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Critical Review on Biochar-Supported Catalysts for Pollutant Degradation and Sustainable Biorefinery

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Biochar (BC) is a material synthesized from biomass by thermochemical conversion. Physicochemical and functional properties of BCs can be enhanced by several methods of activation or functionalization. The activated and functionalized BCs with a large surface area and abundant surface functional groups can serve as effective catalysts or catalyst supports for various chemical transformations as well as for adsorption/sorption/enrichment of low-concentration pollutant streams. Among them, remediation of environmental contaminants and production of a range of bioproducts in biorefineries have attracted much attention in the context of achieving green and sustainable development. Although the applications of BC as adsorbents in removal of pollutants have been discussed extensively, there is a lot of untapped potential with new applications of BCs as catalysts or catalyst supports for advanced oxidation processes (AOPs) and sustainable biorefineries. In this review, the production and activation/functionalization of BCs are scrutinized. The mechanisms of activated and functionalized BC and BC-supported catalysts in degradation of organic contaminants via AOPs assisted with hydrogen peroxide (H_2O_2), peroxydisulfate (PDS), and peroxymonosulfate (PMS) are reviewed. Emerging applications of BC as catalyst for production of biodiesel and high-value chemicals, tar removal, bio-syngas reforming, and energy storage and conversion devices are discussed in detail.

1. Introduction

Biochar (BC) is a carbonaceous material, produced by thermochemical conversion of biomass under an inert environment.[1] The thermochemical processes for synthesis of BC from biomass includes hydrothermal carbonization (HTC) and pyrolysis.[2–4] In comparison with other carbonaceous materials synthesized by complicated and energy-consuming processes, BC is a greener carbonaceous material derived from waste biomass by cost-effective synthesis processes and thus reduces environmental impacts.[5–7] The applications of as-synthesized BCs are closely related to their physicochemical characteristics.[8] To improve the physicochemical characteristics of the as-synthesized BCs, various activation and functionalization methods have been studied so far.[7,9,10] The activated and functionalized BCs have extensive applications in diverse fields such as soil reclamation, carbon dioxide (CO_2) sequestration, removal of heavy metals (HMs), and degradation of organic pollutants,[10–13] as shown in **Figure 1**.[14] More significantly, BCs after activation and functionalization can obtain larger surface area along with abundant chemical-active functional groups, thus displaying remarkable roles as catalysts, catalyst supports, and adsorbent/sorbent in various chemical processes.[10,15–17]

Snowballing level of pollutants in the environment has become a major area of concern these days. There are various approaches of degradation and removal of pollutants that have been reported. In comparison with other approaches, advanced oxidation processes (AOPs) are gaining more attention for removal of organic pollutants in the environment these days.[16–18] AOPs can generate hydroxyl ($^{\bullet}OH$) as well as sulfate ($SO_4^{\bullet-}$) radicals during the degradation, having robust redox potential and enormous reactivity.[19–21] Principally, AOPs include two types of catalytic processes: i) homogeneous catalysis, including chemical activation of peroxymonosulfate (PMS) as well as peroxydisulfate (PDS), Fenton,[19–21] photo-Fenton,[22] and several other chemical reactions in which oxidizing free radicals are produced, and ii) heterogeneous catalysis such as carbonaceous materials[23] and nanoscale zero-valent iron (nZVI),[24] etc. Among all heterogeneous catalysts, nZVI could be applied as an efficient enhancer of $^{\bullet}OH$ when

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combined with hydrogen peroxide (H_2O_2) for catalytic oxidation of environmental pollutants, due to its higher surface-to-volume ratio.[24] However, nZVI can be easily oxidized, passivated, and agglomerated,[25,26] while the resultant reduction in mobility of nZVI leads to decreased catalytic efficiency.[24,27] To overcome such limitations of nZVI and improve its practical utility, several materials such as zeolite, amorphous activated carbon, and BC have been applied as catalyst supports.[28] Due to higher porosity and diverse oxygen-containing functional groups (OCFGs) such as carboxyl (—COOH) and hydroxyl (—OH) on its surface, BC can be easily applied to disperse and stabilize the nanoparticles.[18,19,24] Moreover, the higher specific surface area and better porosity make BC an efficient adsorbent to remove environmental contaminants.[3,29] Therefore, by using BC-supported catalysts (e.g., BC-conjugated nZVI (nZVI/BC), Fe_3O_4/BC, and iron-impregnated-BC (Fe-BC)), organic contaminants were effectively degraded via AOPs with improved efficiencies.[18,30,31]

Along with application of BCs as catalysts/catalyst supports in degradation of organic pollutants, it can also be applied in biorefinery for production of range of value-added products. Various bioproducts such as syngas, bio-oils, bio-hydrogen, and BCs can be produced by thermochemical conversion of the biomass.[9,10,32,33] Although the purity of products obtained from biomass could limit its further utilization to some extent, it has been reported that both the rate and selectivity of the conversion reaction could be enhanced by application of appropriate catalysts, such as BC.[34,35] Cheng and Li overviewed the environmental application of BCs as well as suitable catalysts for applications in integrated biorefinery.[9] Ala'a et al. reported the production of biodiesel by applying carbon-based catalysts, and they found that this carbon-based material showed exceptional catalytic properties as well as catalyst support due to higher surface area, better thermal stability, and its cost-effectiveness.[36] Cao et al. and Xiong et al. also reviewed upgradation of biomass for production of value-added chemicals and byproducts by applying BC-based catalysts.[7,10] Even with numerous advantages of BC as catalyst or catalyst support in upgradation of biomass, the utilization of BCs has not been thoroughly investigated yet. Hence, an inclusive review is required to infer the application of BC or BC-supported catalysts in conversion of biomass in to value-added products along with catalytic degradation (mineralization or simultaneous adsorption and degradation) of pollutants via AOPs.

This review precisely summarizes the preparation, modification, and catalytic application of BC and BC-supported catalyst in degradation of environmental pollutants by AOPs along with upgradation of biomass. The prime objectives of this review are to describe 1) the application and mechanism of BC and BC-supported catalysts in degradation of organic contaminants via H_2O_2-, PDS-, and PMS-assisted degradation; and 2) application of BC/BC-supported catalyst in biorefinery for production of range of chemicals compounds, their production processes, and future prospects.

2. Production of BC

BC is generally produced from lignocellulosic or algal biomass as feedstock via the thermochemical/pyrolysis process at 300–800 °C in an inert atmosphere, as shown in **Figure 2**.[14] The major products of the conventional carbonization process include CH_4, H_2, CO, bio-oil, and some syngas.[4] This process requires long residence time (>1 h) and low heating rate (5–7 °C min^{-1}). In the case of fast pyrolysis, the heating rate is much higher (>200 °C min^{-1}); the residence time is shorter (<10 s); and the main product is bio-oil.[4,37] Due to incomplete carbonization of biomass, the produced BC displays lower surface area along with entrapped tar-like constituents in the pores.[38] Gasification is another process for preparation of BC

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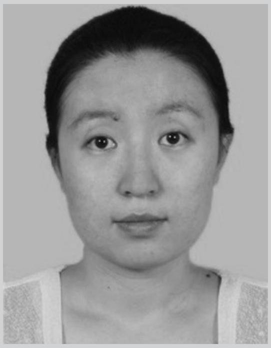

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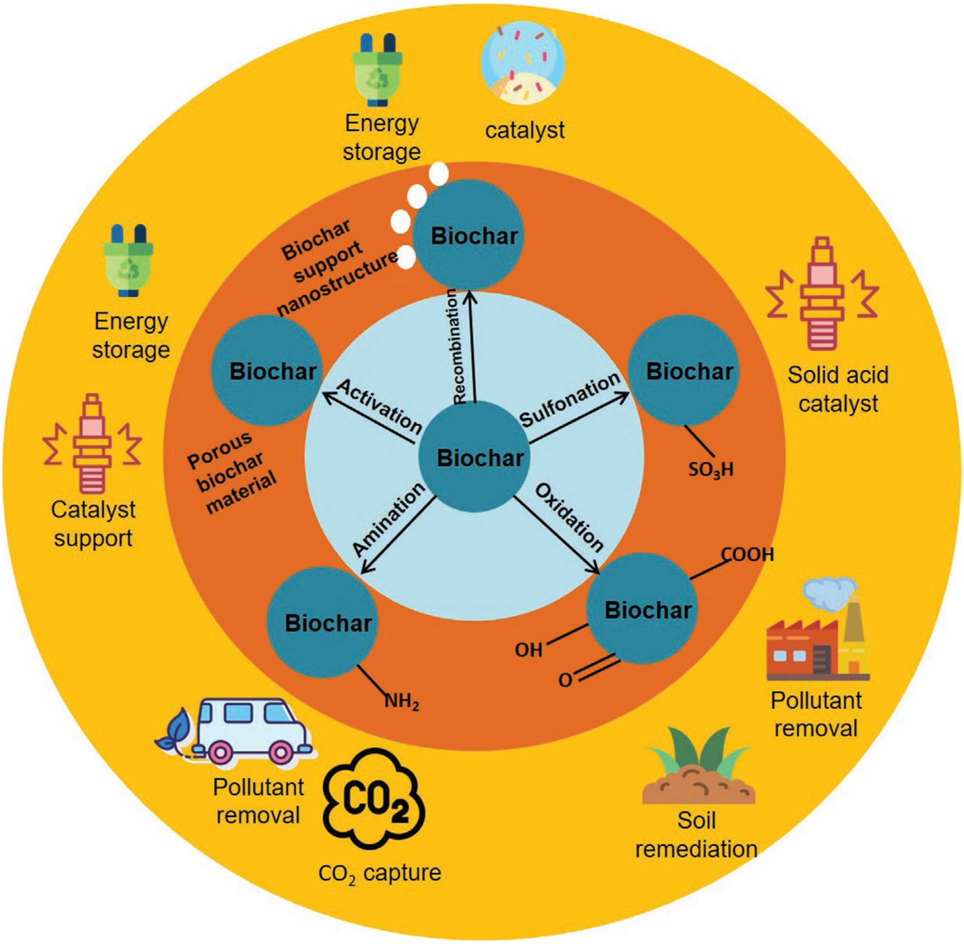

Figure 1. Biochar as carbonaceous material for the synthesis of various functional materials and their potential applications. Reproduced with permission.[14] Copyright 2015, American Chemical Society.

performed at higher than 700 °C in the presence of O_2 or steam as oxidants, which produces syngas as the major product.[2,3] BC can also be produced as secondary product from tar reforming, which displays similar mechanism as pyrolysis and gasification.[9,10] HTC of biomass at lower temperatures (180–250 °C) in pressurized water condition generates hydrochar, which is considered as BC analog.[39] The HTC process eliminates the energy-intensive drying step of feedstock, and thus it is considered to be cost-effective.[39]

3. Activation and Functionalization of BC

Generally, BCs synthesized from pyrolysis of biomass display relatively low specific surface area, inadequate porosity, and limited OCFGs.[19] These inherent characteristics of BC hamper its application as catalysts/catalyst supports to some extent. To improve the above-mentioned properties of BC, appropriate activation or functionalization methods are required.[3] There are numerous original research articles and well-organized reviews published recently on activation and functionalization of BCs, describing the applications of BCs as catalysts/catalyst supports for environmental application.[10,18,19] Since this review mainly discusses BC/BC-supported materials for catalytic removal/degradation of pollutants and biorefinery, therefore, here we focus on activation and functionalization of BCs for promoting these processes (i.e., organic degradation via AOP and biomass valorization).

3.1. BC Activation

The foremost objective of BC activation includes increasing specific surface area and porosity. This improvement can be achieved by the development and formation of new internal porous structure during activation.[4] Based on the activation agents/environment/temperature/time applied, the process can be generally separated into two categories: physical activation and chemical activation.[40]

3.1.1. Physical Activation

In the process of physical activation, the pyrolyzed BCs are kept in measured flow of steam and/or CO_2 at >700 °C. At high temperatures, the gaseous agent leads to gasification via the C–H_2O and/or C–CO_2 reaction, thus partially changing the carbonaceous

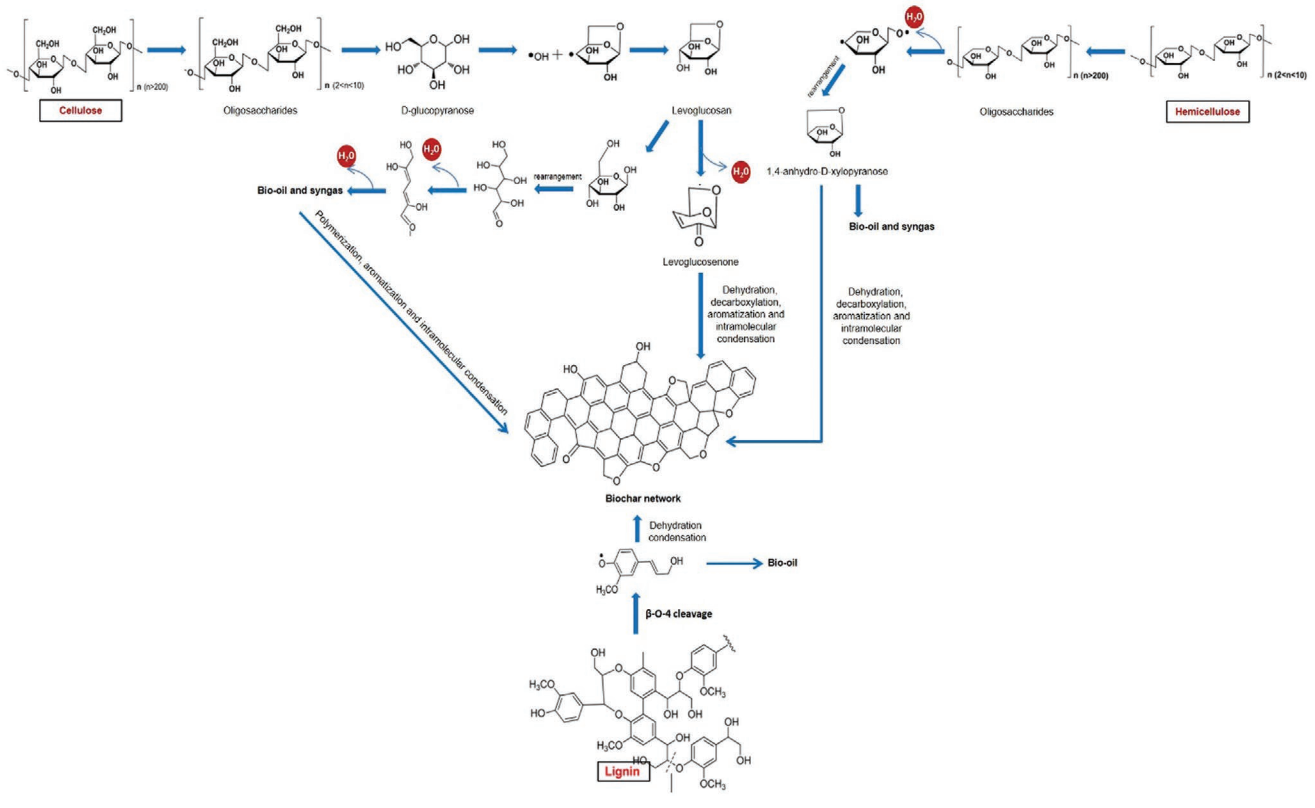

Figure 2. Thermochemical synthesis of biochar from biomass (cellulose, hemicellulose, and lignin). Reproduced with permission.[14] Copyright 2015, American Chemical Society.

matrix of the pyrolyzed BC.[40,41] The major reactive carbonaceous parts of the BC are specifically removed and widen the pore sizes by connecting one pore to another during the activation process.[42] Subsequently, the specific surface area can also be expressly enhanced, and a sharp microporous structure with little involvement of mesopores is visualized.[40,42] The specific surface area, pore size distribution, and porosity of the activated BCs are mainly governed by the type of feedstocks, gaseous agent for activation, and activation conditions.[10] For example, Koltowski et al. found that both the steam and CO_2 activation could significantly improve the surface area and porosity of the BC.[43] There are several articles and reviews available related to selection of feedstocks, gaseous agent, and activation conditions of BCs.[7–10,41,42] So, we are not discussing much about these here.

3.1.2. Chemical Activation

In the process of chemical activation of pyrolyzed BCs, BCs are first impregnated in acid/alkaline/metal salt solutions containing activating chemicals such as H_2SO_4, H_3PO_4, KOH, $ZnCl_2$, and K_2CO_3; afterward, the dried solids are pyrolyzed in presence of inert gas.[40,44,45] The mechanism of chemical activation is more complicated in comparison with physical activation. These chemical agents may encourage the formation of new pores by eliminating the partial carbon atoms of the BC matrix, suppressing tar synthesis, and facilitating the formation of volatile organic compounds.[14] In comparison with physical activation, the overall activation of chemical activation is more effective with higher surface area and enhanced porosity of BC, and this operation takes place at relatively lower temperatures.[40,46] However, after the process, a washing procedure is necessary to eliminate the agents applied in impregnation and their respective salts.[47] Apart from several advantages of chemical activation process, there are certain issues that limit their application to some level, including equipment corrosion, recycling of chemical, and generation of secondary pollutants.[46] The chemicals applied in activation process are highly corrosive in nature, and this property is enhanced at elevated temperatures. Important factors in the processes of chemical activation include activation temperature, the characteristics and quantity of the chemicals, and biomass type, etc. These parameters significantly influence the specific surface area, pore size distribution, and porosity of the activated BCs.[40,41]

3.2. Functionalization of BC

To improve the OCFGs of BC and facilitate it with catalytic activity for specific reactions, appropriate functionalization process is a prerequisite for the BC expected to be a catalyst. Mostly, catalytic properties of BCs can be improved by surface alteration or deposition of active materials.[3,41] BC functionalization can be simply done by introducing specific chemical functional groups, commonly acid functional groups, onto BC surface. One of the most commonly used methods

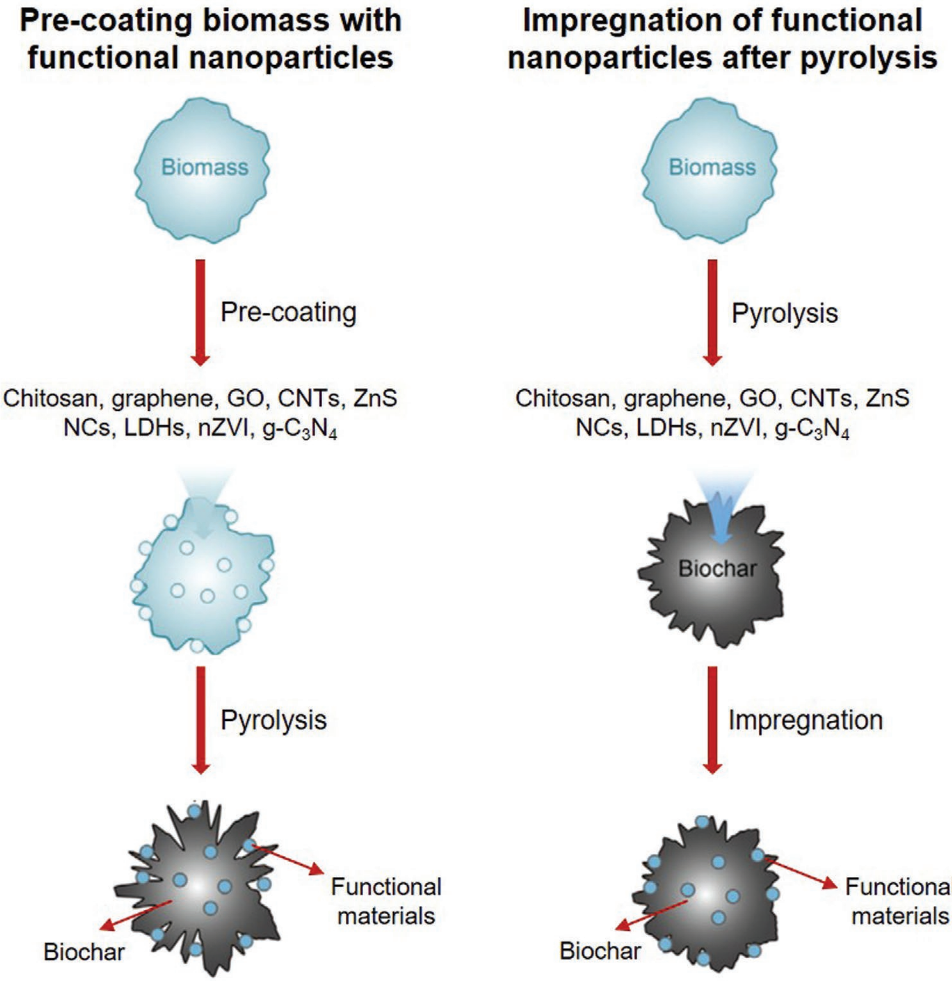

Figure 3. Synthesis of functional nanocomposite biochar. Reproduced with permission.[52] Copyright 2016, Elsevier.

is sulfonation, which attaches BC with $-SO_3H$ groups by concentrated sulfuric (H_2SO_4) or its derivatives (e.g., fuming sulfuric acid and gaseous SO_3).[10] The sulfonated BCs can be extensively applied as solid acid catalysts for biomass hydrolysis, dehydration, and biodiesel production, etc.,[9,10] which will be discussed in Section 5. In addition to the $-SO_3H$ group, other weak acid functional groups such as the carboxyl ($-COOH$) functional group can also be incorporated into the BC matrix.[9] The catalytic property and reusability of these solid acid catalysts showed better performances in comparison to nonfunctionalized BCs.[9]

In addition to application of BCs as catalysts, they are also applied as catalyst supports.[48] To improve the catalytic properties of metals and/or metal oxides, these materials can be preloaded onto biomass matrix before pyrolysis[49] or in other way the pyrolyzed BCs are impregnated with the metal precursors.[15,50]

3.3. Functional Nanoparticles-Coated BC

The functional nanomaterials, such as graphene, graphene oxide, chitosan, carbon nanotubes (CNTs), zinc sulfate (ZnS) nanocrystals, double-layered hydroxides, nZVI, and graphitic C_3N_4, can be successfully coated on BC surface to combine the advantages of both BC matrix and the functional nanoparticles,[24,48,51–53] as shown in **Figure 3**.[52] These synthesized composite materials could obtain improved OCFGs, specific surface area, porosity, and thermal steadiness, which may enhance their contaminants removal efficiency.[48,52] Principally, BC-supported nanocomposites can propel the concurrent adsorption and degradation of organic contaminates via AOPs. There have been two methods reported so far, through which coating of functional nanoparticles on BC surface can be achieved, as discussed below in detail.

3.3.1. Precoating Biomass with Functional Nanoparticles

Various functional nanoparticles have been used to pretreat feedstock prior to pyrolysis, as shown in Figure 3.[52] Commonly, feedstock can be pyrolyzed to BC-supported functional composites after a dip-coating procedure.[54] A newly engineered BC-coated graphene was synthesized via annealing derivative of graphene/pyrene-treated feedstock. The findings showed that the thermal steadiness of the composites was significantly improved due to the graphene “skin,” and the efficiency of methylene blue (MB) removal was enhanced.[55] Besides, a graphene/BC composite was fabricated via slow pyrolysis of graphene-pretreated wheat straw biomass.[56] The observation confirmed that the phenanthrene removal efficiency of the composite was higher than the pristine BC. Inyang et al. applied different concentrations of carboxyl-functionalized CNT solutions to fabricate a multiwalled-CNT-coated BC before the slow pyrolysis.[57] The experiment results inferred that addition of CNTs to BC led to improved thermal stability, specific surface area, and porosity of BC.

3.3.2. Impregnation of Functional Nanoparticles After Pyrolysis

Impregnation of functional nanomaterials onto fresh BC after pyrolysis can also improve the performance of BC-nanomaterial composites (Figure 3). Mg/Al-layered double hydroxide,[58–60] nZVI,[48,61] hydrogel beads, chitosan,[62,63] and ZnS nanocrystals[64] were generally applied in this fabrication process. The fabricated composites have higher efficiencies than the individual BCs and nanomaterials. Nevertheless, coating of functional nanomaterials may lead to partial obstruction of the BC pores. Fortunately, the novel characteristics of functional nanoparticles can compensate for this possible shortcoming. For example, the chitosan-modified BCs synthesized by chitosan coating onto BC surfaces showed shared properties of BC's porous system as well as comparatively larger surface area and higher chemical affinity property of chitosan;[63] however, drastic reduction in the surface area of the BC was also observed due to partial blockage of BC pores by the chitosan. Therefore, explicit researches should be required to curtail the unwanted effect of a fabrication technique on other beneficial characteristics while impregnating the desirable nanomaterials.

4. Application of BC and BC-Composites in Degradation of Organic Contaminants by AOPs

Several organic contaminants, such as chlorinated congeners, persistent organic pollutants (POPs), and pesticides, are existing in aquatic and terrestrial environments.[48] There are various mechanisms such as complexation, reduction, oxidation, dichlorination, and sorption, which are involved in removal of organic pollutants by BCs and BC-supported-catalysts,[10,24,65] as depicted in **Figure 4**. Adsorption can only remove the pollutants by allocating them from one medium to another. Comparatively, when BC-based composite materials are used as catalysts, contaminants can be easily mineralized or fragmented into smaller forms with lesser toxicity and improved degradability than its original form.[19] Therefore, BC/BC-supported materials as catalysts in degradation of organic contaminants are gaining attention these days. Huang et al. synthesized sludge-derived BC to activate PMS for degradation of pollutant.[66] Approximately 80% of bisphenol A (BPA) was mineralized within 30 min after application of the BC–PMS system. Generation of several free radicals is a prerequisite for degradation of pollutants via AOPs. The properties of BC in activation and generation of free radicals will be described in the following sections in detail.

4.1. Abundant OCFGs

BC comprises ample OCFGs throughout the surface. The distribution and abundance of OCFGs largely depend on the biomass feedstocks, pyrolytic temperature, and pyrolytic duration.[18,20] Overwhelming OCFGs on BC surface may significantly contribute to effective activation of PDS, PMS, and H_2O_2 to form reactive oxygen species (ROSs),[18,24] which give BC an efficient catalytic capability in Fenton-like systems. The generation procedure of ROSs is systematical displayed in Equations (1)–(4). In the beginning, PDS/PMS transforms to $SO_4^{\bullet-}$ by gaining electrons from OCFGs (Equations (1) and (2)); after that, $^{\bullet}OH$ can be produced by reaction of $SO_4^{\bullet-}$ with OH^- or H_2O (Equation (3)). The catalytic degradation of contaminants was mainly performed by the $SO_4^{\bullet-}$ and $^{\bullet}OH$ free radicals.[65] BC derived from sludge is full of OCFGs due to the presence of various metal components in sludge, which can trigger the activation of PDS/PMS to generate different oxidants.[65] The C—OH presenting on BC surface facilitates the decomposition of H_2O_2 into $^{\bullet}OH$ free radicals by liberating $^{\bullet}CO$ radicals (Equation (4)). Yan et al. reported effective degradation of trichloroethylene (TCE) from the generated $^{\bullet}CO$ and $^{\bullet}OH$ free radicals[24]

$$BC_{surface} - OOH + S_2O_8^{2-} \rightarrow BC_{surface} - {}^{\bullet}OO + SO_4^{\bullet-} + HSO_4^- \quad (1)$$

$$BC_{surface} - OH + S_2O_8^{2-} \rightarrow BC_{surface} - {}^{\bullet}O + SO_4^{\bullet-} + HSO_4^- \quad (2)$$

$$SO_4^{\bullet-} + H_2O_2/OH^- \rightarrow HSO_4^-/SO_4^{2-} + {}^{\bullet}OH \quad (3)$$

$$BC_{surface} - OH + H_2O_2 \rightarrow {}^{\bullet}CO + {}^{\bullet}OH + H_2O \quad (4)$$

4.2. Generation of Persistent Free Radicals

During biomass pyrolysis for synthesis of BC, plenty of phenol or quinone moieties are formed from the phenolic lignin component of biomass, and they can further participate in electron transfer to metals (mostly transition metals) to generate persistent free radicals (PFRs) on BC.[67] The generation of PFRs is mainly governed by the pyrolytic temperature and duration. Photocatalytic oxidation of contaminants is facilitated by PFRs, and PFRs participate in induction of ROSs in Fenton-like reaction.[68] PFRs also play an important role in generation of $^{\bullet}OH$ free radicals. Fang et al. investigated the importance of PFRs in H_2O_2 activation for generation of ROSs.[69] PFRs participated in catalytic decomposition of PDS/PMS to form $SO_4^{\bullet-}$ by electron transfer from PFRs to $S_2O_8^{2-}$.[70] Afterward, reaction between the $SO_4^{\bullet-}$ and H_2O or OH^- leads to the generation of $^{\bullet}OH$. Both diversity and the concentrations of PFRs encourage the generation of $SO_4^{\bullet-}$. Because of PFRs on the surface, BC is able to effectively catalyze the activation process of H_2O_2 and PDS/PMS.[18]

4.3. BC-Catalyzed AOPs

The degradation potency of BC was reported by several researches via activation of H_2O_2, for example, a pine-needle-derived BC that was proved to activate H_2O_2.[69] The degradation

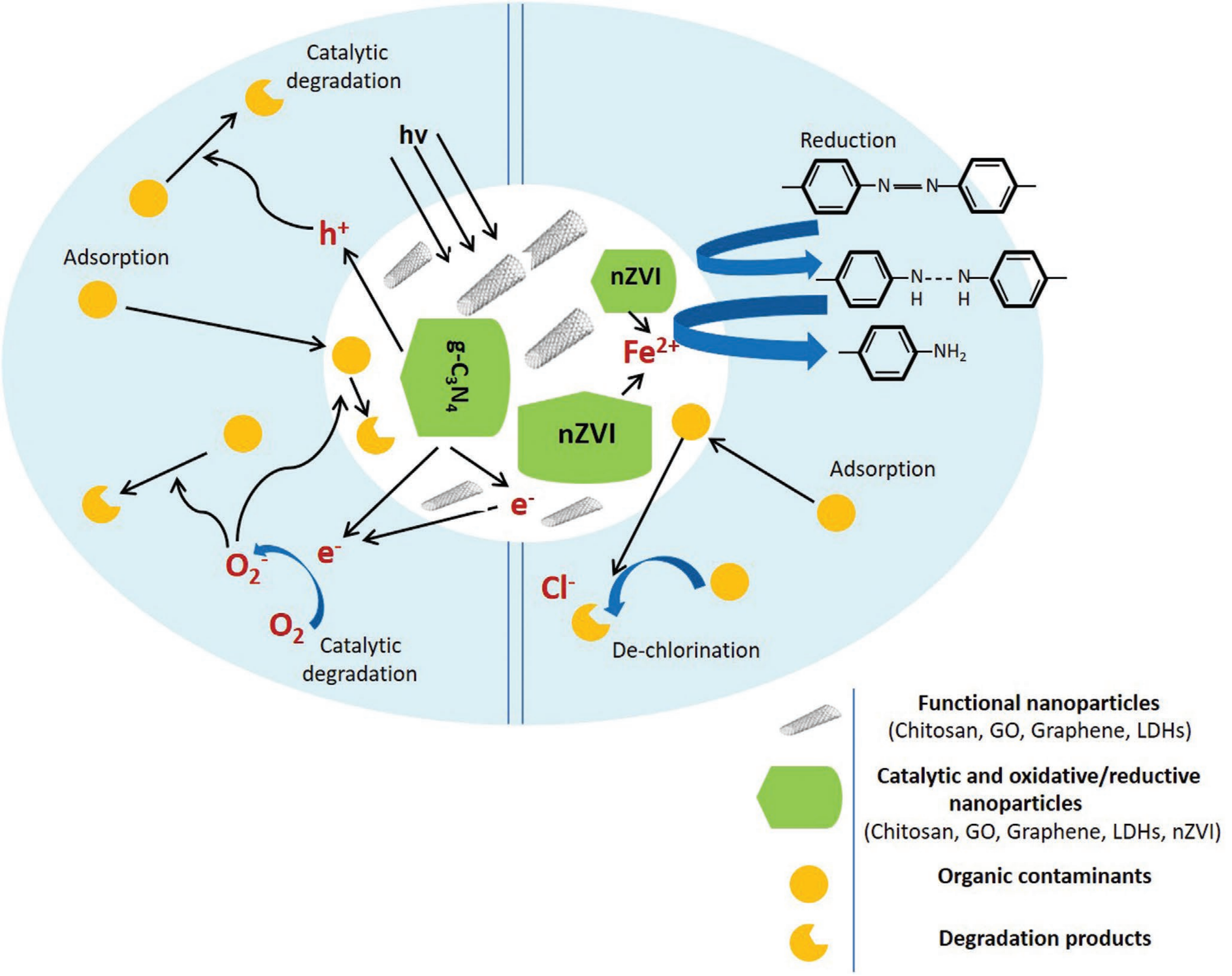

Figure 4. Simultaneous adsorption and degradation of organic contaminants catalyzed by oxidative /reductive nanoparticle-coated biochar. Reproduced with permission.[52] Copyright 2016, Elsevier.

efficacy of 2-chlorobiphenyl (2-CB) by H_2O_2 and BC systems separately was relatively low. However, when BC–H_2O_2 system was applied, the degradation potency was enhanced gradually. Liu et al. prepared a novel catalyst derived from sewage sludge (SS), applied it in the H_2O_2 aqueous system for degradation of norfloxacin (NOR) via the Fenton-like process, and reported 98.8% degradation[71] (**Table 1**). The synthesis temperature of BC plays a crucial role in the activation of H_2O_2.[28] The generation of $^{\bullet}OH$ from H_2O_2 increased gradually when the pyrolytic temperature gradually increased from 300 to 800 °C. Similarly, the trend of sulfamethazine (SMT) degradation also increased from 93.4% to 100%, with the degradation rate increasing from 0.0211 to 0.427 min^{-1}. This study suggested the importance of higher pyrolytic temperature in activation of H_2O_2-based system and improvement of ROSs' generation. Several researches also reported that the AOPs based on the $^{\bullet}OH$ system showed better degradation efficiency of diverse groups of organic emerging contaminants,[30,72] as summarized in Table 1.

Recently, noticeable advantages and importance of the $SO_4^{\bullet-}$ radical in AOPs have been investigated owing to its comparatively higher oxidation potential ($E^0 = 2.5–3.1$ V) than that of $^{\bullet}OH$ ($E^0 = 2.8$ V),[20] and its reaction with diverse groups of contaminants.[90] In addition, $SO_4^{\bullet-}$ free radicals have longer lifetime (30–40 µs) in comparison to $^{\bullet}OH$ free radicals (0.02 µs), and they are able to degrade more pollutants.[91] Furthermore, their high solubility may lead to convenience in transportation and also can be applied as solid PMS/PDS oxidants. These days, different approaches have been applied in activation of PMS/PDS to generate radicals because of lower oxidation potential ($E^0 = 2.01$ V) of the PMS/PDS.[19,21] Owing to some novel characteristics of BC (discussed in Sections 4.1 and 4.2), recently, BCs are gaining more attention in activation of the PMS/PDS system (Table 1). Yu et al. used sludge-derived BC as catalyst for activation of the PMS system.[92] The findings revealed that PMS made negligible contribution to the generation of $SO_4^{\bullet-}$ radicals. In contrast, when BC was applied as the catalyst of the PMS system, the generation of $SO_4^{\bullet-}$ radicals was enhanced and the PMS concentration was simultaneously reduced. Additionally, more than 60% of dissolved organic carbon (DOC) was eliminated by the PMS–BC system. Obtained results showed

Table 1. Degradation and removal of environmental contaminants by biochar as catalyst/catalyst support by advanced oxidation processes.

Catalyst	Contaminant	Conditions	Activation/ mechanisms	Removal efficiency	Refs.
H_2O_2-based system					
Pine needles BC	2-chlorobiphenyl	$[H_2O_2] = 10$ mmol, BC = 1.0 g L^{-1}, pH = 7.4, 2-CB = 10.6 = 10^{-6} M	${}^{\bullet}OH$/Fenton-like degradation	100	[69]
Sewage sludge-derived char (SSBC)	Norfloxacin (NOR)	$H_2O_2 = 1.5$ mmol, SSBC = 1 g L^{-1}, NOR = 20 mg L^{-1}	${}^{\bullet}OH$/Fenton-like oxidation	98.8%	[71]
nZVI/BC	Trichloroethylene (TCE)	$[H_2O_2] = 1.5$ mmol, nZVI/BC = 1.13 g L^{-1}, pH = 6.2, TCE = 0.10 mmol L^{-1}	${}^{\bullet}OH$/Fenton-like oxidation	TCE = 98.9%, TOC = 78.2%	[24]
Magnetic biochar composite (MBC)	Methylene Blue (MB)	$[H_2O_2] = 1$ mL L^{-1}, MBC = 100 mg L^{-1}, MB = 100 mg L^{-1}	${}^{\bullet}OH$/Fenton-like reaction	COD = 47%, TOC = 49%	[30]
Fe-loaded rice husk biochar (Fe-RHB)	Acid red 1 (AR1)	$[H_2O_2] = 16$ mmol, Fe-RHB = 5 g L^{-1}, pH = 3, AR1 = 50 mg L^{-1}	${}^{\bullet}OH$/Fenton-like reaction	AR1 = 97.6%, TOC = 84.2%	[31]
Fe-loaded coir pitch BC (Fe-CPB)	Acid red 1 (AR1)	$[H_2O_2] = 16$ mmol, Fe-RHB = 4 g L^{-1}, pH = 3, AR1 = 50 mg L^{-1}	${}^{\bullet}OH$/Fenton-like reaction	AR1 = 99.1%, TOC = 86.7%	[31]
N-TiO_2–Fe_3O_4–BC	MB	$[H_2O_2] = 1.28$ mol L^{-1}, catalyst = 1 g L^{-1}, pH = 7, MB = 400 mg L^{-1}	${}^{\bullet}OH$, O_2^{2-}/adsorption, photodegradation, Fenton-like reaction	99.99%	[72]
nZVI/BC	Sulfamethazine (SMT)	$[H_2O_2] = 20$ mmol, SMT = 10 mg L^{-1}, pH = 3, nZVI/BC = 1.2 g L^{-1}	${}^{\bullet}OH$/sorption, Fenton-like degradation	74.0%	[28]
Iron sludge calcined at 600 °C (Fe-600)	Rhodamine B (RhB)	$[H_2O_2] = 10$ mmol L^{-1}, RhB = 10 mg L^{-1}, pH = 5.44, Fe-600 = 1 g L^{-1}	${}^{\bullet}OH$/Fenton-like degradation	99.0%	[73]
Fe-impregnated sugarcane biochar (FSB)	Orange G (OG)	$[H_2O_2] = 0.075$ g L^{-1}, OG = 0.1 g L^{-1}, pH = 5.5, FSB = 0.5 g L^{-1}	${}^{\bullet}OH$/Fenton-like degradation	99.7%	[74]
Sludge-derived porous carbon (SPC)	1-diazo-2-naphthol-4-sulfonic acid (1,2,4-Acid)	$H_2O_2 = 15$ mmol, 1,2,4-acid = 1×10^{-3} M, pH = 3, SPC = 0.5 g L^{-1}	${}^{\bullet}OH$/adsorption and Fenton-like degradation	94.0%	[75]
Magnetic sludge-based carbons (MSBCs)	Methyl orange (MO)	$H_2O_2 = 15$ mmol, MO = 1 mmol, pH = 3	${}^{\bullet}OH$/Fenton-like reaction	96.1%	[76]
PDS-based system					
Bamboo BC + Fe_3O_4	4-Nonylphenol (4-NP)	[PDS] = 0.23 mol, pH = 3, catalyst = 3.33 g L^{-1}	PDS-Fenton-like reaction	85.0%	[77]
Wheat straw-derived BC	*P*-Nitrophenol	$[PDS]_0 = 10$ mmol L^{-1}, *P*-nitrophenol = 10 mg L^{-1}, pH = 6.4, BC = 0.8 g L^{-1}	–	82.9%	[78]
Rice husk BC/nZVI	Nonylphenol (NP)	[PDS] = 5 mmol, NP = 20 mg L^{-1}, BC/nZVI = 4 g L^{-1}	$SO_4^{\bullet -}$ and ${}^{\bullet}OH$– Fenton-like degradation	96.2%	[79]
Pine needle BC +*n*Fe_3O_4	1,4-Dioxane	$[PDS]_0 = 8$ mmol, 1,4-dioxane = 20.0 µmol, BC +*n*Fe_3O_4 = 1 g L^{-1}	$SO_4^{\bullet -}$ and ${}^{\bullet}OH$–Fenton-like degradation	98.0%	[80]
Magnetic sludge-derived biochar (MSDBC)	Acid orange 7	[PDS] = 1.85 mmol, Acid orange 7 = 0.06 mol, pH = 5.22, MSDBC = 1 g L^{-1}	$SO_4^{\bullet -}$ and ${}^{\bullet}O^-$ Fenton-like degradation	98.1%	[81]
BC/nZVI	Bisphenol A (BPA)	[PDS] = 0.75 mmol, BC-nZVI = 1 g L^{-1}, pH = 3, BPA = 10 mg L^{-1}	Fenton-like reaction	>95.0%	[82]
nZVI/BC	TCE	[PDS] = 4.5 mmol, TCE = 0.15 mmol, nZVI/BC = 4.5 mmol L^{-1}	Fenton-like degradation	99.4%	[83]
Sludge-derived BC nanocomposites (SBCNs)	Orange G (OG)	[PDS] = 0.5 g L^{-1}, OG = 20 mg L^{-1}, SBCN = 0.2 g L^{-1}	PDS-based AOPs	95.0%	[84]
SBC	4-Chlorophenol	[PDS] = 1.85 mmol, 4-chlorophenol = 0.039 mmol, pH = 6.30, SBC = 1 g L^{-1}	Adsorption and AOPs	92.3%	[65]
SBC	SMX	[PDS] = 1.5 mmol L^{-1}, SMX = 40 µmol, pH = 5.0, SBC = 2.0 g L^{-1}	${}^{1}O_2$–assisted nonradical oxidation	94.6%	[85]
Anaerobic digestion sludge BC (ADSBC)	Sulfathiazole (STZ)	[PDS] = 10 mmol, STZ = 20 mg L^{-1}, ADSBC = 0.5 g L^{-1}	Nonradical pathway via electron transfer	100%	[86]

Table 1. Continued.

Catalyst	Contaminant	Conditions	Activation/ mechanisms	Removal efficiency	Refs.
N-doped BC (N-BC900)	Phenol, SMX, and BPA	[PDS] = 2 mmol, BPA = 20 mg L^{-1}, phenol = 20 mg L^{-1}, N-BC900 = 0.2 g L^{-1}	Nonradical oxidation	100%	[22]
N-doped BCs (NBCs)	Sulfadiazine (SDZ)	[PDS] = 0.25–3.0 mmol, SDZ = 1–50 µmol, pH = 3–11, NBC = 0.5–3.0 g L^{-1}	$^1O_2$-dominated nonradical pathway via electron transfer	85.6–97.1%	[87]
PMS-based system					
Fe-functionalized biochar composite (Fe-BC)	BPA	[PMS] = 0.2 g L^{-1}, BPA = 20 mg L^{-1}, pH = 8.2, Fe–BC = 0.15 g L^{-1}	PMS-based AOPs	100%	[88]
Sludge BC (SBC)	BPA	[PMS] = 0.1 g L^{-1}, BPA = 10 mg L^{-1}, SBC = 0.2 g L^{-1}	PMS-based AOPs	TOC = 80.0%	[66]
SBC	Triclosan (TCS)	[PMS] = 0.8 mmol, TCS = 0.034 mmol, SBS = 1 g L^{-1}, pH = 7.2	PMS-based AOPs	TOC = 32.5%	[18]
$MnFe_2O_4$/BC	Orange II	[PMS] = 0.5 g L^{-1}, Orange II = 20 mg L^{-1}, pH = 5.8, $MnFe_2O_4$/BC = 0.05 g L^{-1}	$SO_4^{\bullet-}$,$^{\bullet}OH$, and $^1O_2$ nonradical degradation	93.0%	[89]

that BC could efficiently participate in activation of PMS toward generation of $SO_4^{\bullet-}$ radicals. Further, catalytic performance of rice straw BC (RSBC) was evaluated by Wu et al.[93] The results established the degradation of aniline RSBC via PDS activation. Nearly 94.1% degradation efficiency was achieved by this system. Moreover, higher mineralization efficiency and total organic carbon (TOC) removal were attained within 80 min.

Nowadays, PMS/PDS-based AOPs are gaining much attention in degradation of various organic pollutants.[94–96] Predominantly, due to its lower cost, better solubility, higher redox potential, and improved stability in comparison to PMS, PDS has been propelled for in situ remediation of soil and removal of water pollutants.[97] The PDS system generated strong ROSs via efficient activation processes such as photolytic, sonolytic, thermal, and transition metal-assisted activation.[82,85] Among all the transition metals that assisted PDS activation, Fe^{2+}-assisted activation is considered as the most reliable and efficient methods for homogeneous PDS activation.[98] Nevertheless, various limitations of the above-mentioned techniques have subsequently been reported, such as leaching of toxic metals ion resulting in secondary pollutants' generation, energy intensiveness, and poor steadiness of the materials.[99] Additionally, there have been various opinions regarding the mechanism of PDS activation. Generation of some radicals or nonradical oxidant species by PDS activation may lead to degradation of pollutants by the radical and nonradical AOPs.[85] The general route of PDS activation is assisted by the $SO_4^{\bullet-}$ or $^{\bullet}OH$ radical oxidation. The emergence of nonradical activation of PDS system was acknowledged recently, with better performance in comparison to radical-based oxidation pathways.[99] A study on thermal-activated PDS systems reported generation of the predominant $SO_4^{\bullet-}$ radical for degradation of organic contaminants.[100] On the contrary, Zhang et al. reported that the activation of PDS system by CuO can degrade the water contaminants via nonradical oxidation process.[101] In addition, combined radical and nonradical mechanism for degradation of emerging contaminants was reported by applying nitrogen-doped bamboo-like CNTs with Ni-encapsulated materials.[87]

As for BC application in the activation of PDS, selection of the proper feedstock is a prerequisite condition. The utilization of SS as feedstock for synthesis of BCs is gaining much more attention these days due to its cost-effectiveness and waste management.[72,81] Since SS contains a huge quantity of biomass, some transition metal species including Fe, and some other active stuff, it would be a better choice for BC synthesis for the PDS system.[102] Wang et al. adopted the sludge-derived biochar (SDBC)/PDS system for degradation of 4-chlorophenol with excellent performance via simultaneous adsorption and degradation[65] (Table 1). Similarly, a ZVI–SDBC composite was successfully fabricated from municipal sewage sludge without external Fe doping, and demonstrated excellent performance in removal of acid orange (AO7), TOC, and ammonia in the presence of PDS via both radical and nonradical routes.[103] Recently, SDBC has been applied by Yin et al. for degradation of sulfamethoxazole (SMX) via the SDBC/PDS system.[85] According to them, SDBC alone can remove up to 16.5% SMX, while 10.1% was eliminated via direct oxidation by PDS alone. When the SDBC/PDS system was applied together, the drastic enhancement in degradation (94.6%) of SMX was observed, which would be due to activation of PDS by SDBC (Table 1). The rate constant of SDBC/PDS system was 48.3 times higher than the PDS and the SDBC system. Yin et al. also described that N-doping and Fe-loading into the carbon matrix might form the imperative active sites for degradation of SMX by the graphene-like SDBC material via the PDS system.[85] More importantly, in the SDBC/PDS system, in comparison to the frequently generated $SO_4^{\bullet-}$ or $^{\bullet}OH$ free radicals, singlet oxygen ($^1O_2$) was the principal reactive species. This finding might lead to a novel nonradical oxidation pathway by the SDBC/PDS system.

4.4. BC-Composites Catalyzed AOPs

Application of transition metals as catalytic agents in degradation of organic pollutants is gaining popularity recently.[19,80] Fe-based transition metal catalyst has been widely applied in the AOPs, because of its higher efficiency, less toxicity, and greener characteristics in comparison to other transition metals.[88,91] nZVI is considered as a possible alternative that generates Fe^{2+} ion, and it has been effectively applied in activation of $^{\bullet}OH$ free radicals for the catalytic degradation of diverse groups of organic contaminants.[28,71] Nevertheless, because of its strong magnetic interaction as well as high surface energy, nZVI leans to aggregate and forms microscale particles, leading to diminishing reactivity.[51,104] Due to large surface area, porous nature, and cost-effectiveness, BC has been considered as a catalyst support to stabilize nZVI,[105] which enhances the catalytic performance of nZVI.[51] For example, BC derived from rice hull (RHBC) at 350 °C was applied for activation of H_2O_2 via nZVI/BC composite by Yan et al.[24] The OCFG of BC and the Fe^{2+}/Fe^{3+} redox action of nZVI make this composite a virtuous catalyst for activation of H_2O_2. Also, lamellar-structural BC prevents agglomeration of loaded nZVI on its surface, leading to excellent activation efficiency of $^{\bullet}OH$ radicals. The degradation efficiency of TCE and TOC removal efficiency were also estimated by nZVI/BC–H_2O_2 system (Table 1). Yan et al. reported the PDS/PMS activation of nZVI/BC composite and its further application in degradation of TCE.[83] Owing to abundant OCFGs of BCs, which can mediate the electron transfer among Fe^{2+}/Fe^{3+} of nZVI, PDS/PMS can be efficiently activated, resulting in the generation of $SO_4^{\bullet-}$ and $^{\bullet}OH$.[106,107] The process of generation of $^{\bullet}OH$ and $SO_4^{\bullet-}$ by nZVI/BC composite has been described in Equations (5)–(8). Initially, degradation efficiency of TCE by the nZVI–PDS system was just 56.6%, but after deployment of the nZVI/BC composite, the degradation efficiency of TCE reached 99.4% within 5 min by nZVI/BC composite, due to the enhanced generation of $^{\bullet}OH$ and $SO_4^{\bullet-}$ (Table 1). The significant improvement established the importance of the nZVI/BC system in PDS activation[83]

$$Fe^0 + 2S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{\bullet-} + 2SO_4^{2-} \tag{5}$$

$$Fe^0 + S_2O_8^{2-} + 2H_2O \rightarrow 2SO_4^{2-} + Fe^{2+} + 2^{\bullet}OH + H^+ \tag{6}$$

$$BC_{surface} - OOH + S_2O_8^{2-} \rightarrow BC_{surface} - OO^{\bullet} + SO_4^{\bullet-} + HSO_4^- \tag{7}$$

$$BC_{surface} - OH + S_2O_8^{2-} \rightarrow BC_{surface} - ^{\bullet}O + SO_4^{\bullet-} + HSO_4^- \tag{8}$$

Magnetite (Fe_3O_4) is also considered as an alternate source of Fe^{2+}, which can be effectively applied with BC for the generation of $^{\bullet}OH$ free radicals. Ouyang et al. effectively applied the Fe_3O_4/BC composite to activate PDS and generate $SO_4^{\bullet-}$ and $^{\bullet}OH$ free radicals.[80] The generation of $SO_4^{\bullet-}$ and $^{\bullet}OH$ free radicals could be governed by the following three processes: 1) the available OCFGs on the surface of BC contributed to activation of PDS and subsequently generation of free radicals; 2) consistent ketonic or quinonic organic functional groups in BC were generated via the pinacol rearrangement process, which further participated in activation of PDS; and 3) Fe_3O_4 activated PDS via electron transfer from Fe^{2+} to PDS system. Almost 98.0% degradation of 1,4-dioxane was achieved within 120 min[80] (Table 1). They also reported the importance of pyrolytic temperature and mass ratio of Fe_3O_4 to BC in activation of PDS system. Heterogeneous Fenton-like degradation of MB by Fe_3O_4/BC via activation of H_2O_2 system was reported by Zhang et al.[30] When the pH of MB solution was <3, the degradation achieved almost 98%. Furthermore, practical application of Fe_3O_4/BC/H_2O_2 system was also demonstrated. The real wastewater treatment by this composite revealed 49 ± 2.7% and 47 ± 3.3% reduction of the TOC and chemical oxygen demand (COD), respectively, which established the importance of the Fe_3O_4/BC/H_2O_2 system (Table 1). Along with the Fe_3O_4/BC and nZVI/BC composites, various Fe-impregnated catalysts have been successfully applied in Fenton-like degradation of organic contaminants. Rubeena et al. successfully synthesized an iron-impregnated BC (Fe–BC) via the sonication method.[31] The Fe–BC/H_2O_2 system showed 99.1% degradation of acid red 1 (AR1), and almost 86.7% TOC removal efficiency was archived under the optimal conditions (Table 1). Furthermore, the Fe–BC system displayed much better stability and recyclability along with less leaching of Fe.

In addition to the most ubiquitous Fe- and Fe-oxide-incorporated BC, copper and titanium could provide unique strategies for producing metal–biochar with mild catalytic properties. Wan et al. recently proved that the Cu species on BC surface formed metastable oxyanion complexes, which directly oxidized oxyanion molecules and organic pollutants.[108] The incorporated Cu nanoparticles on BC surface also induced generation of $^1O_2$ benefiting from the graphitic BC structure. Similarly, Lu et al. prepared the TiO_2/BC composite for photocatalytic degradation of methyl orange. Increased decolorization and mineralization efficiency by 20.8% and 51.0%, respectively, were found at the optimized biochar-to-TiO_2 ratio.[109]

Moreover, N-functionalized BCs with N-doping were reported to be highly reactive in redox reactions with good catalytic performance in AOPs. For example, the N-doped graphitic BC derived from co-pyrolysis of reed mixed with urea under 900 °C enhanced the PDS activation via a nonradical two-electron process.[110] Ho et al. fabricated a novel N-doped BC from direct pyrolysis of C-phycocyanin extracted *Spirulina* residue under 900 °C. The inherent protein contents in algae provide self-doping of graphitic N, which contributed to efficient electron transfer to PDS molecules.[111]

5. Application of BC Catalyst in Biorefinery

To substitute the traditional chemical production involving petrochemical processes, thermochemical conversions of biomass into diverse ranges of chemicals and biofuels are gaining much more attention these days, as shown in **Figure 5**. BC is playing a significant role as catalyst in various fields, the list of which is continuously increasing.[5,6,50] The additional efforts done to study the activation and functionalization of this carbonaceous material have revealed its chemical stability and possibility of modified structural properties, which make it an appropriate catalyst/catalyst support.[7,10] Depending upon the usage of BC, its surface chemistry can be altered to act as catalyst/catalyst support for biomass hydrolysis, bio-oil upgrading, catalytic esterification, bio-syngas reforming, and biodiesel production.[7,9,10]

5.1. BC as Catalyst in Production of Biodiesel

Biodiesel is a renewable fossil source with properties similar to fossil diesel but with additional advantages of no toxicity and environmentally friendly nature.[112–114] The production reaction involves esterification and transesterification of free fatty acids (FFAs) and vegetable oils with alcohols (commonly ethanol and

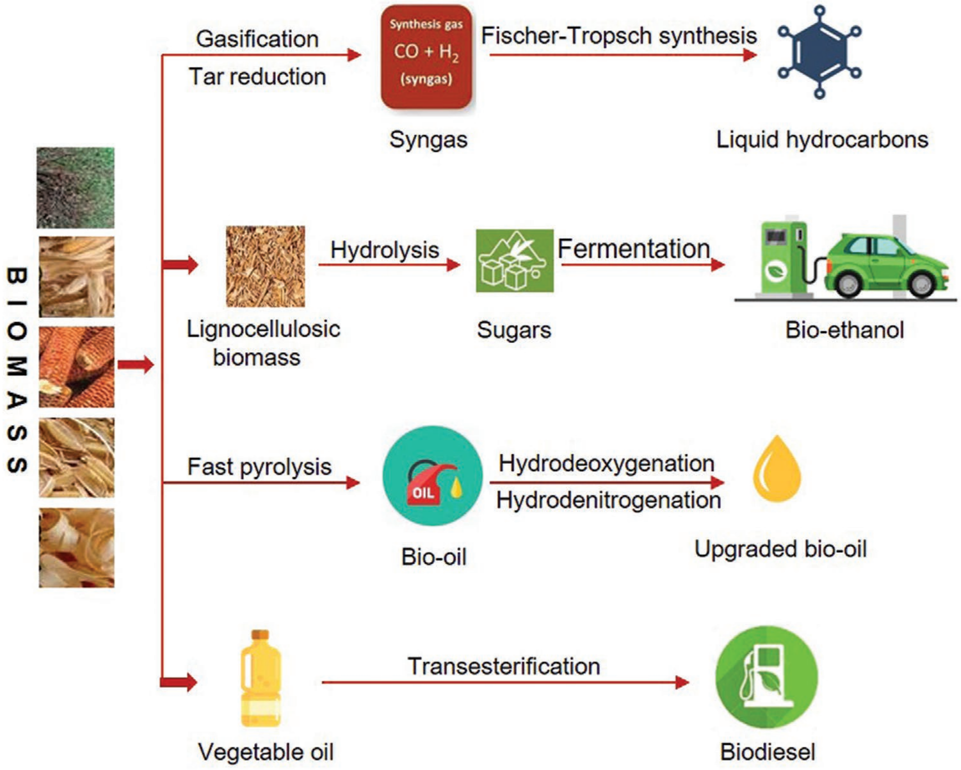

Figure 5. Primary conversion reactions of biomass to biofuels.

methanol) (**Figure 6**), respectively.[115–118] There are two sets of catalysts used during the process: homogeneous and heterogeneous. Homogeneous catalysts such as NaOH, KOH, and H_2SO_4 are easily available, but they have the limitations of poor recycling and product purification. Heterogeneous catalyst, for example MgO, $CaZrO_3$, ZnO, and CaO, can be used several times and are easily separated from products, but it comes with their own cost limitation as these metal oxide catalysts require expensive metal precursors.[9] To overcome the above-mentioned limitations, it was found that activated BC will be a good option as it can be applied as catalysts/catalyst supports for biodiesel production.[7,9,10] BC as catalysts are categorized as 1) solid acid catalysts and 2) solid alkali catalysts.

5.1.1. Solid Acid Catalysts

The conventional preparation of solid acid catalysts is done by sulfonating BC with gaseous SO_3 or liquid H_2SO_4 (Section 3). **Table 2** depicts the acid-catalyzed production of biodiesel

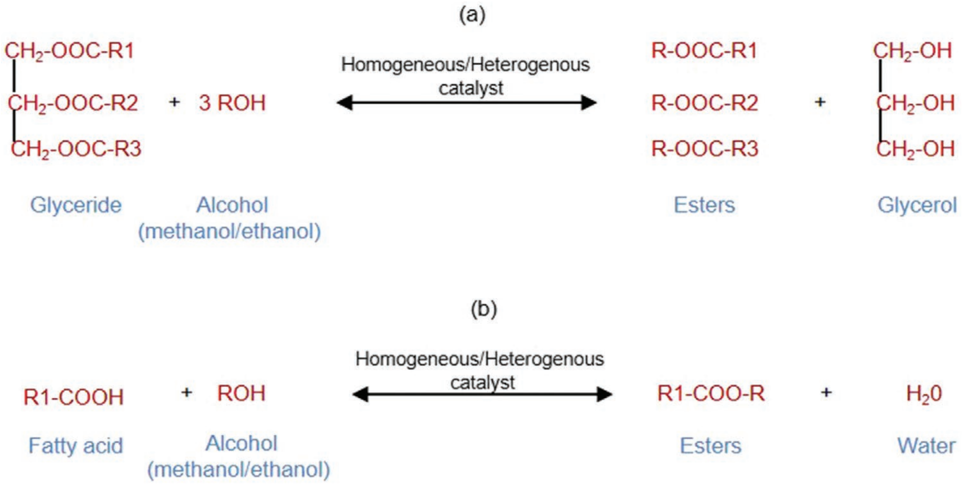

Figure 6. Reactions for biodiesel production: a) transesterification of glyceride with alcohol and b) esterification of fatty acid with alcohol.

Table 2. Biochar as catalyst for production of biodiesel/FAMEs.

Biochar feedstock	Synthesis and functionalization conditions	Reactants	Reaction conditions	Biodiesel/FAMEs yield [%]	Refs.
Maize residue	–	Waste cooking oil	300 °C, 50:1 alcohol:oil 2 w/v% catalyst	90	[119]
Oat hull biochar	Sulfonated with H_2SO_4, 100 °C for 30 min	Waste cooking oils	140 °C, 30 min, 10:1 alcohol:oil	28	[120]
Wood	Biochar activated with KOH at 675 °C; sulfonated with SO_3 at 150 °C for 15 h	Canola oil	150 °C, 3 h, 1.52 MPa, 15:1 alcohol:oil	44.2	[121]
Palm kernel shell	Calcination at 800 °C for 2 h, activated with CaO	Sunflower oil	65 °C, 9:1 alcohol:oil 3 wt% catalyst	99.8	[122]
Oat hull biochar	Sulfonated with H_2SO_4 140 °C for 30 min	Waste cooking oils	140 °C, 30 min alcohol:oil 10:1	72	[101,120]
–	Biochar, activated with KOH at 675 °C; sulfonated with SO_3 at 150 °C for 15 h	Canola oil and oleic acid	150 °C, 1.52 MPa, 3 h canola oil: oleic acid:ethanol 3:1:30	48.1	[123]
Rice husk	Sulfonated with H_2SO_4	Waste cooking oil	110 °C, alcohol:oil 20:1, 5 wt% catalyst	87.57	[124]
–	Biochar sulfonated with H_2SO_4 at 150 °C for 24 h	Vegetable oils	60 °C, 3 h, alcohol:oil 18:1	77–89	[125]
Coconut shell	Carbonized at 422 °C (4 h), sulfonated with conc. H_2SO_4 at 100 °C for 15 h	Palm oil	60 °C, 6 h, alcohol:oil 30:1	88.15	[126]
Glucose	Biochar sulfonated with H_2SO_4 at 160 °C for 12 h	Palm fatty acid	65 °C, 134 min, alcohol:oil 12.2:1	92.4	[127]
Rice husk	Biochar sulfonated with H_2SO_4 at 70–150 °C for 0.25–4 h	Oleic acid	110 °C, 2 h, alcohol:oil 4:1	98.7	[128]
–	Waste egg shells as CaO source, fly ash as support, wet-impregnation method	Soybean oil	70 °C, 5 h, alcohol:oil 6.9:1	96.97	[129]
Corn straw	Biochar sulfonated with fuming H_2SO_4 at 180 °C for 4 h	Oleic acid	60 °C, 4 h, alcohol:oil 7:1	98	[130]
Glucose–starch mixture	Biochar sulfonated with H_2SO_4 at 150 °C for 5 h	Cotton seed oil	80 °C, 12 h, alcohol:oil 20:1	>80	[131]
Bovine bone waste	Calcined at 750 °C for 6 h	Soybean oil	65 °C, 3 h, alcohol:oil 6:1	97	[132]
Peat	Biochar loaded with K_2CO_3	Palm oil	65 °C, 1.5 h, alcohol:oil 8:1	95.2–98.6	[133]
–	Carbonized at 350 °C and functionalized with $CaCO_3$	Waste cooking oil	350 °C, alcohol:oil 20:1	95	[134]
Flamboyant pods	Biochar Impregnated in KOH solution	*Hevea brasiliensis* oil	60 °C, 1 h, alcohol:oil 15:1	89.3	[135]

and its yield. In a study conducted by Zeng et al., a partially carbonized peanut shell was sulfonated to synthesize a solid acid catalyst with a stronger acid strength than HZSM-5 (Si/Al = 75). Following this, the same catalyst was used to transesterify cottonseed oil with methanol, where it was observed a significant reusability and a conversion rate of 90.2%.[136] Employing waste or low-grade oils containing high amount of FFAs in the process hampers the reaction rate and decreases the yield, which urges the need for efficient catalysts to promote esterification and transesterification simultaneously.[35,137] This was achieved by Dehkhoda and Ellis, who synthesized a catalyst to esterify and transesterify a mixture of oleic acid and canola oil simultaneously at 1.52 MPa and 150 °C. With the condition of maintaining an appropriate concentration of three reactants, the yield of alkyl ester was expected to be 48% in 3 h.[123] The BC-based acid catalysts are gaining much attention as their efficiency rate is quite comparable to conventional acid catalyst, and they have a wider scope of modifications, which increases their field of application. This has been recently quoted by Dawodu et al., who observed 99.0% conversion of nonedible seed oil, *Calophyllum inophyllum* (15% FFAs), using a sulfonated BC catalyst.[138] González et al. used a microwave reactor to prepare a sulfonated catalyst with $-SO_3H$ groups and used to esterify and transesterify waste cooking oil, resulting in 75% methyl ester yield in 15 min.[120]

There are different parameters that govern the functioning of a BC-based acid catalyst, such as $-SO_3H$ leaching, BC characteristics, crude oil impurities, and the number as well as accessibility of active acid sites. Among these, the number of active acid sites is a significant factor to determine the efficiency of catalytic activity. It was concluded that the number of $-SO_3H$ groups is directly proportional to the yield of biodiesel.[120] Similar observation was obtained in another study, where the catalytic efficiency increased with the number of acid sites, but this also demanded a BC with high porosity and large surface area.[9] Zaccheria and Nicoletta found that intrinsic acidic groups of BC also accounted for the total number of active acid sites.[139] There are other parameters, for example, carbonization conditions, that can affect the surface-active groups and surface area, which eventually affect the transesterification rate and efficiency. Carbonization temperature is directly proportional to the surface area, but it shows inverse proportion to total acid density.[139] Increase in carbonization temperature also increases the rigidity of the BC carbon sheet, ultimately hampering the inclusion of $-SO_3H$ groups. This can be concluded that a moderate temperature (600–700 °C) is most suitable for preparing an efficient acid catalyst from BC. This is consistent with an observation that an optimized catalytic performance was found from a BC catalyst carbonized at 675 °C rather than those at 450 or 875 °C.[140] Therefore, a partially carbonized BC at moderate physical conditions usually favors for synthesizing solid acid catalysts.[141] In another study, canola oil was transesterified by BC acid catalyst sulfonated from two different forms of acid.[106] The catalytic activity of the catalyst sulfonated with fuming H_2SO_4 was higher in comparison to the one treated with concentrated H_2SO_4. Kastner et al. validated that BC sulfonated with SO_3 (gaseous) at 23 °C returned a greater $-SO_3H$ density than with conc. H_2SO_4 at 100 °C.[142] This concluded that sulfonation conditions involving reagent and their properties also have an impact on formation of active sites and thus transesterification activity.[120]

Leaching of $-SO_3H$ is a significant cause for the loss of catalytic activity. A hydrated sulfonic group is easily leached down as H_2SO_4 in an aqueous system, and can be stabilized by using a hydrophobic BC matrix that will avoid the hydration of $-SO_3H$ group.[143,144] Additionally, the presence of different electron-withdrawing groups such as carboxylic acid ($-COOH$) can increase the electron density strength between carbon and sulfur, which will eventually decrease the leaching rate.[139] On the contrary, impurities (such as phospholipids and chlorophyll) of crude oil as well as FFAs and water content of vegetable oils lead to leaching and decreasing the catalytic efficiency of the acid catalysts for the transesterification process.[9,141,145] In addition to organic contaminants, inorganic elements present in microalgae-derived BC such as chlorine (Cl) and phosphorous (P) also potentially disrupt the catalytic performance and impair biodiesel quality.[145] To avoid all these disrupting contaminations, it is suggested that biodiesel production should always be succeeded with crude oil refinement.[145]

5.1.2. Solid Alkali Catalysts

Biodiesel production can also be assisted by biomass-derived and BC-supported solid alkali catalysts. Table 2 lists their catalytic efficiency and potential yield of biodiesel/fatty acid methyl esters (FAMEs). In a research conducted by Kostic et al. and Bazargan et al., $CaCO_3$-rich palm kernel shell was used to synthesize a CaO–BC catalyst, which can be reused for three repeated cycles with no substantial activity loss.[122,146] When CaO (3 wt%) was used in a combination with a methanol-to-oil ratio of 9:1, it achieved 99% methanolysis of sunflower oil at 65 °C. It was realized that CaO was showing a good catalytic efficiency, so efforts were made to produce CaO–BC composite catalyst using a cost-effective substrate. Cost-effective substrates such as crab shell and bovine bone waste were used to synthesize CaO–BC catalysts through calcination, and soon they became a striking alternative to existing transesterification catalyst systems with good reusability and high biodiesel yield (94% and 97%, respectively).[132,147] Other molecular compounds such as K_2CO_3 or KOH were also applied to produce potent catalysts.[9] Flamboyant pods were impregnated with KOH to form a BC-assisted KOH catalyst, which was used to transesterify *Hevea brasiliensis* oil and attained 89.3% biodiesel yield.[135] Similarly, Wang et al. used the wet impregnation method to create a peat-BC-supported K_2CO_3 catalyst.[133] Maximum biodiesel yield (98.6%) was achieved at 30% K_2CO_3 loading and 600 °C activation temperature (Table 2).

5.2. Catalytic Conversion of Lignocellulosic Biomass into Value-Added Chemicals

Lignocellulosic biomass is an excellent raw material comprising of aromatic (lignin) and carbohydrate polymers (cellulose and hemicellulose), while the inter- and intramolecular hydrogen bonding interactions occurring between the components assist in the formation of platform chemicals and value-added products such as biofuels (Figure 5). The conversion and valorization of lignocellulosic biomass occur over a series of transformation reactions such as hydrolysis, isomerization, dehydration, and rehydration, which are found to be facile using a BC-based catalyst (**Table 3**).[7,10,148]

5.2.1. BC as Catalyst in Hydrolysis of Biomass

Biomass hydrolysis is an initial step to convert biomass to its catabolic components, monosaccharides, or oligosaccharides, which will be eventually transformed to platform chemicals (e.g., furfural (FF)) and biofuel (e.g., ethanol).[158,159] Hydrolysis is catalyzed by various solid acids, liquid mineral acids, and enzymes. For example, Brønsted acid catalyzes biomass hydrolysis within 90–260 °C.[33,160] According to Zhou et al. and

Table 3. Biochar-assisted catalytic conversion of lignocellulosic biomass into value-added chemicals and products.

BC	Functionalization	Reaction conditions and solvent	Feedstock	Yield [%]	Conversion [%]	Refs.
Corn stover BC	Sulfonated with H_2SO_4 at 150 °C for 15 h	170 °C, 1 h, dichloromethane/water	Perhydrolysate of corncob	81.1 (FF)	–	[149]
Bamboo BC	Sulfonic acid functionalization	80 °C, 3 h, Water	Cellulose	27.9 (HMF)	–	[32]
Bamboo BC	Ionic liquid (IL)–Zn functionalization	100 °C, 2 h, dimethylacetamide–LiCl/water	Cellulose	30.4 (HMF)	–	[150]
Corncob BC	Sulfonated with 0.5 м H_2SO_4 at room temperature for 24 h under the assistance of ultrasonic vibration	180 °C, 2.83 h, water	Corncob	37.8 (FF)	62.0 (xylan)	[151]
SnO_2–Co_3O_4/BC	SnO_2–Co_3O_4 (Sn/Co molar ratio was 0.5–4.0)	180 °C, 3.33 h, water	Corncob	30.0 (FF)	–	[152]
Bamboo BC	IL-Cu sulfonic acid functionalization	110 °C, 2 h, water	Cellulose	35.6 (TRS)	–	[153]
Bamboo BC cellulose	Functionalized by 80% H_2SO_4 at 80 °C for 3 h and 50 wt% SO_3 at 80 °C for 2 h	90 °C, 1 h, water	Cellulose	27.5 (TRS)	–	[154]
Bamboo BC	IL–sulfonic acid functionalization	90 °C, 3 h, water	Cellulose	34.9 (TRS)	–	[154]
Bamboo BC	Functionalized by concentrated H_2SO_4 at 180 °C for 12 h	150 °C, 0.45 h, water	Bamboo hemicellulose	55.7 (XOS)	–	[155]
Pine chip BC	Functionalized H_2SO_4 at 100 °C for 12–18 h	120 °C, 2 h, water	Birchwood xylan	–	85	[156]
Corn stover BC	Sulfonated with H_2SO_4 at 150 °C for 24 h	100 °C, 6 h, water	Corn stover, prairie cordgrass, and switch grass	–	67.9–80.5 (xylan) 18.8–21.8 (glucan)	[157]

Zhang et al., Brønsted acid releases its protons to attack the oxygen moiety of glycosidic linkage, and forms a cyclic carbonium ion that further accepts an OH ion to subsequently produce a mono- or oligosaccharide.[160,161] Mineral acids are quite difficult to recycle, while enzymatic hydrolysis is very expensive and limited to strict operating conditions. Comparatively, sulfonated BC is a promising alternative owing to its significant catalytic activity, inexpensive feasibility, better recyclability, and sustainable nature.[9,148] A typical example includes a BC acid catalyst prepared by Jiang et al. using hydrolyzed corncob residues that were used to hydrolyze corncob under microwave radiation.[162] It was observed that corncobs were efficiently hydrolyzed giving a yield of 100% arabinose, 77.3% xylose, and 34.6% glucose at 110–140 °C with the possibility of reusing the same catalyst three times with no substantial activity loss.

Li et al. examined the hydrolysis of prairie cord grass, switch grass, and corn stover using corn stover BC-based catalyst, and compared it with a similar concentration of H_2SO_4 as catalyst.[157] The results showed that BC solid acid catalyst was preferably more selective toward xylose, glucose, and total reducing sugar (TSR), and also depicted better glucan conversion as compared to H_2SO_4. In a similar study performed by Qi et al., HTC of sulfosalicylic acid and glucose was used to synthesize a BC-based solid catalyst employed in the cellulose hydrolysis in ionic liquid.[155] The study achieved a yield of 59.4% TSR in 3 h at 130 °C, which was not significantly reduced (57.4%) even after five recycle runs, concluding the catalyst stability and effectiveness. There are many examples quoted to validate the BC catalyst stability, for example, a sulfonated bamboo BC catalyst was used for transforming bamboo hemicelluloses into xylooligosaccharides (XOS) with a mass ratio of 1:200 for solid acid catalyst to water solvent. A yield of 54.7% XOS was achieved after 45 min at 150 °C (Table 3).[155] Liu et al. also prepared a sulfonated BC using saccharide and lignocellulose residues to study its effect on corncob hydrothermal degradation.[151] The study obtained 62% corncob conversion and 37.75% FF yield. The functional groups presenting on the surface of the BC play a significant role in determining its catalytic performance. For example, functional groups such as phenolic —OH and —COOH exhibit strong affinity to β-1,4-glycosidic bonds, which increases the accessibility of β-1,4-glucans to the sulfonate groups, performing an effective catalysis in hydrolysis.[10] Pore volume of BC also affects the catalytic activity. According to Ormsby et al., a higher turnover frequency for xylan hydrolysis was obtained using a BC catalyst with lower $-SO_3H$ density than using Amberlyst 15 (sulfonated commercial resin).[156] The reason was an appropriate volume and large surface area of the selected catalyst for xylan. Every parameter has a threshold value, and below or above and the active site feasibility is constrained; therefore, only the threshold value works properly for an optimized activity.

5.2.2. BC as Catalyst for Isomerization and Dehydration

BC can also catalyze other biomass valorization reactions including isomerization and dehydration. Once a BC is functionalized, it can be used to dehydrate glucose to 5-hydroxymethylfurfural (HMF) and/or isomerize glucose to fructose.[10,163] Zhang et al. prepared a sulfonated BC catalyst modified by ionic liquid, which showed 27.9% HMF yield and a moderate selectivity of 62% from cellulose at 80 °C within 3 h in water (Table 3).[32] The catalytic performance was credited to adducted ionic liquid, which increased acidity, accessibility, and thermal stability of the sulfonated groups. According to Kang et al., catalytic activity can be enhanced by altering the solvent. For example, lignin-based sulfonated hydrochar was used over inulin in ionic liquid for 60 min at 100 °C and gave a yield of 65% HMF, which is comparable to conventional solid acid catalysts such as sulfated zirconia and Amberlyst.[164] Similarly, Deng et al. hydrolyzed corncob using sulfonated BC in 60 h at 170 °C, which realized 81.1% FF yield in biphasic co-solvent (Table 3).[149] This allowed a significant furfural extraction in the organic phase, cutting off the humins formation, and increasing the furfural yield. After five subsequent runs, there was a decrease in the catalytic activity of BC from 81.0% to 24.6% due to the increase in the humins-to-catalyst ratio (94.0%) and decrease in $-SO_3H$ group density (91.4%). Therefore, to maintain an efficient performance of the catalyst, it should be regenerated in high concentration of sulfuric acid at temperature around 150 °C.

In addition to sulfonation, a BC catalyst can be impregnated with mineral ($SnO_2-Co_3O_4$) for increased efficiency. Liu et al. synthesized a mineral-adducted BC catalyst, which hydrolyzed corncob in water and formed 30% furfural at maximum.[152] Multivalent metals play an important role in isomerization and dehydration reactions. For example, they function as Lewis acid sites to isomerize xylose into an extra reactive xylulose followed by facile dehydration. In addition to providing Lewis acid sites, the metals also react with the OH ion of water and generate Brønsted acid, which facilitates hydrolysis of glycosidic bond of sugars (xylose) and dehydration of the transformed product (xylulose).[152] Therefore, Lewis and Brønsted acids proceed in a cooperative manner to activate all the required reactions and generate furfural efficiently. The catalytic conversion of biomass is exceptionally favored by the introduction of Lewis and Brønsted acids. The acid ratio is an important parameter to decide the selectivity and product yield. Research demonstrated that system components such as temperature and solvent also play a significant role in determining an optimized ratio of Brønsted to Lewis acid for HMF production from glucose over niobium oxides and zeolites.[33,165] According to Osatiashtiani et al., a bifunctional (acid and base) catalyst also gets affected by the acid-to-base ratio.[166] Additionally, this ratio also governs the direction of the reaction and avoids unessential side reactions.[167] Hence, important parameters during designing the active sites for BC catalysts include acid-to-base ratio, pore structure (decides substrate accessibility), etc.

Sulfonated carbons with hierarchically ordered macropores and mesopores (SCHOP) achieved higher fructose yield (100%) in 18 min than conventional sulfonated carbons with regular micropores (52.4%) and mesopores (71.9%).[168] Unlike the catalysis on meso- and microporous carbon, SCHOP allows movement between the macrochannels, which increases the contact between active sites and fructose, and thus assists the product separation. Though the mechanism is unknown, it has been found that the hierarchically ordered pore structure is efficient to increase the active site resistance against humins. Interestingly, an acidic mesoporous carbon (CMK-5) with small pore size (2.67–3.38 vs 7.5 nm) and less acid sites (0.9 vs 2.3 mmol g^{-1}) showed a turnover frequency (TOF) of 0.069 min^{-1} for dehydrating fructose to HMF, in comparison to silica-based catalyst (TOF = 0.048 min^{-1}).[144,169] It has been inferred that bimodal pore structure and higher surface area (616 vs 218 m^2 g^{-1}) of CMK-5 are responsible for its lower deactivation rate and more effective performance. The above findings and observations emphasize the importance of catalytic site positioning and pore structure for sustainable biomass valorization processes.

5.2.3. BC as Catalyst for Rehydration of Biomass

Along with hydrolysis, isomerization, dehydration, and rehydration (discussed in earlier sections) are also one of the processes to form different value-added products, such as levulinic acid (LA). LA is produced from cellulose degradation and is a potent precursor for the synthesis of polymers and fuels.[170] To the best of our knowledge, there are no available studies for LA synthesis using BC-based catalysts. However, during valorization of biomass using an activated BC for prolonged reaction time and increased temperature, LA acid was detected as a byproduct.[32,35] Potent candidates like inorganic salts (e.g., $FeCl_3$), mineral acids (e.g., HCl, H_2SO_4, and H_3PO_4), zeolites, and solid acid exhibit significant potential to give promising yield of LA.[35,170,171] Therefore, these functionalities can be altered to recognize BC application for facile synthesis of LA from biomass.

5.3. Tar Decomposition

Biomass obtained from different sources can be used to produce syngas through gasification. Syngas is a significant source of fuel and power, but its production process leads to generation of concentrated tars. According to Xiong et al., tar is a combination of aromatic hydrocarbons with molecular weight higher than benzene, which are formed from partial or thermal oxidation.[10] The composition and quantity of tar change with parameters such as feedstock, gasification conditions, and the type of gasifier. However, the most common composition of syngas tar includes benzene, phenol, styrene, toluene, naphthalene, and polyaromatic hydrocarbons (PAHs).[172,173] It has been a consistent problem to deal with the excessive tar formation. Traditionally, syngas cleaning was done through water scrubbing, filtration, catalytic, and thermal cracking, while currently catalytic removal of tar or transformation to syngas constituents is gaining significant attention.[172,174] Transformation and catalysis are more practical solutions than any thermal or physical treatment. There have been wide ranges of catalysts used in removing tar such as alkali metals, iron ores, dolomite, zeolites, calcined rocks, and Ni-supported and noble-metal-based catalysts.[175] Nickel-based catalysts show significant catalytic reactivity, due to which they are favored over others, but they are usually assisted with metal oxides (e.g., MgO and Al_2O_3) or natural substrates (e.g., olivine), which unfortunately make them unsustainable and expensive.[175–178] Interestingly, BC can be a fair alternative and work as a sustainable support for tar exclusion.[179] BC helps in dealing with excessive tar components using a catalytic procedure.[10] Mani et al. studied pink bark slowly pyrolyzed at 950 °C to synthesize BC capable of decomposing toluene, a principle tar component.[173] In comparison to thermal cracking, activation energy was decreased by fourfolds, and 94.0% conversion of toluene was achieved.

During the catalytic cracking of toluene at 900 °C, benzene was identified as an intermediary chemical with a selectivity of 28.0%. In comparison to BC, metal catalysts such as Ni/dolomite and Ni/olivine have higher tar removal rate, but BC's performance can be improved by attaching active metals on its surface.[157,162,175,180] Previous researches observed that the presence of different alkali metals such as Fe (significant contributor), Na, K, and Ca on the surface of a BC is responsible for its catalytic efficiency toward tar removal.[10,173,175] This was also reported by Kastner et al. when decomposing toluene using a Fe-supported BC catalyst at 600–900 °C.[50,53] With the increase in catalyst loading and temperature, the toluene decomposition and conversion rate were also linearly increased.[53]

5.4. Bio-Syngas Reforming

Syngas is produced from thermochemical conversion of biomass. It is a composite gaseous mixture of H_2, carbon monoxide (CO), CO_2, and volatile hydrocarbons. Bio-syngas can be used as an effective fuel source through its conversion to hydrocarbons such as alcohols and ethers.[10,172,181] The activation energy of syngas reforming process can be decreased in the presence of an effective catalyst, and carbonaceous materials are gaining a lot of attention. They possess easily modifiable surface and structural properties as well as chemical stability.[15] In a study performed by Yan et al., BC was used to produce carbon-encapsulated iron nanoparticles, which efficiently performed the Fischer–Tropsch synthesis.[182] The solid and gaseous products generated as a result of biomass thermochemical conversion can be applied for methanation.[183] Menéndez et al. studied the direct conversion of biogas to syngas. They employed coffee hulls to produce potassium-rich biochar pellets by pyrolysis via gasification of CO_2 and CH_4 (1:1 ratio).[184] The gasification process releases H_2 that increases due to the addition of BC support, because it has inorganic minerals with catalytic activity.[185,186]

5.5. Energy Storage and Conversion Device

With technological advances and needs, there is an alarming requirement for alternate energy sources. BC after activation can be used as energy storage and conversion device with high capacitance.[187] The conventional supercapacitors work on the availability of porous structure, while meso- and microporous have always shown an enhanced performance.[188,189] An activated microporous structure with a high surface area validates a superior capacitance activity.[190,191] The process of activating BC holds significant importance in deciding its activity efficiency. Gupta et al. have observed that as compared to an untreated BC, there was 2.8 times rise in the capacitance of BC activated with oxygen plasma attributed to broadly distributed pores and increased surface area.[191] Similarly, Dehkhoda et al. tested a BC activated with KOH for energy storage process and wastewater treatment by exploiting its capacitive deionization activity.[190] The electrodes of activated BC were applied to double-layer adsorption of NaOH/NaCl electrically, and it showed a high capacitance of 222–245 F g^{-1} owing to a microporous structure. With increased introduction of mesoporous structure, BC capacitance decreased to 182–240 F g^{-1}, but it showed an improved capacitive activity and substantial decrease in electrode resistance.[190] Along with modified pore structure, activated BC is chemically improved, which also enhances its application in supercapacitors. For example, a seven-time capacitance increase was reported for a BC activated with diluted HNO_3 (at room temperature).[188,192] The capacitance performance of activated BC has been found to be comparable and even superior than carbon materials such as graphene, commercial activated carbon, and CNTs; thus, BC can be a potent alternative for cost and environment friendly supercapacitors.[193–195] In another study, Koutcheiko and Vorontsov tested a physically activated BC as an electrode to measure the production and electrochemical characteristics of fabricated stack coin as single supercapacitors.[196] The activated carbon was found to be appropriate for supercapacitor electrode fabrication with 1200 mg g^{-1} iodine number (maximum) and 1500 m^2 g^{-1} Brunauer–Emmett–Teller surface area. Single coin supercapacitors displayed consistent and stable functioning with characteristics (3 F, <1 Ω equivalent series resistance) equivalent to commercial devices with similar size and forms.[196] A renewable BC thermally treated at 675 and 1000 °C and chemically activated with 7 M KOH was used in electric double layer (EDL) applications.[197] To evaluate the effectiveness and sustainability of the activated BC electrodes, the total capacitances were calculated and compared with expensive electrode systems using cyclic voltammetry analysis. It was realized that the total capacitance of BC systems was 50-fold greater than Vulcan electrodes and quite competitive with graphene-based and graphene electrodes. Additionally, Jin et al. also observed the superior performance of KOH-activated BC over commercial graphene, ordered mesoporous carbons, and general bioinspired activated carbons.[198]

6. Conclusions and Prospects

The current review emphasizes the importance of BC-based catalysts as a sustainable solution to overcoming the energy barrier of some reactions that are spontaneous at high temperatures. The effectiveness of BC as a potent catalyst can be enhanced by activation and/or functionalization processes by improving its physiochemical properties such as porosity, surface area, and functional groups. The introduction of active functional groups in BC increases its selective adsorption and rate of catalytic degradation. There are many potential catalytic applications of activated and functionalized BCs including organic pollutants degradation by AOPs and biorefinery. There are physicochemical parameters such as production conditions, biomass type, and activation or functionalization conditions, which govern the dynamic nature of activated BCs. BCs and BC composites have been extensively studied, but their productions and applications on industrial scale require more technoeconomic analysis. The commercial and environmental applications of BC are very sensitive for the biorefinery point of view. Type of feedstock, accessibility and transportation cost, capital and operational costs, taxation, BC types and its market demands, crop types and product prices, and biomass and biofuel logistics have major impacts on application of BC in biorefinery. Also, to make the BCs and BC composites practical for degradation of organic contaminants in soil and waste system by AOPs, cost is a crucial factor. In Fenton-like degradation, the utilization of oxidant incurred extra cost, specifically at the industrial level. For AOPs via photocatalysis, the major cost incurred includes operating cost, electricity cost, and cost involved in purchase of a xenon lamp. Similarly, in sonocatalytic AOPs, the major cost contains electricity consumption and purchase of an ultrasonic cleaning bath system, which increase the total cost of the process. To make BC/BC-supported catalysts a feasible option for AOPs at large scale, technoeconomic analysis is required in future researches. A life cycle analysis (LCA) for the BC production process (pyrolysis) and applications will help in evaluating the sustainability of the whole process. Additionally, the combined application of functionalized/activated BC in catalytic degradation along with biomass valorization is attracting a lot of attention. But still these researchers are at lab-scale only. This advantageous carbonaceous material demands more efforts and consideration to achieve co-production of BC and bioproducts from biomass at industrial level.

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Conflict of Interest

The authors declare no conflict of interest.

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