

Review Article

Recent Advances in Biochar-based Catalysts: Air Purification and Opportunities for Industrial Upscaling

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ABSTRACT The preparation of eco-friendly carbon-rich (biochar) materials by thermal pyrolysis of waste biomass has been recognized as one of the most economical and effective strategies for gas purification in recent years. Through control of synthesis and activation methods, the surface features and catalytic sites in biochar can be engineered for diverse heterogeneous catalytic reactions. Nonetheless, its commercial utilization in air pollution control has yet been limited to a large extent because of (i) the shortage of databases related to the actual catalytic performance of biochar and (ii) the complexity involved in industrial upscaling. Herein, the merits and demerits of biomass-to-biochar catalyst conversion are discussed, along with the factors to consider in the synthesis stage for enhancing catalytic activities toward air purification applications. This paper also offers an in-depth evaluation of the techno-economic and environmental aspects of biochar-based catalysts and their catalytic reactions for air pollution control and energy production. Lastly, a contemporary perspective is offered to help develop novel biochar-based catalysts for real-world applications in air purification fields.

KEY WORDS Biochar catalysts design, Heterogeneous catalysis, Air purification, Energy applications, Industrialization challenges, Sustainability

1. INTRODUCTION

The concept of waste-to-energy (WtE) is a smart technique used globally for waste management with a beneficial impact on both the economy and the environment. In particular, the gasification/pyrolysis of biomass wastes (as renewable resources) to generate heat, fuels (e.g., biogas, biodiesel, and bioethanol), or value-added economic products have attracted a good deal of research interest worldwide (Guo *et al.*, 2020; Balajii and Niju, 2019).

In the context of renewable resources, biomass materials include a variety of macromolecular organic matters (e.g., agriculture wastes, forest woods, sewage, and food products) with carbon, oxygen, and hydrogen as major elemental constituents. In the last five years, the global annual production of waste biomass was approximately 140 Gt, in which 580, 451, 682, 605, and 716 Mt (fresh weight)/year were generated by the European Union (EU) member states, Brazil, USA,

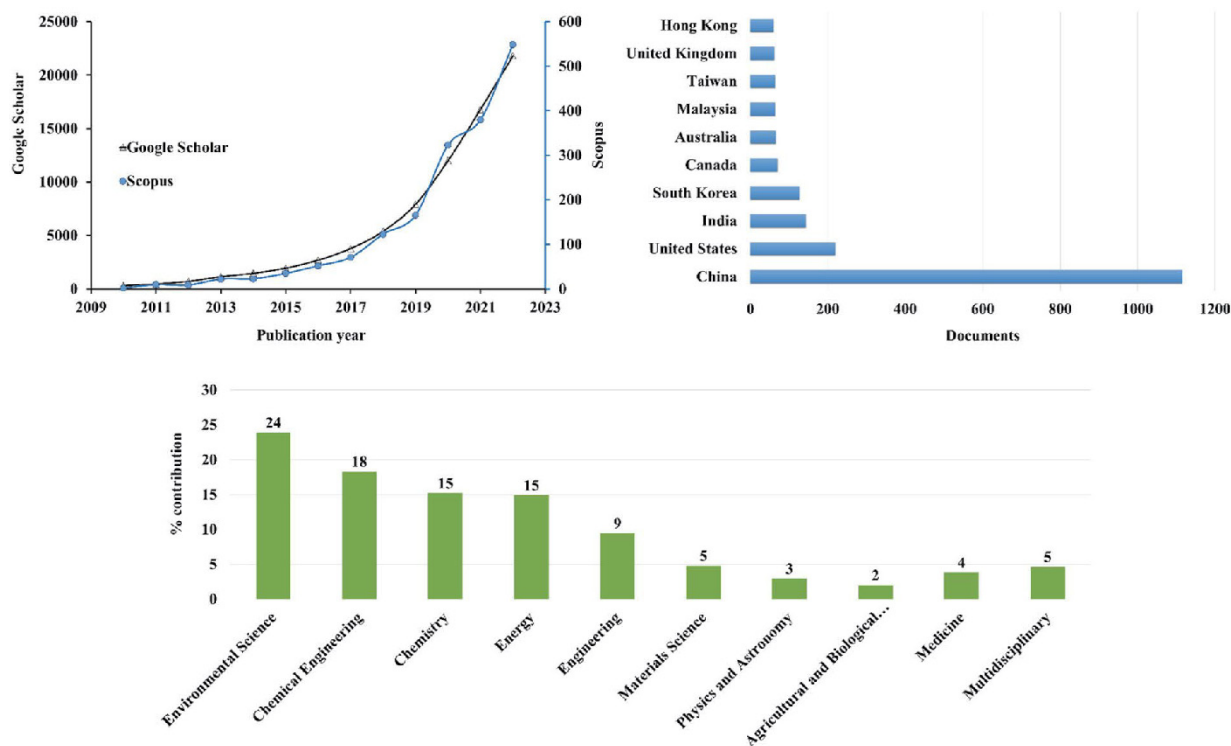


Fig. 1. Meta-analysis of the research databases (Google scholar and Scopus) available for publications with “Biochar” and “Biochar catalyst” as keyword indexes over the last decade (2010–2022).

India, and China, respectively (Casson Moreno *et al.*, 2020; Tripathi *et al.*, 2019). Such an issue is a significant management problem as it has high negative impacts on the economy and environment (e.g., > 2 Gt waste residue is burned, accounting for 18% of global CO₂ emissions). The direct/indirect conversion of biomass to bioenergy (or WtE) has been an appealing option to manage this problem, as it can account for an approximate share of 96%, 59%, 65%, and 65% of total primary energy supplies in 2019 for Africa, USA, EU, and Asia, respectively, based on global bioenergy statistics (GLOBAL BIOENERGY STATISTICS-World Bioenergy Association, 2019). However, it should be noted that two challenges are facing the current WtE management protocols: (i) environmental pollution like the high emission of greenhouse gases (GHGs) like CO₂ (> 47 Mt/year) and generation of high quantities of particulate ash/black carbons (Tripathi *et al.*, 2019) and (ii) high capital cost for the installation of WtE power plants (400 to 6,100 USD/kW), depending on the feedstock biomass cost, type of technology, and country/region (Ghosh, 2016). Hence, it is essential to

maximize the structure/efficiency of WtE power plant technologies to reduce CO₂ emission and bioenergy production costs at the same time. In this respect, the generated ash/black carbon residues are can be utilized as sustainable carbon-negative products to capture point-source CO₂ produced during the incineration process. The capital cost of bioenergy production can also be reduced by using sustainable, low-cost feedstock that can be generated onsite (such as black liquor in the papermaking industry) or transported over short distances (e.g., agriculture waste-byproducts collected from nearby farmland).

Thermo-chemical conversion of biomass wastes to biochar (BC) has become one of the most sustainable and effective protocols for the management/recycling of waste biomass in the last decade (Fig. 1). BC is a low-cost, sustainable, and eco-friendly porous carbon-rich solid with high chemical stability, low bulk density, tunable electrical/photonic responses, and abundant surface oxygen functional groups (OFGs; e.g., OH, C = O/C-O, and COOH) (Do Minh *et al.*, 2020). The main constituents of BC are carbon, hydrogen, oxygen,

and ash, with quantitative ranges of 60–89% (fixed aromatic carbon \approx 10.7–86.4%), 1–7%, 9–36%, and 0.2–40%, respectively. BC products also contain a good number of inorganic mineral elements (e.g., N, S, P, Na, K, Ca, Mg, Fe, Zn, Cd, As, Se, and Si) that exist as micronutrients in the raw feedstock biomass (Chen *et al.*, 2019; Liu *et al.*, 2015). The morphological structure of BC products is turbostratic graphite-like layers with porous networking structures. These inherent features of BC are strongly dependent on the raw biomass sources, activation methods, and pyrolysis conditions (e.g., characteristic features of yielded products). Accordingly, the recent progress in the synthesis and application of BC-based materials has been recognized in various fields (Fig. 1) such as agro/environment (Shaheen *et al.*, 2022; Younis *et al.*, 2021), adsorption/separation for environmental contaminants (Lee *et al.*, 2018; Xiong *et al.*, 2017), electrochemistry (Guo *et al.*, 2020), heterogeneous catalysis (Lee *et al.*, 2017), photocatalysis (Mian and Liu, 2018), air pollution control (Fawzy *et al.*, 2021; Gwenzi *et al.*, 2021, CO₂ capture and utilization (CCU) technologies (Guo *et al.*, 2022; Zhang *et al.*, 2022c), and energy storage/conversion (Bolan *et al.*, 2022; Liu *et al.*, 2019).

In particular, the development of BC-based catalysts has received global attention in the fields of biodiesel production, refinery (syngas cleaning/conversion), and air/water pollution control (Bolan *et al.*, 2022; Younis *et al.*, 2020). Recently, several research studies have been published to help boost the utilization of BC in those mentioned heterogeneous catalytic applications (Wang *et al.*, 2019; Cheng and Li, 2018; Xiong *et al.*, 2017). According to reports made by Grand View Research statistics (Size, 2020) and BCC Research (McWilliams, 2015), the global market for catalysts in environmental and energy fields is projected to reach \$35.8 billion in 2020, with an annual growth rate of 4.4% to 2027. This is due to the key role of catalysts in developing technologies to generate value-added chemical (or biorefinery) products and to control environmental pollution. Despite the potential utility of BC, most recent studies have been directed to the following key parameters: (i) the synthesis or post-synthesis modification strategies to derive BC-based catalysts and (ii) the interrelations between the physicochemical properties of BC materials and their catalytic performances in target catalytic reactions (Anto *et al.*, 2021; Do Minh *et al.*, 2020; Shan *et al.*, 2020). However, it was found that the techno-econom-

ic/fate-life cycle assessments of BC-based catalysts were rarely addressed when evaluating production scale-up (e.g., from lab- to industrial-scale) for solving global energy and environmental problems. To help expand our knowledge in this research field, the potential upgrade of BC-based catalysts as alternative low-cost commercial catalysts in environmental applications is discussed by highlighting: (i) biochar-based materials for air pollution control, (ii) the factors involved in the synthesis of BC catalysts and production scale-up, (iii) the pros and cons of BC-catalysts in heterogeneous catalysis (relative to traditional metal-based catalysts) for CCU technology, and (iv) the fate-life cycle and techno-economic aspects of BC catalysts during manufacturing and in applications.

2. ADVANCES IN BIOCHAR-BASED MATERIALS FOR AIR PURIFICATION

2.1 Mitigation of Volatile Organic Compounds (VOCs)

To date, biochar is considered one of the most commercially viable porous carbon materials in environmental pollution control with the aid of its unique physicochemical features (e.g., large surface area with good porosity, high cation exchange capacity (CEC), and high thermochemical stability). It is widely used as an effective adsorbent for the control of the emission of VOCs to the indoor/outdoor environment based on the two key mechanisms: adsorption and partitioning in carbonized/non-carbonized organic regimes, respectively (Yue *et al.*, 2021; Zhang *et al.*, 2017), as shown in Fig. 2. Likewise, the adsorption mechanism of VOCs over biochar could involve chemical (e.g., covalent and H-bondings) and/or physical mechanisms (e.g., dipole, Π , columbic, and hydrophobic interactions), depending on the interactive relationship between physiochemical properties of biochar and the nature of VOC adsorbates.

The applicability of biochar for the enhanced adsorption removal of VOCs from the atmosphere and/or gas flue is determined by (i) the factors affecting its textural (porosity), morphological, and chemical features (O/C and H/C molar ratios) such as the raw feedstock, pyrolysis/synthesis conditions, and surface modification and (ii) the operational parameters for VOCs adsorption (e.g., target VOCs, air/gas composition, bed temperature, bed height, humidity, and flow velocity). It should be noted that the O/C and H/C molar ratios could con-

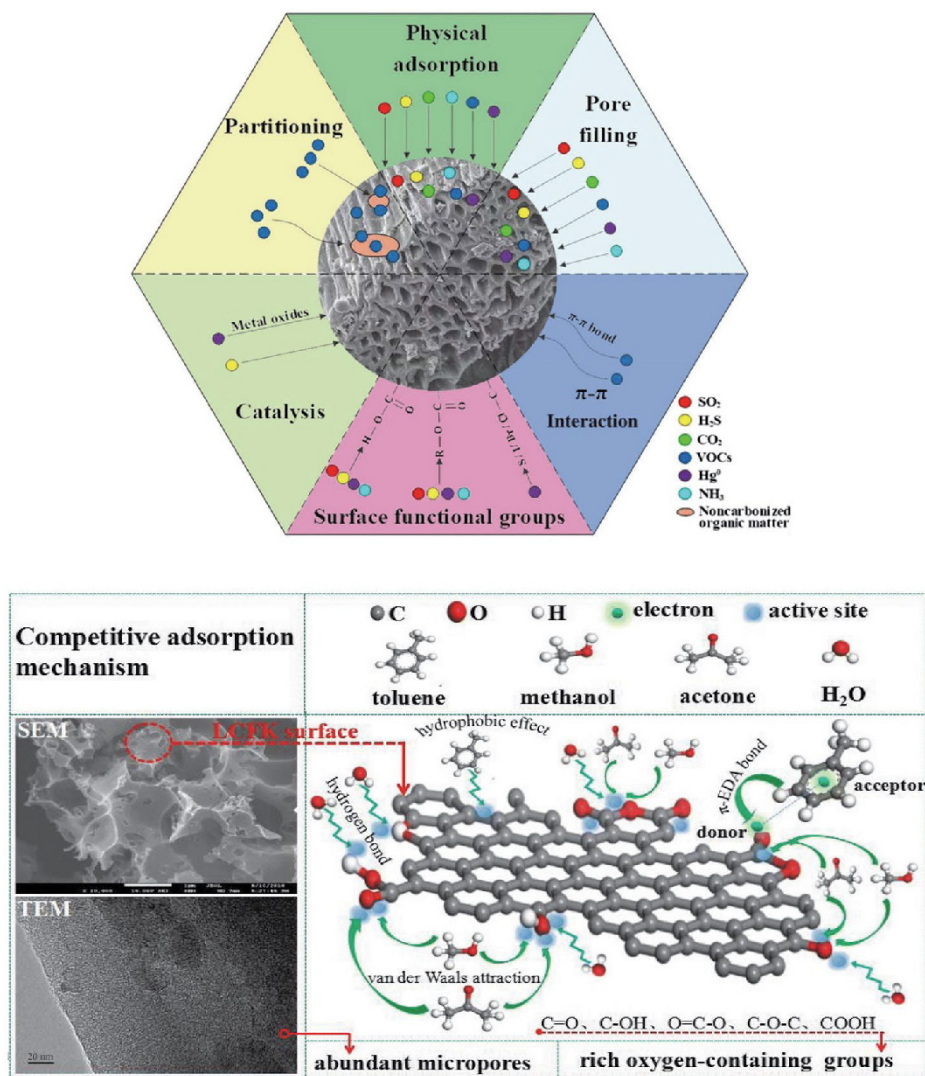


Fig. 2. The contribution of oxygen-containing surface functionalities and porosity of carbon adsorbents like biochar in the adsorption mechanisms of VOCs (Zhao *et al.*, 2022; Meng *et al.*, 2019).

control the adsorption selectivity of biochar for targeted VOCs as they refer to the polarity and quantization aromaticity levels of biochar. For example, altering the feedstocks could significantly affect the surface porosity and surface area of prepared biochars, even if they are synthesized at the same pyrolysis temperature. In this regard, the derived biochars from pine wood, hickory, cotton, corn straw, alfalfa, wheat straw, switchgrass, and rice husk at 600°C had different surface areas of 312, 256, 2.2, 61, 0.2, 182, 15, 168 m² g⁻¹, respectively (Yue *et al.*, 2021). An increased surface area and porosity could help biochar adsorbents to enhance the capacity for GHGs adsorption via the pore diffusion mechanism (Thangarajan *et al.*, 2018). Altering the feedstock from corn straw

to rice husk was reported to change the aromaticity level (H/C molar ratio) of derived biochar from 0.002 to 0.04. On the contrary, the biochar derived from switchgrass showed the highest surface polarity (O/C molar ratio of 0.37) compared with that of hickory wood biochar (O/C = 0.03) (Uchimiya *et al.*, 2010; Abe *et al.*, 2000). The surface polarity of biochar also decreased with a rise in the pyrolysis temperature due to the accelerated removal of oxygen-containing functional groups (OCFGs) (Monga *et al.*, 2022). As the surface polarity decreased, the aromaticity increased to promote the adsorption potential of hydrophobic VOCs. For instance, the effects of physicochemical properties on the adsorption applicability of different biochars (n = 15)

were assessed against varying types of polar and nonpolar VOCs (e.g., acetone, ethanol, methanol, cyclohexane, hexane, benzene, xylene, and toluene) (Yue *et al.*, 2021). Accordingly, an interactive relationship between surface area and the ratio of carbonized/non-carbonized organic matter was observed to be crucial to control their adsorption property against diverse VOCs. In particular, the adsorption affinity of biochar for polar VOCs (e.g., acetone) was maximized (capacity = 483.09 mg g⁻¹) via promoting pore diffusion and physical interactions in the adsorption mechanism along with increases in carbon pore structure and in non-carbonized organic matter (e.g., increase in O/C ratio) (Li *et al.*, 2012).

Among air pollution control strategies, the utilization of biochar to sequester and mitigate CO₂ in soils is well-reported in many reviews (Smith, 2016; Thomazini *et al.*, 2015). However, it was noted that the sorption capacity of pristine biochar for CO₂ was low via a weak physisorption mechanism (e.g., van der Waals forces). The affinity of biochar for CO₂ capture is greatly dependent on its physiochemical features such as surface porosity, hydrophobicity, aromaticity, and basicity (i.e., the content of Lewis base active sites). These physicochemical features of biochar could be adjusted by controlling the pyrolysis and/or synthesis conditions as well as the type of feedstock (Gwenzi *et al.*, 2021). Because of the low CO₂ affinity of pristine biochar, numerous studies have been focused on engineering its surface features (e.g., doping with metal oxides and heteroatoms) to improve CO₂ sequestering potential for industrial applications (i.e., from flue gases at high-temperature conditions). For instance, doping biochar with a basic nitrogen group was carried out to accelerate the uptake rate of CO₂ by approx. 55% relative to bare biochar (Xu *et al.*, 2019).

In light of the great potential of metallic constituents of biochar in the chemisorption of CO₂ and its transformation reaction, the catalytic oxidation/reduction reactions of such biochar-based composites have been studied against GHGs (like NO_x, SO_x, CO₂, and VOCs) under thermal and nonthermal (photo and plasma) conditions (Xu *et al.*, 2016). As such, compared to pristine biochar, engineered biochar-supported metal oxides have attracted great research interest as catalysts with enhanced chemisorption capacity for GHGs (e.g., CO₂) (Gwenzi *et al.*, 2021). A number of chemical and physical activation/modification methods have been applied to improve the catalytic efficiency of biochar catalysts in mitigating VOCs/GHG emissions as a prospective

solution to control the climate shift (Abhishek *et al.*, 2022; Do Minh *et al.*, 2020; Kumar *et al.*, 2020c).

As a good example, the intercalation of bone char with ZnO nanoparticles (nano-ZnO NPs) was reported to improve their photocatalytic activity towards the formaldehyde (2.5–25 mg m⁻³) to attain 75.5% of removal from the humidified indoor air (at 35% relative humidity) under ultraviolet light irradiation (Rezaee *et al.*, 2014). At higher humidity levels, the photocatalytic decomposition of formaldehyde by nano-ZnO@bone char decreased due to the competitive inhibition effects of water vapor for adsorption sites and a downward band bending of ZnO to increase the recombination rate of photogenerated charge carriers (i.e., the photoactivity decreased). A synthesized composite of biochar with g-C₃N₄ nanosheets by co-thermal pyrolysis of melamine and cellulose precursors also accelerated the photocatalytic removal rate of formaldehyde by 130% higher than that of pristine g-C₃N₄ nanosheets “Chrysanthemum” under visible light irradiation (Li *et al.*, 2019). Such observation was accounted for by the fact that the high electron storage capacity of biochar skeleton should be imparted by the π -conjugation system (as an effective electron acceptor) and improved charge carriers separation capacity (i.e., extended lifetime of excited electrons). In another study, doping a sawdust char (SDW) with MnO_x nanocatalyst was carried out to accelerate the oxidative destruction of toluene (89.7% after 100 min) (Cha *et al.*, 2022). The enhanced catalytic activity of MnO_x/SDW composite was accounted for by the high redox potential of Mn³⁺ and the abundance of Ov (vacancy oxygen)/OL (lattice oxygen) generated on the SDW surface upon doping. In summary, although some VOCs might release into the atmosphere during biochar formation, the engineered biochar with high adsorption/catalytic properties appears to be a promising candidate for the effective control of GHGs and VOCs emitted from industrial sectors (flue gases).

2.2 CO₂ Capture and Utilization (CCU Technology)

The chemical activation and doping of biochar (BC) with metal oxides played vital roles in CCU reactions (catalytic conversion of CO₂ to renewable fuels and other chemicals). Hence, over the last decade, the utility of multiple chemical agents has been investigated for the activation of BC materials, such as KOH, KHCO₃, and amine agents (Zhang *et al.*, 2022a; Chatterjee *et al.*, 2020,

2019; Ding and Liu, 2020). As the first step in the CCU technology involves CO₂ capture, these chemical activations were used to improve the textural features (microporosity and surface area) and surface functionalities (i.e. g., surface basicity and Lewis base sites) of BC materials for the enhancement of adsorption capacity toward CO₂. In the second step of CCU technology, the catalytic activity of BC materials is mainly considered with respect to the metal contents and properties (e.g., oxidation state, dispersion patterns, and morphological features) (Shrestha *et al.*, 2022).

In this respect, doping BC with metal oxides is a growing area of research interest for developing sustainable and cost-efficient catalysts from waste sources for the ultimate applications toward selective catalytic CO₂ reduction reactions (CO₂-RR). For example, biochar-ZnO composite has been prepared to have a stable and selective electrocatalytic activity in the CO₂-RR to CO (85.8%) at -1.09 V versus the RHE in a batch reactor (Lourenço *et al.*, 2021). Likewise, in light of the high carbon and energy density, biochars have been used as reducing agents to enhance CO₂-RR into O₂-free fuel gas (21.3–27.1%) in an atmospheric plasmatron via the Boudouard reaction (CO₂+C → 2CO, ΔH = 172 kJ mol⁻¹) (Zhang *et al.*, 2022b; Huang *et al.*, 2021). It is noted that the contribution of Boudouard reaction (i.e., in the presence of biochar) in the overall CO₂-RR under an atmospheric plasmatron is approx. >96.0%. Accordingly, the use of biochar in CO₂ splitting processes via Boudouard reaction in non-thermal plasmas could offer a more efficient route for the effective purification of industrial flue gases. Because the direct thermocatalytic reduction of CO₂ (CO₂ → CO+1/2O₂, ΔH = 280 kJ mol⁻¹) requires high thermal energy conditions (> 850°C at 1 atm) that can limit its flexibility of the scale.

The photocatalytic CO₂-RR over BC-based catalysts has also attracted research interest as one of the effective, inexpensive, and environmentally friendly strategies for CO₂ conversion to value-added solar fuels (e.g., HCO₂H, CH₂O, CH₄, and CH₃OH) under solar irradiation condition (Bhavani *et al.*, 2022; Lin *et al.*, 2022; Rangarajan *et al.*, 2022). Hence, several types of BC-based composite photocatalysts have been introduced in recent years to study their role in boosting CO₂-RR pathways. For instance, the developed BC-templated g-C₃N₄/Bi₂O₂CO₃/CoFe₂O₄ composite (BCBF) heterojunction showed promising photocatalytic activity for CO₂-RR into CH₄ (~119 μmol g⁻¹) and CO (~131

μmol g⁻¹) in 8 h under visible light irradiation (Kumar *et al.*, 2018). The boosted photocatalytic activity of BCBF is attributable to the uniform dispersion of Bi₂O₂CO₃/CoFe₂O₄ nanocatalysts with low bandgap energies (i.e., solar light harvester), high capability of g-C₃N₄ (with Lewis base sites) for CO₂ capture onto the catalytic surface, and the mediator role of BC template in reducing the electrons-holes (e⁻/h⁺) recombination rate (Fig. 3). In another study, the Ag-g-C₃N₄/biochar nanocomposite with a hollow bird's nest-like carbon (BN-C) structure was prepared with a selective photocatalytic CO₂-RR to CO at a production rate of 33.3 μmol h⁻¹ g⁻¹ which was far higher (e.g., by around three folds) than the pristine g-C₃N₄ counterpart (CO production rate of approx. 10.3 μmol h⁻¹ g⁻¹) under visible light (Li *et al.*, 2022). In this case, the high photocatalytic activity of the former was assigned to the localized surface plasmon resonance (LSPR) effect of Ag NPs to endow an efficient utilization of solar light energy and to produce more active "hot electrons. In addition, the co-existence of Ag NPs and conductive BN-like carbon structure may impart more surface active sites to enhance CO₂ capture, electron trap states, and charge separation efficiency, which, in turn, accelerates photo-induced electrons of g-C₃N₄ photocatalyst with great potential for the CCU process. Multiple Cu-doped hydrochar (Cu-HTCC) photocatalysts were also developed by hydrothermal carbonization (HTCC) of different biomass feeds (such as rice, straw, glucose, and cow dung) in the presence of CuSO (Hu and Liu, 2020). The developed Cu-HTCC photocatalysts exhibited an outstanding performance for catalytic conversion of CO₂ to CO, with a production rate of 564.8 to 643.5 μmol h⁻¹ g⁻¹, which is superior to the above-mentioned BCBF catalyst and 32-time higher than commercial P25-TiO₂ photocatalyst. The improved photoactivity of Cu-HTCC was accounted for by the HTCC sp²-hybridized structures that promoted catalytic reduction of CO₂ reduction with the enhanced solar light harvesting capacity (e.g., over Cu co-catalyst).

3. FACTORS AFFECTING BIOMASS-TO-BIOCHAR CONVERSION FOR CATALYTIC APPLICATIONS

Although the source materials and production methods of biochar are similar to activated carbon (AC), their distinctions are apparent. For example, the production

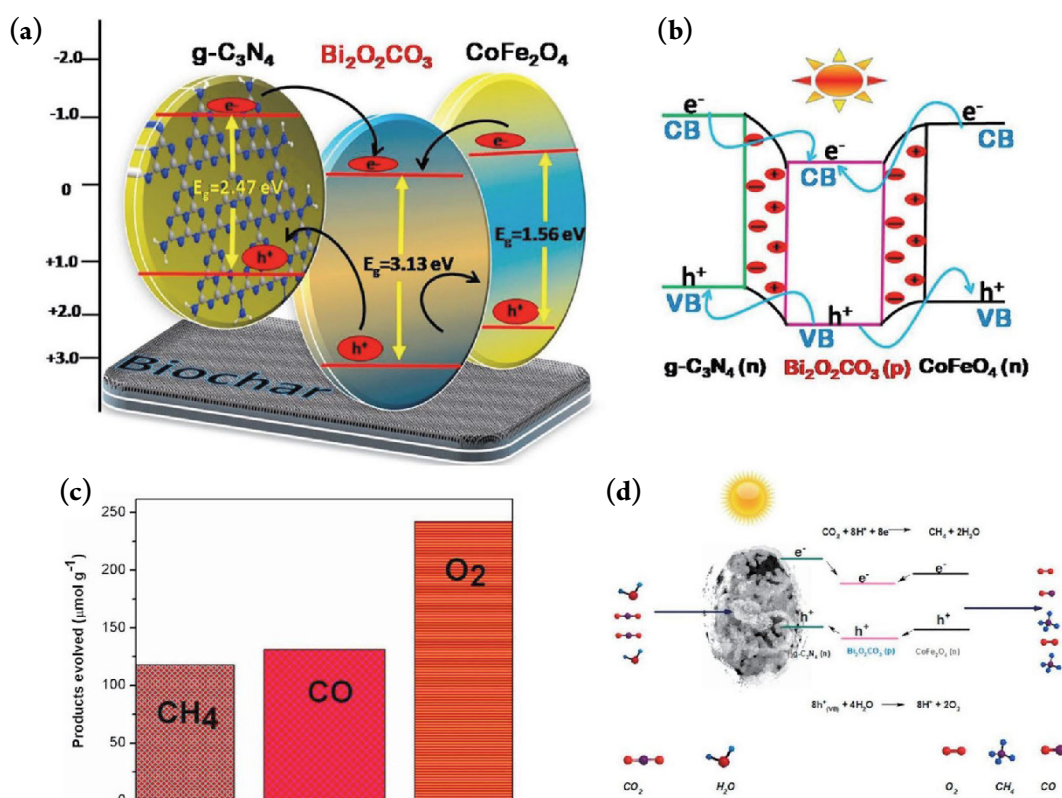


Fig. 3. Photocatalytic reduction mechanism of CO_2 into solar fuels by BC templated $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{O}_2\text{CO}_3/\text{CoFe}_2\text{O}_4$ photocatalyst: (a, b) charge carrier's transfer, (c) CO_2 -reduction products, and (d) CO_2 -RR scheme (Kumar *et al.*, 2018).

temperature of biochar (e.g., less than 700°C) is much lower than that of AC (e.g., up to 900°C) (Zhang *et al.*, 2017). Besides, the process of activation is unnecessary during biochar production, while it is crucial for AC production. In addition, the break-even price of biochar is about US $\$246/\text{ton}$, which is only 1/6 of that for commercial AC (Awasthi, 2022; Amusat *et al.*, 2021).

At present, several thermo-chemical methodologies have been reported for the development of BC from biomass wastes such as slow/fast pyrolysis, hydrothermal carbonization, microwave-assisted heating, gasification, rectification, and torrefaction methods (Guo *et al.*, 2020; Qian *et al.*, 2015). Briefly, the slow pyrolysis method (e.g., low temperature (at $350\text{--}600^\circ\text{C}$) for long residence times (hours to days) in oxygen-limited conditions) is the most widely used method for BC production with specific surface areas in the range of 1.5 to $241 \text{ m}^2 \text{ g}^{-1}$ (Kumar *et al.*, 2020a; Wang *et al.*, 2019). Chemical activation of raw biomass is also commonly used before thermal pyrolysis to control Brønsted-to-Lewis acid/base ratios (using H_2SO_4 , KOH , NaOH , or H_3PO_4) or to

anchor catalytic sites (using NiCl_2 , ZnCl_2 , $\text{Sn}(\text{OH})_4$, $\text{Co}(\text{OH})_2$, or MnCl_2) for target catalytic reactions. This method is also adopted to improve the physicochemical features of BC materials (e.g., increases in the swelling/hydrolysis of lignocellulosic contents) before thermal pyrolysis. In this case, the BC products should show improved texture properties (e.g., porosity, pore volume, and surface area), high aromaticity (e.g., greater fixed carbon and lower crystallites), and low content of undesired components (e.g., ash or volatile carbon). For instance, the adjustment of KOH : biomass char ratios from 1 : 1 to 1 : 3 can increase the surface area (from 853 to $1686 \text{ m}^2 \text{ g}^{-1}$) and pore volume (from 0.34 to $0.64 \text{ cm}^3 \text{ g}^{-1}$) to favorably improve catalytic reactions (Cha *et al.*, 2016). Similarly, hydrothermal treatment and/or oxygenation of raw biomass can also be used to increase the texture (e.g., surface area and porosity) properties of BC products.

In typical pyrolytic conditions (at $< 500^\circ\text{C}$ for 12 h or $> 500^\circ\text{C}$ for 1 h, with a yield of 30–40%), about 700 kg of BC can be synthesized from the pyrolysis of two tons

of biomass (Liu *et al.*, 2015). This shows that BC can be scaled-up for practical applications in multiple fields as catalysts. However, it should be noted that the catalytic activities of pristine BC materials (without pre- or post-synthesis modification) are rarely reported, especially in photocatalysis and thermocatalysis. This is mainly due to the absence or deactivation of inherent catalytic sites (Brønsted acid/base or semiconducting metal sites) during the pyrolytic synthesis of BC. For example, the catalytic capacity of BC could dramatically decrease when using a high pyrolytic temperature ($>$ volatilization temperature of minerals) for longer reaction times during thermochemical synthesis due to the gradual cracking of phenolic (e.g., quinone/hydroquinone) constituents and to the deactivation/volatilization of inherited metallic sites associated with catalytic activity in BC (Lyu *et al.*, 2020). Further, the utilization of feedstock biomass with a high content of mineral elements can also significantly decrease the stability and electrical conductivity of BC, which is required to improve heterogeneous photocatalytic activity. This observation is attributed to the destruction of conjugated aromatic carbon or preventing its formation in the presence of high mineral content (like Si) during pyrolytic synthesis (McBeath *et al.*, 2015). These findings suggest that the catalytic efficiency of BC is dependent on its physicochemical properties (surface area, porosity, hydrophobicity, and surface functionality) and the availability of inherent catalytic sites (Brønsted acid/base sites or semiconducting metal sites). It is thus essential to understand the fundamentals associated with the production of BC to develop BC catalysts with promising performance in target catalytic reactions.

There are many contrasting factors to consider for controlling BC catalytic activity (Kumar *et al.*, 2020a; Xiong *et al.*, 2017). For instance, the use of a feedstock with high lipid/ash content can lead to a reduction in aromaticity, porosity, and surface area (unfavored) of the produced BC. On the other hand, biomass with rich lignin/cellulose content increases porous graphitic structure and carbon stability (favored for catalysis). Notably, the weight ratios of water to biomass in hydrothermal carbonization are found to have a direct effect on the catalytic capacity of BC materials. This is due to the significant role of water in the pyrolysis of biomass and the formation of persistent free radicals (PFRs: e.g., sulfate ($\text{SO}_4^{\cdot-}$) or hydroxyl (HO^{\cdot})) on the BC surface (Lyu *et al.*, 2020). Note that the concentration of PFRs is dependent on the metal and phenolic content in BC. In this

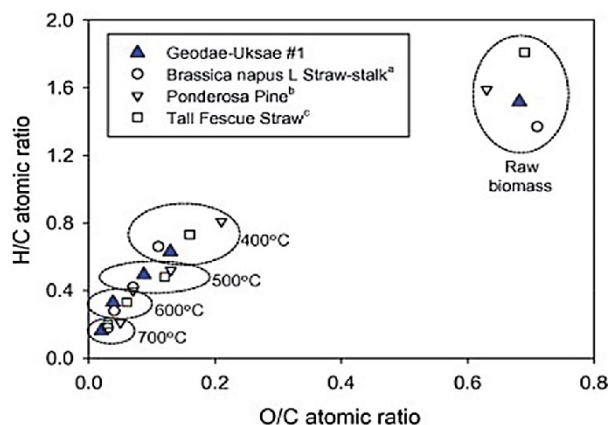


Fig. 4. Van Krevelen diagram for the effect of pyrolysis temperatures on the characteristics of BC produced from diverse raw biomass materials (Lee *et al.*, 2013).

context, the use of high water: biomass ratio (e.g., 1 : 2.5) is suggested to increase the concentration of PFRs (i.e., to accelerate hydrolysis and radical reaction mechanisms). On the other hand, using low water content could lead to a reduction in the pyrolyzation rate, which would require long residence times to achieve complete biomass pyrolysis. In terms of thermal pyrolysis conditions, pyrolytic temperature (relative to the heating rate and residence time) plays a critical role in determining characteristics/morphological structures of BC products by controlling H/C and O/C ratios (Fig. 4) (Lee *et al.*, 2013). An increase in pyrolysis temperature ($>$ 500°C) can reduce catalytic activities in biorefineries as it causes a significant reduction in the BC yield, H/C and O/C ratios, porosity, and Brønsted acid sites (Cha *et al.*, 2016). The fast pyrolysis driven at high temperatures can also reduce the yield of porous BC while increasing the yield of bio-oil (heating value of 17 MJ kg^{-1}) and hydrochar with poor texture properties. This observation is due to accelerated pyrolysis reaction mechanisms (decomposition/depolymerization (cracking) of lignocellulosic biomass, inter-molecular rearrangements, decarboxylation/dehydration, aromatization, and condensation reactions) (Liu *et al.*, 2015). On the other hand, the Brønsted bases, ash content, and carbon stability of BC formed at high pyrolytic temperatures can increase when using a feedstock with high pH and cellulose content (e.g., seaweeds, manures, and crop residue) (Kumar *et al.*, 2020b; Cha *et al.*, 2016). These features are useful in the adsorption removal of heavy metals and acid dyes (i.e., water pollution control). An overview of

the parameters controlling the pyrolysis reaction mechanism and their associated impact on the yield and properties of BC products is given elsewhere (Kumar *et al.*, 2020a, b; Xiu *et al.*, 2017; Liu *et al.*, 2015).

4. BIOCHAR-BASED CATALYSTS: ADVANTAGES VS. LIMITATIONS

In most heterogeneous catalysis, BC can serve as a promising medium to make various heterojunctions/composites with high catalytic activities, especially in photocatalysis for environmental remediation (e.g., air/water pollution control) (Kumar *et al.*, 2020b; Lee *et al.*, 2019, 2017; Wang *et al.*, 2019). The construction of BC-supported heterojunctions/composites can be achieved by post-synthesis impregnation of noble metals and/or transition metal oxides NPs (e.g., Pt, Pb, Ru, Ni, TiO₂, CuO₂, MnO_x, ZnO, FeVO₄, Fe₃O₄, and BiOX) onto the BC surface through sol-gel, sonochemistry, thermal polycondensation, solvothermal, and hydrolysis methods (Mian and Liu, 2018).

Among these post-synthesis strategies, the solvent-free-ultrasonic approach is recommended as an effective clean impregnation method. However, the use of high-input ultrasound waves could cause cracking in the BC structure (i.e., reduce the quality and performance of BC-based catalysts). In terms of the techno-economic aspect, solvothermal/thermal condensation methods are ineffective options to develop BC-based catalysts due to the high energy consumption (high cost), high probability for agglomeration of catalysts, and the risk of secondary waste generation (large quantities of solvents used in synthesis and washing procedures). To overcome such disadvantages, the pre-synthesis modification of raw biomass can be used, followed by co-calcination/carbonization under nitrogen flow at low temperature (100–200 °C) for a long reaction time (10–38 h) (Kumar *et al.*, 2020b; Xiong *et al.*, 2017). These pre-synthesis modification options are frequently used to increase the number of active sites and surface functionalities in the obtained BC catalysts through (i) doping with semiconducting or noble metals (e.g., Pt(OH)₂, Pd(OH)₂, Ni(NO₃)₂, Sn(OH)₄, Cu(OH)₂, Zn(NO₃)₂, and Co(OH)₄) needed for improving thermo-/photo-catalysis and (ii) anchoring Lewis acid/base sites (*viz.* sulfonation, phosphorylation, amination, oxidation, acid/base treatment, ionic liquid grafting, or other hetero-atom

doping) required to promote biorefinery/acid-base catalytic reactions. It should be noted that all the impregnation/modification methods mentioned above can alter the surface functionalities of BC-based catalysts due to their active role in the binding of newly loaded metal/metal oxides or other functional sites anchored on the surfaces. Although pre-/post-synthesis modification methods appear to significantly affect the physicochemical features of the BC support and its inherited catalytic sites, the performance of BC-based catalysts was generally covered without considering such critical factors in almost all systematic reviews made in this area to date.

BC can play an active role to improve the catalytic activities of heterogeneous BC-based heterojunction/composite catalysts by increasing the surface area and porous structures (pore volume and pore size distribution), providing the required accelerated mass transport and increasing the binding capacity of target organic/inorganic reactants (Fig. 5) making them closer to surface catalytic sites (Do Minh *et al.*, 2020). As electroconductive carbon, the use of BC supports can also improve the photocatalysis via (i) shuttling the flow of excited electrons (e⁻) to suppress the fast recombination of e⁻/h⁺ pairs and (ii) improving the optical response of incorporated photocatalysts in the UV-visible region (Mian and Liu, 2018). The high density of O, N, and S-type functional moieties on BC surfaces also enhances acid-driven catalytic reactions in biorefinery reactions (e.g., biofuel production: trans-esterification, hydrolysis, and dehydration reaction) (Kumar *et al.*, 2020b; Wang *et al.*, 2019). Similarly, the synthesis of BC with functionalities rich in *p*-block heteroatoms (e.g., N, P, S, and B) is also preferred in the design of visible/solar-driven BC-based photocatalysts. This is because these non-metal elements can modulate the electronic states (conduction band) of BC to promote electro-photo-chemical catalysis (Do Minh *et al.*, 2020). Hence, besides inherited functionalities, doping surface functionalities onto pristine BC materials by pre-/post-synthesis modification strategies is an effective route to increase the catalytic activities of BC-based catalysts in biorefinery (Xiong *et al.*, 2017) and photocatalysis applications (Cui *et al.*, 2020; Mian and Liu, 2018). Further, the interaction between the impregnated catalytic sites and graphitic carbon with a high dispersion of minerals significantly enhanced the catalytic activity of BC-based catalysts. However, in some cases, the high mineral content (e.g., Si) in raw biomass could have a negative role in the cata-

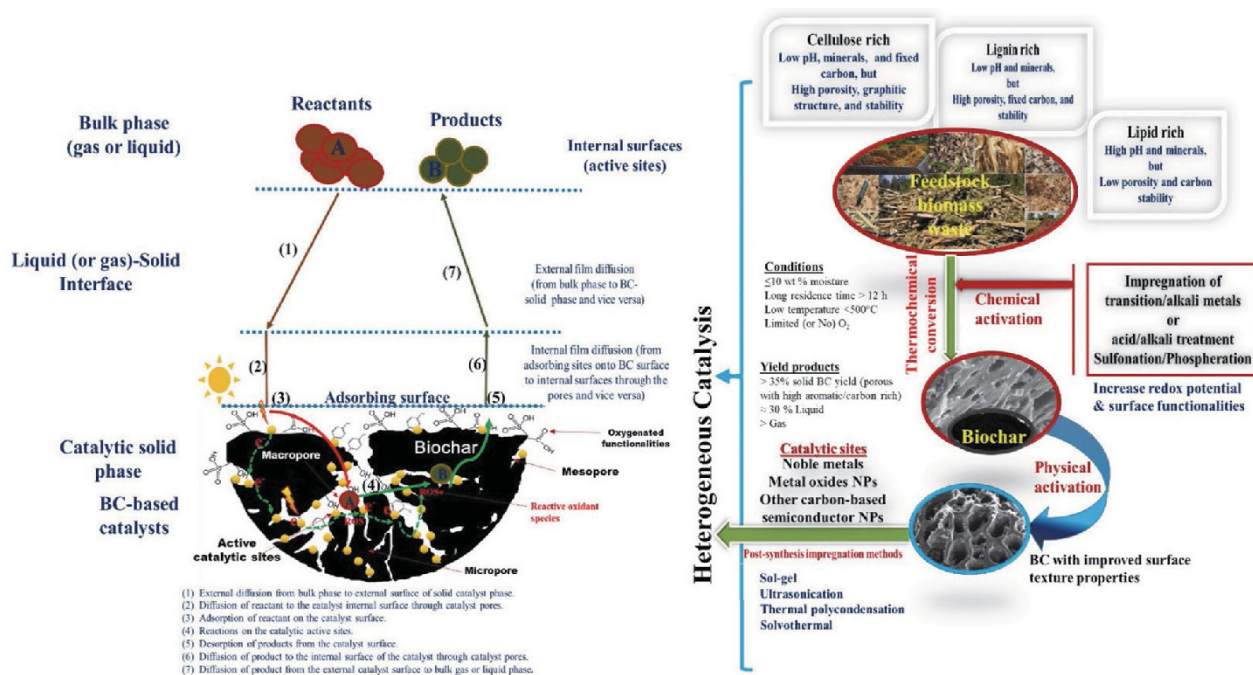


Fig. 5. Schematic for the synthesis/activation of BC-based catalysts and the associated catalytic reaction steps in heterogeneous catalysis.

lytic activities of BC catalysts as it promotes alkali/transition metal sintering at high temperatures (agglomeration) when using steam-containing thermal pyrolysis (Cheng and Li, 2018). On the other hand, the synthesis of BC through the gasification of biomass in CO_2 can address such a drawback and increase metal dispersion.

The texture properties of BC are a critical part of enhancing the catalytic activities by accelerating the mass diffusion step, as seen in Fig. 5. It was noted that most synthesized bare BC supports have lower surface areas ($1.5\text{--}241\text{ m}^2\text{ g}^{-1}$) and pore volumes ($0.01\text{--}0.39\text{ m}^3\text{ g}^{-1}$) than other carbon supports (like activated carbon, graphene oxides, and carbon nanotubes). Further, all post-impregnation/surface functionalization methods are known to reduce the surface porosity, and surface area of BC supports to a certain degree due to pore blocking with anchored materials with non-metals, noble metals, or metal/metal oxides on the surface. To resolve this problem, physical activation of BC by steam treatment under high-temperature conditions ($\geq 700^\circ\text{C}$ for 1–8 h) is frequently proposed as a favorable post-modification option to increase the surface area and to increase the channel (pore) volume (e.g., a factor of > 122 improvements) (Xiong *et al.*, 2017). More importantly, the co-activation method (*viz.* pre-chemical and post-physical activation) showed a more preferable synthesis

scenario to improve the physicochemical/texture features of the final BC supports (in terms of mesoporosity, high surface area $> 1000\text{ m}^2\text{ g}^{-1}$, and an increase in the number of Lewis acid/base and metal catalytic sites) (Liu *et al.*, 2015). Nonetheless, we should keep in mind that such a physical activation process is energy-intensive and time-consuming, leading to an increase in the production cost of BC-supported catalysts.

Among catalysts reported in the energy field (Fig. 6, e.g., biomass hydrolysis reactions, esterification, and methanation), the improved dispersibility ($> 70\%$) of Ru catalyst on activated BC (ABC) support with a high surface area of $728\text{--}757\text{ m}^2\text{ g}^{-1}$ was highly effective in the methanation reaction (e.g., conversion of $55\%\text{ CO}_2$: $97\%\text{ CO}$ to CH_4 onto Ru/ABC with 92% selectivity) (Xiong *et al.*, 2017). Sulfonated biochar (BC- SO_3H) has been recommended strongly for promoting the esterification/transesterification reactions of free fatty acid (FFA) in acid oils to biodiesel, with a conversion efficiency in the range of $97\text{--}98\%$ (using refined microalgal oil at 100°C) to $77\text{--}89\%$ (using waste vegetable oils at 60°C) (Xiong *et al.*, 2017). These results indicated that the effectiveness of BC catalysts in biodiesel production is mainly dependent on the oil source and operation conditions. Also, it should be noted that the high catalytic performance of BC- SO_3H in esterification/transesterification reactions

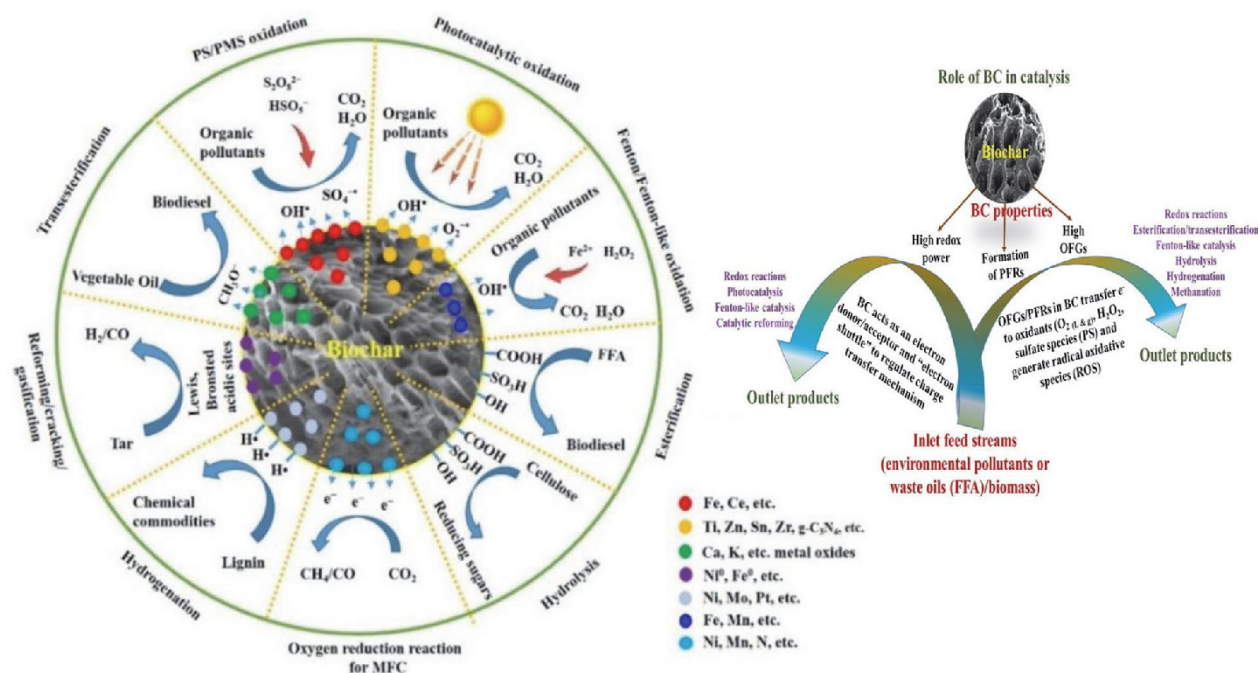


Fig. 6. The catalytic mechanisms of BC-based catalysts in environmental and energy applications and the role of BC surfaces in these heterogeneous catalytic reactions. Adapted from Ref. (Shan *et al.*, 2020).

was attributed to the presence of a high acid site density (like $-\text{SO}_3\text{H}$, $-\text{COOH}$, and $-\text{OH}$ groups) on the BC surface (referred to as a solid acid catalyst). Likewise, it was found that the BC- SO_3H catalyst had high performance in the catalytic hydrolysis of biomass to value-added glucose product, with yield efficiencies at 19.8% (Liu *et al.*, 2015) and 85.4% (Shan *et al.*, 2020). This difference in the catalytic activity of BC- SO_3H is attributed to two main reasons: (i) the difference in the loaded density of $-\text{SO}_3\text{H}$ sites (e.g., 1.99 and 0.196 mmol g^{-1}) in the BC, along with its textural characteristics and (ii) the change in catalytic conditions (e.g., mass: catalyst ratio, reaction temperature, and time). To improve the properties of BC- SO_3H acid catalysts, the use of gaseous sulfonation (using $>20\%$ SO_3 gas) is a preferable option to that of liquid (95% H_2SO_4) sulfonation to increase the loaded density of $-\text{SO}_3\text{H}$ sites on BC, while the latter is favored to improve the textural features of BC over the former (Lee *et al.*, 2017).

For catalytic applications in environmental engineering (Fig. 6), BC-based catalysts are useful to induce various advanced oxidation processes (AOPs, like Fenton-like reaction, sonocatalysis, electrocatalysis, photocatalysis, and redox reactions) of multiple emergent organic pollutants (Do Minh *et al.*, 2020; Lyu *et al.*, 2020; Wang

et al., 2019). Among reported BC-based catalysts, one decorated with graphitic carbon nitride (BC@g-C₃N₄) as core-shell spheres was found to significantly improve visible-driven photocatalysis against bisphenol A (91% removal with a rate of $8.86 \times 10^{-3} \text{ min}^{-1}$) and provide good stability up to 5 cycles (Lyu *et al.*, 2020). In this case, the BC acted as a charge carrier to stabilize the active species and enhance e^-/h^+ pair separation in g-C₃N₄ (i.e., prolonged exciton lifespan) to accelerate photo-redox reactions. In sonocatalysis, the synthesis of lanthanide $\text{CeO}_2\text{-H@BC}$ catalysts exhibited a high catalytic capacity for enhanced degradation (98.5%) of organic dye (e.g., RR84) under mild sonolysis conditions (at 450 W and pH 6.5) for 1 h. Further, the increased FBR concentration in BC with high iron (Fe) content could improve oxidative redox reactions (via Fenton-like catalysis) against various organic contaminants in water solutions in the presence of homogenous oxidants (like H_2O_2 , HSO_5^- , or $\text{S}_2\text{O}_8^{2-}$) (Shan *et al.*, 2020). More interestingly, BC materials have recently been utilized either as supports or catalysts in many coupling catalytic processes for the practical treatment of real industrial wastewater, such as in bio-electrochemical, bio-electro-Fenton, and photo-bio-electrochemical combined technologies (Do Minh *et al.*, 2020). Detailed catalytic perfor-

mance analysis of BC-based catalysts was not the key aim of this work. Hence, interested readers may refer to the reviews organized to evaluate the catalytic performances of many synthesized BC-based catalysts in energy (biofuel/biorefinery) production (Kumar *et al.*, 2020b; Xiong *et al.*, 2017; Qian *et al.*, 2015) and environmental protection (Do Minh *et al.*, 2020; Lyu *et al.*, 2020).

From the above findings, we concluded that designing a broadly active BC catalyst for different catalytic reactions is a challenging process, either in energy or environmental fields. The major hurdles in the design of the BC catalyst are the complex nature of biomass waste, the activation process, and establishing pyrolytic operation conditions. However, the low cost and sustainability of raw biomass substrates are the keys to increasing the probability of engineering BC catalysts as industrially viable options to replace traditional catalysts (like metal-based or other carbon-based catalysts) in environmental and energy fields. Therefore, one needs to consider the following aspects in the development of commercial BC-based heterogeneous catalysts: (i) selection of appropriate raw biomass (determine elemental composition) with low initial cost and (ii) optimization of synthesis conditions for BC (controlled surface and texture features) prior to the pre-/post-impregnation/functionalization methods.

5. COMMERCIALIZATION: TECHNO-ECONOMIC ASPECT AND FUTURE PERSPECTIVE

Before realizing the scalable production of commercialized BC catalysts, it is essential to provide a holistic techno-economic analysis related to the thermochemical conversion of biomass to BC-driven catalytic materials and their environmental impacts. To accurately compute the techno-economic aspects, one should consider four parameters during BC catalyst synthesis: (i) the collection, chipping, and pelletization of raw feedstock precursors, (ii) processing, activation, or modification processes (i.e., pre-/post-synthesis strategies), (iii) energy consumption during carbonization set up (conversion method), and (iv) economic (based on mass/energy balances) and environmental (greenhouse gas emission (GHG) as an indicator) performance indicators (inputs-to-outputs) observed during synthesis (Casson Moreno *et al.*,

2020). In terms of economic performance, the estimated average investment costs were in the ranges of 11.35–24.80 USD/ton for biomass collection and 380–580 USD/ton for production of BC using pyrolysis/gasification processes (Do Minh *et al.*, 2020). The low cost-production of BC is due to the exothermic nature of the pyrolysis process (i.e., requiring a low energy of ≈ 85 MJ ton⁻¹ biomass) (Kumar *et al.*, 2020a). The mass-to-energy balance was also approximated at 30.3 MJ kg⁻¹ when using olive trees with a high heating value under thermal conversion at 700°C with a mass flow of 6 kg h⁻¹ (Casson Moreno *et al.*, 2020). Globally, the revenue-cost ratio of bare BC (sale/production) is positive at 1.02, indicating the significant benefits of BC synthesis from an economic viewpoint. BC catalysts made via thermal pyrolysis are also expected to have a positive impact on the environment if the pyrolytic char by-products (or spent BC catalysts) are not disposed of in a landfill but are used as a soil amendment for non-edible agriculture.

The fate-life cycle of BC materials in their applications could also show substantial benefits for both environmental and economic performance indicators through reutilization as a reactive carbon for capturing GHG in the environment and as fertilizers in soil (Matušík *et al.*, 2020). In China (Guizhou and Henan provinces), a new pilot-scale rotary kiln has recently been built for the co-production of heat and BC (600 kg h⁻¹) using the syngas generated during the biomass pyrolytic process. Other Chinese companies operated a semi-closed sub-high-temperature anoxic carbonization furnace for the co-production of BC, bio-oil, heat, and electricity during thermopyrolysis of biomass (Chen *et al.*, 2019). Using these technologies, the produced energy was higher than that of energy required for the thermal pyrolysis of biomass-to-BC catalysts (i.e., positive net energy). Accordingly, the profits of biomass-to-BC catalyst production (heat, bio-oil, and electricity generation) could compensate for the GHG generated during the pyrolysis process. Results also revealed that the scenario of co-production of BC and biofuel (bio-oil and syngas) during pyrolysis provided a revenue of 24.2 million USD based on historic energy market prices. The total revenue was 5.5 million USD in terms of the biomass waste management scenario (Kumar *et al.*, 2020a). In environmental protection applications, the projected costs for employing BC catalysts in wastewater treatment (1000 gallons) were approximately 14, 8648, and 15536 USD for Fenton-like reactions, photocatalysis, and sonocatalytic processes,

respectively (Wang *et al.*, 2019). The high estimated treatment cost in photocatalysis and sonocatalytic processes may mainly reflect high electrical consumption and the need to purchase experimental tools (like ultrasound and UV-vis lamps). In the Fenton reaction, the homogenous oxidant represents the major part of the total treatment cost. These findings suggest the beneficial aspects of BC catalysts, as cost-effective and sustainable materials in environmental protection and energy applications, especially at a large industrial scale.

As a net conclusion, the techno-economic analysis of BC production suggests it has a bright future for large-scale applications of BC catalysts as inexpensive heterogeneous catalysts. However, the performance of those catalysts in environmental/energy fields is still in the research and development stage. This is mainly due to the low catalytic selectivity and stability of BC catalysts with complex surface chemistry (e.g., chemical/elemental composition, texture features, surface functionalities, redox potential, and total acidity), which is dependent on the factors controlling the synthesis (See Section 3). Hence, it is fundamentally important to optimize those parameters for scalable production and commercialization to maximize the techno-economic efficiency and surface chemistry of BC catalysts for enhanced catalytic performance. To meet such a goal, one should consider and understand the synergistic effect between the elemental composition of biomass and pyrolysis conditions (e.g., for synergistic increases in the number of generated catalytic sites and surface functionality (OFGs and PFRs) in pristine BC materials). Further, a deep understanding of the role of the co-activation (physical and chemical activation) in improving texture properties of pristine BC is crucial, as such information should help enable the design of inexpensive and effective BC catalysts for target catalytic reactions without the need for post-synthesis modification that can increase production cost while limiting scaled production.

6. CONCLUSIONS

Biochar (BC) and its composites have shown promising potential for applications as solid catalysts in various heterogeneous catalytic reactions (e.g., acid-base reaction, biorefinery reactions, hydrogenation, methanation, photo-electro-catalysis, bio-electrochemical reactions, and advanced oxidation reactions). Nonetheless, BC-

based catalysts are still confined to the research and development stage (e.g., lab-scale studies) in which their performance is assessed under favorably adjusted experimental conditions rather than what is actually encountered under real-world conditions. Further, it was found that the basic properties of the same BC-based catalysts (e.g., inherited functionalities/catalytic sites) were significantly different from one report to another due to the subtle differences in the synthesis environments of pristine BC. As such, it is difficult to assess the best-performing BC-based catalysts for industrial applications.

The direct use of pristine BC as a catalyst is not possible for all types of catalysis but can be realized in some heterogeneous catalysis, especially in energy generation applications (e.g., catalytic pyrolysis/gasification, esterification/transesterification, and hydrolysis reactions). However, the direct use of BC in those catalytic reactions depends on the conditions of thermochemical conversion (e.g., from waste biomass to BC) and their effect on the generated active sites (e.g., high surface acidity, OFGs, and PFRs sites). In this context, it should be noted that the presence of active sites in BC-based catalysts is dependent on the following factors: (i) the relationship between the nature of the precursor (e.g., the elemental composition of waste biomass) and pyrolysis conditions, (ii) the actual effect of such interrelated factors on the physicochemical properties of BC (i.e., texture and elemental active sites), and (iii) the effect of pre-synthesis conditions (e.g., pre-chemical activation and moisture/water content of biomass) on the surface chemistry of BC catalysts (total acidity, OFGs, and PFRs sites).

In environmental and air pollution control, BC is frequently utilized as a low-cost template to design various heterojunctions/composites to enhance reactivities in diverse processes (e.g., thermocatalysis, photocatalysis, electrocatalysis, and redox reactions) for pollution control. In this respect, many different types of post-synthesis modification (PSM) methods have been utilized to impregnate/incorporate organic catalytic nanoparticles, transition metals/metal oxides, and non-metal active sites on the surface of the BC support. The catalytic performance of those BC-based composites employed in environmental catalysis was dictated by the combined effects of several factors such as: (i) the physicochemical features of BC (surface functionality, conductivity, and texture properties) and (ii) the catalytic activity of catalysts doped/incorporated on the BC surfaces. In con-

trast, most PSM strategies led to changes in the pristine BC surface properties with an increase in the production cost of BC-based catalysts that can be crucial in the catalytic treatment of environmental pollutants. For example, as a semiconductor with a graphene-like skeleton, BC can serve as (i) an electron reservoir to improve charge separation of electrons and holes to carry out visible-light-driven photocatalysis and (ii) an adsorbent to capture organic/inorganic contaminants for the acceleration of catalytic degradation/reduction during photo/electro-catalysis (or redox reactions). Hence, prior to the design of BC-based catalysts for environmental application, the effect of the PSM strategy should be considered to ensure that the physicochemical features of BC supports can be improved most cost-effectively.

From a techno-economic viewpoint, large-scale thermochemical conversion of biomass to BC product is favored because it provides many environmental/economic advantages in terms of waste management, production of eco-friendly low-cost value-added products, abatement of environmental pollution and GHGs, high energy generation, and soil reclamation. Accordingly, future research should consider the following technical and economic aspects to improve the production of BC-based catalysts for industrial-scale applications in environmental/energy fields: (1) optimization of the synthesis conditions for the BC-based catalysts should be performed to maximize their catalytic performance with the lowest production cost, (2) future research should be carried out under industrially relevant experimental conditions (e.g., similar to target industrial operation) to maximize the applicability of BC-based catalysts in industry, (3) the PSM strategies should be employed with the least negative impact on the inherent properties of BC templates and to help develop BC-based composite catalysts, and (4) the development of BC-based catalysts and their composites for future catalytic studies should include environmental and techno-economic assessments that are compared to other nanoscale or commercial catalysts produced at industrial scales. In summary, a systematic understanding of the parameters affecting the inherent properties of biochar materials (e.g., synthesis procedures, biomass precursors, and modification strategies) will assist in designing efficient biochar-based catalysts for environmental applications, in particular for air pollution control.

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