

# Characterization, Modification and Application of Biochar for Energy Storage and Catalysis: A Review

Shuangning Xiu, Abolghasem Shahbazi,\* and Rui Li

*Department of Natural Resources and Environmental Design, North Carolina A & T State University, 1601 East Market Street, Greensboro, NC 27411, United State*

Received January 6, 2017; Accepted February 6, 2017; Published February 7, 2017

Biomass can be converted to biofuels and bioproducts via thermochemical processes. Biochar is one of the major products of thermochemical conversion of biomass. The efficient use of biochar is critical to improving the economic viability and environmental sustainability of biomass conversion technologies. Applications of biochar for both agricultural and environmental benefits (e.g. as soil amendment, for inorganic pollutant removal) have been studied and reviewed extensively. However, biochar for energy storage materials and catalytic applications has not been widely reviewed in the recent past. This review aims to present the more significant recent advances in several biochar utilizations such as catalysts and supercapacitors. Discussions on biochar production technologies, chemistry, properties, characteristics, and advanced functionalization techniques are provided. It also points out barriers to achieving improvements in the future.

**Keywords:** *Biochar; Hydrochar; Catalysis; Supercapacitor; Thermochemical conversion of biomass; Mechanism of biochar formation; Feedstock choice; Characterization; Biochar modification*

## Introduction

Energy crisis, environmental pollution, and global warming are serious problems that are of great concerns throughout the world. Sustainable development requires discovering economically viable and environmentally friendly energy sources with the aim of solving these problems.

One important aspect of such research is to synthesize a range of materials that can be used to resolve many of the challenges encountered (e.g., environmental pollution and global warming). For example, materials with catalytic functionalities can be developed to convert renewable sources to fuel or chemicals. Absorbents or catalytic materials can be developed to capture CO<sub>2</sub> or remove pollutants. Materials with high storage capacities can be produced for the storage of low-cost clean renewable energy (such as solar, wind, and bioenergy) [1]. Carbon-based materials have attracted considerable interest in many energy-related applications, such as energy storage in supercapacitors and Li-ion batteries, catalysis/electrocatalysis, absorption, and gas separation and storage, due to their abundance, chemical and thermal stability, processability, and the possibility of tuning their textural and structural characteristics to fulfill the requirements of specific applications.

\*Corresponding author: ash@ncat.edu

Different routes have been used to synthesize carbon-based materials, such as chemical vapor deposition, arc discharge synthesis, and carbonization of synthetic or natural polymers. However, these methods usually require tedious synthetic methods as well as organic solvents and electrochemical treatment. In addition, they often rely on relatively expensive fossil fuel-based precursors, the use of metal catalysts, and complicated apparatus involving high processing temperatures, none of which are environmentally and economically sustainable. These drawbacks lead to high production cost and limit the large-scale production and commercialization of such carbon materials. Alternatively, thermochemical conversion (*e.g.* pyrolysis and hydrothermal carbonization) of biomass is a promising route, offering low-cost, low temperature, and environmentally friendly production of novel carbon materials from natural precursors without the need to use toxic chemicals [2].

Biomass is a naturally abundant renewable resource that has great potential as a raw carbon material for synthesizing various carbon materials [2]. Considerable attention has been given to lignocellulosic biomass such as agricultural residues, woody biomass and energy crops [3]. Recently, biochar, a product from biomass thermochemical conversion, has received increasing attention for the use in several applications due to the cheap, abundant, and sustainable advantages. The most common biochar application is soil amendment to mitigate greenhouse gas emission and improve soil health. Recent developments in activation procedures and/or precursors allow a better control over the pore structure and surface property. These characteristics have widened the use of biochar to more demanding applications, including use biochar as a precursor for making catalysts, energy storage, gas storage and contaminant adsorbents. These new high-value applications are still in their infancy, and further research and development are needed to reach commercialization.

This review addresses the opportunities and advantages of using new technologies to convert biomass into biochar-based functional materials with applications in energy storage and catalysis. Discussions on biochar production technologies, chemistry, properties, characteristics and advanced methods to modify its structure and properties are also provided.

## Biochar Production

### Overview of the biochar production technologies

Research to date has shown biochar to be a carbonaceous solid consisting of an aromatic, furanic, and aliphatic backbone and numerous oxygen defects. The international Biochar Initiative defines biochar as “a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment” [4]. Biochar is produced in solid form by dry carbonization, pyrolysis or gasification of biomass, and in slurry form by hydrothermal carbonization (HTC) of biomass under pressure. Typical operating conditions and char yields of different thermochemical processes are shown in Table 1 [5]. An advantage of the thermochemical process is that it is relatively simple, usually requiring only one reactor, thus having a low capital cost.

Pyrolysis is the most common method to produce biochar, which can be categorized into slow pyrolysis and fast pyrolysis depending on the heating rate and residence time. Slow pyrolysis, also called conventional carbonization, produces biochar by heating biomass at a low heating rate for a relatively long residence time (up to several

days). According to the literature, the production of biochar from carbonization of biomass can be dated back for centuries [6].

**Table 1.** Different thermochemical processes and typical char yields from these processes

Process	Temperature (°C)	Residence Time	Char Yield (wt%)
Slow Pyrolysis	400-600	min to days	20-50
Fast Pyrolysis	400-600	~1 s	10-20
Gasification	800-1000	5-20 s	~10
Hydrothermal Carbonization	160-350	1-12 h	30-60

On the other hand, fast pyrolysis involves the rapid thermal decomposition of organic compounds by heat in the absence of oxygen, which results in the production of biochar, bio-oil, and gaseous products. Fast pyrolysis produces biochar at a high heating rate (above 200 °C/min) and short residence time (less than 10 s). The major differences between the two pyrolysis methods are the yields of biochar and bio-oil: Fast pyrolysis favors a high yield of bio-oil, while slow pyrolysis favors a high yield of biochar.

Gasification is different from general pyrolysis processes. For gasification, the biomass is converted into primarily a gaseous mixture (containing CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and smaller quantities of higher hydrocarbons) by supplying a controlled amount of oxidizing agent under high temperature (greater than 700°C). The resulting gas mixture is known as synthetic gas or syngas. The typical biochar yield of gasification averages about 10 wt% of biomass [7].

Hydrothermal carbonization (HTC) is also called wet pyrolysis, direct liquefaction, hydrothermal upgrading/pyrolysis, and solvolysis. The use of water as a solvent obviates the need to dry biomass and permits reactions to be carried out at lower temperatures in comparison with pyrolysis. HTC of biomass takes place in water at elevated temperatures (160–350 °C). Since the water temperature is above 100°C, the reaction pressure also must be elevated (more than 1 atm) to maintain the water in a liquid form. Low-temperature HTC can mimic the natural coalification of biomass, although the reaction rate is higher and the reaction time is shorter compared to the hundreds of years of slow natural coalification of biomass. Char yield of low-temperature biomass HTC varies from 30% to 60% depending on the feedstock properties, reaction temperature, and pressure [8]. Since HTC requires water, this may be a cost-effective biochar production method for feedstocks with high moisture content.

The char produced from HTC often is called hydrochar. It is important to differentiate biochar from hydrochar because the chemical and physical properties differ significantly from each other. Chemical properties of biochars from gasification or pyrolysis were compared to hydrochars from HTC in the publication of [9]. The observations showing that hydrochars have lower proportions of aromatic compounds than biochars (less stable) but are rich in functional groups (higher cation exchange capacity) than biochars [9].

### Mechanism of biochar formation in the biomass thermochemical conversion process

Biomass undergoes series of chemical reactions that are highly complicated and partially understood during the biochar or hydrochar production. The understanding of

the mechanism involved in biochar formation is essential in order to make it possible to tune the morphology, functionality, and porosity of the resulting biochar.

The overall mechanism of biochar formation consists indirectly of the pyrolysis/HTC mechanisms of the main biomass components, namely, cellulose, hemicellulose, and lignin. However, the reaction mechanisms of these two processes are different, which have been studied by many investigators [10, 11]. The HTC occurred in an aqueous medium which involves complex sequences of reactions including solvolysis, dehydration, decarboxylation, hydrogenation of functional groups, etc. The hemicelluloses were partly undergoing hydrolysis at lower temperatures and results in the formation of biochar/hydrochar through polymerization (water solubility homogenous reaction). For pyrolysis, the reaction mechanism is characterized by decreasing degrees of polymerization through homogeneous reactions in the gas phase. A number of pyrolysis mechanisms of cellulose, hemicellulose, and lignin have been proposed in [12, 13].

Several factors can influence the production and properties of biochar, of which the reaction temperature and the nature of biomass feedstock are the main factors [14]. The properties of biochar can be tuned by modifying the thermochemical operating conditions such as temperature, substrate concentration, residence time, and catalysts. Further studies are required to develop efficient catalysts for the conversion of biomass to biochar with the desired functional groups and porous structure.

#### Feedstock for biochar production

A number of lignocellulosic biomass materials have been used as feedstocks for pyrolysis and HTC. For example, Minowa *et al.* [15] tested twenty species of forest and agricultural residues with different lignin, hemicellulose, and cellulose contents. However, animal wastes and aquatic materials with low lignin and cellulose contents have not been studied as extensively as the high lignin and cellulose content biomass due to their difficult handling conditions. Besides, Giant Miscanthus as a bioenergy feedstock has gained importance in the recent few years [16].

Managing animal and crop wastes from agriculture poses a significant environmental burden that leads to pollution of ground and surface waters [17, 18]. These wastes, as well as other biomass, are usable resources for biochar production. Not only can energy be obtained in the production process, but the volume and weight of these wastes are significantly reduced, which is an important aspect of managing agricultural wastes [19].

Biomass with different chemical compositions (*i.e.* different contents of hemicellulose, cellulose, and lignin) are thought to have a significant impact on the biochar surface composition, reactivity with the chemical activating agent, and yields. A detailed comparative study on biochar produced from different feedstocks will be of great importance to identify common features and develop appropriate protocols for biochar-based materials production. Furthermore, it will be of immense interest to develop a correlation between the surface characteristics of biochar and composition of starting material with the change in thermochemical parameters.

## Biochar Characterization

Physical, chemical, and mechanical properties of biochars can vary with production conditions and raw feedstock. It is very important to characterize biochar because its characterization plays a vital role in determining their applications in industry and environment.

### Proximate, elemental composition and Inorganic fraction characterization

The proximate analysis can provide the weight fractions of moisture, volatile matter, ash, and fixed carbon. There are standardized methods for performing a proximate analysis (ASTM, ISO, DIN, and SB) [20]. Apart from the proximate analysis, the elemental composition of biochar are usually determined using analytical devices, such as an elemental analyzer. The principal elements of biochar are C, H, and O, with N sometimes included. The exact content differs greatly depending on the nature of the biomass feedstock. Usually, the carbon content of a typical biochar is in the range of 45-60 wt %, the hydrogen content 2-5 wt %, and the oxygen content about 10-20% [21].

In addition to the proximate and the bulk elements, various inorganic elements present in biochar also substantially influence its properties. Several analytical techniques can be applied to characterize the inorganic elements: inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray fluorescence (XRF), and X-ray diffraction (XRD). ICP-AES can be used to determine the absolute concentrations of the inorganic elements (K, Mg, Ca, Na, Si, Al, Fe, Mn, etc.). XRF is often used to determine the inorganic (ash) compositions in terms of weight fraction of oxides and XRD can be used to identify the crystalline minerals in ash [22, 23]. The contents and species of inorganic elements are highly dependent on the nature of the biomass feedstock and reaction conditions (*e.g.*, temperature).

### Textural characterization and morphology

The structure of biochar can be analyzed using a broad suite of analytical techniques. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are techniques commonly used for the general characterization of biochar (*e.g.*, particle structure and surface topography) [24]. X-ray diffraction (XRD), Raman spectroscopy, and energy dispersive X-ray (EDX) spectroscopy are the most widely used methods for the characterization of the biochar microstructure [25]. Surface area and pore structure can be analyzed by using the Brunauer, Emmett, and Teller (BET) method, in which N<sub>2</sub> and CO<sub>2</sub> are the most widely used sorbate gas [20]. It is also suitable for the characterization of the biochar textural features, such as surface area and porosity. In addition to the above-mentioned routine characterization methods, there are also some in-depth characterization techniques used to understand the biochar fine structure. For example, solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) is a commonly used technique for carrying out comparisons that do not rely on peak ratios [26, 27]. As it has already been mentioned in the earlier sections, the biochars produced in pyrolysis usually exhibit very different structures than those obtained from the HTC process.

### Surface functionality characterization

The surface functionality can be characterized by X-ray photoemission spectroscopy (XPS), FTIR, and temperature programmed desorption (TPD) techniques [28- 30]. The detailed surface chemistry of biochar, surface functionalities, and

composition can be obtained from these technologies. Surface functional groups play an important role in the application of biochars as functional materials, *e.g.*, catalysts, adsorbents, and electrode materials. The surface chemistry of biochar is very variable due to its highly heterogeneous composition. The main contribution to the reactivity of biochar is the fact that the surface usually exhibits a range of hydrophilic and hydrophobic functional groups both acidic and basic [31].

Although substantial progress has been made in the development of different techniques for the analyses of the structure, composition, and surface chemistry of biochar, future research efforts are required in order to explore the existence of various categories of biochar with unique molecular compositions and physical architectures. Future investigation into the effects of both charring conditions, such as charring duration and heating rates, as well as the nature of biomass (wood and grass) on the properties and yields of individual biochar categories may help refine the present classification scheme.

## Biochar Modification

### Tuning of surface properties

Typical biochars produced from a thermochemical conversion process present limited polar oxygenated surface groups such as C–O, C=O, and OH and possess very limited porosity and surface area (usually <math>150\text{ m}^2/\text{g}</math>) [32]. These inherent disadvantages limit the wide application of biochar as a useful functional material. For example, an abundant surface functionality is highly desirable for biochar destined to be used as a catalyst or adsorbent, because it may provide more active sites for catalysis or pollutant adsorption. Porosity and large surface areas are favorable for biochar used as an energy storage material or catalyst because they facilitate high mass transfer fluxes and high active loading.

Therefore, in order to enhance the performance of functionalized biochar materials, a suitable modification process is essential. The flexibility of biochar materials is that such groups can be easily tuned, and this offers a promising platform for synthesizing various functional materials. A number of functional materials synthesized through the functionalization/modification of the biochar materials are shown in Table 2.

**Table 2.** Typical functionalization/modification processes for tuning surface properties of biochar materials

Functionalization /Modification process	Surface functional group (characteristics)	Applications
Surface Oxidation	C=O, OH, and COOH	Pollutant removal; soil remediation
Surface Amination	NH <sub>2</sub>	Pollutant removal; CO <sub>2</sub> capture
Surface Sulfonation	SO <sub>3</sub> H	Solid acid catalyst
Surface and Pore structure modification	Porous biochar materials	Energy storage; CO <sub>2</sub> capture; catalyst support
Surface recombination	Biochar support nanostructure	Energy storage; CO <sub>2</sub> capture; catalyst

Surface oxidation is the most widely used method for creating oxygenated functional groups on the surface of biochar. Several types of oxygenated functional groups, such as carboxyl, phenolic hydroxyl, lactones, and peroxides, can be formed by surface oxidation treatments [33]. Oxygenated functional groups such as C=O, OH, and COOH are important for enhancing biochar performance in various applications. For example, Xu *et al.* found that surface OH and COOH groups can greatly enhance the adsorption capacity when biochar is used as an adsorbent for heavy-metal removal [34]. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), ozone (O<sub>3</sub>), potassium permanganate (KMnO<sub>4</sub>), and nitric acid (HNO<sub>3</sub>) are the most frequently used surface oxidation reagents [35-37].

Besides oxygenated functional groups, basic amino groups on the surface of biochar have also been shown to greatly improve its performance in applications such as CO<sub>2</sub> capture and pollutant adsorption [38]. Surface amination is one of the most widely used methods to introduce amino groups into biochar. Ammonia (NH<sub>3</sub>) treatment at high temperatures is a conventional surface amination technique that has been used extensively for decades [39]. Alternatively, chemical modification using some amino containing reagents is an environmentally friendly method also used for the surface amination of biochar. Compared to NH<sub>3</sub> treatment and chemical modification, the direct pyrolysis/HTC of nitrogen-rich biomass is a more sustainable method for the preparation of N-enriched biochar, because it does not require the use of NH<sub>3</sub> or expensive chemical reagents.

Sulfonic groups (SO<sub>3</sub>H) are the main functional group in solid acidic materials. These are widely used as alternatives to liquid acids for the catalyzation of many chemical reactions [40]. Surface sulfonation of biochar using concentrated sulfuric acid or its derivatives (*e.g.*, oleum and chlorosulfonic acid) is the most commonly used method for the preparation of biochar-based solid acids [41].

### Pore structure tailoring

One limitation of the biochar materials is that they often possess only a small number of micropores with a small surface area compared to conventional activated carbon. For applications in energy storage in supercapacitor, catalysis/electrocatalysis, and CO<sub>2</sub> capture or H<sub>2</sub> storage, controlled porosity and a high surface area are highly desirable. Thus, to facilitate their application in these fields, a variety of techniques have been developed to control the porosity and increase the surface area of biochar.

One of the most commonly used techniques for tuning the pore structure of biochar is *in situ* catalytic pore formation during biomass pyrolysis. The process is catalyzed by certain chemicals typically an acid, strong base or a salt, such as ZnCl<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> [42-44]. The chemicals are impregnated into the biomass prior to pyrolysis at a temperature of 450-900 °C. H<sub>3</sub>PO<sub>4</sub> activation can not only introduce microspores but also P-containing functional groups into biochar, which can greatly improve the performance of the biochar materials in electrochemical energy storage. It has been found that ZnCl<sub>2</sub> can greatly increase the surface area and porous volume of the biochar produced [43].

In addition to *in situ* catalytic pore formation during biomass pyrolysis, pore structure tailoring through post activation also were used to tailor the pore structure. Two steps are commonly involved in the post activation process: (1) direct pyrolysis/HTL of the biomass to produce original biochar with a very low pore volume and surface area and (2) activation of the biochar using physical or chemical methods to improve its porous structure and surface area. Post activation mainly includes physical activation with different oxidizing gases (*e.g.*, air, O<sub>2</sub>, CO<sub>2</sub>, steam or their mixtures) and chemical

activation with KOH, NaOH, H<sub>3</sub>PO<sub>4</sub> or ZnCl<sub>2</sub>. In the physical activation process, a carbon precursor is first exposed to pyrolysis in an inert atmosphere at 400-900 °C to eliminate the bulk of volatile matter, followed by partial gasification using an oxidizing gas at 350-1000 °C. The chemical activation process consists of the heat-treatment of a mixture of the carbon precursor and the activating agent at a temperature normally in the 450-900 °C range [45]. In addition to conventional physical and chemical activation, some other approaches, such as templating, also have the potential to introduce porosity into biochar, although to date no such reports on biochar pore structure tailoring have appeared [46]. Two stage activation processes consisting of chemical activation step followed by physical activation have also been used to further enhance the porosity development and tune the pore structure [47].

### Biochar nanocomposites

Controlled synthesis of carbonaceous nanocomposites has become a hot research area, due to their improved hybrid properties with high potential values in many fields. As a result of the recombination of specific nanostructures on their surfaces, biochar-based nanocomposites can be imparted with hybrid properties that in turn open up potential applications in many fields. The final nanocomposites have been shown to be utile in many application fields, including catalysis, fuel cells, drug delivery, and bio-imaging [48].

Two main methodologies are identified for the synthesis of such biochar-based nanocomposites: post-modification and in situ synthesis. The post-modification method implies coating of performed nanostructures (*e.g.*, silica sphere, Fe<sub>3</sub>O<sub>4</sub>) or incorporation of inorganic nanostructures onto biochar materials (*e.g.*, Ag, Au, Pt, and Pd) [48-51]. The in situ synthesis method implies of loading of metal nanoparticles directly to the biochar via a simple one step approach [8].

### Application of Biochar Materials

The most promising feature of the biochar-based material is that it's sustainable and easily scalable allowing the production of different functionalized carbon and hybrid nanostructures with a range of practical applications. To date, the application of biochar was primarily focused on using biochar as a soil amendment. New state of the art applications of biochar is emerging, although most of the applications are still in their infancy. These applications include but not limited to energy production, agriculture, carbon sequestration, wastewater treatment, biorefinery, etc. Since many of the review articles have summarized the advances of activated carbon or biochar materials in environmental protection, and agriculture applications, we will not cover this topic in detail in this review. Here, we briefly summarize recent progress and the state of art in applications of biochar in catalysis and energy storage.

#### Catalytic application

Biochar containing SO<sub>3</sub>H groups, also called biochar-based solid acids, represents a type of metal-free catalyst that is ubiquitously used in a wide variety of chemical reactions. The biochar-based solid acids have been demonstrated to be efficient catalysts for various acid-catalyzed reactions, such as the esterification of organic acids in an aqueous medium, acylation of alcohols and amines, and the alkylation of aromatics, as



well as the hydrolysis of biomass itself [52]. Biodiesel production through esterification is a typical reaction catalyzed by solid acids.

It is well-known that the performance of metal nanoparticle catalysts is greatly affected by their supporting materials. Biochar materials have been straightforwardly studied as supports to stabilize metal nanoparticles for different catalytic applications due to their high surface areas and functionalities, such as syngas cleaning and conversion of syngas into liquid hydrocarbons via Fischer-Tropsch synthesis [53]. Table 3 summarizes the recent studies on biochar catalytic applications.

**Table 3.** Biochar unitization for catalytic applications

Application	Biochar type	Effect	Reference
Syngas cleaning	Pine bark (950°C)	Tar reduction	[54]
Syngas cleaning	Ni-Fe catalyst supported on rice husk biochar	In-situ catalytic conversion of tar	[55]
Syngas cleaning	Acidic surface activated carbon from switchgrass	Tar, NH <sub>3</sub> , H <sub>2</sub> S removal	[56]
Fischer-Tropsch synthesis of syngas into liquid hydrocarbons	Biochar-based iron nanoparticle from pine wood pyrolysis	High efficiency of converting syngas into liquid hydrocarbon	[57]
Methane reforming	Pt-Ru alloy nanoparticles supported on HTC biochar of furfural	Hydrocarbon catalytic oxidations; heterogeneous catalysis	[58]
Biodiesel production	Biochar-derived acid catalyst prepared by sulfonating biochar with concentrated sulfuric acid	Transesterification of canola oil with alcohol and oleic acid due to high surface area and acid density	[59]
Biodiesel production	Biochar-based catalysts made from peanut hulls, pine residues, and wood chips	High efficiency in esterification of free fatty acids of vegetable oil and animal fat with methanol and high reusability due to their particle strength hydrophobicity, high surface area, and sulfonic acid group density.	[60]
Hydrolysis of biomass	Biochar sulfonic acid catalysts prepared from bamboo, cotton, and starch	High turnover number values for cellulose hydrolysis due to the multifunctional action of strong –SO <sub>3</sub> H, –COOH, and –OH groups	[61]
Catalysis of various oxidation and reduction reactions	Carbonaceous nanofibers (CNFs) prepared through a template-directed HTC process	Displayed the persistent catalytic ability in a continuous-flow mode	[62]
Acylation reaction	Starch biochar-silica composites bearing SO <sub>3</sub> H as the heterogeneous catalysts	Reactants with NH <sub>2</sub> , OH, SH groups can be quickly acylated to yield target products with very high yields.	[63]

As shown in Table 3, biochar-based catalysts demonstrate favorable catalytic performance in various reactions. Besides, it can be recycled for several runs without significant loss of activity. However, it has relative low efficiency and low abrasive resistance compared with the commercial catalyst. In addition, the inorganic species in biochar may cause catalyst poisoning, thus decreasing the catalytic activity in some organic or electrochemical reactions [64]. Therefore, there is a need to develop new and sustainable ways to tailor the physicochemical properties of such catalysts in order to adopt them for specific applications.

#### Energy storage application (Supercapacitor)

Supercapacitor, an energy storage device, has received attention to harvest energy due to its high-power density, long cycle life, and quick charge/discharge capability [65]. Supercapacitor can be used as uninterruptible power sources in electric vehicles, digital communications system, etc. The microstructure of supercapacitor electrodes has a great influence on supercapacitor performance. Carbon material with high surface area and rich porous structure are the primary raw materials for making supercapacitors due to its wide availability and low environmental impacts [66]. Producing attractive, high quality carbon material at low cost is critical for the development of the supercapacitor industry [67]. Table 4 listed some recent research activities regarding to the fabrication of supercapacitors using biochar from different feedstocks.

**Table 4.** Supercapacitor performance of electrodes made from various precursors

Material	Surface area (m <sup>2</sup> /g)	Capacitance (F/g)	Reference
Activated carbon from rubber wood sawdust	<920	8-139	[68]
Carbon nanotubes(CNTs) from oil palm fruit bunches	1656	111	[69]
Nanoporous carbons from sunflower seed shell	2509	311	[70]
Functional microporous conducting carbon from dead leaves	3404	273	[71]
Templated carbon from acrylonitrile	1680	340	[72]

Results indicated that the use of biochar is promising as an electrode due to its low cost and satisfactory performance. One of the great challenges in the development of supercapacitor technology is the relatively high cost when compared to other energy devices. Thus, future research should be directed towards the development of biochar-based functional materials with high charge capacity and minimum equivalent series resistance in a cost-effective way. One-step synthesis without an additional activation process to obtain high density carbon or composite materials would be beneficial for the compact design of high power energy sources.

## CONCLUSIONS

Recent advances in the biochar production, formation mechanism, and characterization are discussed in detail in this review. It is essential to modify the surface functionality and the porosity of biochar in order to enhance the performance of biochar materials for various applications. Processes used for turning the surface functionalities and pore structure of biochar, including surface oxidation, amination, sulfonation, pore structure modification, and recombination, are summarized and discussed. Abundant functional groups (e.g., C=O, -COOH, NH<sub>2</sub>, and SO<sub>3</sub>H), metal nanoparticles and inorganic nanostructures can be introduced onto the biochar surface. This allows the production of materials with different functionalized carbon and hybrid nanostructures for a range of practical applications. Recent progress and the state of art in applications of biochar in catalysis and energy storage are reviewed. Biochar-based catalysts exhibit favorable catalytic properties in a variety of reactions. In addition, the development of novel biochar materials, such as carbon nanotubes, functional microporous carbon, and activated carbons remain a primary choice for the construction of electrodes for commercial supercapacitor due to its low cost and satisfactory performance. Overall, the use of biochar as sustainable high-value materials seems to have a very promising future, and biochar properties need to be further improved and tailored for the appropriate applications.

## ACKNOWLEDGMENTS

This research was supported by a grant from the USDA-CSREES-Evans-Allen Project, Grant No. NCX-303-5-17-130-1.

## CONFLICTS OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

## REFERENCES

- [1] Boo Linares, N., Silvestre-Albero, A. M., Serrano, E., Silvestre-Albero, J., Garcia Martinez, J. (2014). Mesoporous materials for clean energy technologies. *Chem. Soc. Rev.* 43, 7681– 7717. DOI: 10.1039/c3cs60435g
- [2] Hu, B.; Wang, K.; Wu, L.; Yu, S.-H.; Antonietti, M.; Titirici, M.-M. (2010) Engineering carbon materials from the hydrothermal carbonization process of biomass. *Adv. Mater.* 22, 813– 828. DOI: 10.1002/adma.200902812
- [3] Xie, J., Hse, C., Shupe T., Hu, T. (2015). Physicochemical characterization of lignin recovered from microwave-assisted delignified lignocellulosic biomass for use in biobased materials. *Journal of Applied Polymer Science*, DOI: 10.1002/APP.42635
- [4] Initiate IB. (2012). Standardized product definition and product testing guidelines for biochar that is used in soil. *International Biochar Initiative*. <http://www.biochar->

- [international.org/sites/default/files/Guidelines\\_for\\_Biochar\\_That\\_Is\\_Used\\_in\\_Soil\\_Final.pdf](http://international.org/sites/default/files/Guidelines_for_Biochar_That_Is_Used_in_Soil_Final.pdf) (Accessed on 2/2/2017)
- [5] Qian, K.; Kumar, A.; Zhang, H.; Bellmer, and Huhnke, R. (2015) Recent advances in utilization of biochar. *Renewable and Sustainable Energy Reviews*. 42, 1055-1064. DOI: 10.1016/j.rser.2014.10.074
- [6] Namaalwa, J.; Sankhayan, P. L.; Hofstad, O. (2007) A dynamic bio-economic model for analyzing deforestation and degradation: An application to woodlands in Uganda. *Forest Policy Economics* 9, 479– 495. DOI: 10.1016/j.forpol.2006.01.001
- [7] Meyer, S.; Glaser, B.; Quicker, P. (2011). Technical, economical, and climate-related aspects of biochar production technologies: A literature review. *Environ. Sci. Technol.* 45, 9473– 9483. DOI: 10.1021/es201792c
- [8] Titirici M-M; White RJ; Falco C; Sevilla M. Black perspectives for a green future: hydrothermal carbons for environment protection and energy storage. (2012). *Energy Environ. Sci.* 5, 6796-6822. DOI: 10.1039/C2EE21166A
- [9] Wiedner, C.; Rumpel, C.; Steiner, A.; Pozzi, R.; Maas, B. Glaser. (2013) Chemical evaluation of chars produced by thermochemical conversion (gasification, pyrolysis and hydrothermal carbonization) of agro-industrial biomass on a commercial scale. *Biomass Bioenergy*, 59, 264–278. DOI: 10.1016/j.biombioe.2013.08.026
- [10] Xiu S.; Shahbazi A. (2012) Bio-oil Production and Upgrading Research: A Review. *Renewable and Sustainable Energy Reviews*, 16(7), 4406-4414. DOI: 10.1016/j.rser.2012.04.028
- [11] Kambo, H.S.; Dutta, A. (2015) A comparative review of biochar and hydrochar in terms of production, physical-chemical properties and applications. *Renewable and Sustainable Energy Reviews* 45, 359-378. DOI: 10.1016/j.rser.2015.01.050
- [12] Shen, D. K.; Gu, S. (2009) The mechanism for thermal decomposition of cellulose and its main products. *Bioresour. Technol.* 100, 6496– 6504. DOI: 10.1016/j.biortech.2009.06.095
- [13] Peters, B. (2011). Prediction of pyrolysis of pistachio shells based on its components hemicellulose, cellulose and lignin. *Fuel Process. Technol.* 92, 1993– 1998. DOI: 10.1016/j.fuproc.2011.05.023
- [14] Antal, M. J.; Grønli, M. (2003). The art, science, and technology of charcoal production. *Ind. Eng. Chem. Res.* 42, 1619–1640. DOI: 10.1021/ie0207919
- [15] Minowa, T.; Kondo, T.; Sudirjo, S.T. (1998) Thermochemical liquefaction of Indonesian biomass residues. *Biomass & Bioenergy*, 14(5-6), 517-524. DOI: 10.1016/S0961-9534(98)00006-3
- [16] Xiu S.; Zhang B.; Shahbazi A. (2011). Biorefinery Processes for Biomass Conversion to Liquid Fuel. In: *Biofuel's Engineering Process Technology*; Marco A.D. Bernardes, Ed.; InTech, pp: 167-190.
- [17] Carpenter, S. R.; Caraco, N. F.; Correll, D. L.; Howarth, R.W.; Sharpley, A.N., Smith, V. H. (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications* 8, 559–568. DOI: 10.1890/1051-0761(1998)008[0559:NPOSWW]2.0.CO;2
- [18] Matteson, G. C.; Jenkins, B. M. (2007) Food and processing residues in California: Resource assessment and potential for power generation. *Bioresour. Technol.*, 98, 3098–3105. DOI: 10.1016/j.biortech.2006.10.031
- [19] Cantrell, K.; Ro, K.; Mahajan, D.; Anjom, M.; Hunt, P.G. (2007) Role of thermochemical conversion in livestock waste-to-energy treatments: Obstacles and

- opportunities. *Industrial and Engineering Chemistry Research* 46, 8918–8927. DOI: 10.1021/ie0616895
- [20] Joan J., Manyà. (2012) Pyrolysis for biochar purposes: A review to establish current knowledge gaps and research needs. *Environmental Science & Technology*, 46, 7939–7954. DOI: 10.1021/es301029g
- [21] Brown, T. R.; Wright, M. M.; Brown, R. C. (2011). Estimating profitability of two biochar production scenarios: slow pyrolysis vs fast pyrolysis. *Biofuels, Bioprod. Biorefin.* 5, 54– 68. DOI: 10.1002/bbb.254
- [22] Liao, C.; Wu, C.; Yan, Y. (2007). The characteristics of inorganic elements in ashes from a 1MW CFB biomass gasification power generation plant. *Fuel process. Technol.*, 88, 149–156. DOI: 10.1016/j.fuproc.2005.06.008
- [23] Li, R.; Zhang, B.; Xiu, S.N.; Wang, H., Wang, L.J.; Shahbazi, A. (2015). Characterization of Solid Residues Obtained from Supercritical Ethanol Liquefaction of Swine Manure. *American Journal of Engineering and Applied Sciences*, 8.4: 465–470.
- [24] Brewer, C.E.; Schmidt-Rohr, K.; Satrio, J.A.; Brown, R.C. (2009). Characterization of biochar from fast pyrolysis and gasification systems. *Environ. Prog. Sustainable Energy*, 28, 386–396. DOI: 10.1002/ep.10378
- [25] Spokas, K. A.; Novak, J. M.; Masiello, C. A.; Johnson, M. G.; Colosky, E. C.; Ippolito, J. A.; Trigo, C. (2014). Physical disintegration of biochar: An overlooked process. *Environ. Sci. Technol. Lett.* 1, 326–332. DOI: 10.1021/ez500199t
- [26] Sharma, R. K.; Wooten, J. B.; Baliga, V. L.; Lin, X.; Geoffrey Chan, W.; Hajaligol, M. R. (2004). Characterization of chars from pyrolysis of lignin. *Fuel* 83, 1469–1482. DOI: 10.1016/j.fuel.2003.11.015
- [27] Freitas, J. C. C.; Bonagamba, T. J.; Emmerich, F. G. (2001). Investigation of biomass and polymer-based carbon materials using  $^{13}\text{C}$  high-resolution solid-state NMR. *Carbon* 39, 535– 545. DOI: 10.1016/S0008-6223(00)00169-X
- [28] Mukome, F. N. D.; Zhang, X.; Silva, L. C. R.; Six, J.; Parikh, S. J. (2013). Use of chemical and physical characteristics to investigate trends in biochar feedstocks. *J. Agric. Food Chem.* 61, 2196–2204. DOI: 10.1021/jf3049142
- [29] Gao, Y.; Wang, X.H.; Yang, H.P.; Chen, H.P. (2012). Characterization of products from hydrothermal treatments of cellulose. *Energy*, 42, 457–465. DOI: 10.1016/j.energy.2012.03.023
- [30] Qian, L.; Chen, B. (2014). Interactions of aluminum with biochars and oxidized biochars: Implications for biochar aging process. *J. Agric. Food Chem.* 62, 373–380. DOI: 10.1021/jf404624h
- [31] Lehmann, J.; Joseph, S. (2009). *Biochar for environmental management: science and technology*; Earthscan: London.
- [32] Liu, W.J.; Zeng, F.X.; Jiang, H.; Zhang, X.S. (2011). Preparation of high adsorption capacity bio-chars from waste biomass. *Bioresour. Technol.* 102, 8247–8252. DOI: 10.1016/j.biortech.2011.06.014
- [33] Li, Y.; Shao, J.; Wang, X.; Deng, Y.; Yang, H.; Chen, H. (2014). Characterization of modified biochars derived from bamboo pyrolysis and their utilization for target component (furfural) adsorption. *Energy Fuels* 28, 5119– 5127. DOI: 10.1021/ef500725c
- [34] Xu, D.; Zhao, Y.; Sun, K.; Gao, B.; Wang, Z.; Jin, J.; Zhang, Z.; Wang, S.; Yan, Y.; Liu, X.; Wu, F. (2014). Cadmium adsorption on plant- and manure-derived biochar

- and biochar-amended sandy soils: Impact of bulk and surface properties. *Chemosphere*, 111, 320–326. DOI: 10.1016/j.chemosphere.2014.04.043
- [35] Anfruns, A.; García-Suárez, E. J.; Montes-Morán, M. A.; Gonzalez-Olmos, R.; Martin, M. J. (2014). New insights into the influence of activated carbon surface oxygen groups on H<sub>2</sub>O<sub>2</sub> decomposition and oxidation of pre-adsorbed volatile organic compounds. *Carbon*, 77, 89–98. DOI: 10.1016/j.carbon.2014.05.009
- [36] Wu, L.; Sitamraju, S.; Xiao, J.; Liu, B.; Li, Z.; Janik, M. J.; Song, C. (2014). Effect of liquid-phase O<sub>3</sub> oxidation of activated carbon on the adsorption of thiophene. *Chem. Eng. J.*, 242, 211–219. DOI: 10.1016/j.cej.2013.12.077
- [37] Gokce, Y.; Aktas, Z. (2014). Nitric acid modification of activated carbon produced from waste tea and adsorption of methylene blue and phenol. *Appl. Surf. Sci.*, 313, 352–359. DOI: 10.1016/j.apsusc.2014.05.214
- [38] Adelodun, A. A.; Lim, Y. H.; Jo, Y. M. (2014). Stabilization of potassium-doped activated carbon by amination for improved CO<sub>2</sub> selective capture. *J. Anal. Appl. Pyrolysis*, 108, 151–159. DOI: 10.1016/j.jaap.2014.05.005
- [39] Shafeeyan, M. S., Wan Daud, W. M. A., Houshmand, A., Arami-Niya, A. (2012). The application of response surface methodology to optimize the amination of activated carbon for the preparation of carbon dioxide adsorbents. *Fuel*, 94, 465– 472. DOI: 10.1016/j.fuel.2011.11.035
- [40] Takagaki, A.; Tagusagawa, C.; Hayashi, S.; Hara, M.; Domen, K. (2010) Nanosheets as highly active solid acid catalysts for green chemical syntheses. *Energy Environ. Sci.* 3, 82. DOI: 10.1039/B918563A
- [41] Dehkhoda, A. M., West, A. H., Ellis, N. (2013). Biochar based solid acid catalyst for biodiesel production. *Appl. Catal., A.*, 382, 197– 204. DOI: 10.1016/j.apcata.2010.04.051
- [42] Taberna, P.-L., Gaspard, S. (2014). CHAPTER 9. Nanoporous Carbons for High Energy Density Supercapacitors. In: *Biomass for Sustainable Applications: Pollution Remediation and Energy*, S. Gaspard, and M. C. Ncibi, eds., The Royal Society of Chemistry, pp: 366–399. DOI:10.1039/9781849737142-00366
- [43] Sun, L.; Tian, C.; Li, M.; Meng, X.; Wang, L.; Wang, R.; Yin, J.; Fu, H. (2013). From coconut shell to porous graphene-like nanosheets for high-power supercapacitors. *J. Mater. Chem. A*, 1, 6462– 6470. DOI: 10.1039/C3TA10897J
- [44] Hulicova-Jurcakova, D.; Puziy, A. M.; Poddubnaya, O. I.; Suárez-García, F.; Tascón, J. M. D.; Lu, G. Q. (2009). Highly stable performance of supercapacitors from phosphorus-enriched carbons. *J. Am. Chem. Soc.*, 131, 5026– 5027. DOI: 10.1021/ja809265m
- [45] Sevilla, M.; Mokaya, R. (2014). Energy storage applications of activated carbons: supercapacitors and hydrogen storage. *Energy & Environmental Science*, 7, 1250– 1280. DOI: 10.1039/C3EE43525C
- [46] Gaspard, S., Passe-Coutrin, N., Durimel, A., Cesaire, T., and Jeanne-Rose, V. (2014). CHAPTER 2 Activated Carbon from Biomass for Water Treatment. In: *Biomass for Sustainable Applications: Pollution Remediation and Energy*, S. Gaspard, and M. C. Ncibi, eds., The Royal Society of Chemistry, pp: 46-105. DOI: 10.1039/9781849737142-00046
- [47] Hu, Z.; Guo, H.; Srinivasan, M.P.; Yaming, N. (2003). A Simple Method for Developing Mesoporosity in Activated Carbon. *Sep. Purif. Technol.* 31, 47-52. DOI: 10.1016/S1383-5866(02)00148-X

- [48] Hu, B.; Yu, S.H.; Wang, K.; Liu, L.; Xu, X.W. (2008). Functional carbonaceous materials from hydrothermal carbonization of biomass: an effective chemical process. *Dalton Trans.*, 5414-5423. DOI: 10.1039/B804644C
- [49] Sun, X.M; Li, Y.D. (2004). Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles. *Angew Chem., Int. Ed.*, 43, 597–601. DOI: 10.1002/anie.200352386
- [50] Qian, H. S.; Antonietti, M.; Yu, S. H. (2007). Hybrid “Golden Fleece”: Unique approaches for synthesis of uniform carbon nanofibres and silica nanotubes embedded/confined with high population of noble metal nanoparticles and their catalytic performance. *Adv. Funct. Mater.*, 17, 637–643.
- [51] Hu, B.; Zhao, Y.; Zhu, H.Z.; Yu, S.H. (2011). Selective chromogenic detection of thiol-containing biomolecules using carbonaceous nanospheres loaded with silver nanoparticles as carrier. *ACS nano*, 5 (4), 3166-3171. DOI: 10.1021/nn2003053
- [52] Zhou, C.H., Xia, X., Lin, C.X., Tong, D.S., Beltramini, J. (2011). Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. *Chem. Soc. Rev.* 40, 5588-5617. DOI: 10.1039/C1CS15124J
- [53] Wang, S., Wang, H., Yin, Q., Zhu, L., Yin, S. (2014). Methanation of bio-syngas over a biochar supported catalyst. *New J. Chem.* 38, 4471– 4477. DOI: 10.1039/C4NJ00780H
- [54] Mani, J.R; Kastner, A; Juneja. (2013). Catalytic decomposition of toluene using a biomass derived catalyst. *Fuel Process Technol*, 114, 118–125. DOI: 10.1016/j.fuproc.2013.03.015
- [55] Shen, Y.; Zhao, P.; Shao, Q.; Ma, D.; Takahashi, F.; Yoshikawa, K. (2014). In-situ catalytic conversion of tar using rice husk char-supported nickel-iron catalysts for biomass pyrolysis/gasification. *Appl Catal B: Environ*, 152–153, 140–151. DOI: 10.1016/j.apcatb.2014.01.032
- [56] Bhandari, P.N.; Kumar, A.; Huhnke, R.L. (2013). Simultaneous removal of toluene (model tar), NH<sub>3</sub>, and H<sub>2</sub>S, from biomass-generated producer gas using biochar-based and mixed-metal oxide catalysts. *Energy Fuels*, 28, 1918–1925. DOI: 10.1021/ef4016872
- [57] Yan, Q.; Wan, C.; Liu, J.; Gao, J.; Yu, F.; Zhang, J. (2013). Iron nanoparticles in situ encapsulated in biochar-based carbon as an effective catalyst for the conversion of biomass-derived syngas to liquid hydrocarbons. *Green Chem*, 15, 1631–1640. DOI: 10.1039/C3GC37107G
- [58] Matosa, J.; Rosalesa, M.; Rezan, D.C., Titiricib, M.M. (2010). Methane conversion on Pt–Ru nanoparticles alloy supported on hydrothermal carbon. *Appl. Catal., A*, 386, 140-146. DOI: 10.1016/j.apcata.2010.07.047
- [59] Dehkhoda, A.M.; Ellis, N. (2013). Biochar-based catalyst for simultaneous reactions of esterification and transesterification. *Catal Today*, 207, 86–92. DOI: 10.1016/j.cattod.2012.05.034
- [60] Kastner, J.R.; J. Miller; D.P. Geller; J. Locklin; L.H. Keith; T. Johnson. (2012). Catalytic esterification of fatty acids using solid acid catalysts generated from biochar and activated carbon. *Catal Today*, 190, 122–132. DOI: 10.1016/j.cattod.2012.02.006
- [61] Wu, Y.; Fu, Z.; Yin, D.; Xu, Q.; Liu, F.; Lu, C.; Mao, L. (2010). Microwave-assisted hydrolysis of crystalline cellulose catalyzed by biomass char sulfonic acids. *Green Chem*, 12, 696-700. DOI: 10.1039/B917807D

- [62] Liang, H.W.; Zhang, W.J.; Ma, Y.N.; Cao, X.; Guan, Q.F., Xu, W.P.; Yu, S.H. (2011). Highly Active Carbonaceous Nanofibers: A Versatile Scaffold for Constructing Multifunctional Free-Standing Membranes. *ACS Nano*, 5 (10), 8148–8161. DOI: 10.1021/nn202789f
- [63] Gupta, P.; Paul, S. (2011). Amorphous carbon-silica composites bearing sulfonic acid as solid acid catalysts for the chemoselective protection of aldehydes as 1,1-diacetates and for N-, O- and S-acylations. *Green Chem.* 13, 2365-2372. DOI: 10.1039/C0GC00900H
- [64] Bhandari, P. N.; Kumar, A.; Bellmer, D. D.; Huhnke, R. L. (2014). Synthesis and evaluation of biochar-derived catalysts for removal of toluene (model tar) from biomass-generated producer gas. *Renewable Energy*, 66, 346– 353. DOI: 10.1016/j.renene.2013.12.017
- [65] Xiao, Y.H.; Zhang, A.Q.; Liu, S.J. Zhao, J.H.; Fang, S.M. Jia, D.Z. (2012). Free-standing and porous hierarchical nanoarchitectures constructed with cobalt cobaltite nanowalls for supercapacitors with high specific capacitances. *J Power Sources*, 219, 140–146. DOI: 10.1016/j.jpowsour.2012.07.030
- [66] Liu, M.C.; Kong, L.B.; Zhang, P.; Luo, Y.C.; Kang, L. (2012). Porous wood carbon monolith for high-performance supercapacitors. *Electrochim Acta*, 60, 443–448. DOI: 10.1016/j.electacta.2011.11.100
- [67] Zhang, L.; Zhao, X.S. (2009). Carbon-based materials as supercapacitor electrodes. *Chemical Society Reviews*, 38, 2520-2531. DOI: 10.1039/B813846J
- [68] Taer, E.; Deraman, M.; Tali, I.A., Awitdrus, A.; Hashmi, A.; Umar, A.A. (2011). Preparation of a Highly Porous Binderless Activated Carbon Monolith from Rubber Wood Sawdust by a Multi-Step Activation Process for Application in Supercapacitors. *International journal of electrochemical science* 6(8):3301-3315.
- [69] Basri, N.H.; M. Deraman; S. Kanwal; I.A. Talib; J.G. Manjunatha; A.A. Aziz. (2013). Supercapacitors using binderless composite monolith electrodes from carbon nanotubes and pre-carbonized biomass residues. *Biomass Bioenergy*, 59, 370–379. DOI: 10.1016/j.biombioe.2013.08.035
- [70] Li, X.; Xing, W.; Zhou, S.P.; Zhou, J.; Li, F.; Qiao, S.Z.; Lu, G.Q. (2011). Preparation of capacitor's electrode from sunflower seed shell. *Bioresour. Technol.* 102(2):1118-1123. DOI: 10.1016/j.biortech.2010.08.110
- [71] Biswal, M.; Banerjee, A.; Deo, M.; Ogale, S. (2013). From dead leaves to high energy density supercapacitors. *Energy Environ. Sci.* 6, 1249-1259. DOI: 10.1039/C3EE22325F

**Article copyright:** © 2017 Shuangning Xiu, Abolghasem Shahbazi, and Rui Li. This is an open access article distributed under the terms of the [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use and distribution provided the original author and source are credited.

