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Introduction to Biomass-Derived Carbon Materials

Sources, Production, Activation, and Cost Analysis

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1.1 Introduction

The transformation in climate and demand for energy encourages us to concentrate and cultivate a new technique for generating and storing energy via clean and green technologies. In order to fulfill our requirements for both energy generation and storage, it is necessary to produce high-performance materials [1–4]. Due to their less cost, comparatively simple preparation, richness, eco-friendly credentials, decent conductivity, and stability in chemical and thermal environments, carbon materials are placed at the topmost position in the list among other materials. The supply of different waste biomasses is growing globally, and the disposal of this biomass is an issue. It is mostly disposed of by burning materials in open spaces, which, by releasing greenhouse gases, directly affects our atmosphere. The conversion of biomass into useful materials is a beneficial alternative for waste management.

Because of the waste to richness principles, the carbons extracted from biomass attracted additional interest. In addition, the carbon materials derived from biomass demonstrated beneficial properties that broadened their applications. At present, by enhancing benefit of their physical and functional diversity, carbon materials, such as graphene, carbon nanotubes, activated carbon (AC), and porous carbon, are used in the energy storing area. However, demands for green and renewable energy storage materials have been spurred by the growth of advanced science and technology. As a source of electrode materials, biomass-derived carbon gained considerable attention due to its structural diversity, modifiable physical/chemical properties, environmental friendliness, and significant worth in trade and industry [5–10].

Since nature adds bizarre microstructures to biomass, the carbon materials derived from biomass also exhibit natural structural diversities, such as 0D spherical, 1D fibrous, 2D lamellar, and 3D spatial structures. In addition, it is important to

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mold the characteristics of the bio-derived carbon materials (B-d-CMs) according to their application. Different approaches for manufacturing and modifying carbon materials are pursued.

There are several general properties of carbon materials that make them attractive in different applications. Carbon is a common commodity, indicating that it has long been used by individuals. Graphite, carbon black (CB), and AC materials are included in these long-used traditional carbon materials [11–14]. New carbon materials with customized properties have been developed in the past century. This included carbon fibers, graphite that was strongly focused, and several others.

Much more sophisticated nanosized or nanostructured carbon materials have been developed in recent decades. Carbon materials are currently being intensively researched, in particular the newest nanocarbons, but also macroscopic carbons such as carbon fibers [15, 16]. Due to their distinguished physicochemical properties, innovative carbon materials namely graphene and its derivatives, fullerene, and carbon nanotubes have gained significant interest in the area of energy storing nowadays. They have good conductivity, outstanding chemical stability, porosity that can be tuned, large specific surface area, and enriched electroactive sites enriched. Porous carbon nanomaterials have gained significant attention because of their physiochemical properties and high surface area. The carbon with different

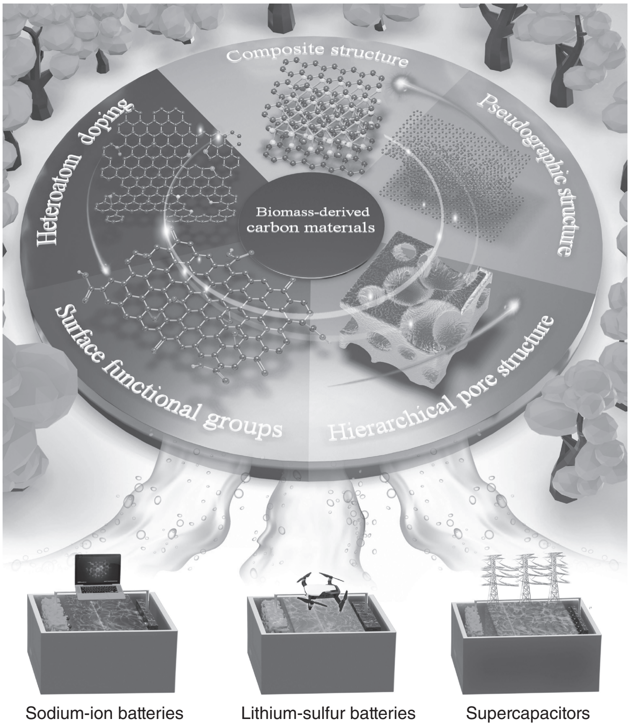

Figure 1.1 B-d-CMs structure strategies for different EES applications. Source: Ref. [19] / American Association for the Advancement of Science / CC BY 4.0.

pore sizes has attracted significant attention for highly efficient electrochemical storage applications [17, 18].

However, these carbon materials depend on precursors based on fossil fuels using energy-consuming synthetic methods (e.g. chemical vapor deposition, discharge of electric arcs, and laser ablation) that are toxic and expensive to the atmosphere. While these synthetic methods are advanced technology on a bench scale, due to complex synthetic processes, they are not yet ready for commercialization. Consequently, the establishment of more effective, environmentally sustainable and economic approaches to the processing of carbon materials is important.

B-d-CMs are showing great importance, and efforts have been devoted for enhancing the performance of electrochemical storage applications [19]. It is essentially to know how the structure design and diffusion kinetics of B-d-CMs are affecting the performance of electrochemical energy storage (EES) devices. It is shown in Figure 1.1.

1.2 Biomass Resources and Composition

Biomass refers to animal- and plant-based materials or by-products that may serve as a potential energy source. Protein, carbohydrates, starch, lignin, and lipids constitute biomass and are such components that differ dependent on the geographic situation and source. Proximate and final studies have shown that biomass is abundant in carbon, hydrogen, oxygen, and nitrogen, and traces of chlorine and sulfur are also shown. Biomass-derived carbon has many crucial advantages associated with additional electrode materials for energy and ecological applications, such as cheap and plentiful supply, environmentally safe, in situ nanoporous structure establishment, and processing elasticity [20–24]. As the source affects the finishing carbon return and its structural features, which are mandatory for energy storing and ecological applications, the option of a biomass precursor is crucial.

Agro-residues from crop production, solid waste from municipal, and further agro-based manufacturing units are key sources of precursors. Owing to the large availability and less cost, these precursors have gained a lot of attention. They do, however, have various chemical functionalities, creating them an ideal choice for a wide range of morphologies for the proposal of carbon materials. Biomass derivative carbons are deliberated to be favorable electrode materials for different forms of electrochemical energy storing and transformation systems due to the aforementioned advantages, including lithium batteries, supercapacitors, potassium batteries, sodium batteries, and fuel cells [25–29]. Given the quick growth in this sector, a thorough analysis and comparison of their manufacturing approaches, features, applications, and performance in these electrochemical energy storing applications are not only necessary but also urgent.

The carbon powder that comprises egg white, bacterial cellulose, mushrooms, peels of orange, human hair, dry elm samara, chitin, catkin, etc. has been used to manufacture a wide variety of biomaterials. These biomass products, however, can be classified into four main groupings, i.e. biomass based on microorganisms,

Table 1.1 Difference between biochar, activated carbon, and carbon black.

	Biochar	**Activated carbons**	**Carbon black**
Precursors	Biomass	Coal, asphalt, and biomass.	Petroleum, coal tar, and asphalt.
Carbon content	40–90%	80–95%	>95%
structural features	Amorphous and porous carbon with enriched surface functionalities	Amorphous carbon and highly porous	Microcrystal or amorphous carbon particles
Preparation method	Medium temperature pyrolysis (400–600 °C), followed by physical or chemical activations	High-temperature carbonization (700–1000 °C) with physical or chemical treatments	Combustion process with little or without air

Source: Ref. [30] / with permission of American Chemical Society.

animal based, plant based, and food based. It becomes more difficult to predict the concluding arrangement and construction of a derived biochar. Generally speaking, it is difficult to understand the awareness of the elemental and chemical composition of biomass as the responses can happen in the phases of carbonization and stimulation. The morphology and structure of resulting carbon could eventually be changed by these induced reactions. Table 1.1 lists the difference between activated, biochar, and CB [30].

Significant research studies are done in pursuit of biomass that at the same time receives functional groups containing oxygen or nitrogen, interrelated micro or mesoporous arrangements, and similarly has a large carbon content production that amplifies the application of the environment and resources. Most advanced precursors, however, end up with low yields. The biochar is a derivative of willow catkins, for example, proved excellent presentation in performance, capacitance, and cycling as energy storage devices. The final carbon outcome was significantly lesser (5.5% wt.) relative to similar biomass precursors including rice straw, considering these benefits [31–34]. The biochar outcome, heteroatom, and doping of the biochar depend greatly on the precursors' basic composition and chemical structure. It is thus important to discover and understand different precursor-related properties in order to enhance biochar outcome to create it appropriately in energy storing and ecological applications. The different biomass resources are given in Figure 1.2.

1.2.1 Plant-Based Biomass

The numerical chemical composition of plant-based biomass varies according to geographic factors, categorizations of organisms, and organ dependency. Still, cellulose, lignin, hemicellulose, and extractives consist of the qualitative chemical configurations of plant-based biomass [35, 36]. For instance, seed shells, palm, areca, etc. consist of substantial lignin and 83% of cellulose. Whereas, for

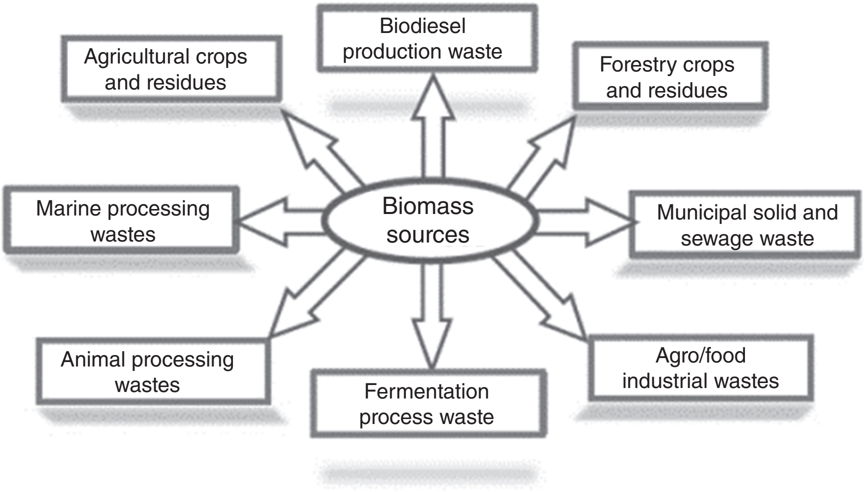

Figure 1.2 Popular biomass resources.

instance, plant's bast fibers are good in cellulose, and in cotton, jute, and fax, bast comprises 67, 64, and 56% comparatively higher cellulose with respect to other parts of the plant. Figure 1.3 shows the chemical composition of lignin, cellulose, and hemicellulose. Investigations on the basic composition of precursors, such as the involvement of microstructure, capacitance, and conductivity in precursors of oxygen and nitrogen content.

High oxygen content in precursors has been determined to yield low crystallinity and larger defects, and more unstable mixes are produced in the process of pyrolysis and thermal decay; however, higher levels of nitrogen content could yield enhanced electrochemical featured nitrogen-doped carbon.

Compared to lignin, cellulose and hemicellulose offer less stability in thermal decomposition and lead to considerably less carbon yields. Nevertheless, lignin hemicellulose and cellulose components contribute to biochar yield porosity. It was noted in the process of thermal pyrolysis at 500 °C that no noteworthy relations between hemicellulose and cellulose were seen, but obvious interactions between the components of lignin and cellulose were observed.

Therefore, in order to get biochar outcome with worthy conductivity, controllable faults, and a high degree of graphitization to make it suitable for application in ecological and energy storing, it is important to choose plant biomass precursors rich in nitrogen content and less in oxygen content, cellulose fraction, and lignin fraction.

1.2.2 Fruit-Based Biomass

The quantifiable elemental and chemical composition of fruit-based biomass can vary with regard to geographical parameters and species. The main fruit-based biomass components are sugars, lipids, ash, crude proteins, and fibers. The lipid quantity in the peels and pulp varies from 0.7 to 9.96% and 1.4 to 28.6%, while the

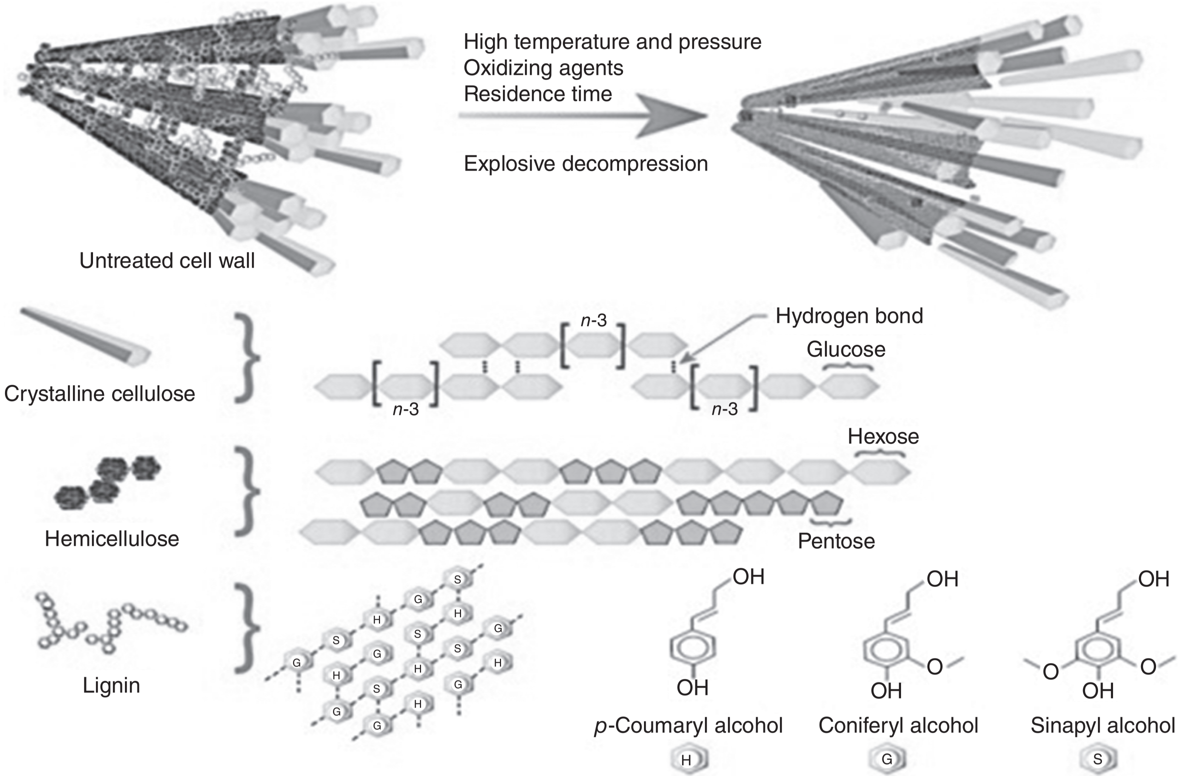

Figure 1.3 Plant-based biomass constituents. Source: Ref. [36] / with permission of Elsevier.

crude protein yields 3.5 to 28.6% and 5.8 to 43.4%, respectively. Larger levels of proteins and crude lipids, however, lead to disadvantages in the ultimate biochar outcome, as these proteins and crude lipids start degrading when temperature is low, exempting unstable compounds namely water vapors, methyl esters, olefins, carbon dioxide, and ammonia fumes. On the other hand, the presence of nitrogen and phosphorous content in proteins and crude lipids can lead to heteroatom-doped carbon production [25, 37, 38]. The crude fibers of lignin, hemicellulose, and cellulose are the main providers to the processing of carbon. The mass portions of crude fibers, however, are considerably less and typically good in cellulose, which affects the graphic structure and biochar yield.

1.2.3 Microorganism-Based Biomass

New measurements open up the prospect of using microorganisms derived from biochar, such as bacterial cellulose and fungi. The fungi, such as mushrooms and yeasts, have evidenced to be improved precursors of reformative biomass for biochar derivation, attributing their rapidly increasing capacity and their ease of use in environment to bulk. Carbohydrates, crude proteins, fibers, and fats are the main elements of microorganism-based biomass. Plant- and fruit-derived biomass are the key components found in the microorganism-based biochar. But the individual compounds and elements from these modules are considerably different.

The carbohydrates existing in the microorganism include chitins that establish a glucan cross-link, serving as the main source of carbon in the process of pyrolysis, while sucrose and starch are the source of carbohydrates in non-cross-linked plants with the lowest thermal stability. In microorganisms, crude fibers are primarily made of cellulose, which shows the same plant or fruit biomass carbonization behavior.

The main precursors are mushrooms based on microorganism-based precursors. Compared to other elements such as mycelium, the fruiting section of the mushroom is most commonly used for processing as it goes into depth. Owing to the existence of large nitrogen content, mushrooms are an attractive choice. The mushroom's nitrogen content varies from 3 to 10% and 17% nitrogen content is observed for some species. As they are able to generate carbon derived from nitrogen-doped biomass, the mushroom precursors are promising [39–41]. Geographical factors, however, have a major effect on the composition of the elements and can differ from region to region.

1.2.4 Animal-Based Biomass

Chitin is an alternative positive bio-precursor for a widespread variety of applications owing to the existence of larger nitrogen concentrations, chemical stability and large existence in the environment. Chitin is capable of creating chitin-catecholamine and chitinglucan complex cross-link networks and is able to form intermolecular hydrogen bonds. Compared with cellulose, chitin has larger thermal stability and carbon outcome. Chitin extraction can be used for the popular animal species containing mollusks, pests, and crustaceans. The crustaceans consist of a substantially high amount of chitin content ranging from 17 to 72%, i.e. *Carcinus*, *Pandalus*, *Carangon*, and *Cancer* [42, 43].

Likewise, the cuticles and sloughs of many types of insects, such as, butterflies *Holotrichia parallela*, and silkworms, have extraordinary chitin content concentrations ranging from 18.4 to 64%.

Chemical demineralization, deproteinization, and mechanical crushing are used to remove the chitin content from the biomass. The final extraction yield depends on biomass precursors, and it ranges from 4 to 40% in the processing system. Chitin's nitrogen content is extracted from animal biomass and matches with that of microorganism-based biomass with nitrogen concentrations, capable of its appropriateness in energy and ecological applications [44, 45].

1.3 Condition for Precursor Selection of Biomass-Derived Carbon

The following conditions must be addressed in order to synthesize good-quality biochar by means of superior conductivity and porosity and to satisfy the needs for huge ecological and energy applications.

The existence of nitrogen content improves nitrogen-doped carbon production with greater conductivity and enhanced cycling stability. Still, it is important to select precursors having less oxygen content, or else the aromatic carbon formation would be obstructed. The existence of strongly cross-linked, large molecular weight with thermal stability biomacromolecules including lignin, keratin, and chitin enables the formation of aromatic carbon and in the process of carbonization provides superior biochar. Aliphatic compounds must be prevented by the existence of little contents of noncrosslinked and molecular weight, otherwise they hinder aromatic carbon formations.

1.4 Production Methods of Biomass-Derived Carbon

Numerous activation and various methods of carbonization can be used to turn biomass into carbon. In order to turn biomass into value-added carbon goods, physical, chemical, and a combination may be used [16].

In carbon materials, many factors including surface properties, temperature, time, reagents, and availability cause an effect. The key processes used to extract carbon from biomass are pyrolysis and hydrothermal carbonization (HTC). Pyrolysis is performed at a defined temperature level in a restricted oxygen or inert atmosphere environment, whereas a thermochemical mechanism is used for transforming biomass into carbon. Temperature, temperature ramping rate, catalyst, and particle size are the products obtained from biomass pyrolysis. HTC is done with or without the use of a catalyst in a pressurized aqueous atmosphere at less temperature range from 120 to 250 °C. Compared to natural biomass coalification, the HTC procedure

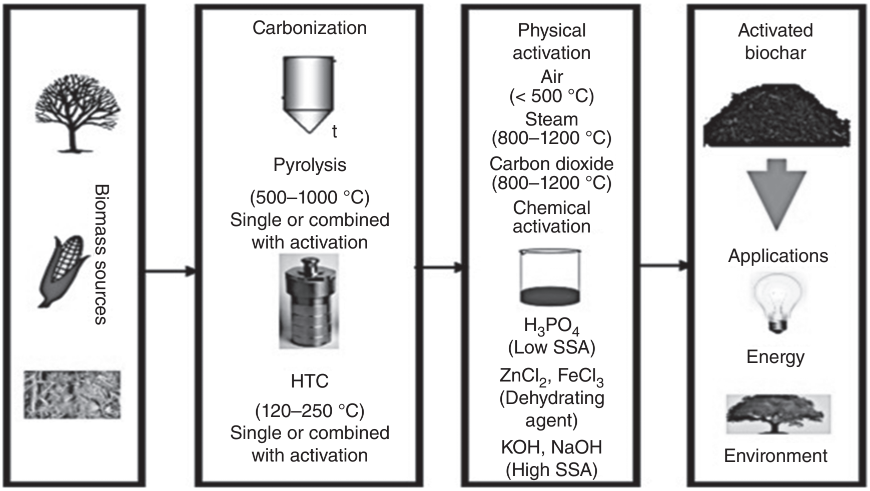

Figure 1.4 Overview of overall production methods of B-d-CMs. Source: Ref. [36] / with permission of Elsevier.

is done at a rate of higher reaction added with a smaller reaction length. Various publications have studied hydrothermal conversion in recent research [46–48].

The overview of different production methods of B-d-CMs is shown in Figure 1.4.

HTC is a thermochemical conversion method that requires a variety of components including precursor concentration, catalyst, residence period, and temperature. It uses subcritical waters to transform biomass to carbon products for successful dehydration and hydrolysis of hydrochar precursors with high-oxygen-rich functional groups. Through the use of additives or doping-containing precursors, other functional groups, including nitrogen groups, may also be added to hydrochars. Recovered carbon products have attracted interest in a wide range of uses, including energy harvesting, catalytic, and trap technologies.

The method used for transforming carbon materials into AC is activation. For activation, chemical and physical methods may be introduced. Physical activation by pyrolysis is achieved at 1200 °C in the presence of carbon dioxide. In the presence of a chemical agent, chemical activation takes place at temperatures between 450 and 900 °C. The most used chemical activators are NaOH, KOH, K_2CO_3, $FeCl_3$, H_3PO_4, and $ZnCl_2$ [48].

1.4.1 Carbonization

1.4.1.1 Hydrothermal Carbonization

The hydrochar material produced by the method of HTC is partly carbonized and contains oxygen groups of large density. The final yield, however, depends on the precursor features employed. For energy storage applications, hydrochars are straightaway used as electrodes. Poor porosity and small specific surface area are naturally present in the hydrochar formed by HTC. Consequent initiation or carbonization is compulsory to change its chemical and physical properties.

For supercapacitor applications, Zhu and his team created electrodes derived from fungi by hydrothermal-assisted pyrolysis [49]. Initially, at 120 °C, HTC is done for six hours. With large oxygen composition and less surface area, the particles obtained differ between 50 and 200 nm.

Hydrochar is exposed for three hours to additional pyrolysis at 700 °C in order to increase electronic conductivity and enhance porosity. A fixed surface area of $80\,m^2\,g^{-1}$ with an oxygen content of 5 wt. is the final carbon product obtained. Compared with other industrial AC, the content displays a particular capacitance of $196\,F\,g^{-1}$. The porous carbon materials dependent on hydrochar exhibit a high number of heteroatoms. Via activation using KOH, Salinas-Torres and research work group established AC by doping with O and N heteroatoms [50]. At large current densities, the existence of both nitrogen and oxygen groups increases charge transmission and capacitance. Uniform oxygen has been developed by Wei et al., which shows a large specific surface area and porous structure.

The complete overview of carbonization methods of producing B-d-CMs is shown in Figure 1.5.

1.4.1.2 Pyrolysis

In an oxygen-limited atmosphere, biomass pyrolysis is carried out when the temperature ranges from 300 to 1200 °C. Pyrolysis is categorized into fast pyrolysis and slow pyrolysis depending on the range of heating. The method of slow pyrolysis has a longer residence period and lower heating rates. It is carried out at the temperature of

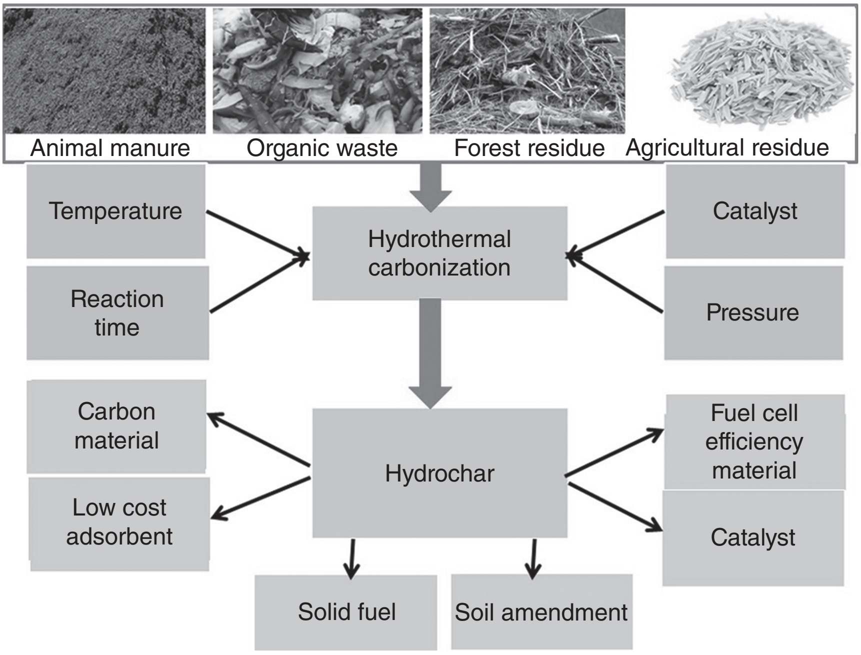

Figure 1.5 Complete overview of carbonization process. Source: Ref. [51] / with permission of Elsevier.

400–600 °C, resulting in maximized biochar yield and low bio-oil and syngas product yields [52]. Quick pyrolysis, on the other hand, possesses larger heating rate and lower residence period, providing the value of maximized bio-oil outcome upto 75%. Temperature is a main parameter in regulating the pyrolysis process and then affecting the behavior and biochar outcome, relative to rate of heating, reaction time, and particle size of feedstock.

Growing pyrolysis temperature decreases the yield of biochar, the ability of cation exchange, and the quality of nutrients, but increases its degree of aromatization, specific surface area, larger range of heating value, and solution pH. In addition, biochar generated at a lower temperature of pyrolysis has a lower stable fraction ratio than biochar produced at higher temperatures [53]. Due to its less conductivity, poorer pore characteristics, and less specific surface area, biochar developed at lower temperature pyrolysis is not appropriate for use as energy storing and conversion materials. Therefore, surface alteration and activation procedures are required prior to their implementation [54].

1.5 Biomass-Derived Carbons (B-d-CMs) Activation Methods

The two basic methods that are applied to achieve AC based on biomass are physical and chemical activation. Physical activation is easier and more environmentally friendly than the chemical activation, which is normally done at higher temperatures.

1.5.1 Physical Activation

Overall, various suitability and acceptable activation methods could be altered and material features could be different. It is a famous fact that, as opposed to physical activation, chemical activation needs less activation period and temperature. Chemical activation, however, has shown many significant drawbacks comprising of water washing step after activation that is needed and needed to eradicate≪Revise as "…that is needed to eradicate…" impurities. Normally, physical activation deploys a two-step procedure. Biomass content is initially pyrolyzed to create biochar, which is then triggered using gases, namely steam, CO_2, air, or their mixture by controlled gasification [23, 56]. Disorganized carbons are made in the process of pyrolysis from tar decomposition, blocking biochar pores, and minimizing their particular surface area.

The complete overview of different activation methods is shown in Figure 1.6.

The successively regulated gasification is able to promote further decomposition of the as-prepared biochar and get a fully created, usable, and interrelated porous structure. Porosity production also yields from carbon calcination and generation of volatile substances, and depending heavily on the triggering gas. CO_2 is safe and easy for usage, so it is always used. Activation period, temperature, rate of gas flow, and furnace selection can influence the degree of carbon calcination. By activation

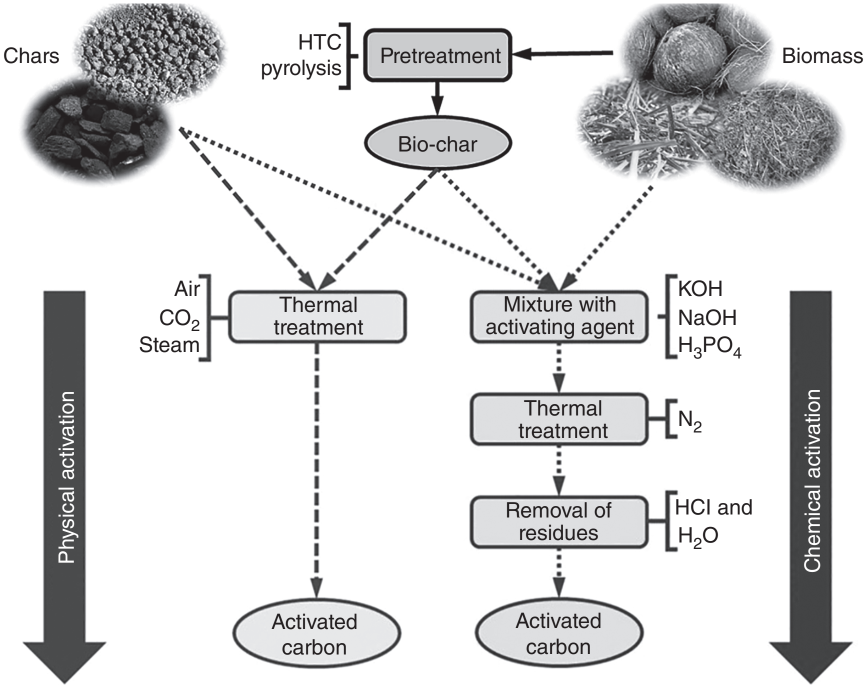

Figure 1.6 Overview of complete activation methods. Source: Ref. [55] / Frontiers Media S.A. / CC BY 4.0.

of CO_2, Zhang et al. [57] developed carbons derived from biomass from various forestry area and agricultural residue types. In general, higher surface areas and micropore volume can benefit from the higher activation temperature. Guo et al. [58] researched the activation of carbon-based coconut shell by CO_2 and methodically observed the effects on the particular surface region, micropore volume, and total volume of activation temperature flow rate and time.

Their findings showed that increasing activation temperature aided the formation of pores, expanded pore diameter, and increased generation of mesopores. In addition, the generation of micropores and mesopores was favored by increasing activation time, but excessively lengthy activation period led to pores collapsing and deteriorating. Taer et al. [59] investigated the CO_2 activation of carbon extracted from rubber wood and tested the capacitive and electrochemical characteristics of the AC content. With the rise in activation temperatures, the conductivity and basic capacitance of their findings increased. The increased specific surface area induced by the increasing temperature of activation was straightway connected to the rise in the volume of micropores in the carbon precursor. Though, pore deformation resulted from a larger temperature above 900 °C [60, 61]. Second, due to its cheap price and ease, steam is often used in biomass materials as an activation agent.

Demiral et al. [62] examined olive bagasse steam activation, and their findings exhibited that rise in activation period (30–45 minutes) and temperature (750–900 °C) could increase the total pore volume of the specific surface region.

Still, additional enhancement in activation period (60 minutes) decreased total volume and the real surface area of the pore, as the creation and expansion of micropores were less successful than the worsening of high porosity. Chang et al. [63] and Okada et al. [60] published similar findings. The pore structures were mainly contributed by micropores, close to CO_2 activation, and the ratio of micropore volume to total pore volume (Vmicro/VT) was between 0.63 and 0.84. Thus, all methods of activation of CO_2 and steam led to well-built microporosity. Compared to CO_2 activation, however, steam activation favors the widening of microporosity and increases the growth of mesopores at the cost of microporosity.

1.5.2 Chemical Activation

Air activation needs less temperature compared to the CO_2 and steam activation mentioned earlier. Nevertheless, since they commonly grow a hierarchical porosity, steam and CO_2 activations are often used. Research on biomass physical activation is still incomplete, in comparison to chemical activation. There is a need for further methodical research and evaluations of CO_2, air, and steam activations of carbons derived from biomass, particularly in the application scenarios in the field of electrochemical energy storing. Thermal preparation of the biomass carbon precursor and the triggering agent in the 450–900 °C temperature range is part of the process of chemical activation. In contrast to physical activation, chemical activation needs lesser pyrolysis temperature, improved carbon outcome, carbon yielded with large surface area, and properly arranged and defined microporous structure [64].

The large surface area and properly arranged and defined microporous structure of the carbon generated show a vital role in ecological and energy storing applications. KOH is widely used as an agent for chemical activation, performing as an oxidant and forming oxygen functional groups on biochar. Therefore, not only electrochemical double-layer capacitance but also pseudo-capacitance can be contributed by KOH-ACs. KOH first dehydrates into K_2O at 400 °C in the activation phase. Then, with the development of H_2, carbon reacts with H_2O, followed by CO_2 formation. K_2O reacts and forms K_2CO_3 with CO_2. Once the temperature is increased beyond 600 °C, it responds completely to KOH. K_2CO_3 begins to decompose above 700 °C and is absent from the system at 800 °C [65]. Simultaneously, metallic potassium is formed. To generate CO at higher temperatures, the CO_2 produced will react with carbon.

The three key mechanisms for porosity production by activation of KOH are generally accepted. A redox reaction decomposes the carbon matrix with KOH, leading to the formation of abundant micro- and mesopores. The formation of H_2O and CO_2 helps in the production of porosity. After extracting the metallic potassium and other potassium substances by rinsing, as shown in the figure, expanded carbon lattices integrated with intermediate metallic K are unable to restore their original structure. Therefore, on the basis of the synergistic effects of physical and chemical activation, microporosity, carbon lattice expansion, and high specific surface area are formed. Various precursors are developed into porous carbon material by means of distinguishing morphological characteristics, pore texture, and surface functional

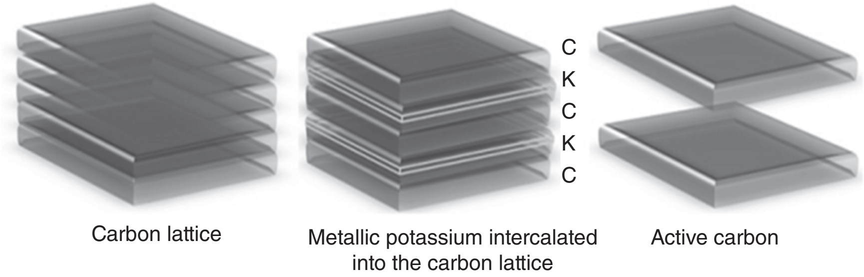

Figure 1.7 KOH activation mechanism. Source: Ref. [66] / with permission of Elsevier.

groups by controlling the activation parameters, further influencing the behavior of KOH-ACs in their electrochemical energy storing system applications [66]. The KOH activation mechanism is shown in Figure 1.7.

Peng et al. [67] developed carbons through leftover tea leaves via large temperature carbonization and activation process with KOH. The carbon materials demonstrated a porous structure with a large specific surface area ranging from 2245 to 2841, and when measured in a three-electrode device in a 2 M KOH electrolyte solution it showed perfect capacitive behaviors with a maximum specific capacitance of 330 F at a current density of 1 A. To enhance specific surface area and pore volume further, the KOH activation method is combined with CO_2 activation. The arrangement of CO_2 gasification, however, leads to a decrease in functional groups of oxygen, decreasing the contribution of pseudo-capacitance to the overall real capacitance (up to 30% loss). Therefore, the grouping of activation of KOH and CO_2 yields very complicated effect on the electrochemical features of biomass-derived carbon.

1.5.3 Combination of Physical and Chemical Activation

The combination of both physical and chemical activation shows better pore size distribution and porosity development of AC than the individual one. This two-stage mechanism comprises of initial chemical activation using different agents then followed by physical activation. The high mesopore content and surface-area-modified AC are obtained and reported by several authors, which is utilized in both chemical and physical activation processes [68–70].

1.5.4 Modification and Structural Control of B-d-CMs

The electrochemical performance of B-d-CMs depends upon their consistency of surface functionalities. The micro-, meso-, and macropore-sized ACs are produced based on their applications with choosing suitable activation process that is already known. The double-layer properties such as capacitance, self-charge characteristics, electrical conductivity, and wettability can be altered by surface functionalities of B-d-CMs with oxygen-containing carboxyl, hydroxyl, and phenolic groups [71–74]. There are several methods available to improve the electrochemical performance of B-d-CMs via surface functionalities modification, heteroatom doping, surface

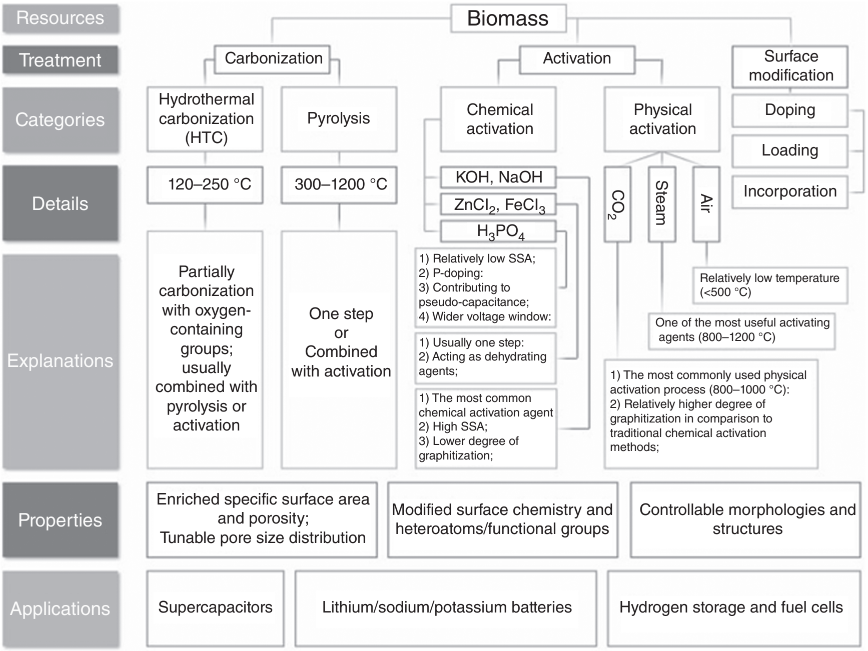

Figure 1.8 Complete overview of production methods converting biomass into carbon materials for EES devices. Source: Ref. [66] / with permission of Elsevier.

incorporation with nanostructures, and surface loading with oxides including physical and chemical activation. The complete production methods and structural modification of B-d-CMs are shown in Figure 1.8.

1.5.4.1 Surface Modification and Heteroatom Doping of B-d-CMs

Several authors investigated the surface modification of B-d-CMs using functional groups or doping different heteroatoms such as nitrogen, phosphorus, oxygen, sulfur, and boron. They have reported that the surface modification and heteroatom doping B-d-CMs are enhancing the double-layer properties, which include pseudo-capacitance, wettability, effective surface area, etc. for energy (supercapacitor electrodes, fuel cells, and batteries) and environmental (wastewater treatment) applications [75–78].

Instead of single heteroatom doping, codoping (two heteroatoms with B-d-CMs) is increasing the electrochemical performance of B-d-CMs because of synergistic effect. Among all heteroatoms, the nitrogen-containing groups (amide, pyrrolic, pyridinic, imide, and lactame) doped B-d-CMs show significance and excellent performance in CO_2 capture, catalyst, electrochemical storage, and environmental applications [79].

1.5.4.2 B-d-CMs Surface Loading of Metal Oxides or Hydroxides

The surface of bio-mass derived carbon (BM-DCs) is also modified by loading different transition metal oxides or hydroxides such as NiO, MnO_2, RuO_2, and

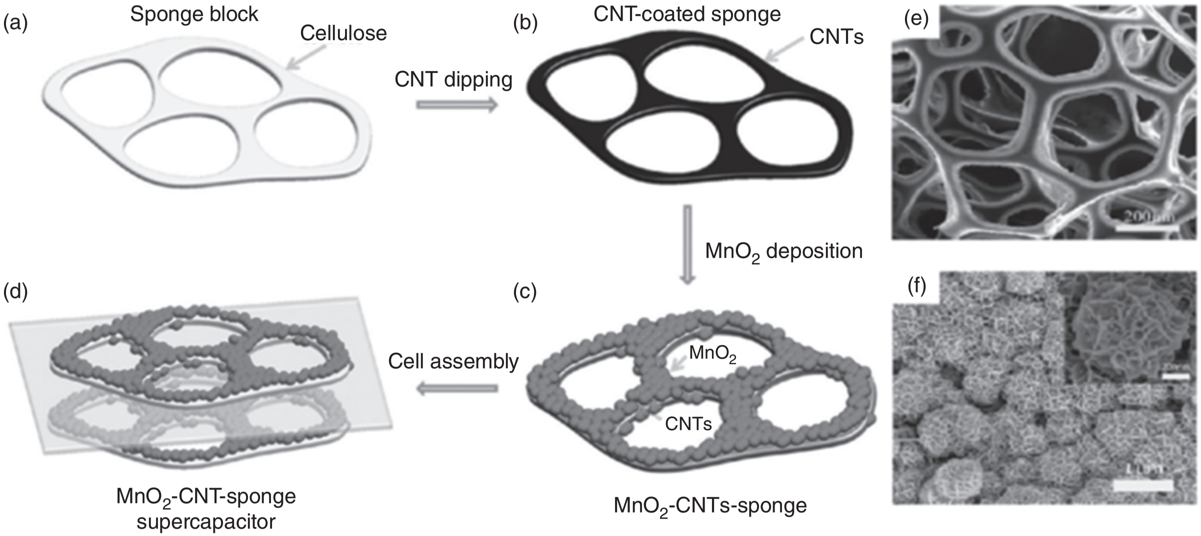

Figure 1.9 (a–d) The complete hybrid MnO_2/CNT sponge electrode fabrication (Source: From Ref. [83] / with permission of American Chemical Society) and (e and f) representation of the scanning electron microscope (SEM) and high resolution scanning electron microscope (HRSEM) images showing flower-like individual MnO_2 nanoparticles. Source: Ref. [83] / with permission of American Chemical Society.

Co_3O_4 [80, 81]. Due to loading of metal oxides into the BM-DCs, the agglomeration of metal particles is reduced, but the surface redox activity can be enhanced, which is useful to improve the electrochemical performance of B-d-CMs. Among all metal oxides, the NiO is a promising significant electrode material for energy applications because of its unique properties and availability.

1.5.4.3 Surface Incorporation with Different Nanostructures

The B-d-CMs are incorporated with different nanostructures, such as carbon nanotubes (CNTs) and graphene, which are important electrode materials for electrochemical storage applications. Deng et al. [82] investigated cellulose/carbon nanotube nanocomposite fibers followed by deacetylation and carbonization, and as-prepared active nanofibers were used as electrodes for supercapacitors. Chen et al. [83] studied that the MnO_2 nanoparticles are incorporated with CNT sponge hybrid electrode for supercapacitor applications. The complete diagrammatic representation of fabrication of hybrid MnO_2/CNT electrode is used for supercapacitor applications as shown in Figure 1.9.

1.6 Production Process Description

The abundant amount of AC, carbonaceous materials are prepared from various biomass wastes such as pecan shell, coconut shell, rice waste, bamboo cane, and peat [84–86] because these ACs are mainly used as odors, removal of colors, and metal ions. In general, the production cost of steam-AC is lower than that of acid-AC. The economic estimation of production of AC process depends upon the various raw materials is considered using the economic criteria namely return on investment, net present value, simply payback period, and internal rate of return. The profitable is attained in the stand-alone case indicated by economic indices and more attractive in the integrated plant. They found that cost estimation was sensitive to KOH cost, plant capacity, and product selling price.

In terms of product output and activation route, AC plant economies are mostly extremely sensitive. The economy is also significantly impacted by the price of the product, based on its quality (adsorption capacity) and not quantity (weight). The raw material costs and plant capability are also factoring that affect the costs of the raw materials. Calculations showed that pet coke complies with all these requirements and will be the best option for the manufacture of AC [87].

Large capacity manufacturing facilities are necessary to produce appealing economics for the other materials examined and this might offer challenges in small markets. The study might start with a plant capacity determined at the moment of breakeven. The conclusion is that the highest raw material yield should be chosen, a chemical activation scheme should be adopted, and the product price based on product-surfaced areas (or more generally on product adsorption capacity of adsorbate) be considered for attractive investment in AC production.

Weight-based cost calculation, large output of CB, which is reflected in substantially improved economic indices near pet coke and charcoals, makes chemical activation more appealing than physical activation. The utilization of wood and tires is the last to be evaluated economically owing to their poor yield. When expenses are referred to on a productive surface basis, the picture is again substantially changed. The most appealing raw materials are pet coke, followed by wood and lignite, as they have large surface areas and yield compared to black carbon, wood, and used tires, with lower surface areas despite strong yields.

It may be stated that the price of the carbon products on the basis of surface area, such as pet coke, charcoal, and lignite, is better compared to the economic indices. In contrast to others for which these characteristics have values that result in worse economic results, this material mix results in high yields with large surface area. Economic improvement in chemical activation is significantly more obvious than in physical activation because carbon development with extremely high surface areas uses zero expenses for start-up material to manufacture ACs [88, 89].

Here the various product yields and surface areas of the raw material used in physical and chemical activation are listed in Tables 1.2 and 1.3 [90].

Table 1.2 Raw materials used, product yield, and surface areas in physical activation (chemical activation).

Raw material	Pyrolysis yield, wt.%	Activation yield, wt.%	Total carbon yield, wt.%	BET surface area, m^2/g
Wood	25	50	12.5 (22)	800 (800)
Used tires	30	50	15 (20)	500 (700)
Pet coke	90	70	63 (45)	1000 (3000)
Carbon black	95	50	47.5 (60)	500 (500)
Charcoal	90	50	45 (44)	900 (2000)
Lignite	52	30	15.6 (25)	800 (2500)

Source: Ref. [90] / with permission of Elsevier.

Table 1.3 The raw materials and their production cost calculation based on heating value.

Raw material	Heating value, kcal/kg	Raw material cost, $/kg	Product price, $/kg (physical activation)	Product price, $/kg (chemical activation)
Wood	4541	0.808	1.54	1.54
Used tires	8760	1.558	0.96	1.34
Pet coke	7833	1.394	1.92	5.76
Carbon black	8202	1.459	0.96	0.96
Charcoal	6667	1.186	1.72	3.84
Lignite	4156	0.739	1.54	4.22
Diesel oil	10 250	1.26	—	—

Source: Ref. [90] / with permission of Elsevier.

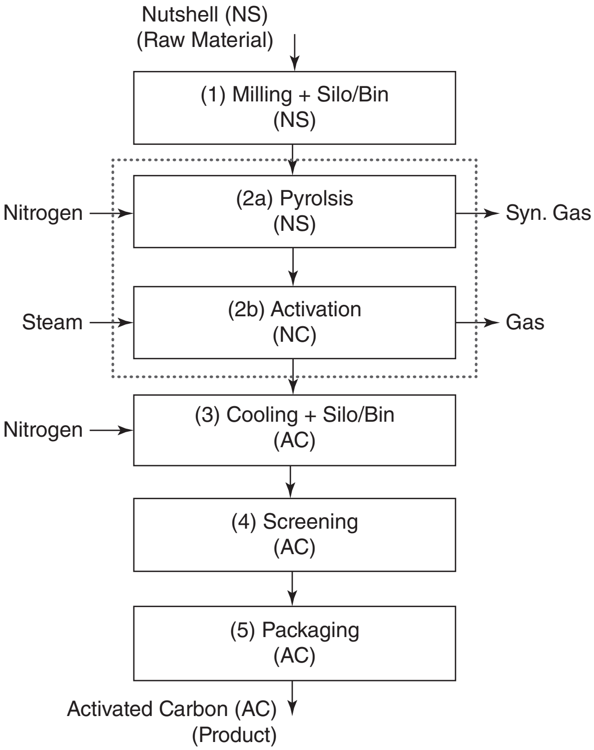

Figure 1.10 Proposed design equipment for the production of activated carbon from industrial waste nutshells. Source: From Ref. [91] / MDPI / CC BY 4.0.

1.7 Cost Analysis

Cost can be measured in a number of different ways, and each way of accounting for the cost of producing ACs from biomass in its own insights. The cost can be estimated for including equipment and its installation, financing cost, and maintenance cost for focusing particular applications such as batteries, supercapacitors, and fuel cells.

Leon et al. [91] developed the conceptual design of the industrial production plant of AC (6.6 ton/day) from waste nutshells (31.15 tons/day) by physical activation method in terms of different stages. The cost of the design included the cost of main equipment, nutshells price, basic operations, and services. Several authors designed different plants based on the yield of AC, low-cost production, and high surface area for EES devices.

The complete production process and the cost estimation of AC from industrial waste nutshells are shown in Figure 1.10.

1.8 Summary

Carbon materials are the most used material in the electrochemical storage devices such as fuel cells, lithium batteries, and especially supercapacitors.

Among others, the biomass is one of the promising candidates for producing carbonaceous materials, which is used for electrochemical storage system because of its microstructure, cheap price, and abundance. The various carbon materials are produced using different biomass resources for boosting the electrochemical performance of batteries, supercapacitors, etc. The efficiency of EES devices completely depends on porosity, high specific surface area, and morphology of B-d-CMs. The physiochemical properties and microstructure of B-d-CMs can be enhanced by selecting the biomass materials and applying suitable carbonization–activation–surface modification processes. The carbon yield is more in the chemical activation method than in the physical activation method. Considering practical applications of B-d-CMs in EES is still challengeable. The product description and cost analysis are also discussed. The computation of capacity at break-even points, i.e. at the capacity, where production costs are equal to revenue may be an alternate approach of handling the challenge of finding the optimal plant capacity. It may be observed that capacity is typically reasonable and relative size depends upon the criteria such as product yield and activation route. Finally, B-d-CMs are undoubtfully increasing the performance of EES system in the future similar to graphite in lithium-ion batteries.

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