of biochar (Ippolito et al., 2020; Li et al., 2018). MSWs from various regions if processed under similar operating conditions result in biochar displaying varying functions (Abylkhani et al., 2019; Yin Ding et al., 2021). Table 1 depicts the variation of the yield of biochar, from 19.4 % to 48.4 %, which can vary due to the properties and composition of MSW (Hasan et al., 2021).

2.5. Sewage sludge (SS)

Sewage sludge is a by-product of wastewater treatment plants and can serve as feedstock for biochar production. More than 80 % water is present in SS along with various organic and inorganic matter (i.e., Al_2O_3 , Cao, MgO , and SiO_2 , etc.). The high concentration of heavy metals in SS can be a cause of groundwater and soil contamination as a result of leaching (Meng et al., 2016). Therefore, the American Environmental Protection Association has labelled SS as a pollutant (Gong et al., 2014; Yuan and Dai, 2017). According to a detailed study (Ding et al., 2021), in 2018 China's SS output was approximately 228 million tons per annum, having a capita of 0.45 kg/person/day. Processing such large amounts via conventional pathways is not viable due to strict relevant rules and regulations.

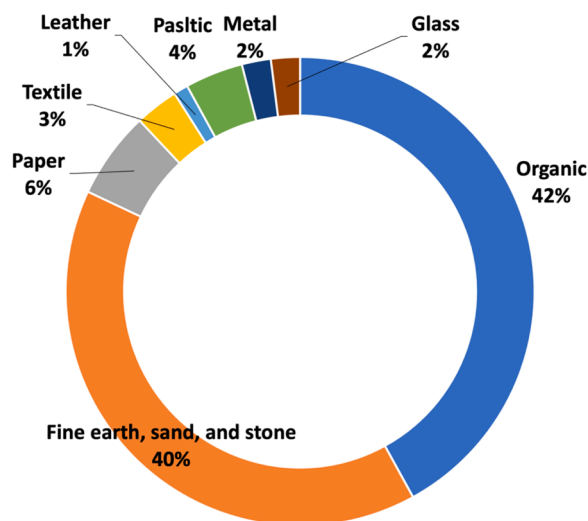


Fig. 2. Composition of municipal solid waste (Carnimeo et al., 2023; Demuner et al., 2019).

Therefore, thermal treatment of SS has gained attention in recent years due to various unique disposal methods, resource recovery, and economic benefits (Gherghel et al., 2019). Thermochemical pathways are preferred as they can handle large volumes of SS, due to their overall efficiency, and are economically viable. A study from 2020 by Gao et al. (Gao et al., 2020), entails a detailed review of SS treatment via three thermochemical methods. Table 2 displays various thermochemical techniques employed for biochar production from SS as the feedstock. Pre-treated SS for biochar can be activated to further enhance its characteristics such as Brunauer, Emmett, and Teller (BET) surface areas, pore structure, and surface functional groups (Singh et al., 2020). Sewage sludge biochar has attracted the attention of the scientific community owing to its properties, low cost, and ability to be utilized in energy-related applications.

2.6. Animal manure

The livestock sector contributes to more than 90 % of the pathogens present in the environment. These impose a severe threat to the health of both animals and humans (Gudda et al., 2022; Rechsteiner et al., 2021, 2020). Estrone, 17α -estradiol, 17β -estradiol, estriol, and predominantly persistent estrogens are found in animal dung. Few soil-based microorganisms are capable of degrading estrogen and soil exposure to high amounts of it can have negative effects on the soil's microbial activity (Wei et al., 2021).

Transforming animal dung to biochar, via thermal treatment, has risen as a suitable alternative to mitigate the above-mentioned issues. High temperature ($>400^\circ\text{C}$) operating conditions can make pathogens and organic matter (e.g., steroids, antibiotics) inactive and can decrease the concentration of potentially toxic elements (PTEs) in the environment. Treating manure at a higher temperature (>600 – 650°C) via pyrolysis is not preferred as it can result in losing nutrients such as nitrogen and phosphorous. Therefore, biochar produced from animal manure exhibits low amounts of PTEs and releases nutrients at a slower rate to the soil as compared to animal manure.

2.7. Aquatic biomass

Aquatic biomass, such as algae, seaweed, kelp, and microflora, is known as a third-generation biofuel substrate (Dutta et al., 2022). River floors, ponds, and lakes are rich sources to find such bioresources. As a result of fishing and other water-based activities, significant amounts of waste are generated. Among the various aquatic organisms, algae are a prominent species that is capable of growing in freshwater and seawater or even damped oils. They can be either multicellular or unicellular.

Algal-based biomass has some merits when compared to dry land-based biomass as a substrate for producing biochemicals or biochar. Combined processes of biological and thermochemical methods are suggested to increase the utilization of algae biomass (Dutta et al., 2022). Biochar obtained from algae is nutritionally richer than biochar from lignocellulosic biomass (Bird et al., 2011). These are macronutrients (i.e., K, P, N, Mg, and Ca) and micronutrients (Mo). The characteristics and properties of algal biochar vary from those of lignocellulosic biochar. The pH is higher for algae biochar than lignocellulosic biochar (Yu et al., 2018). Preparing carbon materials from algae is possible due to its inherent heteroatom functional groups. However, algae-based biochar has its limitations due to the high cost of algae cultivation and collection. Apart from this, algae utilization is already in demand due to applications in agar, alginate, food, and cosmetics which are economically more attractive. Therefore, using algae as a feedstock for biochar production cannot compete with its existing market demands (Roberts and de Nys, 2016). Nonetheless, various types of algae have been investigated for the production of biochar via pyrolysis for supercapacitor application as shown in Table 3.

When considering various types of biomass feedstocks, the operating conditions such as temperature and atmosphere conditions are the most

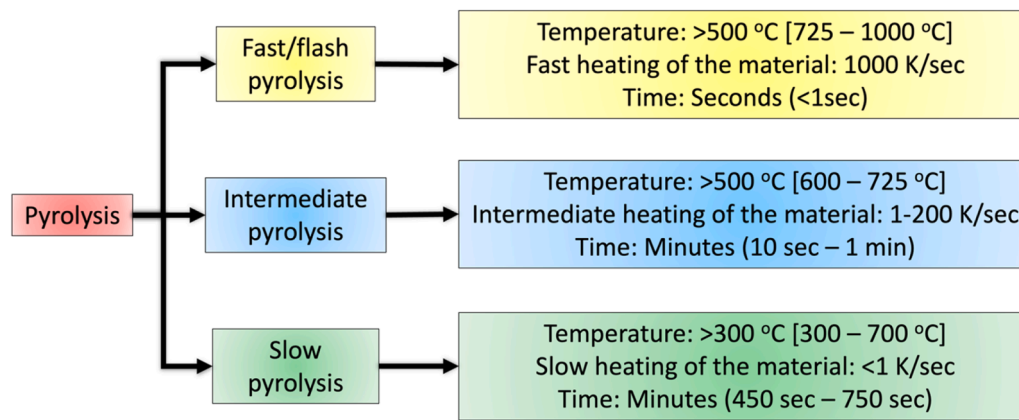


Fig. 3. Required operating conditions for different pyrolysis pathways.

Table 1

Biochar yield obtained via pyrolysis of MSW from various countries.

Substrate	Biochar yield (%)	Operating conditions	Ref.
Australia	48.4	Slow pyrolysis at 500 °C	(Kabir et al., 2015)
China	26.4	Fast pyrolysis at 600 °C	(Yan et al., 2020)
	19.4	Fast pyrolysis at 800 °C	
Korea	27.2	Slow pyrolysis at 500 °C	(Lee et al., 2013)
UK	36.0	Slow pyrolysis at 500 °C	(Buah et al., 2007)

influential factors affecting the properties of biochar (Luo et al., 2015). With the increase of temperature leads to the formation of biochar consisting of higher fixed carbon content with low yield (Manyà, 2012). As reported in literature (Luo et al., 2015), the biochar surface area tends to drastically increase above 400 °C suggesting that cellulose and lignin do not decompose pyrolytically around 300 °C (Keiluweit et al., 2010). To be more precise, cellulose crystallinity within biomass has documented to vanish at temperatures above 350 °C, whereas aromatic crystallites were determined to evolve near 400 °C. The high surface area and pore volume formation were formed due to highly ordered aromatic structures which were facilitated by the formation of narrow pores in biochar resulting at elevated temperatures (Al-Wabel et al., 2013). The most active temperature range for biochar processing lies

from 250 to 350 °C, at this range almost all properties of biochar experience change as a result of hemicellulose decomposition and partial decomposition of cellulose along with lignin (Weber and Quicker, 2018). When compared to operating temperature and atmosphere, heating rate and time have relatively low effect on biochar properties. Temperatures higher than 400 °C with heating time of 5 mins and more result in almost all holocellulose (i.e., mixture of water-insoluble carbohydrates with components of cellulose and hemicellulose). With short residence times (2 mins and less) some parts of the holocellulose are conserved and can be identified in biochar synthesized at elevated temperatures. Holocellulose is reported to be decomposed completely at temperature above 650 °C even when the residence time is short. Furthermore, temperatures required to decompose lignin are significantly higher as compared to holocellulose (Weber and Quicker, 2018). Biochar has been synthesized from various biomass feedstocks, however the phenomena taking place during the synthesis process are not completely investigated and understood. Therefore, there are many contradicting conclusions in literature and reported results are found to vary significantly.

3. Methods for biochar production

Biochar production is usually achieved via thermochemical

Table 2

Operating conditions for various thermochemical techniques to obtain biochar from SS (Xiao et al., 2022).

Thermochemical technique	Operating conditions			
	Temperature	Heating rate	Residence time	Atmosphere
Combustion	800 °C	10–40 °C/min	5–30 min	Air
HTC	150–240 °C	~10 °C/min	5 min – 24 hrs.	Ar/N ₂
Gasification	700–1000 °C	> 10 °C/sec	< 30 min	O ₂
Slow pyrolysis	300–700 °C	0.1–1 °C/sec	5–30 min	N ₂ /CO ₂
Fast pyrolysis	400–600 °C	10–200 °C/sec	0.1–0.3 sec	N ₂ /CO ₂
Flash pyrolysis	750–1000 °C	> 200 °C/sec	< 1 sec	N ₂ /CO ₂

Table 3

Different types of algae utilized for pyrolytic biochar production for supercapacitor application.

Algae type	Pyrolysis temperature (°C)	Activation agent	Specific capacitance (F g ⁻¹)	Ref.
S. Platensis	650–750	KOH	200	(Sevilla et al., 2013)
Kelp	600	KOH	277	(Zeng et al., 2017)
	700	NH ₃	> 360	(Li et al., 2015)
Cladophora	-	Polypyrrole polymerization	181–127	(Wang et al., 2015)
	-	Ni(OAc) ₂ ·4 H ₂ O	103	(Zhou et al., 2019)
Nanochloropsis salina	550	Co(OH) ₂	296–347	(Zhou et al., 2017)
Chlorella zofingensis	600	KOH	353	(Zhu et al., 2018)
Nostoc flagelliforme	600–900	KOH/HF acid	283	(Wang et al., 2019)
C. glomerata	900	HNO ₃	376.7	(Pourhosseini et al., 2018a)

techniques. The latter has benefits in terms of substrate selection but is hindered by the slow reaction rate and feedstock requirements (Zhang et al., 2023). Pyrolysis, hydrothermal carbonization (HTC), flash carbonization, and gasification are some of the most widely applied methods. It is formed when biomass is burnt either naturally (i.e., wildfires) or intentional manmade processes (i.e., HTC, gasification, pyrolysis, etc.) in an oxygen-controlled environment. A technique for biomass transformation is selected on the basis of feedstock characteristics, yield, and quality of biochar. Operating conditions such as temperature, residence time, and heating rate are very important in terms of the yield and quality of biochar.

3.1. Pyrolysis

In pyrolysis, the substrate is treated at elevated temperatures in the absence or in limited oxygen. Solid carbon (i.e., biochar), gases, and liquid (i.e., bio-oil) are the products of pyrolysis. The biochar yield is dependent on the substrates' nature and the process parameters (Wei et al., 2019). Agro-/forest-based biomass constitutes cellulose, hemicellulose, and lignin. Cellulose can be pyrolyzed at a temperature of 350 °C, whereas lignin melts above 350 °C (Czernik and Bridgwater, 2004). Therefore, the viable temperature range for pyrolyzing biomass is 350–700 °C (Suárez-Abelenda et al., 2017). Temperature, residence time, and heating rate can be used to categorize the process into fast and slow pyrolysis. Furthermore, flash, vacuum, and microwave are also types of pyrolysis.

3.1.1. Fast pyrolysis

Fast pyrolysis is carried out at a high heating rate (100–200 °C min⁻¹) and has less residence time (Dhyani and Bhaskar, 2018). High liquid product recovery and less residence time are benefits of fast pyrolysis over slow pyrolysis, but a relatively lower biochar yield is normally obtained. The product yield of pyrolysis as per literature is around 60 % bio-oil, 20 % syngas, and 20 % biochar (Dai et al., 2017; Huang et al., 2016). Different studies entail producing biochar by fast pyrolysis from various sources like sewage sludge (Dai et al., 2017), coconut shells, rice husks, Palmyra nutshell (Jegajeevagan et al., 2016), and pine sawdust (B. Li et al., 2023b).

3.1.2. Flash pyrolysis

Flash pyrolysis is considered an upgraded technique of fast pyrolysis. In this method, biochar is produced in a short time (i.e., mostly less than a minute) by decomposing biomass at temperatures higher than 1000 °C. To achieve biochar in such a short time, normally a very high heating rate is set. Flash pyrolysis is carried out at temperatures between 900–1200 °C which allows biomass transformation to biochar within seconds (Roy et al., 2001; Tripathi et al., 2015). A short residence time and a rapid heating rate led to a high yield of bio-oil. However, this results in a lower biochar yield (Tripathi et al., 2015). Due to high temperature and high heating rate operation, the reactor construction (i.e., twin screw reactor and fluidized bed reactor) limits its ability to be employed at the industrial scale.

3.1.3. Slow pyrolysis

Slow pyrolysis is also known as conventional pyrolysis, in this type, biomass is treated at a temperature between 300–600 °C with a heating rate of 5–7 °C min⁻¹ having a residence time of more than 450 s (Lai et al., 2013a). For slow pyrolysis, the main product is biochar (35–45 %, with syngas (20–30 %) and bio-oil (25–35 %). In slow pyrolysis, due to low heating rate secondary pyrolysis and cracking process are reduced for both lignin and lignocellulosic-based biomass. This leads to biochar production as the main product. When the heating rate is less than 10 °C min⁻¹, the breaking of chemical bonds takes place affecting the biomass structure. This is in accordance with a study carried out with a heating rate of 10 °C min⁻¹, the volatile matter was reduced from 25.2 % to 11.5 % as the temperature was increased from 400 °C to

600 °C (Angin, 2013). Slow pyrolysis of nut shells and paper sludge has been used for producing biochar (Lai et al., 2013b; Méndez et al., 2015). In a comprehensive study carried out by Mendez et al. (Méndez et al., 2015), they investigated the effect of feedstock type on the quality and physiochemical properties of the obtained biochar and concluded that characteristics of the required biochar should be studied prior to selecting the substrate.

3.1.4. Vacuum pyrolysis

Pyrolysis carried out under low pressure, or vacuum is termed as vacuum pyrolysis. Temperature and pressure are kept in the ranges of 450–600 °C and less than 1 atm respectively (Carrier et al., 2011; Roy et al., 2001; Tripathi et al., 2016), whereas the heating rate is kept low. Although both the heating rate and temperature are comparable to slow pyrolysis, the products vary for both of the methods. This difference can be related to the efficient removal of vapor during vacuum pyrolysis. The negative pressure i.e., vacuum facilitates in reducing the boiling point of substrates, hence, reducing the required temperature for devolatilization of volatiles during the process (Guo et al., 2019; Tripathi et al., 2016; Wan Mahari et al., 2018). Moreover, the vacuum environment during the process diminishes the need for a carrier gas (e.g., helium, nitrogen), making the overall cost of vacuum pyrolysis less (Liew et al., 2019). The effect of vapor removal has a positive effect on the yield and quality of the char and liquid products. Thus, high-quality biochar is obtained by exhibiting high porosity which can be applied to applications such as energy storage for supercapacitors (Uras et al., 2012).

3.1.5. Microwave pyrolysis

In microwave pyrolysis, heating is carried out by using microwave radiation at temperatures ranging between 300–800 °C. The heat from microwaves allows for the thermal degradation of substrates into conventional pyrolysis products i.e., char, oil, and gases (ethaib et al., 2020). Microwaves are not only a source of heat but also facilitate in breaking down of heavy hydrocarbons (i.e., C₅₁–C₅₇), this is accomplished through the chain-end scission pathway which takes place during microwave pyrolysis (Lam et al., 2016). Zhu et al. (Zhu et al., 2015) performed a study comparing slow and microwave-assisted pyrolysis using corn stover as a biomass substrate. Biochar obtained via microwave pyrolysis exhibited a larger surface area and higher carbonyl groups present on the surface. Menéndez et al. (Menéndez et al., 2005) utilized sewage sludge for biochar which displayed fewer micro and mesopores when prepared by microwave pyrolysis as compared to conventional pyrolysis.

Microwave pyrolysis reduces the cost of operation by removing pre-treatment (i.e., drying and size reduction) as it can process large and moisture-containing substrates (Motasemi and Gerber, 2018). It is to be noted that using microwaves in this method poses danger to the surroundings due to microwaves, however, this can be avoided through suitable measures such as using a Faraday cage. Another point to consider for this technique is the type of materials that can be used for the design and manufacturing of the reactor. Metallic materials should not be entertained as this can lead to arcing which can cause damage to personnel and the overall pyrolysis setup.

3.2. Hydrothermal carbonization (HTC)

Similar to pyrolysis, HTC can be performed by varying the operating conditions to successfully convert biomass into products i.e., char, gases, and liquids. HTC is carried out at a temperature range between 180–250 °C and pressure ranging between 2–10 MPa (Shen et al., 2015). Fig. 4 depicts the different pathways to obtaining biochar and hydrochar. Carbon produced via conventional pyrolysis is termed as biochar, whereas carbon obtained through HTC is called hydrochar. The nitrogen present in the biomass converts to N₂O, whereas chlorine, sulfur, and phosphorous form their respective inorganic acids through oxidation.

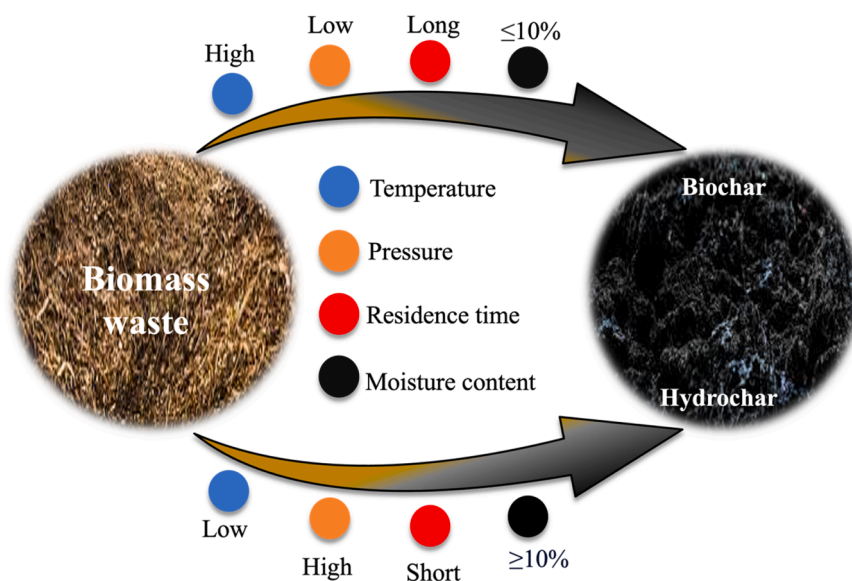


Fig. 4. The various parameters required to synthesize biochar and hydrochar.

These inorganic acids can be countered by adding relevant bases (Peterson et al., 2008). The yield of biochar and bio-oil can be decreased and increased respectively by increasing the temperature up to 250–350 °C and the pressure to 10–30 MPa. This method of obtaining a higher liquid yield is denoted as hydrothermal liquefaction (HTL) (Nizamuddin et al., 2017).

Biomass is depolymerized via hydrolysis due to the ionization of water at high temperatures (Kumar, 2010). During the process the nature of water to act simultaneously as both acid and base permits hydrolysis to convert biomass into desired biofuels (Akiya and Savage, 2002). This is supported by the fact that HTC produces more quantities than pyrolysis which does not involve water (Zhang et al., 2009). Water weakens specific bonds in organic matter, leading to the formation of new molecular portions that alter the overall reaction environment. As this is ongoing, water acts as an acid-based catalyst, hastening various reactions (Nizamuddin et al., 2017) leading to the formation of various chemicals and hydrochar. Hydrochar obtained via HTC varies considerably from biochar. Its structure is rich in alkyl portions whereas, biochar consists of more aromatic fractions (Fu et al., 2019; Kumar et al., 2020b). Hydrochar and biochar when prepared from the same substrate, it was found that hydrochar consists of more oxygen fractions (Liu et al., 2010). Recently it was determined that the functional groups on the hydrochar surface can be replaced or modified by tempering the solution mixture HTC. In a study carried out by Nunes et al. (Nunes et al., 2020), they imposed sulphonate groups on the char structure using Kraft lignin as the substrate. Most of the carbon (i.e., hydrochar) obtained via HTC remains in soluble form (Hu et al., 2010). Merits of the HTC over pyrolysis lie in the characteristics of the hydrochar obtained. It (i.e., hydrochar) includes a noteworthy reduction in the C/O ratio, the char obtained can be grounded easily, enhanced calorific value, and increased hydrophobicity (Gao et al., 2013). As it has a low fiber structure and a high heating value it is comparable to coal, furthermore, the elemental contents are almost similar to sub-bituminous or lignite coal (Nizamuddin et al., 2017). Table 4 presents an overview of various substrates employed through HTC for hydrochar formation at varying operating conditions.

3.3. Flash carbonization

Conventional pyrolysis usually is carried out at elevated temperatures and often it can be a lengthy process. Comparatively, flash carbonization is done at lower temperatures (i.e., 400 °C), once the

Table 4

Hydrochar synthesized from various biomass substrates via HTC, adopted from reference (Nizamuddin et al., 2017).

Biomass substrate	Temperature (°C)	Time (mins.)	Type of reactor	Yield (%)
Microalgae	190–210	30–120	Parr stirred stainless steel	25.3–45.7
Mix wood	215–295	5–60	Parr stirred stainless steel	50.1–69.1
Eucalyptus sawdust	250	120	Autoclave	40
Poplar wood	180–230	480	Stainless steel autoclave	51.9–89.9
Empty fruit bunch	150–30	20	Parr stirred pressure batch reactor	49–76
Olive mill wastewater	180 and 220	840	Lab scale autoclave	~30
Switchgrass	300–400	60–180	Cylindrical metal container	35.2–82.0
Palm shell	180–260	30–120	Amar autoclave batch reactor	38.7–63.0

targeted temperature is achieved, the obtained biochar is introduced to air for around 10–20 mins. This method was invented by Prof. Michael J. Antal from the University of Hawaii (Antal et al., 2003; Uchimiya et al., 2015). In this process, a vessel is used in which the biomass is placed with a pressure of 1–2 MPa, a fire is ignited at the bottom of the substrate opposite to the airflow. Here the carbonization period is reduced with the increase in pressure. In these operating conditions, the volatile content of biomass is transformed into gas-based fuel, while the remaining content is obtained in the form of biochar (Uchimiya et al., 2015). The yield of this process is 40 % and the obtained biochar consists of a more microporous structure as compared to biochar prepared from conventional pyrolysis (Hirst et al., 2018).

3.4. Gasification

This thermochemical technique converts biomass substrate mainly to syngas (CO₂, CO, H₂, and CH₄) at high temperatures in steam or air. The biochar yield is less whereas the syngas yield from gasification is high (Prabakar et al., 2018). Steam gasification results in the partial oxidation of lignocellulose leading to the formation of a highly microporous biochar which is abundant in minerals (Romero Millán et al., 2019). In a

review article published by You *et al.* (You *et al.*, 2017) states that the characteristics of biochar obtained via gasification can be regulated through optimized operating parameters leading to a sustainable pathway for producing both biochar and syngas. It is considered that the biochar formed from gasification is a waste product, although it has many applications in energy storage, dye removal, carbon sequestration, soil healing, and adsorption of chemicals (Al-Rahbi and Williams, 2017; González *et al.*, 2008).

The quality of biochar generated from gasification is related to the carbon content of the biomass substrate (Shackley *et al.*, 2014). Furthermore, Benedetti and the research group (Benedetti *et al.*, 2018) state that biochar quality is influenced by factors like substrate characteristics, equivalence ratio (ER), gas carrier, and pressure. ER is considered the most crucial parameter that affects gasification, in accordance with the physical properties of the selected biomass substrate, its optimized value is 0.25–0.28. Another study conducted by Yao *et al.* (Yao *et al.*, 2018) found that when the equivalence ratio (ER) is increased from 0.1 to 0.6 the yield of biochar decreased from 0.22 to 0.14 kg kg⁻¹, whereas the carbon content of the obtained biochar also decreased from 88.17 % to 71.16 %. Muvhiwa *et al.* (Muvhiwa *et al.*, 2019a) articulates that the carbon content of the obtained biochar reduced from 89 % to 80 % and from 93 % to 86 % for 700 °C and 900 °C respectively. This was done when the flow rate of oxygen increased from 0.15 to 0.6 kg h⁻¹. A higher ratio of ER denotes that more oxygen is provided to the reactor (i.e., gasifier). High ER has merits and demerits on the overall quality of the obtained biochar. It supports heterogeneous reactions resulting in more transformation of solid carbon into gases. This also facilitates the formation of a microporous structure hence, leading to a high specific area of biochar (Kumar *et al.*, 2017). The oxygen can also have a negative effect resulting in reduced mechanical strength of the biochar and an increase in ash content. Recently, various reactor types have been employed for biomass gasification (Table 5) at varying temperatures.

4. Properties of biochar for supercapacitor applications

As discussed above, process conditions such as temperature, residence time, and heating rate can significantly impact the characteristics of the desired biochar like surface area, porosity (i.e., porous structure), and functional groups. The presence of aromatic moieties, hydroxyl, and carbonyl groups on biochar has been confirmed through analysis techniques such as X-ray photoelectron spectroscopy (XPS) and infrared (de Figueredo *et al.*, 2017). Normally, when the pyrolysis temperature is increased it results in a reduction of oxygen content, and the final biochar product exhibits a higher surface area (Mendonça *et al.*, 2017). The pH of the biochar can be also altered by tuning the operating parameters. Zhao *et al.* (Zhao *et al.*, 2017) produced biochar from branches of an apple tree at varying temperatures and displayed an incline in pH at elevated temperatures. This resulted in a reduction of carboxyl groups at high temperatures. The fiber structure, carbon matrix, and layered

Table 5

Types of reactors employed for biomass gasification and surface area of the obtained biochar at varying temperatures.

Biomass substrate	Type of reactor	Temperature (°C)	Char BET surface area (m ² g ⁻¹)	Ref.
Wood pellets	Nitrogen plasma torch	900	364.4	(Muvhiwa <i>et al.</i> , 2019b)
Rice straw	Dual fixed bed	800	444.4	(Xu <i>et al.</i> , 2019)
Wood chips	Dual stage gasifier	900	587	(Benedetti <i>et al.</i> , 2018)
Coconut shells	Fluidized bed gasifier	750	1041.8	(Millán <i>et al.</i> , 2019)
Pine	Fixed bed	800	-	(Huang <i>et al.</i> , 2013)

structure of the substrate affect the end structure of the biochar (Chen *et al.*, 2019; Gabhi *et al.*, 2020b; Yang *et al.*, 2019) which satisfies the requirements to be utilized as a material for supercapacitor electrodes. Properties of biochar are not only influenced by its elemental composition but also by the presence of heteroatoms such as P, S, N, etc., which rely on the biomass substrate. These properties can lead to a varying capacity to store charge. The electrical conductivity of biochar is directly associated with its ability to be graphitized, and this can be achieved by pyrolyzing at very high temperatures (i.e., 1000 °C) (Gabhi *et al.*, 2020b).

The specific capacitance of supercapacitors can be enhanced by generating more active sites on the electrode material (i.e., biochar structure) as per the electrochemical double-layer mechanism (Yang *et al.*, 2019). In theory, a high surface area of biochar results in large specific capacitance. A higher number of active sites on the surface of the electrode material can be achieved by increasing the surface area (Guo *et al.*, 2019). However, the increase in the surface area of biochar does not linearly lead to an increase in specific capacitance. A microporous structure (i.e., small pore size) of biochar constitutes most of the surface area and it does not allow large electric ions (i.e., from the electrolyte) to enter and make efficient contact with the porous structure (X. Li *et al.*, 2023). Various studies have stated that biochar with the majority of microporous structure is not suitable for electrochemical performance as it hinders the ion transportation between the two electrodes. This should be considered especially when employing organic electrolytes (Chen *et al.*, 2019). If the pore size and the ion size of the electrolyte are in sync, this will increase the transportation rate leading to enhanced capacitance. The biochar's surface area with suitable pore size can significantly enhance the electrochemical performance of the material (Li *et al.*, 2020). Furthermore, the average pore size distribution plays a crucial role on the electrochemical performance of supercapacitors. Micropores can facilitate in ion adsorption and desorption, while mesopores are used as ion transport channels, whereas macropores act as storage points for electrolytes (Bedin *et al.*, 2016). Therefore, it can be said that unreasonable pore size will not be able to facilitate in ion adsorption and transportation and hence the full potential of the supercapacitor will not be achieved. Additionally, a summary of various electrolytes and their characteristics are provided in Table 6.

Chemical modification of the biochar's surface includes modifying it by introducing oxygen-related functional groups, and metal, or non-metal heteroatoms (Fig. 5). These functional groups and heteroatoms can impact the electrochemical performance by impacting the pseudocapacitance and wettability (Lyu *et al.*, 2019). These functional groups and heteroatoms may also showcase adverse effects in the form of current leakage, high self-discharge, and limited stability of the assembled supercapacitor. The electrode materials' properties may contribute to the device's internal resistance, which is crucial to its overall electrochemical performance (Zhi *et al.*, 2012). Sometimes, biochar can be influenced by specific activators, this will increase the surface area but in turn, may reduce the conductivity. However, high temperatures for biochar production can enhance the degree of graphitization leading to increased conductivity but, this may damage the overall structure of the biochar (Ishii *et al.*, 2017; Sevilla *et al.*, 2013). Therefore, it is necessary to carefully apply the operating conditions in accordance with the biomass substrate by keeping in view the intended application for the prepared biochar.

5. Biochar-derived carbon materials for supercapacitors

5.1. Enhanced porous biochar

Due to the low surface area and lack of active sites on biochar obtained from the above-mentioned thermochemical processes, it is not feasible to apply it directly for electrochemical applications. To achieve biochar in a feasible state to be employed, activation is carried out to

Table 6

Types of electrolytes and their characteristics (Pal et al., 2019).

Electrolyte type	Average ion size (nm)	Viable pore size (nm)	Remarks
Aqueous (KOH, H ₂ SO ₄ , Na ₂ SO ₄ etc.)	~0.6–1	> 1 (Micro and mesopores)	- These electrolytes have higher ion diameter due to hydration. - Commonly employed in low-voltage supercapacitors (1.0–1.2 V).
Solid-state and gel (PVA-H ₂ SO ₄ , polymer electrolytes)	~0.5–2	> 1 (Micro and mesopores)	Ions in gels and solid-state systems have reduced mobility.
Organic (TEABF ₄ in Acetonitrile/ Propylene Carbonate)	~1–2	> 1.5–2 (Micro and mesopores)	- Larger organic ions such as tetraethylammonium, TEA⁺ require larger pore sizes. - Employed in higher voltage supercapacitors (2.5–3.5 V).
Ionic liquid (EMIM-BF ₄ , BMIM-PF ₆)	~1–2.5	> 2–3 (Meso and macropores)	- Ionic liquids consist of large, asymmetric ions with strong ion-ion interactions. - Higher thermal and electrochemical stability (up to 4 V) but suffer from high viscosity.

increase its porosity. The treatment can be done by keeping in view specific characteristics of biochar such as surface area (i.e., porosity) which will enable it to be utilized in energy storage. These treatments can be categorized into physical and chemical activation.

Physical activation is done by reacting biochar with CO₂, steam, ammonia, or a controlled quantity of air. The temperature used for physical activation usually varies from 600 to 1200 °C (Yao et al., 2020). These activating agents interact with the carbon atom present on the top surface. As a result of the carbon (i.e., biochar) and the activating agents, various micropores and mesopores are formed enhancing the surface

area (Sajjadi et al., 2019). As a result, the removal of carbon occurs leading to the formation of a porous structure as depicted in Fig. 6.

Treating the obtained biochar with chemicals such as metals, salts, bases, acids, etc. at a temperature between 450–900 °C is known as chemical activation (Fig. 6). This step is carried out by various agents such as ZnCl₂, KOH, NaOH, and H₃PO₄ etc. Upon completion of chemical activation new surface function groups are distributed on the biochar surface along with more porosity. These outputs can be controlled by tuning the activating agent and process parameters such as temperature and residence time. The ratio of biochar and the activating agent added plays a crucial role in the output of the process (Angin et al., 2013). Biochar produced by employing molten salts can result in the presence of functional groups on the surface which can lead to specific properties for various applications. In a recent article from our research group Li et al. (Li et al., 2024) mentions that biochar produced from rice husk by using LiCl led to the formation of carbonyl groups (C=O) and defects in the biochar structure. These biochar properties prove useful for multi-dimensional applications. Apart from LiCl, carbonate-based molten salts have also been utilized to obtain porous biochar (B. Li et al., 2023c).

Wu et al. (Wu et al., 2016) formed biochar from almond nutshells, and the obtained biochar was chemically activated by HNO₃ and KOH to prepare pore sizes less than 2 nm. Using HNO₃ and KOH the specific surface area obtained was 327.7 and 1363 m² g⁻¹ respectively. The specific capacitance obtained for HNO₃ and KOH-treated biochar was found to be 286.1 F g⁻¹ and 272.3 F g⁻¹ at 1 A g⁻¹ respectively. In some cases, the substrate may possess some elements which will serve as an activating agent. In one study carried out by Gao et al. (Gao et al., 2018), crab shells were used to prepare biochar having a surface area of 630 m² g⁻¹. The CaCO₃ present within the shells acted as an *in-situ* template forming a mesoporous structure as it decomposed and formed CaO and CO₂ during the process at 900 °C leading to the formation of pores. The specific capacitance from the biochar was found to be 220 F g⁻¹. Biomass substrates such as flaxseed and bacterial cellulose have been treated with KOH and thiourea respectively to obtain porous carbon for

Table 7

Biochar obtained from biomass substrates and its characteristics after activation and capacitance when applied to supercapacitor.

Biomass substrate	Activating agent	Activating conditions	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Specific capacitance (F g ⁻¹)	Ref.
Pine nutshell	Steam	900 °C, 75 mins.	956	0.62	128	(Qin et al., 2019)
Flaxseed residue	KOH	700 °C, 1 hr.	3326	1.56	366	(Li et al., 2019)
Mangosteen peel	NaOH	700 °C, 2 hrs.	2623	-	357	(Yang et al., 2019)
Banana flesh	CO ₂	900 °C, 4 hrs.	1414.97	0.746	178.9	(Lei et al., 2018)
Baobab fruit shells	H ₃ PO ₄	800 °C, 2 hrs.	911.7	0.47	355.8	(Deng et al., 2015)
Elaeocarpus tectorius	H ₃ PO ₄	900 °C, 3 hrs.	781	0.43	385	(Nirosha et al., 2019a)



Fig. 5. Schematic illustration of modifying biochar for supercapacitor applications. Reproduced with permission from ref (mehdi et al., 2022). Copyright 2022 MDPI.

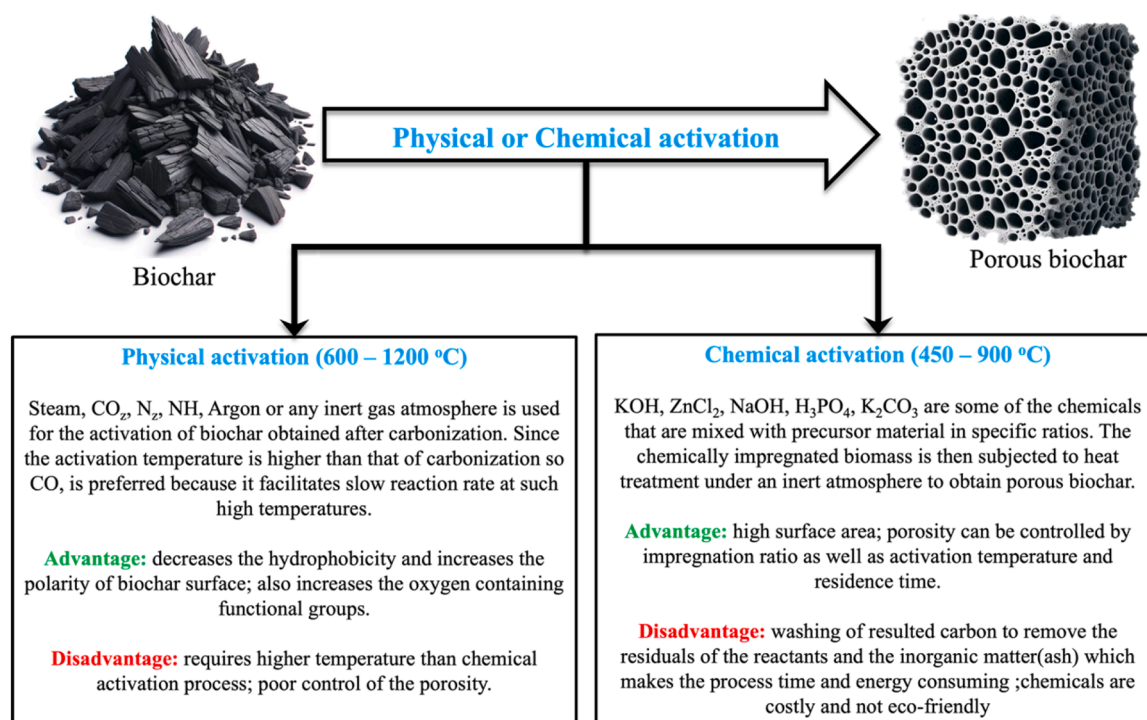


Fig. 6. Transformation of biochar to porous biochar via physical or chemical activation.

supercapacitor applications (Ding et al., 2020; Y. Li et al., 2020). Zhang et al. (Zhang et al., 2019) utilized excretes from silkworms which were pyrolyzed at 700 °C and treated with HCl to obtain a mesoporous matrix of carbon with a specific capacitance of 391.5 F g⁻¹. Hierarchical porous carbon (HPC) can be obtained by treating biochar with various activating agents and has a wide range of pore distribution (i.e., macro, meso, and micropores). The pores are well-connected, and the carbon matrix is suitable for diffusion-based systems such as energy storage. In electric double-layer (EDL) supercapacitors the mechanism for charge storage relies on the adsorption and desorption of electrostatic ions (Inagaki et al., 2014). HPC materials can be obtained from waste biomass substrates and can be employed for energy storage applications (Zhou et al., 2020). Another study done by Deng et al. (Deng et al., 2015) determined a specific capacitance of 253 F g⁻¹ from HPC by treating the biochar (i.e., pyrolyzed at 900 °C) with KHCO₃. Song et al. (Song et al., 2015) reported the preparation of HPC for supercapacitors using corn husk as biomass substrate. The husk was treated with KOH and was carbonized having a specific capacitance of 356 F g⁻¹ at a current density of 1 A g⁻¹. Table 6 summarizes biochar from substrates that are activated (i.e., physical, and chemical activation) using different agents and their characteristics.

5.2. Modified biochar via doping

5.2.1. Heteroatom doping

Organic or inorganic precursors can be utilized to dope biochar with elements. The p-block elements such as O, N, S, or P can be introduced to enhance the interaction between biochar pores and the electrolyte, which leads to enhanced active sites on the biochar surface and wettability when faced with electrolytes (Jiang et al., 2024; Nirosha et al., 2019b).

Biomass substrates can inherently possess these elements, therefore, making it possible to achieve biochar with different elemental compositions. A study done by Yu et al. (Yu et al., 2018) reported that they transformed pyrrolic nitrogen present in biochar to quaternary and pyridinic nitrogen by high-temperature polymerization and condensation. A work published by Zhang et al. (Zhang et al., 2019) revealed that

they were able to significantly enhance the conductivity of biochar obtained from sodium lignosulfonate. The treated biochar displayed a specific and volumetric capacitance of 480 F g⁻¹ and 950 F cm⁻³ respectively at a current density of 1 A g⁻¹ in H₂SO₄ electrolyte. In a study done by Ding and his group (Ding et al., 2021), biochar from bean pulp was activated using CO₂ for 30 min at 500 °C where nitrogen was prevalent. The treatment led to increased porosity and the nitrogen content was observed to be doubled with the increase in CO₂ volume. The resulting biochar exhibited a specific capacitance of 105 F g⁻¹ at a current density of 0.25 A g⁻¹ when employed as a supercapacitor electrode. Lei et al. (Lei et al., 2021) prepared porous heteroatom-doped biochar by utilizing waste biomass as the feedstock in a self-sacrificial template method. The research group applied molten salts (i.e., Na₂CO₃ and K₂CO₃) to activate hydrochar from peanut shells with moderate heteroatom co-doping (i.e., 5.35 at% O and 1.02 at% N). The specific capacitance of the treated hydrochar was 447 F g⁻¹ at 0.2 A g⁻¹ current density. Other studies have showcased similar treatments depending on the characteristics of the biochar where it has been employed for supercapacitor application (Huang et al., 2021; Li and Forciniti, 2020; Pontiroli et al., 2019). Recently, Xue et al. (Xue et al., 2024) was prepared biochar doped with N, O, S, and Cl at 700 °C by utilizing Suaeda Glauca Bunge as the biomass feedstock. The synthesized heteroatom doped biochar displayed a surface area of 658 m² g⁻¹ which resulted in a specific capacity of 638 F g⁻¹ at a current density of 0.5 A g⁻¹. Biomass in the form of oyster shells also present themselves as a carbon precursor for the preparation of doped biochar. In a study (Prabu and Chiang, 2024) bio-waste oyster shells was employed to prepare N/O 3D honeycomb like porous biochar through a two step process involving HTC and pyrolysis. The prepared 3D honeycomb like porous structure was used to assemble a supercapacitor which exhibited an impressive capacitance of 525 F g⁻¹ at a current density of 0.5 A g⁻¹.

As further research is carried out on utilizing biochar as an electrode material, doping with heteroatoms has become a recent trend. Doping of biochar enhances the interaction between the electrode material (i.e., modified biochar) and the specified electrolyte. It is an important direction for the development of biochar as a suitable carbon source for supercapacitor applications. However, the cycle stability of the

introduced elements reduces as the pseudo-capacitance consumes it repeatedly. This hinders wide applications of biochar heteroatom doping but also provides a direction for future research.

5.2.2. Metal doping

The ability of transition metals to be applied for energy storage shows promise as variable oxidation states of metals facilitate electrochemical storage. Whereas, in junction with carbon, the mechanism for storing charge is dominantly electrostatic, leading to the utilization of metal-doped biochar. The carbon structure of the biochar serves as a matrix and provides high surface area and support while specific capacitance is increased as a result of redox reactions due to the metal atoms. Li *et al.* (Li *et al.*, 2020) prepared biochar from waste biomass which was doped with $\alpha\text{-Fe}_2\text{O}_3$ using FeCl_3 via a molten salt route. Pyrolysis was carried out at 800°C for 2 hrs. The obtained biochar hybrid had a specific capacitance of 452.3 F g^{-1} at a current density of 2 A g^{-1} . Thomas and his research group (Thomas *et al.*, 2020) produced magnetic biochar (i.e., at 500°C for 12 hrs.) by using banana stems with FeSO_4 and FeCl_2 . A specific capacitance of 333 F/g was obtained by modifying the biochar surface using magnetite nanoparticles. Pourhosseini *et al.* (Pourhosseini *et al.*, 2018b) prepared algal-derived biochar which was obtained through doping with Fe nanoparticles and activated using KOH. The obtained porous metal-doped carbon interconnected structure exhibited a specific capacitance of 418 F g^{-1} . Similarly, Norouzi *et al.* (Norouzi *et al.*, 2021) produced biochar from algae (i.e., 700°C for 2 hrs.) and activated it using NaOH and doped with it cobalt. At a current density of 1 A g^{-1} the assembled supercapacitor displayed a specific capacitance of 445 F g^{-1} . Wang and their research group (Wang *et al.*, 2017) were able to dope Ni onto biochar obtained from pyrolyzing animal manure and sewage sludge at 600°C for 4 hrs. The treated biochar exhibited an increased specific capacitance of up to two times. It is evident that doping biochar with various metal atoms results in enhanced properties making it suitable to be employed as an active electrode material.

Doping of biochar has reported to enhance pore structure due to the presence of dopant oxides. Ions from doping species not only promote volatilization but also facilitate cracking of tar and volatiles leading to internal pore formation (Jia *et al.*, 2021). Studies have attributed pore formation to the level of graphitization of biochar. Furthermore, less degree of graphitization has led to the formation of well-developed pores (He *et al.*, 2020; Sun *et al.*, 2019). According to a study carried out by Jia *et al.* (Jia *et al.*, 2021), bi-metallic doped biochar doped was determined to possess a well-developed pore structure. Doped biochar serving as the carbon matrix with well-developed pore structure will enhance the electrochemical performance providing optimum pathways for ion transportation when applied for supercapacitor applications.

5.3. Biochar-based carbon nanotubes (CNT)

Carbon nanotubes are a class of carbon materials arranged in a cylinder shape and can be categorized into single-wall CNT (SWCNT) and multi-wall CNT (MWCNT). The diameter ranges between $0.8\text{--}2\text{ nm}$ for SWCNT and $5\text{--}20\text{ nm}$ for MWCNT (Liu *et al.*, 2006; nagai *et al.*, 2011). They have been employed in different domains such as energy storage (i.e., solar cells and fuel cells), microwave absorption, pharmaceutical, air, and water purification (He *et al.*, 2013; Ihsanullah, 2019; Jin *et al.*, 2021; Qi *et al.*, 2015). CNTs recently have been produced by many techniques such as arc discharge, chemical vapor deposition (CVD), and laser ablation (Hong *et al.*, 2003; Nath *et al.*, 2012). The operating conditions like gases, temperature, vacuum pressure, substrate characteristics, inert atmosphere, and residence time make the overall procedures costly (Bajpai and Wagner *et al.*, 2015). Alternative precursors such as synthetic polymers, and products of coal combustion have also been studied for CNT production (Kure *et al.*, 2017; Salah *et al.*, 2016). In 2019, Osman *et al.* (Osman *et al.*, 2019), initially prepared activated biochar from potato peel through a two-step process. The activated

carbon was then treated with a nitrogen and iron-based precursor and treated at 600°C for 2 hrs. and then at 900°C for 1 hr. to achieve CNTs as displayed in Fig. 7a. After this Osman prepared CNTs from lignocellulosic biomass (i.e., *Miscanthus giganteus*) (osman *et al.*, 2020) (Fig. 7b). Here he carried out a similar method to achieve CNTs from biomass-based activated carbon. In 2019, Hidalgo *et al.* (hidalgo-Oporto *et al.*, 2019a) prepared biochar from various biomass wastes (i.e., wheat straw, rapeseed cake, hazelnut hulls, and oat hulls). The obtained biochar was further processed under microwave irradiation at 80°C while employing ferrocene as the catalyst. The use of microwave-assisted pyrolysis was also employed by Shi *et al.* (Shi *et al.*, 2014) for synthesizing CNTs using biomass as the substrate. MWCNTs were synthesized from gumwood via pyrolysis (i.e., 500°C) in the presence of microwave irradiation and silicon carbide. Whereas CNTs were not formed when microwave irradiation was not applied. In another study, Zhang *et al.* (Zhang *et al.*, 2018) processed chitosan as the substrate and used it for nitrogen and cobalt-doped CNTs at 800°C in an inert environment. CO and CH_4 were utilized for CNT synthesis a No-Mg/ Al_2O_3 -based catalyst at 500°C in a fluidized bed reactor. This proves useful as CH_4 and CO are the main products of biomass gasification. They reported that process conditions such as temperature for obtaining biochar play a crucial role in the quality of the CNTs. Furthermore, Baghel *et al.*, (Baghel, Kaushal, 2022) recently utilized biochar from *Prosopis juliflora*, as the substrate for CNTs. CNTs prepared at higher temperatures displayed a higher degree of graphitization, and crystallinity, and were of enhanced quality with fewer defects. Furthermore, there is ample literature available where CNTs have been employed for supercapacitor applications (Ali *et al.*, 2020; Kim *et al.*, 2021; Liu *et al.*, 2018; Pan *et al.*, 2010; Zhang *et al.*, 2020).

Higher concentration of CNTs can be obtained from precursor possessing higher carbon content. Despite precursors with higher concentration of ash content facilitating in CNT synthesis, the purity of the carbon precursor plays a crucial in quality of the CNTs (hidalgo-Oporto *et al.*, 2019b). The presence of nitrogen has reported to act as a catalyst during the process of CNTs formation (Hachimi *et al.*, 2015). The interface catalyst and nanotube interface are stabilised hence the reduction of the interface energy leading to the growth of CNTs. Nitrogen has also reported to enhance the crystallinity of the CNTs and reduces defects formation (Pattinson *et al.*, 2013). Apart from nitrogen, other elements such as alkaline metals (K and Na) also facilitate by offering nucleation sites similar to the chemical vapor deposition (CVD) process (Xu *et al.*, 2014). Hence impurities or the presence of various elements contribute towards CNTs growth however, further investigation is required to have an in-depth understanding of how they impact the CNT growth process.

5.4. Biochar-based graphene

Graphene is a single sheet of graphitic carbon linked by sp^2 bonds as shown in Fig. 5a. Its unique properties such as high surface area, thermal stability, and enhanced conductivity make it an ideal material to be used in supercapacitors. Synthesizing graphene from various biomass-based (i.e., organic) substrates has been recently articulated (Mahmood *et al.*, 2023). Similar to CNT's conventional preparation methods, they are difficult to operate and are costly. Preparing graphene through the chemical exfoliation process is well known and studied due to its suitability, reliability and its potential to be upscaled when required. This process involves the introduction of oxygen into the layered graphite leading to its oxidation. This oxygen increases the interlayer spacing of the graphite leading to delamination of graphene oxide (khai *et al.*, 2013). The initial oxidation stage leads to defects in the structure, hence damaging the conjugation of the carbon basal plane (Russo *et al.*, 2014; Varrla *et al.*, 2014). Additionally, this process (i.e., chemical exfoliation) heavily depends on employing hazardous chemical and in turn yields low graphene materials. To avoid utilizing chemically hazardous chemicals, researchers have studied liquids having a surface energy

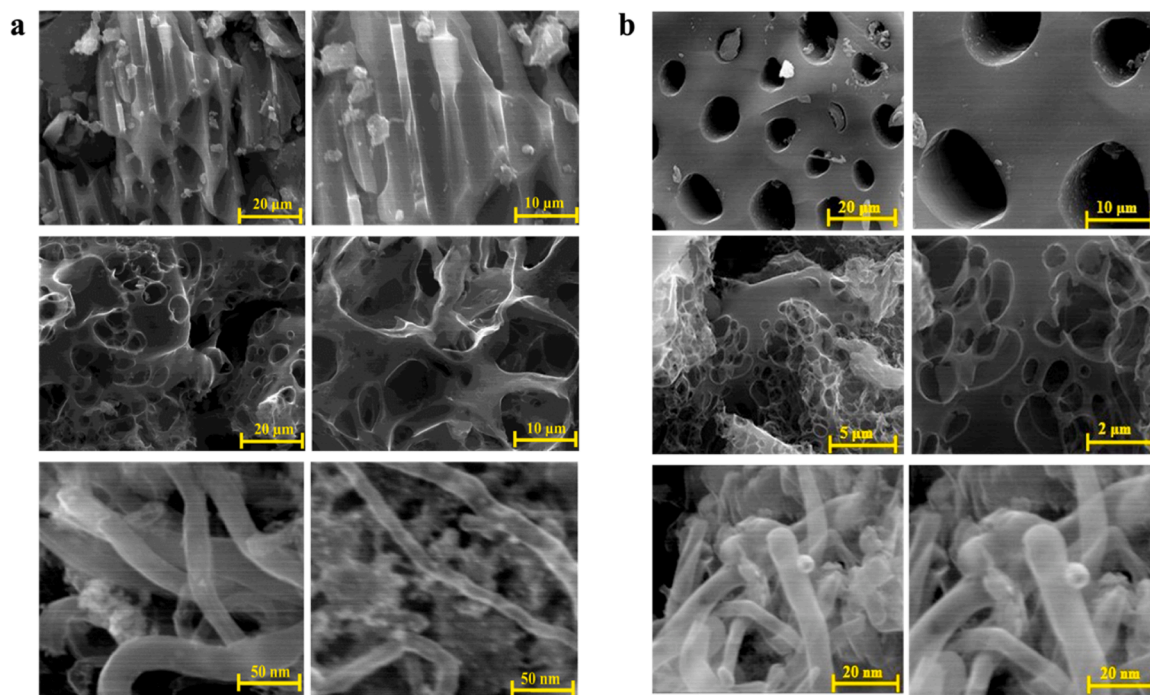


Fig. 7. Synthesized CNTs from activated biochar from (a) potatoo peel (b) Miscanthus. Reproduced with permission ref. (Osman et al., 2019, osman et al., 2020). Copyright 2019 Springer Nature and Nature Portfolio 2020.

similar to graphene i.e., 68 mJ/m^2 (Arao et al., 2016; Coleman, 2013). This method has reported to form defect free graphene (Coleman, 2013). Although N-methyle-2-pyrrolidone (NMP) has been reported to be one of the best solvents to disperse and form graphene (Wei and Sun, 2015), sonication is commonly employed to facilitate exfoliation of graphene layers. Sonication creates instant 5000 K and 20 mPa paired with instant rapid heating to cooling rates of 10^9 K sec^{-1} (Crum, 2007). These severe conditions produce shock waves leading to the separation of graphene layers from graphite (L.A. Crum, 2007). Although, graphene formation

through this method produces high quality graphene but has low yield of around 0.04 g h^{-1} (paton et al., 2014) which remains the largest hurdle in its commercialization. Biomass is an abundantly available renewable and sustainable raw material which can be utilized for graphene preparation. Therefore, biochar preparation and its further processing could be a potential pathway for preparing graphene as discussed.

Pukait et al. (purkait et al., 2017) prepared activated biochar by KOH from peanut shells as shown in Fig. 8a. The biochar was further transformed into a few layered graphene (FLG). This was carried out by

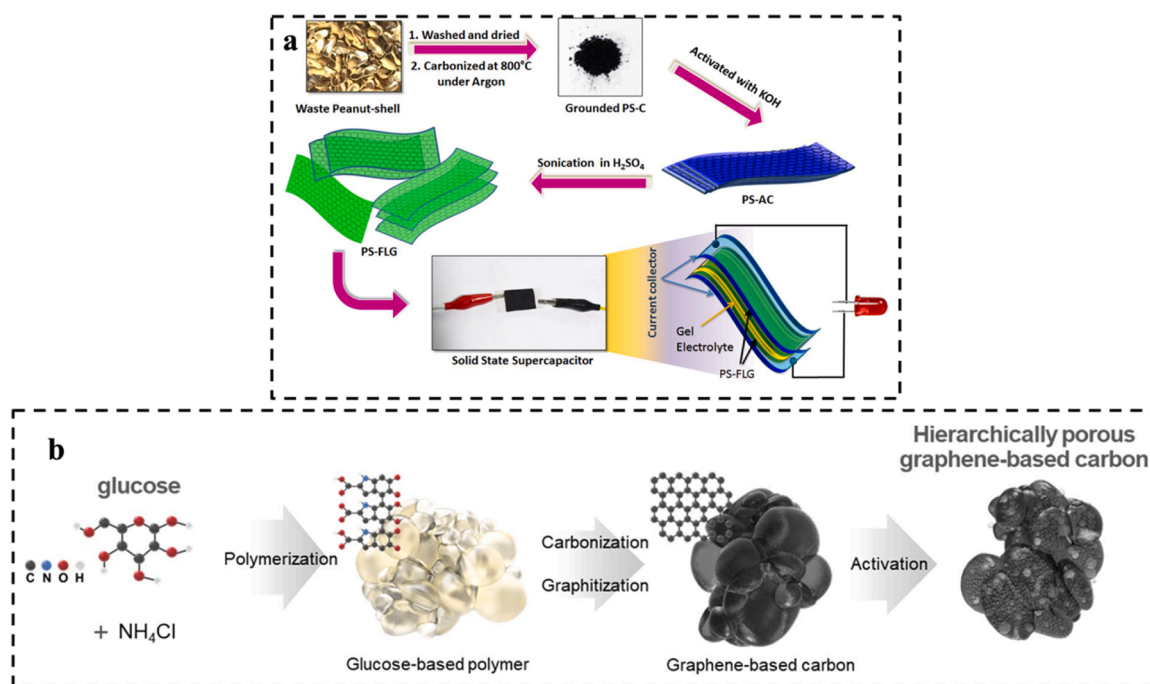


Fig. 8. Schematic illustration of the adopted pathways to synthesize graphene-based carbon from biochar for supercapacitor applications. Reproduced with permission from refs (Sun et al., 2018, Jung et al., 2018). Copyright 2018 Nature portfolio.

mechanical exfoliation and sonication in H_2SO_4 . The FLG was employed as electrode material for a supercapacitor having a specific capacitance of 78.3 F g^{-1} at a current density of 1 A g^{-1} with an energy density of 68 Wh kg^{-1} . Nanaji et al. (Nanaji et al., 2021) reported that using KOH can serve both as a catalyst and an activating agent for graphitizing biochar (from *Hibiscus sabdariffa* sticks) leading to porous graphene sheets showcasing a specific capacitance of 240 F g^{-1} at 1 A g^{-1} . In a study published by Sun et al. (Sun et al., 2018) hydrothermal carbonization (HTC) was employed to obtain graphene sheets from spruce bark by utilizing KOH for activation purposes. Similarly, KOH was utilized as the activating agent leading to a specific capacitance of 398 F g^{-1} at 0.5 A g^{-1} . Fig. 8b depicts graphene synthesized by Jung et al. (Jung et al., 2018) by carbonizing glucose at 400°C with NH_4Cl and activated it with KOH and CO_2 . The capacitance obtained was 175 F g^{-1} with a surface area of $3657 \text{ m}^2 \text{ g}^{-1}$. In a study done by Thomas et al. (Thomas et al., 2021) reported that commercially available biochar can be used for synthesizing carbon-based graphene dots which were employed for preparing carbon aerogels for supercapacitors.

5.5. Biochar derived carbon quantum dots (CQD)

Quantum dots are carbon nanoparticles that have fluorescent characteristics and are a relevant new class of carbon materials. They have multidimensional applications such as biosensors, chemical sensors photocatalysis, nanomedicines, and electrolysis (Lim et al., 2014; Wang et al., 2019). Synthesizing CQDs is normally achieved through either top-down or bottom-up methods, where the latter is widely adopted as it is simple, require minimum equipment and is cost-effective along with being a practical approach. Recently, scientists have studied other pathways such as hydrothermal by employing biomass waste as the carbon precursor (dhongde et al., 2024; Gao et al., 2023; Krishnaiah et al., 2022; Mu et al., 2024). As previously mentioned, biomass as a carbon precursor is both abundantly available and is a cost-effective option. Furthermore, CQDs have gained attention in the domain of supercapacitors when they are used as electrolytes (zhang et al., 2016). In a study done by Nguyen and the research group (Nguyen et al., 2022), CQDs from activated biochar were produced from banana peels. The banana peels were hydrolyzed via HTC and the CQDs were employed in fabricating electrodes of supercapacitors with a specific capacitance of 199 F g^{-1} at a current density of 0.5 A g^{-1} . Jamaludin et al. (jamaludin et al., 2020) also employed HTC for CQDs synthesis from empty fruit bunch as represented in Fig. 9. HTC extraction was done using isopropyl alcohol at 250°C for 1 hr for synthesizing CQD from an empty fruit bunch. Zaman and his research group (Kamarol Zaman et al., 2021) also used biochar from empty fruit bunches to prepare CQDs. In their study, they investigated that the extraction step of CQDs although takes hours can be achieved in minutes by using microwaves. Furthermore, adding

composites can enhance the specific capacitance of the fabricated device. This was confirmed by research done by Hoang et al. (Hoang et al., 2019) prepared a cauliflower-based CQDs composite with reduced graphene oxide which displayed a high capacitance of 278 F g^{-1} at a current density of 0.2 A g^{-1}

6. Challenges and future prospects

The transformation of biomass wastes to biochar has been well-studied for the past few decades. The post-treatment of biochar to obtain activated biochar results in specific desired properties and characteristics which can be targeted towards the intended applications. The type of feedstock and operating conditions play a crucial role in the homogeneity and stability of the biochar which are highly desired. Due to this, the substrate type and its characteristics, the process conditions, the activation agent, and the method should be considered while preparing biochar for any application. The abundance of biomass waste and its carbon content should be considered as this can be important while upscaling production. While preparing and processing biochar for the desired application, products such as gases (i.e., H_2 , CH_4 , CO_2 , and CO , etc.) and liquids (i.e., tar/bio-oil) may be produced, so countermeasures should be placed to obtain maximum biochar yield. Therefore, the processes to obtain biochar, from cheap and abundant renewable resources, and its utilization for preparing various carbon-based materials should be further studied and optimized. Control of the material's surface morphology, phase, and doping of precise functional groups remains a major hurdle to be further investigated.

The energy density of a supercapacitor is proportional to its specific capacitance, which can be enhanced by facilitating the transport of electrolyte ions. Novel and easy-to-carry-out methods for controlling and synthesizing highly ordered hierarchical porous biochar structures require more investigations. Although altering the physical properties (i.e., porosity) or modifying the surface chemistry can facilitate achieving enhanced electrochemical performance. Despite the energy density of electric double-layer capacitors (EDLCs) is limited, it can be improved by forming highly porous carbon which will facilitate the transportation of electrolyte ions during the charging and discharging of the device. Another way to improve it is by preparing composite materials for the electrodes showcasing high performance. Therefore, the interaction between electrode material possessing various properties and electrolytes should be thoroughly investigated. The suitable research work should not only be limited to laboratories but should be adopted at the commercial scale. Processing of biochar to obtain exquisite carbon-based materials such as CNTs, graphene, carbon quantum dots, etc., has proven to be achievable in lab studies. Despite ample studies available, but the issue of commercializing an economically viable synthesis process where high quality and high yield is possible, remains

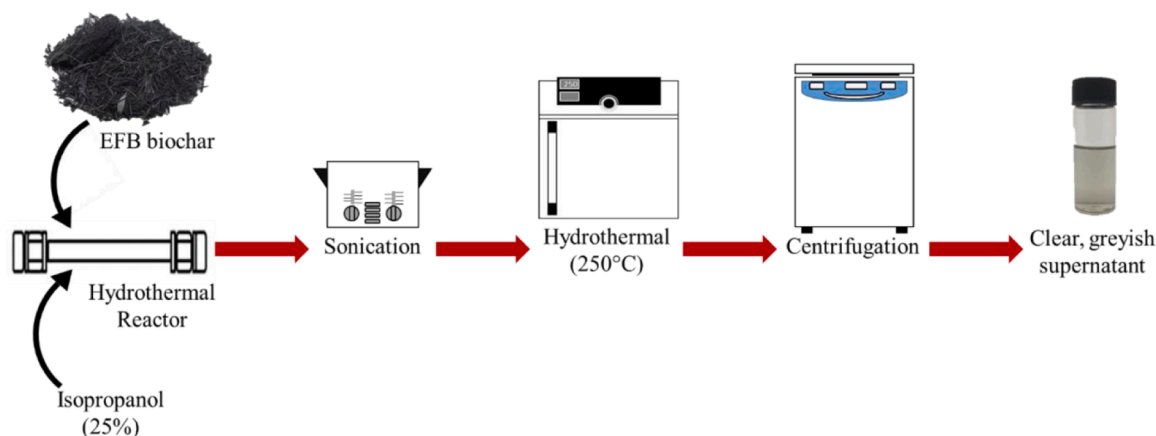


Fig. 9. Illustrated pathway to synthesize CQD from empty fruit bunch. Reproduced with permission from ref. (jamaludin et al., 2020). Copyright 2020 MDPI.

the main obstacle. Therefore, detailed investigations are required to streamline their production from raw materials (i.e., biomass feed-stocks) to achieve high yields by keeping the overall process economically viable.

7. Conclusions

Various biomass substrates can be utilized for the sustainable production of a wide range of applicable carbon-based materials. The operating conditions such as temperature, heating rate, and residence time play a crucial role in obtaining high-quality biochar. The specific characteristics of biochar can be modified to achieve the desired results. Porosity, surface properties of biochar and its ability to be utilized to synthesize superior carbon-based materials make it an attractive carbon source. The detailed carbon materials possess unique properties that make them viable to be employed as electrode materials for supercapacitors. The ability to transform waste biomass to biochar and process it further to obtain various carbon materials for supercapacitors is an interesting pathway of waste to energy that requires further investigation. Moreover, the process needs to be optimized to make it economically viable and environmentally benign on a large scale.

CRediT authorship contribution statement

Mahmood Faisal: Writing – review & editing, Writing – original draft, Visualization. **Ali Mujahid:** Visualization, Validation. **Khan Mustafa:** Writing – review & editing, Validation. **Mbeugang Christian Fabrice Magoua:** Visualization. **Isa Yusuf Makarfi:** Visualization, Validation. **Kozlov Alexander:** Validation, Supervision. **Penzik Maxim:** Visualization, Supervision. **Xie Xing:** Supervision, Resources. **Yang Haiping:** Writing – review & editing, Supervision. **Zhang Shi-hong:** Writing – review & editing, Validation. **Li Bin:** Writing – review & editing, Validation, Resources, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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