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Research review paper

Recent advancements and challenges in emerging applications of biochar-based catalysts

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ABSTRACT

The sustainable utilization of biochar produced from biomass waste could substantially promote the development of carbon neutrality and a circular economy. Due to their cost-effectiveness, multiple functionalities, tailorable porous structure, and thermal stability, biochar-based catalysts play a vital role in sustainable biorefineries and environmental protection, contributing to a positive, planet-level impact. This review provides an overview of emerging synthesis routes for multifunctional biochar-based catalysts. It discusses recent advances in biorefinery and pollutant degradation in air, soil, and water, providing deeper and more comprehensive information of the catalysts, such as physicochemical properties and surface chemistry. The catalytic performance and deactivation mechanisms under different catalytic systems were critically reviewed, providing new insights into developing efficient and practical biochar-based catalysts for large-scale use in various applications. Machine learning (ML)-based predictions and inverse design have addressed the innovation of biochar-based catalysts with high-performance applications, as ML efficiently predicts the properties and performance of biochar, interprets the underlying mechanisms and complicated relationships, and guides biochar synthesis. Finally, environmental benefit and economic feasibility assessments are proposed for science-based guidelines for industries and policymakers. With concerted effort, upgrading biomass waste into high-performance catalysts for biorefinery and environmental protection could reduce environmental pollution, increase energy safety, and achieve sustainable biomass management, all of which are beneficial for attaining several of the United Nations Sustainable Development Goals (UN SDGs) and Environmental, Social and Governance (ESG).

1. Introduction

Energy shortages and environmental pollution are two critical global challenges (Li et al., 2022a; Zhang et al., 2022). The continuously increasing consumption of primary energy worldwide and declining global reserves of fossil fuels have posed severe challenges to energy security (Li et al., 2022c; Liu et al., 2019a), necessitating the development of alternative energy resources to replace conventional fossil fuels. Environmental, air, water, and soil pollution have become inevitable topics of discussion in the 21st century as they pose substantial threats to biodiversity. The Global Burden of Disease study estimates that 4.5 million deaths per year are caused by outdoor air pollution (Murray,

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2020). Soil pollution has caused unexpected direct and indirect negative effects on human, plant, and animal health, as well as entire ecosystems (Palansooriya et al., 2022; Yuan et al., 2021c); moreover, water pollution has catastrophic effects on the environment, mainly affecting aquatic flora and fauna (Wang et al., 2022b; Xiong et al., 2021a).

Numerous studies have addressed the two challenges of energy shortage and environmental pollution. Potential alternatives to fossil energy were investigated, of which biochar has attracted substantial attention as an energy alternative and efficient means to reduce environmental pollution owing to its cost-effectiveness, carbon-neutrality, and long-term persistence (Chen et al., 2022; Ok et al., 2021). According to the International Biochar Initiative (IBI), biochar is a solid material obtained by the thermochemical conversion of biomass in an oxygen-limited environment (IBI, 2015). The major products derived from the thermochemical conversion of biomass are syngas, bio-oil, and biochar, with yields that depend on the specific operating conditions (Li et al., 2022a; Qian et al., 2015). Syngas and bio-oil are widely used for energy production and electricity generation, and biochar is commonly used in gas adsorption (Ok et al., 2021; Yuan et al., 2022b), soil amendment (Chen et al., 2022; Wang et al., 2020b), and wastewater purification (Krasucka et al., 2021; Xiang et al., 2020).

Recent developments have focused on biochar-based catalysts for environmental protection and energy production to achieve a positive, planet-level impact (Minh et al., 2020; Yuan et al., 2021a). As shown in Fig. 1, the number of publications using "biochar catalyst" as a research topic has increased from 127 in 2018 to 591 in 2022, with the total number of citations increasing from 2035 in 2018 to 19,198 in 2022 (accessed on March 15, 2023), highlighting the growing research interest in biochar-based catalytic applications. This implies that biomass serves as an efficient and versatile platform for synthesizing multifunctional biochar-based catalysts, which has led to a paradigm shift in research areas toward other practical deployments for biochar-based catalysts, such as mitigating environmental pollution and solidifying energy security. When searching for "biochar catalyst" as a topic from the "Web of Science Core Collection" database, a total of 2037 publications are available (accessed on March 15, 2023), of which 193 are categorized as review articles, with only 19 of the reviews being on the catalytic applications of biochar for energy production and environmental protection. After examining these 19 reviews (summarized in Table 1), we found that most of them addressed the catalytic applications only in the sub-sections. For example, Qian et al. (2015) and Sakhiya et al. (2020) only reviewed biochar-based catalysts for biodiesel production and syngas cleaning in sub-sections 3.1 and 7.3, respectively; in addition to addressing biodiesel production and syngas cleaning in sub-sections, Cha et al. (2016), Bolan et al. (2021), and Lee et al. (2019) discussed air pollution control in sub-section 4.2, sub-section 5.1, and section 5 (short section), respectively. Moreover, we published two reviews of biochar-based catalysts for sustainable biorefinery (mainly bio-oil and bio-gas production) and pollutant control (mainly NOx reduction and advanced oxidation processes) (Kumar et al., 2020a; Xiong et al., 2017). Therefore, a timely and systematic review is urgently needed to thoroughly address and update the synthesis approaches of biochar-based catalysts for sustainable biorefinery and environmental pollution degradation in air, soil, and water. Fig. 2 displays a scientometric visualization of the keywords (top 300) of the 2037 publications from the "Web of Science Core Collection" database, using the search topic of "biochar catalyst." The major results from this paper suggest that: 1) biochar-based catalysts have been effectively synthesized for biorefinery and pollutant control applications, and 2) biochar-based and catalyst-related research interests have gradually shifted from bioenergy upgradation to environmental protection.

Therefore, this comprehensive review of the preparation methods and practical catalytic applications of biochar addresses the progress and challenges of current biochar-based catalyst research. A novel system of biochar-based catalytic applications is proposed in this review. The detailed mechanisms are discussed for each application, machine learning (ML)-aided syntheses and optimizations of biochar-based catalysts are highlighted; additionally, full assessments on environmental impacts and economic feasibilities are recommended to clarify the sustainability of each catalytic biochar application. This review ultimately promotes the practical application of biochar-based catalysts in energy supply and environmental protection, which may provide key guidelines to policymakers, industry practiontioners, and researchers working on the sustainable management of biomass waste, environmental pollution mitigation, and solidification of energy security. Hence, this body of knowledge may help achieve the UN Sustainable Development Goals (UN SDGs), namely, sustainable mitigation of environmental pollution and continued growth in the use of alternative energy as well as Environmental, Social, and Governance (ESG).

Herein, we explain how we performed this review. To emphasize the

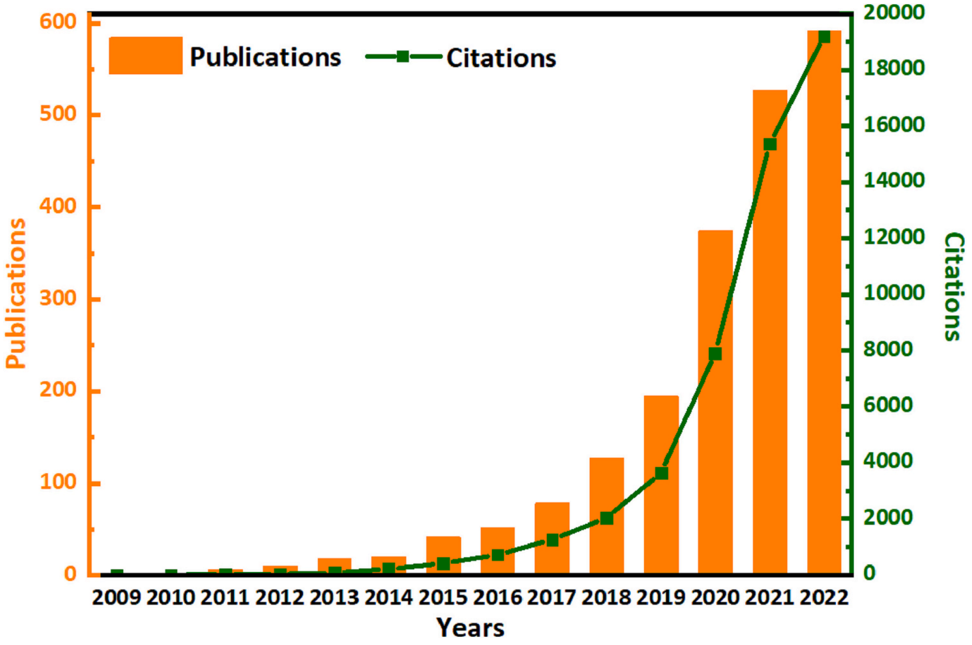


Fig. 1. Publications and citations using the topic "biochar catalyst" from 2009 to 2022, based on the Web of Science database (accessed on March 15, 2023).

Table 1
Synopsis of previous reviews of biochar-based catalysts for both energy production and environmental protection (updated on March 15, 2023).

Review title	Citation	Review summary on catalytic applications	Ref.
Development of Biochar-Based Functional Materials: Toward a Sustainable Platform Carbon Material	866	This review addressed catalysis applications of biochar-based materials in sub-section 4.1 and also made a brief discussion on catalytic applications for energy storage and environmental protection.	Liu et al. (2015a)
Production and utilization of biochar: A review	639	This review briefly discussed the catalytic applications for syngas cleaning, biodiesel production, and air pollution control in sub-section 4.2.	Cha et al. (2016)
Recent advances in utilization of biochar	461	This review addressed the biochar as a catalyst for syngas cleaning and conversion, and biodiesel production in sub-section 3.1.	Qian et al. (2015)
Emerging applications of biochar-based materials for energy storage and conversion	323	Without considering environmental protection, this review addressed biochar-based catalysts for electrocatalytic hydrogen evolution, and oxygen reduction/evolution reactions (ORR and OER) occurring in electrochemical energy storage and conversion processes.	Liu et al. (2019a)
A review of biochar-based catalysts for chemical synthesis, biofuel production, and pollution control	304	This review provided biochar-based catalytic applications of chemical production, biofuel production, and pollution controls.	Xiong et al. (2017)
Insights into biochar and hydrochar production and applications: A review	280	This review briefly addressed biochar as a precursor of catalysts (energy production, waste management) in sub-section 4.2.	Zhang et al. (2019)
Biomass-derived porous graphitic carbon materials for energy and environmental applications	143	This review addressed the biochar as promising candidates as cathode ORR catalyst, catalyst for persulfate activation, and support for photocatalytic materials, separately.	Chen et al. (2020a)
Multifunctional applications of biochar beyond carbon storage	142	In addition to other major applications, this review addressed biochar for catalytic applications including selective catalytic reduction, biodiesel formation, tar removal, and syngas production, air pollutants removal.	Bolan et al. (2021)
Critical Review on Biochar-Supported Catalysts for Pollutant Degradation and Sustainable Biorefinery	94	This review addressed biochar-based catalysts in degradation of organic contaminants (AOPs), and biorefinery (including biodiesel production, biomass-to-chemicals, tar decomposition, and syngas-reforming).	Kumar et al. (2020a)
Production, activation, and applications of biochar in recent times	86	In addition to other major applications, this review briefly discussed biochar as a catalyst for biodiesel production, syngas purification, and tar cracking in sub-section 7.3.	Sakhiya et al. (2020)
Biochar as a support for nanocatalysts and other reagents: Recent advances and applications	63	This review addressed biochar as a support of nanocatalysts for photocatalysis using semiconductors (sub-section 3.3), synthesis of fine chemicals (sub-section 3.4), and syngas reforming reactions (sub-section 3.5).	Lopes and Astruc (2021)
Biomass-derived biochar materials as sustainable energy sources for electrochemical energy storage devices	61	In addition to other major applications, this review addressed biochar as electrocatalysts for metal-air batteries in sub-section 4.5.	Senthil and Lee (2021)
Hydrothermal synthesis and applications of advanced carbonaceous materials from biomass: a review	58	This review addressed biochar as the substitutes for inorganic catalysts for catalysis applications in sub-section 4.1.	Wang et al. (2020a)
Review of the use of activated biochar for energy and environmental applications	49	In addition to other major applications, this review addressed activated biochar for catalytic biomass pyrolysis (section 3) and catalytic applications for lithium-ion batteries and fuel cells (sub-sections 4.2 and 4.3).	Lee et al. (2017b)
Sustainable biochar as an electrocatalysts for the oxygen reduction reaction in microbial fuel cells	33	This review only focused on biochars as oxygen reduction reaction catalysts (nitrogen-doped biochar and other heteroatom-doped biochar) in microbial fuel cells.	Li et al. (2021d)
Recent application of biochar on the catalytic biorefinery and environmental processes	28	This review shortly reviewed catalytic biochar applications for biodiesel production, biomass hydrolysis, syngas upgrading, and atmospheric pollutants mitigations (i.e., NOx, VOCs).	Lee et al. (2019)
Current understanding in conversion and application of tea waste biomass: A review	20	This review discussed tea waste biochar as catalysts for electrochemical energy storage in sub-section 2.2.2.	Guo et al. (2021)
Emerging applications of sludge biochar-based catalysts for environmental remediation and energy storage: A review	11	This review addressed the sludge biochar as photocatalysts and Fenton-like catalysts, in sub-section 3.1 nd 3.2, respectively, and also major existing challenges on biochar-based catalysts are highlighted.	Mian et al. (2022)
Role of Metals in Biochar Production and Utilization in Catalytic Applications: A Review	6	This review mainly discussed the role of metals in the catalytic activity of biochar for tar cracking, biodiesel production, bio-oil upgrading, and NOx reduction.	Shrestha et al. (2021)
Recent advancements and challenges in emerging applications of biochar-based catalysts	–	This review comprehensively addressed emerging catalytic applications of biochar including biorefineries and environmental protections. The detailed mechanisms are discussed for each application, and machine learning-aided syntheses and optimizations of biochar-based catalysts are highlighted. In addition, the assessments on environmental impacts and economic feasibilities are finally needed to clarify the sustainability of each catalytic biochar application.	This review

novelty and necessity of this review, the "Web of Science Core Collection" database (https://www.webofscience.com/wos/woscc/basic-search) was used to investigate current advancements in biochar-based catalytic applications. By searching for "biochar catalyst" as the topic of this review, the research background of this topic and the novelty and necessity of this review was established. The total number of publications and citations are presented by year, which is shown in Fig. 1. Tab-delimited files were exported from the "Web of Science Core Collection" database when using "biochar catalyst" as the topic; thereafter, the VOSviewer software was applied to visualize the key research developments and trends of biochar-based catalytic applications. The built-in function of the co-occurrence of keywords plus was used to analyze the obtained publications, and the analysis results were plotted in overlay visualization, which is displayed in Fig. 2. Moreover, to fully investigate the research advancements in the catalytic applications of biochar-based catalysts, major databases such as SCOPUS and Web of Science were used, and detailed investigations for different purposes are listed in Tables 1–4, including the synopsis of previous reviews as well as the syntheses and applications of biochar-based catalysts.

2. Synthesis and modification approaches of biochar-based catalysts

Carbonaceous materials have been widely used in many commercial processes (Rodríguez-Reinoso, 1998) and are preferred as catalysts because they can be physically and/or chemically altered to various shapes, sizes, and forms (Kumar et al., 2020a). Biochar is one of the most preferred carbon materials for catalytic applications because of its cost-effective production using abundant lignocellulosic biomass and other carbon-rich waste (Bhatia et al., 2021; Tsai et al., 2022). Moreover, the impressive stability of biochar and its flexibility in altering its properties for broader applications make it an attractive catalyst (Oliveira et al., 2017; Patel et al., 2022a). In recent years, several studies have looked at designs and modifications to obtain high-performance biochar for wider practical applications, including environmental protection as well as fuel and non-fuel production (Fig. 3) (Bhatia et al., 2021; Cheng and Li, 2018). Stepwise upcycling approaches for converting biomass and its waste to biochar for catalytic applications are illustrated in Fig. 3. Several techniques, including physical, chemical, and biological activation, are widely utilized to enhance the textural properties and surface functionalities of biochar for specific commercial applications. During these applications, modified biochar demonstrates a variety of interaction mechanisms. Further production details on biochar, and advantages/disadvantages, are presented in Table 2, and applications of biochar-based catalysts are summarized in Table 3.

2.1. *General characteristics of engineered/designer biochar*

Some of the fundamental physicochemical attributes of biochar that make it suitable for various applications are its high surface area and porosity, neutral-to-high pH, low bulk density, high cation exchange capacity, aromaticity, and high carbon content (Oliveira et al., 2017). In addition to its general applications, biochar has recently been designed and modified for various catalytic applications (Ahmed et al., 2016; Kambo and Dutta, 2015), and it is imperative to further develop biochar so that it possesses the desired properties. Recent studies have led to the development of methodologies for the preparation, modification, and characterization of biochar (Oliveira et al., 2017; Patel et al., 2022a,b), which is an excellent candidate as a catalyst or catalyst-support; however, additional efforts are required for its specific design and production (Qian et al., 2015). The mineral content, surface chemistry, pore structure, and other inherent properties (*e.g.,* mechanical strength and cyclic stability) of biochar are critical to its role and performance in catalytic applications (Lam and Luong, 2014; Yuan et al., 2021a). This is mainly because of the charges and radicals found on the surfaces of biochar-based systems and reactive surface functional groups (Xiao et al., 2018). As an ideal catalyst, biochar possesses certain general characteristics, such as a well-developed pore structure, high porosity, good mechanical and chemical properties, excellent electrical conductivity, and environmentally friendly and sustainable attributes, along with lower costs (Wang et al., 2021b). Some studies have used biochar as a catalyst (Wan et al., 2019; Waqas et al., 2018); however, few have demonstrated its potential as a catalyst or catalyst-support and evaluated the connections between its physicochemical properties and catalytic activity (Kostić et al., 2016; Shen et al., 2014b). Furthermore, metal nanoparticles and nanotubes can be added to biochar to create a product with unique physicochemical properties (Hung et al., 2021a; Yang et al., 2019a). These properties can be further altered depending on their commercial applications. Therefore, engineered biochar is a promising catalyst or catalyst-support material, and its design is crucial for catalytic applications. The properties of engineered biochar are defined similarly to those of native biochar, based on synthesis routes and modifications. These properties mainly include the specific surface area (SSA), porosity, density, aromaticity, moisture retention ability, cation exchange capacity, pH, value, and element composition (Oliveira et al., 2017). Moreover, engineered biochar is classified based on upcycling approaches, including physical, chemical or physicochemical, and biological methods (Katiyar et al., 2022; Patel et al., 2022a). Physical techniques (e.g., milling, gas activation, and microwave and sonicator use) improve the properties of biochar by altering its physical parameters (*e.g.,* textural properties, density, and moisture content). The key changes in the physiological structure and characteristics of biochar are well correlated with temperature, pressure, initial pH, and other operating parameters. Several new surface functional groups are generated at high operating temperatures. Physical techniques are accessible, economically viable, and suitable for catalytic applications (Banerjee et al., 2016; Patel et al., 2022a,b). For chemical techniques, acid, alkaline, and metal salt chemical agents are commonly employed (Li et al., 2021e; Yuan et al., 2022b). Chemically modified biochar is commonly adopted as it possesses desirable characteristics, particularly, a well-developed pore structure, which is the most valuable parameter in environmental applications (Panwar and Pawar, 2020). For biological techniques, several processes, such as microorganism immobilization and organic doping, are adopted (Gielnik et al., 2019). Microorganisms have the intrinsic ability to colonize, biodegrade, and facilitate catalysis by exchanging free electrons (Hung et al., 2021b; Patel et al., 2022a).

2.2. *Synthesis approaches of biochar-based catalysts*

Thermochemical approaches, such as pyrolysis, hydrothermal carbonization, and torrefaction, have traditionally been used to upcycle biomass and its waste into biochar. Hydrothermal carbonization is possible for biomass and its waste, which have a high moisture content, while pyrolysis is widely used for feedstocks with a low moisture content. Production operating parameters, such as heating rate, final temperature, pressure, and residence time, significantly affect biochar yield. Moreover, operating parameters affect the characteristics of biochar, such as its porous, amorphous, or crystalline nature and its quality, including its size, shape, and chemical composition. The physicochemical properties of biochar are also affected by the feedstock type (Kumar et al., 2020a; Zhou et al., 2022). Correlation studies revealed that two out of several factors largely affect the final properties of biochar: biochar production operating parameters (e.g., temperature, ramping rate, duration, and inert gas purging) and feedstock type (bearing intrinsic element ratios to provide numerous functional groups) (Oliveira et al., 2017; Patel et al., 2022b). Three approaches that have been widely used in past studies for biochar production and modification include carbonization, activation, and surface functionalization. Carbonization has mainly been used for native biochar synthesis; however, the latter two approaches have been principally applied to enhance the properties of biochar for specific applications.

2.2.1. *Carbonization*

Carbonization refers to the conversion of organic substances into highly carbonized residues through destructive distillation or thermochemical processes. Biochar can be produced from biomass or animal solid waste by different thermochemical processes, such as hydrothermal carbonization, pyrolysis, gasification, and torrefaction (Patel et al., 2022a; Zhou et al., 2021a). Hydrothermal carbonization is the most preferred method for wet biomass and is commonly performed in hot-compressed water or subcritical water at 180–250 °C for 5–240 min under a pressured atmosphere (Yuan et al., 2021a). The carbon material produced from hydrothermal carbonization is commonly termed hydrochar, and exhibits diverse shapes, sizes, and surface functional groups (Hu et al., 2010). Hydrothermal carbonization has been regarded as an alternative approach to dry thermochemical conversion (i.e., pyrolysis and gasification) because pre-drying treatment is no longer needed for biomass with high a moisture content during hydrothermal carbonization (Li et al., 2021a; Li et al., 2021f). Temperature is one of the most critical operating parameters because water properties cause ionic reactions to occur in a subcritical region, and residence time and heating rate mainly affect the yield of hydrochar. For example, less residence time and a low heating rate are beneficial for increasing hydrochar yield.

Biochar is carbonized by dehydrating biomass, producing a carbon-rich material with a highly porous structure (Oliveira et al., 2017; Rajapaksha et al., 2016). Pyrolysis and gasification have been proposed as promising thermochemical approaches for converting biomass into biofuels (including biochar) and chemicals because these processes can be scaled up to recover energy (Kumar et al., 2020a). Among the

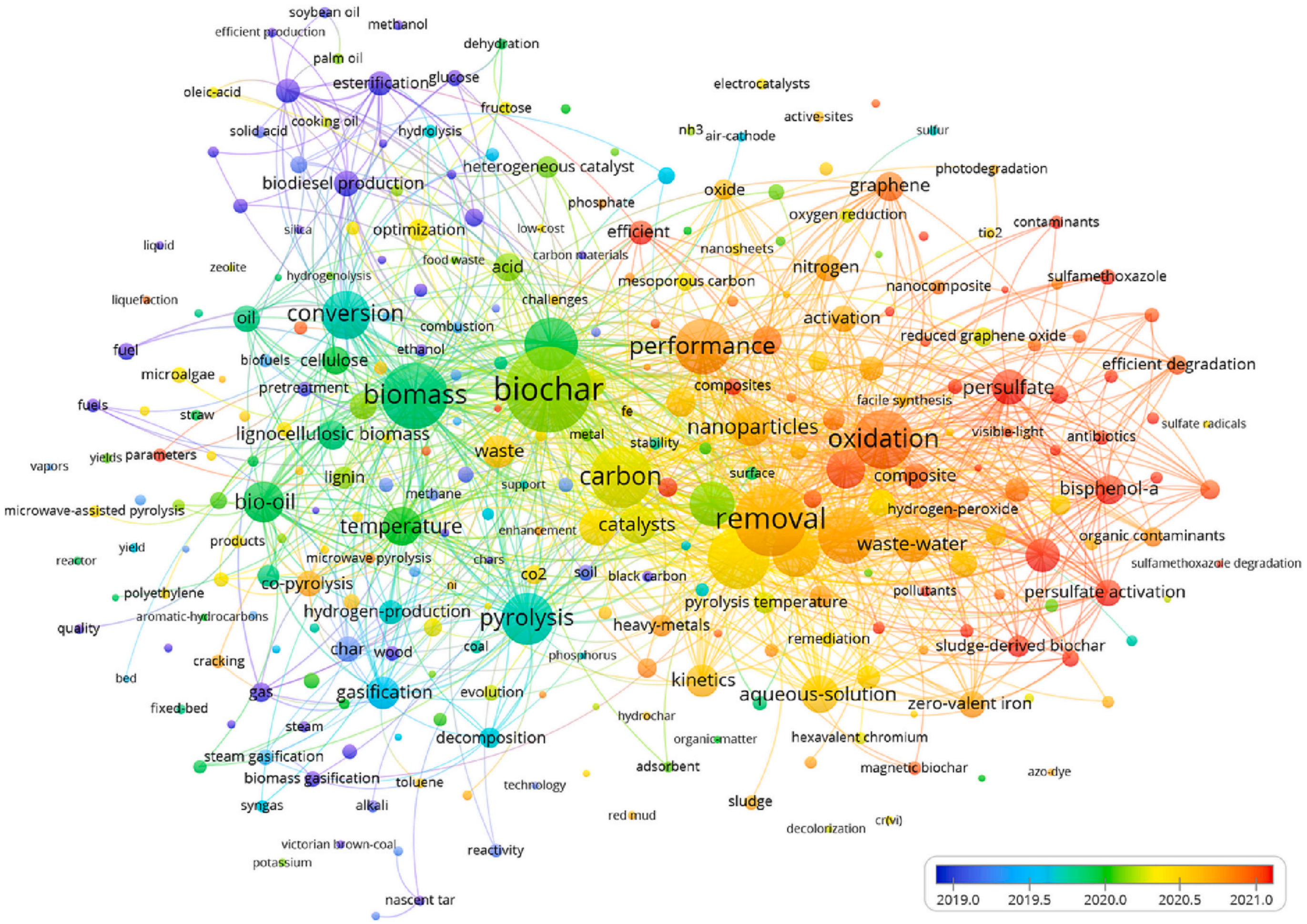


Fig. 2. Scientometric visualization of the top 300 keywords of 2037 publications until 2022 (accessed on March 15, 2023). The selected database is "Web of Science Core Collection." The 2037 publications were collected using "biochar catalyst" as the search keyword (topic). The collected publications were analyzed using the built-in function of co-occurrence of keywords plus and were plotted in overlay visualization (VOSviewer Ver. 1.6.19). Each circle represents a keyword, while its size represents the number of times a pair of keywords have co-occurred in publications. As per the legend, the different colors indicate the average year of the occurrence of each keyword.

thermolytic methods employed for biomass, pyrolysis, unlike gasification, does not use oxidizing agents and transfers most of the heat from carbonaceous feedstocks into combustible syngas, *i.e.*, CO and H_2 (Yuan et al., 2015). Therefore, while these two techniques can be used to produce biochar, the co-production of pyrolytic oil (biocrude) and syngas cannot be avoided. Gasification is carried out at >800 °C using gasifying agents (*i.e.,* air, CO_2, or steam) to produce high-quality syngas; thus, the biochar yield is less than those of gaseous products (Qian et al., 2013). However, pyrolysis is a robust and cost-effective route to obtain a high biochar yield. Pyrolysis techniques are categorized as fast, slow, or microwave-assisted based on the residence time, heating type, and rate (Mašek et al., 2013). Slow pyrolysis occurs between 400 °C and 600 °C and involves slow heating and an extended vapor dwelling period. The biochar yield from this method is the highest (40–60 %) among all pyrolysis methods (Manya, 2012). Slow and fast pyrolysis have approximately the same temperature range, but fast pyrolysis has a high heating rate (≥200 °C/min) and short reaction time, which contribute to a low yield (10–20%) of biochar (Manya, 2012). Fast pyrolysis produces biochar with a high oxygen content, low calorific value, and low surface area. This might result from rapid pyrolysis occurring over a short residence time (Kumar et al., 2020a). In addition, dry torrefaction is a mild pyrolysis route and is commonly performed at 200–300 °C for 30–60 min at a slow heating rate under inert or O_2-deficient conditions (Tumuluru et al., 2021). It is a promising pre-processing step for enhancing the physicochemical properties of biomass and its waste. The mechanism of dry torrefaction includes decarboxylation, dehydration, decarbonylation, demethoxylation, intermolecular derangement, condensation, and aromatization chemical reactions (Acharya et al., 2015). Furthermore, by increasing the operating temperature of dry torrefaction, negative relationships between solid carbon mass yield and both the H/C and O/C molar ratios are found, and the positive relationship with the heating value is verified (Yuan et al., 2021a).

2.2.2. *Activation*

Without activation, biochar exhibits poor catalytic properties owing to its poor morphology and porosity (Shen et al., 2014a). The essential properties for effective catalysis include a greater pore volume, surface area, and basicity/acidity of the biochar-based catalyst. Porosity is an essential parameter in catalysis for exposing active sites for the adsorption, diffusion, desorption, and reaction of various substrates. Tar formation during biochar synthesis reduces porosity; hence, the activation method plays a crucial role in enhancing the pore volume. Various treatments have been proposed for the enhancement of the morphology and porosity of biochar. Physical, chemical, and biological activation have been studied (Yuan et al., 2022a,c). Both physical and chemical methods are used widely for biochar activation; however, chemical activation is generally preferred because it produces well-developed pore structures with large surface areas and various

Table 2
Synthesis approaches of biochar-based catalysts, including their advantages and disadvantages.

Feedstocks	Syntheses		Modifications	Catalytic properties		Ref.
	Main routes	Operating conditions		Advantages	Disadvantages	
Spent mushroom substrate (SMS)	Torrefaction	200–300 °C within 30 min under N_2 atmosphere	Acid washing	More lignin than hemicellulose, low ash content	Recalcitrance towards enzymatic hydrolysis of cellulose	Chen and Aniza (2023)
Mushroom Seeds	Torrefaction + Pyrolysis	320–372 °C within 30 min under N_2 atmosphere	MgO metal oxide catalyst (30%)	Remarkable results of increasing hydrocarbon compounds, upgrading the fuel properties	AC is difficult to separate; biochar is mostly not reusable	Aniza et al. (2022)
Mixture of dried leaves	Slow pyrolysis	470 °C (heating rate: 10 °C/min) within 2 h under N_2 atmosphere	Esterification & Transesterification reaction	Recyclable biochar-based catalyst revealed better activity, Surface area and porosity increase due to breakage of functional group		Chi et al. (2021)
Aesculus chinensis bunge seed (ACBS)	Fast pyrolysis	800 °C within 39.25 s under He atmosphere	Functional group doping nanocatalyst (Fe_2O_3 and NiO)	Enhance the surface area	Porosity, exhibited good catalytic activity	Li et al. (2021d)
Coconut shell	Slow pyrolysis	550 °C (heating rate: 10 °C/min) within 1 h under N_2 atmosphere	KOH activation	Larger molecular structure, increase the amount of grafting group	Weakened surface area	Zhong et al. (2019a)
Coconut shell	Hydrothermal	180 °C within 24 h	Sulfonation	High functionality, short residence time	Low surface area	
Douglas fir (Wood saw dust)	Slow pyrolysis	600 °C under N_2 atmosphere	Sulfonation Acidic	Suitable for refinery process		Dong et al. (2015)
Pine wood chips, peanut hulls	Hydrolysis	120 °C within 2 h	Sulfonated with concentrated H_2SO_4	Biochar has a high potential to replace expensive conventional catalyst		Lee et al. (2017a)
Flamboyant	Gasification	500 °C (heating rate: 10 °C/min) under N_2 atmosphere	Sulfonation Acidic	Good catalytic activity for Tar cracking and reforming		Dhawane et al. (2015)
Coconut shell	Slow Pyrolysis	422 °C within 4 h under N_2 atmosphere	Sulfonated with concentrated H_2SO_4	High functionality, short residence time	Low surface area	Zeng et al. (2014)
Oat hull	Pyrolysis	400 °C within 4 h under N_2 atmosphere	Sulfonated with acid	High functionality, short residence time	Low surface area	Yao et al. (2016)
Rice husk	Flash Pyrolysis	500 °C within 15 min under N_2 atmosphere	Sulfonated with concentrated H_2SO_4	High char yield		Alvarez et al. (2014)
Sugarcane residue	Pyrolysis	600 °C within 4 h under N_2 atmosphere	Impregnation	Large surface area	Porosity, exhibited good catalytic activity	Pajootan et al. (2017)
Cotton linters	Torrefaction	250 °C within 2 h under N_2 atmosphere	Acid activation & Impregnation	Cu-Ru@Pt core–shell PRC/BTC		Lobos et al. (2016)
Wood saw dust	Pyrolysis	750 °C within 30 min under mixed H_2O/N_2 atmosphere	Gas activation	Oxygenated gasification biochar		Ducousso et al. (2015)
Rice straw	Pyrolysis	350–550 °C within 80 min under N_2 atmosphere	Acid washed	Expensive conventional catalyst		Wu et al. (2018)

Noted: SMS (Spent mushroom substrate), He (Helium), N_2 (Nitrogen), AC (activated carbon), MgO (Magnesium oxide).

functional groups (Patel et al., 2022a; Yuan et al., 2022b). Moreover, biological activation is gradually emerging to improve biochar's catalytic performance as well as its sustainable and specific application (Hung et al., 2021b).

Physical methods are endothermic processes, including UV, gaseous (N_2, CO_2, and O_3), thermal, steam, ultrasound, plasma, electrochemical, pressure, and heat activation (Patel et al., 2022a,b; Yuan et al., 2022a). Under these approaches, the physicochemical properties of biochar, e.g., its pore structure, pH, aromaticity, polarity, and ash content, are modified (Anae et al., 2021). In most cases, physical methods are used in combination with chemical methods to modify biochar (Yang et al., 2019a). The activation of biochar with steam has improved its hydrophilicity, primarily by enhancing its microporous structure and effective functional groups, such as -CO, OH, R-O-R, and COO (Rajapaksha et al., 2016). Upon heating, biochar becomes hydrophobic and forms fewer functional groups (Li et al., 2014; Oliveira et al., 2017). Steam favors large macro- and meso-porous volumes; however, CO_2 induces narrow micropores with large micropore volumes.

Chemical activation is performed at a moderate temperature during the thermal process (Kumar et al., 2020a; Yuan et al., 2022b). Activation techniques primarily include chemical oxidation (acid treatment), chemical reduction (alkali treatment), and the impregnation of metals, salts, and oxides, among others. For chemical activation, various compounds, such as KOH, H_3PO_4, H_2SO_4, NaOH, and $ZnCl_2$, are used for biochar activation (Patel et al., 2022b; Yuan et al., 2018). The process comprises five steps with both biochar and biomass as the initial material: (i) chemical impregnation, (ii) carbonization of impregnated biomass/biochar (under N_2 flow), (iii) acid-soaking of carbonized biochar, (iv) neutralization of acidified biochar, and (v) drying of neutralized biochar (Nayak et al., 2017). Chemicals dilate and hydrolyze the biomass or biochar during the soaking stage, preserve the porosity during the carbonization stage, and prevent the production of unwanted products (Kumar et al., 2020a). In an acidic modification, minerals are removed to increase the hydrophobicity of biochar (Zhang et al., 2015). Biochar modified under alkaline conditions generates more positive surface charges (Li et al., 2014). Therefore, chemical modifications have a more significant influence on improving the surface functionality of biochar than steam activation (Yuan et al., 2021a). In particular, alkali-treated biochar exhibits the highest surface functionality (Ahmed et al., 2016; Yuan et al., 2021a). In contrast, acidic treatments enhance the oxygenated functional groups of biochar (Ahmed et al., 2016; Zhang et al., 2015). Moreover, recent studies found that biological activation was effective in improving the catalytic performance of biochar. Microbial diversity and colonization were remarkable in the catalysis of biochar for the degradation of organic pollutants such as 4-nonylphenol (Hung et al., 2021b).

The choice of the activation method is primarily determined by its potential applications. Physical activation (i.e., steam purging at high

Table 3
Production of biochar-based catalysts and their role in catalysis of fuel and non-fuel products.

Catalysts	Feedstock/activator	Process/activation conditions	Applications	Catalytic activities	Ref.
Biodiesel production					
CaO-based PKSB	Palm-kernel-shell and CaO	Calcined at 800 °C for 2 h	Sunflower oil & methanol (1:9), Processed at 65 °C for 300 min	Conversion efficiency 99% (Transesterification)	Kostić et al. (2016)
Heterogenous acidified biochar catalyst	Peanut shell biochar, sulfonic acid	Sulfonation at 100 °C for 1 h	with 5 wt% catalyst loading, MeOH: oil ratio of 20:1 at 65 °C after 4 h	biodiesel yield of 94.91% was obtained (Transesterification)	Behera et al. (2020)
Calcined bovine bone waste	Bovine bone waste	Calcined at 750 °C for 6 h	Soybean oil & methanol (1:6), Processed at 65 °C for 3 h	A fame yield of 97%	Smith et al. (2013)
CaO/CSB	Crab shell	Calcined at 800 °C	Karanja oil & methanol (1:8), Processed at 65 °C for 120 min	Conversion efficiency 94%	Madhu et al. (2016)
SM@650	Swine manure biochar with metallic contents	Three-phase pyrolysis at 500 or 650 °C	Waste cooking oil at 210	Conversion efficiency 99% (Transesterification)	Jung et al. (2020)
Calcined chicken manure biochar	Chicken manure rich in $CaCO_3$	Carbonized at 350 °C	Waste-cooking oil & methanol (1:20) Processed at 350 °C	A fame yield of 95%	Jung et al. (2018)
30 K/AMB-550 catalyst	Pig meat and bone meal	Carbonized at 650 °C, activated by KOH, alkalization with K_2CO_3	Palm oil & methanol (1:7), Processed at 65 °C for 150 min	Conversion efficiency >98% (Transesterification)	Wang et al. (2017)
Tar and steam or gas reforming					
Coked hardwood biochar	Hardwood, temperature activation	Carbonized at 850 °C; 10 h	Used for biomass gasification, toluene, naphthalene, and benzene removal, and syngas cleaning	> 90% toluene, and naphthalene, and > 50% benzene removal	Buentello-Montoya et al., (2020)
Ni/wood char	A mixture of 15 wt% NiO and wood	Carbonized at 650–850 °C; 0.3 s	Used for sawdust gasification, tar removal, and syngas conditioning	> 97% tar removal efficiency from syngas	Wang et al. (2011)
Ni-Fe/rice husk-biochar	Rice husk-Ni-Fe	Carbonized at 800 °C of	Used for biomass pyrolysis, tar removal, and syngas cleaning	92% tar removal efficiency	Shen et al. (2014a)
Switchgrass-biochar	Switchgrass-and KOH activation	Carbonized at 700–800 °C	Used for biomass gasification, toluene removal, and syngas cleaning	81% tar removal efficiency	Bhandari et al. (2014a)
Ar/Mallee wood biochar	Mallee wood	Carbonized at 800 °C; H_2O/Ar for 0–50 min	Used for biomass gasification, toluene removal, and syngas cleaning	Significant tar removal efficiency however not given the exact value	Liu et al. (2021)
Fe/pine bark-biochar	Pine bark and FeO	Carbonized at 800 °C; H_2O	Used for biomass gasification, toluene removal, and syngas cleaning	100% tar removal efficiency	Kastner et al. (2015)
Pine bark-biochar	Pine bark at high temperature	Carbonized at 900 °C; H_2O	Used for biomass gasification, toluene removal, and syngas cleaning	94% tar removal efficiency	Mani et al. (2013)
Miscellaneous applications					
Ni/CC catalysts	Cotton stalk- Ni	Carbonized at 800 °C	Hydrogen production	64.02 vol%, 92.08 mg/g biomass	Yao et al. (2016)
Ni/RC catalysts	Rice straw-Ni	Carbonized at 800 °C	Hydrogen production	H_2 yield: 34.62 mg/g	
Sulfonated biochar catalyst	Forestry wood waste	Chemical (DMSO/DW) based activation	5-hydroxymethylfurfural production	Conversion efficiency: 22%	Cao et al. (2018a)
Sulfonated biochar catalyst	$ClSO_3H$ acidified at 200 W of microwave irradiation	Hydrothermal treatment at 100 °C for 24 h	Spiramycin antibiotic hydrolysis	Conversion efficiency: >17% as compared to native biochar of 12%	Xie et al. (2020)
Ru/ABC	Rice husk	KOH and H_2SO_4 based activation	Syngas methanation	CO conversion efficiency: 100%	Zhu et al. (2015)
SnO_2–CO_3O_4/C biochar catalyst	Lignocellulose residue	Chemical based activation	Corncob hydrolysis	Conversion efficiency: 40.3–60.4%	Liu et al. (2015b)
Biochar solid acid	Corn stover	Chemical based activation	Biomass hydrolysis	Conversion: 18.79–100%	Li et al. (2013)

Noted: Ru/ABC- Ruthenium-activated biochar; Ni/CC- Nickel/cotton carbon; Ni/RC- Nickel/rice carbon; SnO_2–CO_3O_4_Tin(IV) oxide-Cobalt (II, III) oxide.

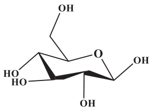
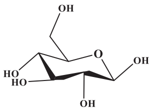
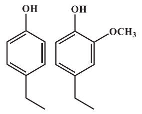
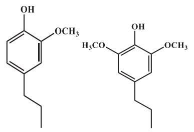
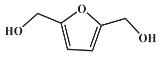
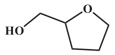
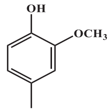
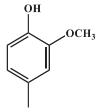
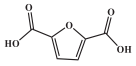
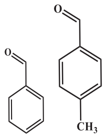
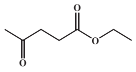
temperatures) is more environmentally friendly and simple compared to chemical activation. However, the textural properties (i.e., low surface area and low porosity) are not well-developed by physical activation. For example, steam purging increases the SSA and total pore volume (TPV), although steam activation is improper for improving the surface functionality of biochar when compared with chemical and impregnation activation. In chemical methods, alkaline activation enhances the SSA and oxygen-containing functional groups of activated biochar, which is desirable for catalytic applications of biochar-based materials (Panwar and Pawar, 2020; Patel et al., 2022a). Metal oxide-modified biochar has better textural properties and environmental applications than physical- or chemical-activated biochar; however, this still needs to be confirmed for catalytic applications (Panwar and Pawar, 2020). Moreover, colonizing specific microorganisms with electron-exchanging ability may be more promising for catalytic applications.

2.2.3. Surface functionalization

Apart from the inherent surface functional groups, additional reactive groups can also be added to biochar via doping. These doping strategies have mainly focused on adding nitrogen, sulfur, phosphate, and oxygen-containing functional groups via processes such as amination (Chen et al., 2021a; Yuan et al., 2020), acidification (Kastner et al., 2012), oxidation (Li et al., 2014), and *in-situ* heteroatom-doping (Gao et al., 2016). These functional-group-doping methods further improve the catalytic performance of native biochar. Some doping treatments have been studied extensively to improve biochar's surface properties, including doping with nitrogen-, sulfur-, and phosphate-rich functional groups, as oxygen-containing groups are considered to be adequately present in biomass-derived biochar (Chen et al., 2021a; Leng et al., 2022).

Doping carbonaceous materials with heteroatoms such as N (Wang et al., 2018), S (Gao et al., 2016), or P (Bose et al., 2019) can alter their physicochemical properties and improve their catalytic, adsorption, or energy-storing performance. Nagy et al. (2016) found that mesoporous carbon aerogels with N-doping efficiently performed oxygen reduction reactions during electrocatalysis. Several methods for incorporating heteroatoms into biochar have been discussed, especially N-doping. However, the direct carbonization of N-containing biomass is more favorable than annealing under NH_3 or NH_4NO_3 because of the large volume availability of N-rich biomass and facile operation (Cheng and

Table 4
Biochar-based catalysts in biorefinery.

Reaction	Biochar preparation	Characteristics	Performance	Product	Ref.
Hydrolysis	One-pot: Pine wood was pretreated by H_3PO_4 85% (*w*/w) and then pyrolyzed at 400–600 °C.	Phosphorus groups (Brønsted acid sites); Surface area of 1547 m^2/g.	High glucose yield of 86.5% at 150 °C for 20 min and HMF yield of 30.2% at 180 °C for 20 min were obtained from the hydrolysis of food wastes by H_3PO_4-activated biochar.	 (Glucose)	Cao et al. (2018b)
Hydrolysis	Two-step: Direct pyrolysis of wood at 700 °C for 15 h was conducted for the preparation of biochar. It was post-modified by 30% *w*/*v* H_2SO_4 at 150 °C for 24 h to synthesize sulfonated biochar catalyst.	-SO_3H groups (Brønsted acid sites); Surface area of 57 m^2/g.	Hydrolysis of maltose with H_2SO_4-activated biochar at 140–160 °C enabled a high glucose yield of 85.4%.	 (Glucose)	Xiong et al. (2018)
Hydrogenation	The activated biochar was prepared by microwave-assisted co-pyrolysis of plastic and biomass at 450 W power (600 °C) and chemical activation. Metal-loaded activated biochar was prepared by impregnation and reduction at 400 °C.	Pd active sites; ZrO_2, MoOx, and WOx (Lewis acid sites); Surface area of 51 m^2/g.	Total phenol monomer yield can reach up to 42.2% by 2Pd-5Mo/ABC catalyst at 240 °C for 3 h under 3 MPa H_2.	 (Phenolic monomer)	Gurrala et al. (2022)
Hydrogenation	Pine powder was firstly carbonized at 450 °C for 3 h and then calcined with melamine and phosphate at 800 °C for 1 h in N_2 to synthesize NP-Char. Ru@NP-Char was prepared by wetness impregnation and reduction at 400 °C for 3 h with H_2.	Ru nanoparticles (3.34 nm); NP-doped carbon; Surface area of 248 m^2/g.	The monomer yields from poplar and pine over Ru@NP-Char were 57.98 wt% and 17.53 wt% under 2 MPa H_2 at 250 °C for 3 h.	 (Phenolic monomer)	Ding et al. (2022)
Hydrogenation	Slow pyrolysis of rice husk at 550 °C for 2 h was conducted to prepare biochar support, which was then impregnated with Pt precursors and reduced by flowing a 5 vol% H_2 at 400 °C for 2 h to synthesize Pt/BC-IM catalyst.	Pt nanoparticles (1.9 nm); 2.6 wt% Pt loading; Oxygen-containing functional groups; Surface area of 9 m^2/g.	Pt/BC-IM catalyst showed the highest yield of DHMF (90.1%) in HMF hydrogenation under 10 MPa H_2 at 160 °C for 10 h.	 (DHMF)	Wang et al. (2021c)
Hydrogenation	Biochar was prepared by the pyrolysis of ammonia solution (3.8 wt%) impregnated sorghum at 550 °C. CO_2 deposition method was used to confine Pt nanoparticles in porous biochar at a low temperature of 40–70 °C.	Pt nanoparticles (2–4 nm); Hierarchically porous biochar; Surface area of 532 m^2/g; Strong metal-support interaction.	3 wt% Pt/C catalyst showed a furfural conversion (80%) with enhanced selectivity to tetrahydrofurfuryl alcohol under 6 MPa H_2 at 140 °C for 3 h.	 (Tetrahydrofurfuryl alcohol)	Hu et al. (2019b)
Hydrodeoxygenation	In chemical activation, the biomass was mixed with $ZnCl_2$ (2:1, *w*/w $ZnCl_2$: biomass), followed by carbonization under CO_2 at 800 °C. Pd-loaded biochar (Pd/C) catalyst was prepared by colloidal synthesis.	Pd nanoparticles (2 nm); Acid groups as H donors (Brønsted acid sites); Surface area of 737 m^2/g.	The highest selectivity of 92% to MMP from vanillin was obtained at 100 °C under 3 MPa H_2 in water with Pd/C catalyst.	 (MMP)	Santos et al. (2020)
Hydrodeoxygenation	Co@NC 700 catalyst was prepared by one-pot pyrolysis of glucose, melamine, and $CoCl_2$ at 700 °C for 4 h.	Co nanoparticles (15–31 nm); 7.9 mol% Co loading; N-doping; Surface area of 381 m^2/g.	Co@NC-700 enabled an excellent conversion rate (95.7%) and a high MMP selectivity in the HDO of vanillin with FA as a hydrogen donor at 180 °C for 4 h under 0.5 MPa N_2.	 (MMP)	Yang et al. (2017)
Oxidation	N-doped carbon was prepared by direct pyrolysis of pomelo peel layer under a mixed flowing NH_3/N_2, and it was then mixed with PVP-stabilized Pt-NPs by rotary evaporation and heated at 900 °C for 3 h under N_2 to synthesize Pt/NC 800 catalyst.	Pt nanoparticles (3–10 nm); 1.12 wt% Pt loading; N-doping; Surface area of 809 m^2/g.	Nearly full HMF conversion (100%) and high selectivity of 83.9% to FDCA can be obtained by Pt/NC 800 catalyst with 2 equiv. of Na_2CO_3 under 0.5 MPa O_2 at 110 °C for 24 h.	 (FDCA)	Yang et al. (2020)
Oxidation	Soluble starch (5 g) and phosphoric acid (5.8 g) were pyrolyzed at 700 °C for 2 h in N_2 and then treated with boiling water for 2 h to synthesize P-modified biochar catalyst.	-P-O-C active sites; Surface defects by P doping (0.98 at.%); Surface area of 1613 m^2/g.	Secondary aromatic alcohols showed the higher reactivity than alicyclic and heterocyclic alcohols over the PC-700 catalyst under 1 atm O_2 at 120 °C.	 (Alicyclic and heterocyclic alcohols)	Hu et al. (2019a)
Esterification	Carbon cryogel was prepared by mild pyrolysis of urea-furfural gel (1:2 mol/mol) at 500 °C for 2 h and acid treatment with concentrated H_2SO_4 at 150 °C for 15 h. The carbon support was further impregnated with $FeCl_3•6H_2O$ and calcined at 300 °C for 5 h to synthesize UCCS-Fe-300 catalyst.	-SO_3H functional groups (Brønsted acid sites); Fe doping (Lewis acid sites); Surface area of 108 m^2/g.	The EL yield from LA can reach up to 92.4 mol% at 80 °C for 4 h by UCCS-Fe-300 catalyst.	 (EL)	Zainol et al. (2021)

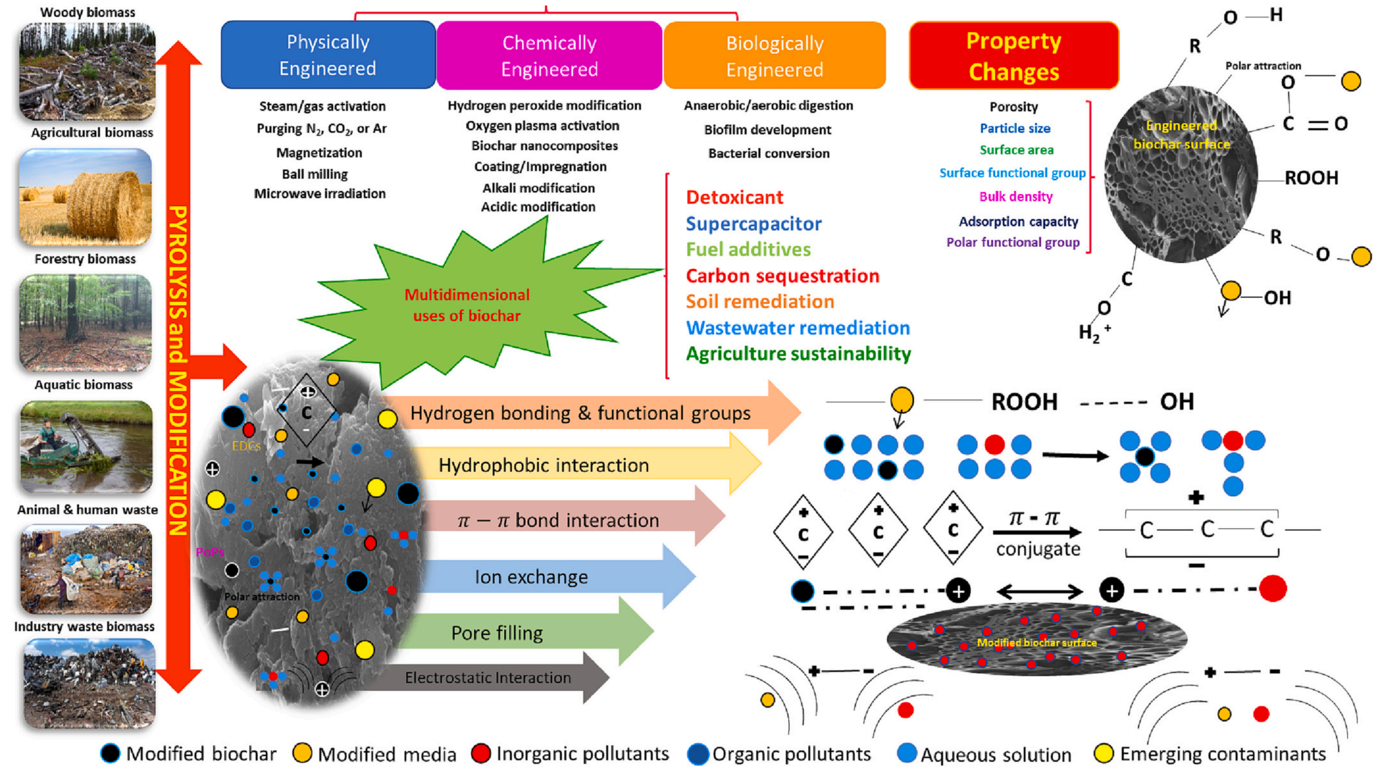


Fig. 3. Upcycling biomass and its waste into biochar for various catalytic applications.

Li, 2018).

To investigate the isomerization of glucose to fructose, Chen et al. (2018) prepared a high-performance catalyst using the N-doping treatment on biochar, improving selectivity by up to 84% for fructose. Chemical reactions were catalyzed by lone pairs of electrons, which attracted hydrogen atoms near water molecules. Yu et al. (2019) also synthesized the aluminum–biochar composite using *in-situ* heteroatom-doping treatment, exhibiting the best catalysis with 21.5 mol% fructose (selectivity up to 74%), which is comparable to those of novel and costly inorganic solid catalysts. Possible active sites on the biochar surface to facilitate glucose isomerization through Lewis acid-based catalysis could be, amongst others, Al–O–C, AlO(OH), $Al(OH)_3$, and Al_2O_3. Thus, the unique surface functionalities of biochar reveal new possibilities for its use as a cost-effective and efficient catalyst.

Various doping treatments have their pros and cons depending on the targeted application. Amination reduces the pore size of modified biochar, but enhances the surface area. Adsorption mechanisms rely on functional-group interactions in such modifications and control the adsorption process, during which acid–base interactions and hydrogen bonding interactions are dominant. Doping treatment uses relatively costly chemicals during oxidation and amination treatments, which limits its application. Aminated biochar is more suitable for metal ion removal due to the charged ionic interaction, compared to organic contaminants (El-Nemr et al., 2021).

Acid treatment of biochar destroys the prevailing basic functionalities on the surface of biochar, decreasing phenolic adsorption. Destruction of basic sites ultimately leads to a reduction in catalysis by phenolic groups. Acid treatment enhances metal ion adsorption and weakens organic contaminant adsorption (Rehman et al., 2019). Some studies have shown contrary results following nitric acid treatment, which was revealed later due to adsorbate–adsorbate interactions in the presence of high concentrations of organic pollutants. The main drawback of acidification is that it can only be used for samples present in large quantities (Rehman et al., 2019).

There are many approaches to oxidation, including acid and base treatments; however, gaseous plasma oxidation is readily used for textural specification in modified biochar. Plasma treatment is adopted to generate desired charged species on the biochar surface for specific roles in remediation. High-temperature oxidation in the presence of concentrated H_2SO_4 was found to be efficient in organic adsorption due to an increased mesoporous volume. Chemical impregnation, however, enhances the prevailing properties of the material by improving its built-in capacity for catalytic oxidation. Importantly, the thermal degradation of biomass enhances the electrical conductivity of biochar by producing carbon sheets but removes oxygen-containing functional groups from the biochar (Sharma et al., 2022).

Heteroatom-doping of biochar to modify surface functional groups is a popular approach at the moment. Biochar performance is being improved by tuning textural features along with the generation of numerous functional groups on the surface. This is effective in the adsorbent surface (Rehman et al., 2019). With a wide range of heteroatoms, aromatic carbon can have an acidic or basic surface due to its surface functionalities incorporating heteroatoms and delocalized electrons. Tailoring the surface of biochar with heteroatoms produces the exceptionally high adsorption performance of these materials. The cumulative performance of the primary functional groups of adsorbents is critical to removing organic and inorganic pollutants such as carboxyl, phenols, carbonyl, lactones, and quinones on their surface. The critical drawbacks of these treatments are the modification process using costly and hazardous chemicals. Chemical modification of biochar commonly produces O_2-containing reactive groups, which enhance the redox capacity of the biochar but reduce electrical conductivity (Sharma et al., 2022).

3. Applications of biochar-based catalysts in biorefineries

Various biorefinery processes have been developed to convert lignocellulosic biomass into fine chemicals and fuels efficiently and in an environmentally benign manner. Biomass conversion can be considered a carbon-neutral circular framework to achieve a sustainable society

(Fig. 4). As biomass is a highly functionalized and oxygenated material, there is an ever-increasing demand for catalytic processes that enable the selective production of target products. Heterogeneous catalysis is vital for achieving a sustainable biorefinery. Carbon has been advocated as a leading material for biomass conversion, and biochar-based catalysts are potential candidates because of their exceptional activity, thermal stability, low cost, and environmental benefits (Kumar et al., 2020b; Zhang et al., 2021). They exhibit many superior properties, such as multiple functionalities, tailorable porous structure, large surface area, and acid/alkali resistance (Chen et al., 2020a; Chen et al., 2018). In addition, catalysts prepared from renewable biomass can contribute to achieving carbon neutrality for low-carbon-footprint chemicals and fuel produced from biomass through a self-contained system (Kobayashi et al., 2016; Liao et al., 2020). This section provides a detailed overview of recent advances in the catalytic liquefaction and pyrolysis of biomass using biochar-based catalysts.

3.1. *Catalytic conversion of biomass and its derivatives through liquefaction*

The catalytic liquefaction of biomass and its derivatives to liquid bio-oils and platform chemicals (e.g., monomeric sugar, furfural, 5-hydroxymethylfurfural, and phenolic chemicals) is a cost-effective biorefinery route (Fig. 5). Various biochar-based catalysts (e.g., acidic biochar, metal/metal oxide-loaded biochar, and heteroatom-doped biochar) have been investigated under different liquid-phase reactions (e.g., hydrolysis, hydrogenation, oxidation, hydrodeoxygenation, and esterification) to efficiently convert various feedstocks that selectively produce valuable fuels and chemicals (Table 4).

3.1.1. *Hydrolysis*

In biomass utilization, the first step typically involves hydrolysis of cellulose and hemicellulose to sugars, which can be further converted to building block chemicals. Acids (e.g., mineral acids and solid acids) have been widely explored to promote the catalytic hydrolysis of biomass because of their proton-donating ability (H^+ ions) for Brønsted acid catalysis or they form an electron-pair bond, driving Lewis acid catalysis (Vogt and Weckhuysen, 2022). Using mineral acids as homogeneous catalysts usually produces a high yield but unavoidably introduces various environmental hazards (Li et al., 2013). Biochar-based solid acid catalysts with Brønsted and/or Lewis acidities have demonstrated exceptional catalytic performance in hydrolysis reactions, outperforming mineral acids in sustainable biorefineries. For example, they can promote the adsorption of CH groups in cellulose molecules over the π–electron-rich surface of biochar through a CH–π interaction, and acidic sites facilitate the hydrolysis reaction (Kobayashi et al., 2016). As greener alternatives for unrecyclable mineral acids, these catalysts are available for the hydrolysis of different biomass feedstocks in a more environmentally benign process (Kobayashi et al., 2016; Xiong et al., 2021b).

Generally, Brønsted acid sites can be easily incorporated onto the biochar surface using a one-step approach or an improved two-step

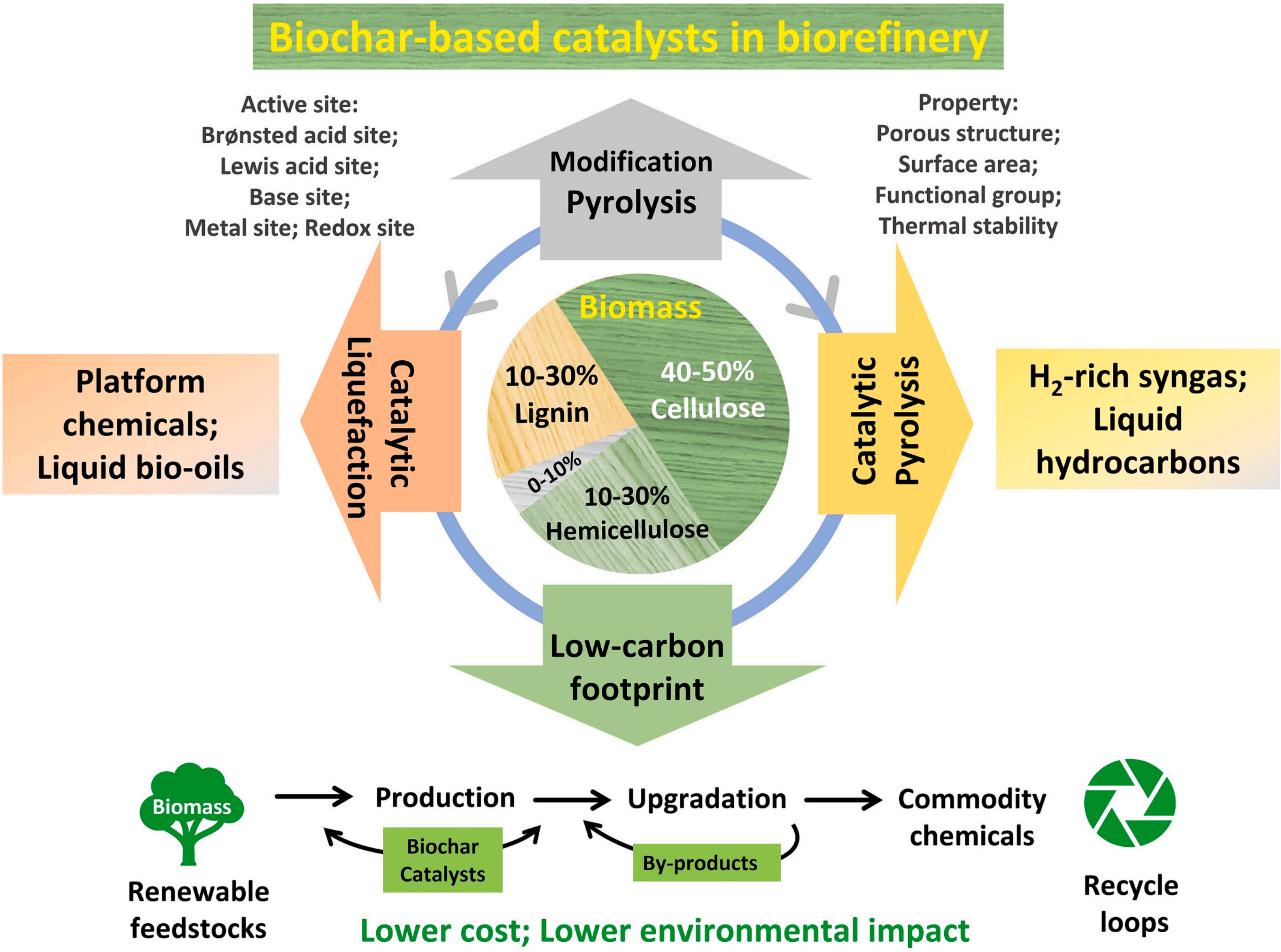


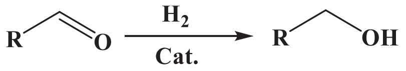
Fig. 4. General overview of biochar-based catalysts in biorefinery.

process that requires post-functionalization of the prepared biochar (Table 3). A phosphoric acid-activated biochar catalyst with a large surface area of 1547 m^2/g was fabricated by one-step pyrolysis of pinewood sawdust with H_3PO_4 (Cao et al., 2018a). Increasing the activation temperature to 600 °C improved the porosity of biochar and enhanced its acidity by incorporating various phosphorus groups (e.g., $-C-O-PO_3$, $-C_2PO_2$, and $-C-PO_3$). Owing to their surface properties, such acidic biochar catalysts promote the hydrolysis of starch and show remarkably high yields of glucose (86.5%) and 5-hydroxymethylfurfural (HMF). Sulfonated biochar catalysts have been recommended as ideal substitutes for H_2SO_4 because the strongly Brønsted acidic SO_3H sites can be covalently linked to the biochar surface. SO_3H-functionalized acidic biochar from wood waste was explored to enhance the hydrolysis of maltose to glucose at 140–160 °C and dehydrate fructose to HMF at a higher temperature range of 160–180 °C. A synergistic effect between $-SO_3H$ groups and O-containing acidic groups (e.g., $-OH$ and $-COOH$ groups) may render the catalyst more polar for substrate adsorption, with $-SO_3H$ groups functioning as effective active sites for hydrolyzing the adsorbed substrates. Therefore, such biochar catalysts with high Brønsted acidity and enhanced adsorption ability exhibit higher activity for the hydrolysis of maltose, achieving an 85% glucose yield (Xiong et al., 2018). A bamboo-based biochar bearing $-SO_3H$, $-COOH$, and $-OH$ groups can enhance hemicellulose hydrolysis to xylo-oligosaccharides, with a maximum yield of 54.7 wt% (Bai et al., 2015). However, leaching of the $-SO_3H$ groups was also observed after several recycling runs, limiting long-term stability. Leaching is a major issue in liquid-phase reactions because it leads to catalyst deactivation and downstream separation. Numerous strategies have been investigated to enhance the resistance to leaching. An ionic liquid (IL)-grafted biochar sulfonic acid catalyst with high thermal stability has been explored for the hydrolysis of cellulose to reducing sugars (Zhang et al., 2012). The enhanced repeatability of the biochar catalyst can be attributed to the formation of intramolecular hydrogen bonds to stabilize $-SO_3H$ groups in IL against the leaching of acidic sites. Compared to a catalyst without IL modification, a much higher turnover number of cellulose hydrolysis (TON, 3.22–6.23) was achieved by forming a strong interaction of functional groups with biochar.

Biochar can be activated for the direct transformation of biomass to sugars by simple chemical activation with several mineral acids. It can also serve as carbon support to improve the dispersion of Lewis acids (e.g., SnO_2, ZrO_2, and Al_2O_3) for producing desirable chemicals (Yang et al., 2019b; Yu et al., 2018). Thus far, studies on the nature of active sites have demonstrated that Lewis acid sites (electron-withdrawing) are intimately linked to Brønsted acid sites (proton-donating). In aqueous systems, the dissociative adsorption of water molecules on Lewis acid sites can form hydronium ions, $H_3O^+(H_2O)_n$, to generate Brønsted acid sites (Vogt and Weckhuysen, 2022). For example, a SnO_2-Co_3O_4-x/C biochar catalyst had an acidity almost equivalent to 4.5% H_2SO_4, but it exhibited a lower SSA of 6.34 m^2/g (Liu et al., 2015b). The reaction mechanism involves H_3O^+ ions that offer Brønsted acidity to hydrolyze corncob hemicellulose to xylose. Multivalent Sn^{4+} and Co^{2+} as Lewis acid sites can promote xylose isomerization and dehydration to furfural (62.7% yield at 180 °C). The Al–biochar catalyst exhibited good catalytic activity towards starch-to-HMF through tandem hydrolysis (Brønsted acids), isomerization (Lewis acids), and dehydration (Brønsted acids) (Xiong et al., 2021b; Yu et al., 2019). Various oxygenated groups on humin-derived biochar served as anchoring sites and were used to improve the dispersion of Al species, together with the enhanced accessibility of substrates to active sites. The resulting catalyst showed an improved selectivity to fructose (61.8–76%) at moderate temperatures (140–160 °C).

3.1.2. Hydrogenation

In hydrogenation reactions, various unsaturated functional groups in biomass-derived products, such as $-C=O$ and $-C=C$ (Eq. 1), must be selectively reduced by H_2 to their corresponding alcohols and alkenes, which are key intermediates for fine chemical industries. The conversion efficiency primarily depends on the temperature, solvent, hydrogen pressure, and nature of the catalyst. Metal catalysts such as Ru, Pt, Pd, and Ni are commonly used because of their high hydrogenation activities. A critical consideration in a hydrogenation reaction is the hydrogen spillover over heterogeneous catalysts, in which catalyst supports provide additional active sites to adsorb hydrogen atoms dissociated from metal sites. Carbon-based materials have shown a great ability to enhance hydrogen evolution and electron transfer. Selective $-C=O$ hydrogenation can easily occur using a biochar-based catalyst.



(1)

Valorizing lignin/lignocellulose into phenolic monomers is essential

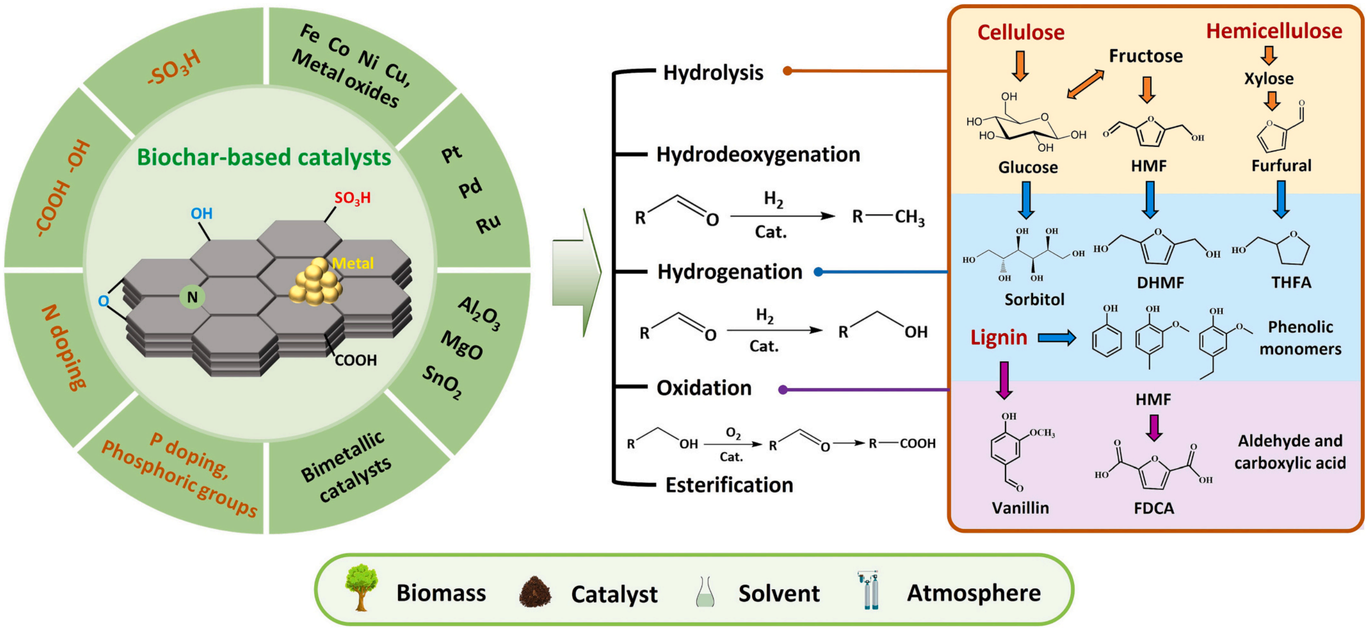


Fig. 5. Catalytic liquefaction of biomass to liquid bio-oils and chemicals.

for sustainable biorefineries (Cao et al., 2020a,b). Palladium-loaded activated biochar was catalytically active in lignin hydrogenation (Gurrala et al., 2022). The activated biochar was prepared by microwave-assisted pyrolysis of biomass and plastics at 450 W power to 600 °C and then oxidized with HNO_3 (Table 3). Introducing additional metal oxides (ZrO_2, WO_x, or MoO_3) as promoters can further improve Pd dispersion and provide more Lewis acid sites for the cleavage of β-O-4 linkages in lignin to produce C_9 monomers. Total phenolic monomer yields can reach up to 42.2% by 2Pd-5Mo/ABC at 240 °C for 3 h with 3 MPa H_2. Recently, surface modification by heteroatom-doping (e.g., N and P) has been studied to tailor the properties of biochar and enhance its hydrothermal stability. N and P were co-doped into the Ru@Char catalyst by high-temperature (800 °C) co-pyrolysis of pine char, melamine/urea (N source), and phosphate (P source). Both physical (small Ru nanoparticles, large specific area of 248 m^2/g, and porous structure) and chemical properties (strong metal-support interaction) significantly facilitated the hydrogenation of lignocellulose to aromatic monomers (Ding et al., 2022). A mechanistic analysis showed that the introduction of N/P atoms is conducive to the electron transfer between Ru and biochar support, forming metallic Ru active sites to participate in reductive depolymerization. The distinct yields of monomers from poplar (57.98 wt%) and pine (17.53 wt%) over Ru@NP-Char indicated that biomass feedstocks affect the catalytic performance and may also need to be considered.

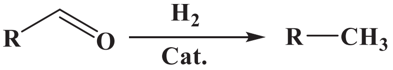
Transition metals such as Ni and Cu exhibit significant activity in selective hydrogenation reactions. In the case of vanillin hydrogenation, the Ni/biochar catalyst enabled a 79.3% conversion with a selectivity of 80.4% for vanillyl alcohol at 170 °C (Wang et al., 2021e). This study also implied a more significant influence of surface chemistry (hydrophobicity/hydrophilicity) on selective hydrogenation. The co-presence of hydrophobic and hydrophilic sites facilitated the adsorption and activation of C=O bonds on vanillin, which could render the Ni/biochar catalyst much higher activity. A bimetallic Ni–Mo_2C/C catalyst was fabricated by one-pot pyrolysis of sawdust with metal salts to increase the Ni dispersion and catalytic stability for lignin hydrogenation (Wang et al., 2016). The combination of Ni and Mo_2C with strong metal-support interactions and the graphitized biochar facilitates electron transfer, allowing catalytic hydrogenation of lignin with a high yield of liquid products (61.3 wt%). After five runs, the yield of the main products in the liquid phase remained almost unchanged, indicating the enhanced stability of the Ni–Mo_2C/C catalyst for lignin hydrogenation.

Furfural is a highly competitive platform chemical. Its derivates can produce bio-based polymers through selective hydrogenation in H_2 or organic solvents. Catalytic stability is significant in liquid-phase reactions. Monometallic Pt nanoparticles loaded on porous biochar were prepared by the pyrolysis of ammonia-treated sorghum at 550 °C and stabilized using a liquid-CO_2 deposition method (Hu et al., 2019b). The Pt/C (3 wt%) catalyst enhanced the catalytic performance in furfural conversion (80%) and selectivity to tetrahydrofurfuryl alcohol at 140 °C for 3 h and displayed no aggregation of metal nanoparticles after four cycles. This study also explored Pd/C and Pt-Pd/C catalysts for the hydrogenation of the −C=O bond. A study of the reaction mechanism indicated that Pd species preferentially transformed the −C=O groups to formic acid through an overoxidation reaction. In the case of such Pt-loaded biochar catalysts for HMF hydrogenation, the highest yield of 2,5-bis(hydroxymethyl)furan (DHMF: 90.1%) compared to other carbon supports (e.g., reduced graphene oxide, graphitic carbon nitride, and carbon nanotubes) was tested at 160 °C for 10 h with 10 MPa H_2 (Wang et al., 2021c). The oxygen-containing functional groups (e.g., OH, C−O, and C=O) in BC may assist in activating the −C=C bond in HMF, thus enhancing the selectivity to DHMF, even though its SSA is relatively low (9 m^2/g).

Biomass source is a key factor, as it can be linked to both physiochemical properties and the composition of biochar. For example, rice husks with a high silica content have been used to fabricate Ni-loaded silica-rich biochar catalysts for the catalytic hydrogenation of furfural (Madduluri et al., 2020). XRD patterns confirmed the formation of the SiC phase in the biochar, and the presence of metallic Ni clusters is probably due to the carbon moiety acting as a reductant for the carbothermic reduction of metal oxides. The production rate of furfuryl alcohol in the presence of a 15 wt% Ni-loaded biochar catalyst was the highest among the biochar-based catalysts. Nitrogen-doped biochar was prepared by fast pyrolysis of N-rich biomass (crushed rubber seed shell), followed by activation with K_2CO_3. It was further used to support Cu^0-Cu_1Ni_3 for the selective hydrogenation of furfural (Fu et al., 2021). There was a slight decline in furfural conversion from 100% to 88.8% after five cycles, and the strong metal-support interaction induced by heteroatom-doping might account for its enhanced catalytic stability. More recently, porous carbon materials with tailorable surface properties have been fabricated using hard/soft templates from liquefiable biomass. A Ru/glucose-derived carbon catalyst was prepared by a CO_2 activation process, and carbon nanotubes were introduced to form a hybrid carbon support and used for the hydrogenation of cellulose to sorbitol (Rey-Raap et al., 2019). A high yield of sorbitol (64.1%) and complete conversion of cellulose were achieved at 205 °C with 5 MPa H_2. This hybrid has a large SSA of 1200 m^2/g, a more stable chemical structure, and basic surface functionalities, which can favor the direct production of sorbitol and prevent its further hydrogenolysis into polyols.

3.1.3. *Hydrodeoxygenation*

Hydrodeoxygenation (HDO) is an important reaction because of its advantages of mild reaction conditions, high-heating-value products, and low coke formation (Cao et al., 2021). Hydrogenolysis of −C−O bonds typically occurs under reducing conditions using H_2 gas or liquid organic hydrogen carriers (e.g., formic acid, methanol, ethanol, and isopropanol) with metal catalysts (Eq. 2). Metal (e.g., Ni, Co, Mo, and W)-loaded or -doped biochar catalysts also show promising potential for HDO reactions.



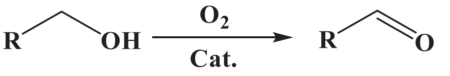
(2)

Aromatic monomers derived from lignin are ideal alternatives for conventional fossil fuels. A pine biochar-modified Ni–V catalyst was explored during HDO of lignin-derived products to produce low oxygen-content aromatics (e.g., toluene and benzene) with a yield of 69.17% (Wu et al., 2021). A strong relationship exists between aromatic selectivity and the essential properties of a catalyst, such as oxygen vacancies and the carbon structure. The graphitic carbon structure in biochar can improve the affinity and adsorption of aromatic reactants. A study of the reaction mechanism suggested that surface vacancies are also favorable for the adsorption of the -OH groups of phenolic compounds, thereby enhancing accessibility to the active sites for the HDO reaction (Wu et al., 2021). Vanillin is a common product in the lignin fraction. Under mild conditions, HDO reactions can be facilitated by noble metals such as Pd, Au, and Ru. For chemical activation, the biomass is mixed with $ZnCl_2$, followed by carbonization under CO_2 at 800 °C to prepare activated carbon. Loading Pd can be used in the HDO of vanillin, and high selectivity of 92% for 2-methoxy-4-methylphenol (MMP) was achieved at 100 °C under 3 MPa H_2 (Santos et al., 2020). Santos et al. (2020) further demonstrated that the catalytic roles of active sites and surface reactions are clearly understood. Their results indicated that surface functional groups (e.g., COOH and OH groups) could act as H donors for −C−O activation via proton transfer from Brønsted acids to oxygen atoms. Chemical activation using KOH also enabled the activated biochar with a large SSA (~2000 m^2/g). A Mo_2C/activated biochar catalyst was evaluated for selective HDO of lignin-derived compounds (Liu et al., 2019b). The oxygen content of the biochar increased when the activation temperature increased to 600 °C, whereas it decreased at 700 °C with increased graphitization. Similarly, in the case of 4-methylphenol (lignin-derived product), surface oxygen groups can facilitate better dispersion of Mo species and serve as active sites to induce direct deoxygenation of C–O bonds.

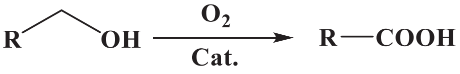
In addition to surface acid sites, catalyst basicity can be tailored by doping biochar materials with heteroatoms such as nitrogen. A cobalt-embedded mesoporous N-doped carbon catalyst (Co@NC-700) was prepared by one-pot pyrolysis of glucose, melamine (N source), and $CoCl_2$ and used for the HDO of vanillin (Yang et al., 2017). In this study, formic acid (FA) was used as a hydrogen donor and a solvent. Heterogeneous N-type species can improve the basicity of carbon materials for FA dehydrogenation and vanillin hydrogenation. Such a bifunctional catalyst enabled 95% vanillin conversion and selective production of MMP at 180 °C for 4 h. In particular, doping with electron-rich N provided a favorable enhancement in stability, without significant loss in catalytic efficiency after five runs. HDO of vegetable oils was used to produce renewable diesel using a biochar-supported bimetallic Mo–W carbide catalyst (Tran et al., 2020). The reaction mechanism suggested that the C-terminated surface for binding atomic H and the altered electronic surface properties of bimetallic carbides (Mo-W) are suitable for the HDO of oxygenates in oils to obtain fuels with a low oxygen content (>95% conversion and >76% yield). This catalyst also possessed an enhanced reusability with a 98% conversion of canola oil after regeneration treatment owing to the strong metal–carbon interaction.

3.1.4. *Oxidation*

Oxidation reactions involve the oxidation of alcohols to aldehydes by reducing the hydrogen content (e.g., Eq. 3) or alcohol oxidation to a carboxylic acid by increasing the oxygen content (Eq. 4). Oxidation reactions are often performed using oxygen, air, and hydrogen peroxide as oxygen suppliers. Metal oxides, such as CuO_2, Co_2O_3, and FeO_x, are commonly used for the oxidative upgrading of biomass derivatives (Cao et al., 2020a; Cao et al., 2019). Carbon-based catalysts might have poor stability compared to other metal oxides under oxidative conditions. Fabricating biochar-supported metal catalysts with high hydrothermal stability to maintain activity and selectivity with time on stream is critical.



(3)

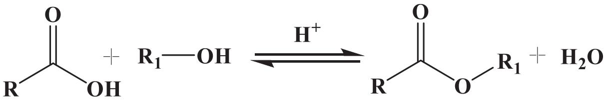


(4)

Tuning the surface oxygen species of the catalyst to stabilize metal particles and promote substrate adsorption and the generation of active oxygen species has been comprehensively studied (Liu et al., 2021). Recently, attention has been paid to N-doped biochar as an efficient metal-free catalyst for the oxidation of HMF to 2,5-furandicarboxylic acid (FDCA), a promising intermediate to replace fossil-fuel-derived terephthalic acid in the production of aromatic polyesters (Feng et al., 2021; Yang et al., 2020). Pomelo peel as a carbon source was polymerized at 800 °C with flowing NH_3 to obtain highly N-doped porous carbon (up to 11.4 wt% of N in the carbon support). Pyridinic and pyrrolic N were the predominant N dopants, and the N-doped carbon surface stabilized the Pt nanoparticles. Near-complete HMF conversion (100%) with high selectivity to FDCA (83.9%) was achieved by the Pt/NC-800 catalyst under 0.5 MPa O_2 at 110 °C for 24 h (Yang et al., 2020). NC-800 support, as a metal-free catalyst, also allowed the HMF conversion to reach 99.9%. However, the carbon balance dropped to 28.4%, probably because of the repolymerization of unstable intermediates in the absence of active metals. Furthermore, numerous experimental investigations demonstrated that the metal-N-C interface could be an active surface for the oxidation of alcohols to aldehydes. Introducing N into the biochar structure could enhance O_2 adsorption, facilitate electron transfer to the surface oxygen from the metal site, and reduce the energy barrier. For example, the Co/Co–N/CN–700 catalyst enabled 92% HMF conversion and 56% FDMC yield at 80 °C within 1 h under 0.1 MPa O_2, and the FDMC yield remained stable after five consecutive runs (Feng et al., 2021). Another example of biomass-derived phosphorus-doped carbon (PC) as a metal-free catalyst was prepared by the co-pyrolysis of soluble starch and phosphoric acid (Table 3). Active P–O–C sites and surface defects induced by heteroatom-doping may be responsible for the enhanced aerobic oxidation of alcohols to their corresponding aldehydes (Hu et al., 2019a). The PC catalyst was further investigated for the selective oxidation of different alcohols (e.g., aromatic, alicyclic, and heterocyclic alcohols) under 1 MPa O_2 at 120 °C for 24 h, and it showed distinct selectivity (>99%), suggesting that aromatic alcohols with electron-donating groups may have higher reactivity (99.6% conversion) than alcohols with election-withdrawing groups (>16.6% conversion). The PC-700 catalyst was evaluated in a recycling test. The high conversion of benzyl alcohol (>99%) persisted even after eight cycles.

3.1.5. *Esterification*

Esterification is an important reaction in the field of organic chemistry. Primary esterification products are biofuels (e.g., biodiesel), organic solvents (e.g., ethyl acetate), and biopolymers. A typical esterification reaction requires carboxylic acids and an excess of alcohol with acid catalysts (Eq. 5). Among these, the Brønsted acid catalyst showed excellent catalytic activity for the esterification reaction.



(5)

Biomass-derived levulinic acid (LA) is the primary feedstock used in esterification reactions to produce ethyl levulinate (EL), which can be a precursor for γ-valerolactone synthesis (Zainol et al., 2021). As a Brønsted acid catalyst, sulfonated biochar has been widely used to esterify LA or other long-chain fatty acids to EL or high-grade biodiesels (da Luz Corrêa et al., 2020; Jenie et al., 2020). An SO_3H-containing carbon cryogel catalyst synthesized from urea and furfural via HTC and mild pyrolysis (300–500 °C) can convert LA to EL (92.4 mol% yield) at 80 °C (Zainol et al., 2021). HMF has been reported to produce EL by acid-driven etherification in the presence of an organosilane-functionalized biochar catalyst with a high acid strength (0.983 mmol/g). Full HMF conversion and EL yield of 84% were achieved at 130 °C (Peixoto et al., 2021). The resulting biochar catalyst showed excellent reusability owing to the strong anchoring of $-SO_3H$ with organosilane groups. Several important factors, such as the density of SO_3H sites and textural properties, have been found to influence the production of fatty acid methyl esters (FAME) from fatty acids, by comparing the activity trends of sulfonated biochar from a diverse variety of biomass feedstocks (Kastner et al., 2012). This study indicated that the SO_3H groups were the key active sites for catalytic esterification. Furthermore, the large SSA (1137 m^2/g) of activated biochar derived from wood could increase the accessibility of substrates to active acid sites, resulting in a high esterification rate (90–100%). The sulfonation conditions were further optimized for different sulfonated biochar catalysts to control esterification of the fatty acids. The best sulfonation conditions for acidic biochar fabrication were obtained at 200 °C for 4 h to allow for highly efficient conversion of feedstocks with yields of up to 97.2% for methyl ester from methanol-oleic acid (da Luz Corrêa et al., 2020).

3.2. *Biochar in catalytic pyrolysis*

Pyrolysis is a feasible and economical way to convert lignocellulosic biomass into gas (e.g., syngas), liquid products (e.g., crude bio-oil), and solid chars (Mishra and Mohanty, 2022). The introduction of catalysts upgrades pyrolytic volatiles through decarbonylation, hydroxylation, carboxylation, and other reactions, thereby improving the quality of target products (Fig. 6). In addition, biomass pretreatment (torrefaction) and heating methods (e.g., microwave heating) can affect biomass pyrolysis reactions and product distribution (Devaraja et al., 2022; Yang et al., 2022). This section reviews the efficient approaches to producing syngas and liquid hydrocarbons via pyrolysis with biochar-based catalysts.

3.2.1. Strategies for in-situ catalysis and ex-situ catalytic upgrading

Catalytic pyrolysis can be conducted via *in-situ* catalysis or *ex-situ* catalytic upgrading; two stages are involved in catalytic upgrading, as shown in Fig. 6. Specifically, feedstocks are decomposed into pyrolytic volatiles in the first stage and then reformed in the second stage. *In-situ* catalytic conversion is a one-step process that entails catalytic pyrolysis and upgrading in a single reactor. *Ex-situ* upgrading is performed in a secondary catalytic reactor and requires reforming pyrolytic volatiles from the initial pyrolysis reactor. An *ex-situ* process can enable ease of implementation and flexibility in process parameter variations. This may separate catalytic upgrading from the initial pyrolysis stage and make it occur under more suitable conditions. For *in-situ* catalysis, the catalyst plays a significant role in both stages in improving the biomass conversion efficiency and adjusting the distribution of volatilized products. For example, the pyrolysis of lignin loaded with 1.0 wt% cobalt can enhance syngas production through an *in-situ* process while producing metal-loaded biochar catalysts for other environmental applications (Cho et al., 2017). However, *in-situ* processes have the disadvantages of low selectivity and high energy consumption, and the vapors formed may not contact the catalyst effectively, limiting its industrialization value. Under *ex-situ* catalytic upgrading, the catalyst is more effective in producing high-quality bio-oils and syngas enriched in H_2, CO, and CH_4. For comparison purposes, one-stage gasification and two-stage catalytic pyrolysis including gasification and volatile reforming were performed (Cay et al., 2019). The results indicate that coffee residue biochars could enhance the production of hydrogen-rich gas (59–64% of H_2) at 850 °C during the *ex-situ* volatile reforming process. *Ex-situ* upgrading of pyrolysis vapors from wheat straw in the presence of biochar catalysts at a lower reforming temperature (750 °C) achieved a high gas yield of 74% with H_2 selectivity of 40% (Di Stasi et al., 2021). Additionally, a two-stage fixed-bed reactor was proposed for a wood chip pyrolysis reaction through *ex-situ* catalysis (Wang et al., 2022a). The biochar catalyst in the second stage of the fixed bed significantly promoted the production of syngas, and high-purity syngas (70.85%) was obtained from poplar. Additionally, *ex-situ* upgrading can avoid direct contact of the catalyst with coke formed at the early stage of biomass decomposition, thereby diminishing catalyst deactivation.

3.2.2. Syngas production via pyrolysis of biomass

H_2-rich syngas (H_2 and CO) can be produced from biomass gasification under oxygen-starved conditions (Wang et al., 2022a,b). Up to 60–70 vol% of H_2 can be achieved in the presence of efficient catalysts (Yao et al., 2016); a Ni-based catalyst with economic feasibility is attractive because of its excellent performance in hydrogen production (Taghavi et al., 2018; Yue et al., 2021). Different Ni loadings in biochar-based catalysts have been investigated to optimize the production of syngas from poplar wood (Wang et al., 2022b). The pyrolysis reaction mainly proceeds by biomass cracking, cracking of oxygenated compounds, and reforming bio-oil oxygenated compounds over the selective catalyst. When the temperature was >500 °C, gases were generated from the reforming reaction. A 10 wt% Ni/biochar catalyst showed the best performance of 34.32 mmol/g for total syngas yield, but the catalytic conversion rates decreased with a 15 wt% Ni/biochar catalyst because of the partial blockage of pores by excessive Ni species. This study highlights the important role of Ni species in both the cracking/reforming reaction of volatile fractions at 300–500 °C and conversion of high-boiling-point compounds at 600–700 °C. Biomass type can affect biochar properties and conversion performance (Yao et al., 2016). Three types of biochar catalysts with 15 wt% Ni loading were synthesized by fast pyrolysis of different grass biomass and used for syngas production by an *ex-situ* conservation process in a two-stage reactor (reactor zone I for biomass pyrolysis: 500 °C, zone II for catalytic gasification: 600–900 °C). All the biochar-based catalysts showed high conversion rates and high concentrations of H_2 and CO (up to 95 vol%). Moreover, the presence of alkali and alkaline earth metals (AAEMs) has been suggested to significantly influence the production of H_2. Notably, the abundant AAEMs in cotton stalk-derived biochar (CC) could contribute to tar decomposition and the water–gas shift reaction. Thus, a high H_2 yield (approximately 90 wt%) was achieved using the Ni/CC catalyst because

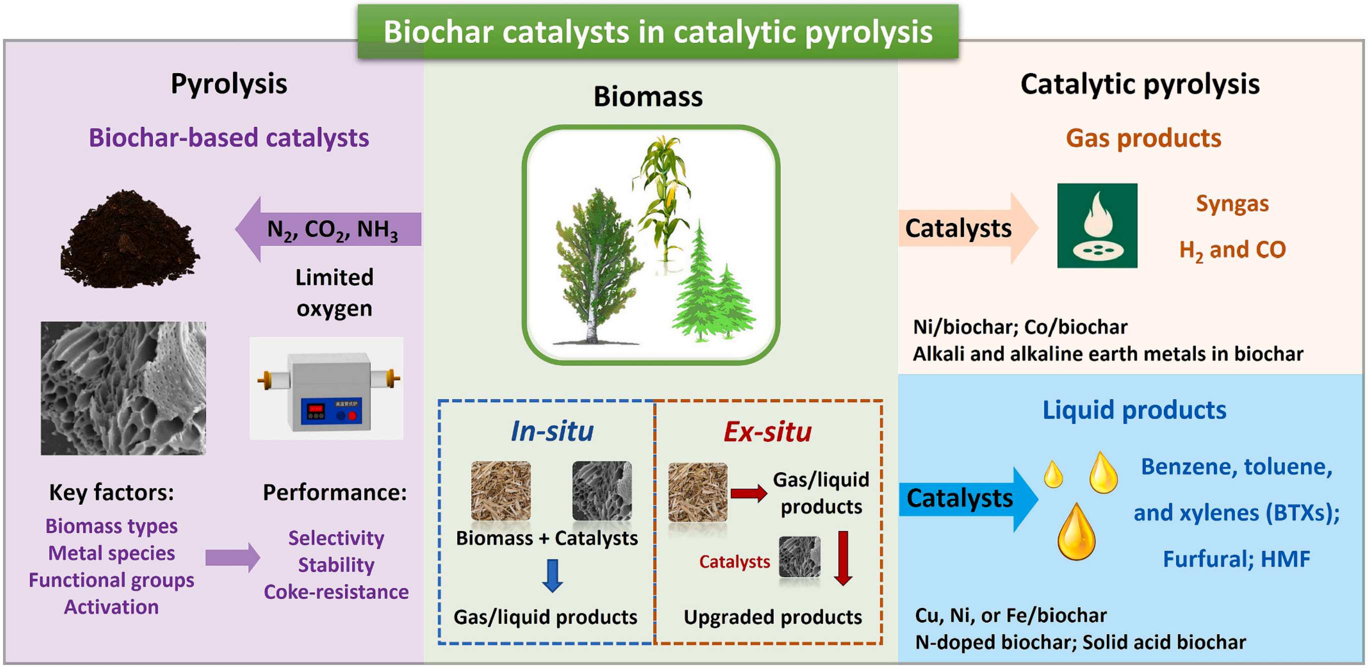


Fig. 6. Main routes for catalytic pyrolysis of biomass.

of the synergistic effect of the active sites (Ni and AAEMs).

A cobalt–biochar catalyst was found to promote the pyrolysis of lignin to syngas through an *in-situ* process (Cho et al., 2017). Syngas production from high-temperature (700 °C) pyrolysis of cobalt salts and lignin was more significant under a CO_2 atmosphere. The DTG curve showed that the thermal degradation rate of cobalt/lignin was significantly delayed in CO_2 compared to that in N_2, indicating the occurrence of surface reactions between biochar and CO_2. Additionally, CO_2-assisted pyrolysis of cobalt/lignin resulted in a large SSA (599 m^2/g) of Co/biochar, which was greater than that of biochar (6.6 m^2/g) produced under an N_2 atmosphere.

3.2.3. Catalytic pyrolysis of biomass to liquid hydrocarbons

Solid biomass can be directly converted into crude bio-oil through pyrolysis, which may require further catalytic upgrading to high-grade fuels owing to low-grade bio-oils having complex compositions and poor properties. Many kinds of catalysts, including alkaline oxide-based, acid, transition metal, and carbon-based catalysts, have been used to produce aromatic hydrocarbons from biomass via a Diels–Alder-type reaction, which is a cycloaddition between a conjugated diene and a substituted alkene (Di Stasi et al., 2021; Maneechakr and Karnjanakom, 2021). Metal-modified biochar catalysts (e.g., Ni, Fe, and Co) have been comprehensively investigated to produce liquid hydrocarbons through the catalytic pyrolysis of biomass (Madduluri et al., 2020). The iron-modified biochar catalyst exhibited high activity and selectivity during corncob pyrolysis (Zeng et al., 2021). Carbonization and chemical activation (H_3PO_4) of the seed powder was conducted to control the surface properties of biochar and to improve its textural properties, particularly for a large SSA (821 m^2/g). As a result of the co-existence of Fe_3O_4 and FeO species in the catalyst, the reverse Mars–van Krevelen mechanism was proposed from abundant oxygen vacancies through the redox cycle of Fe(III) and Fe(II). These properties have proven to enhance the adsorption of oxygen-containing intermediates and their subsequent conversion to phenol-rich bio-oils. Another highly typical reaction, the selective production of benzene, toluene, and xylenes (BTXs) from biomass, is a crucial conversion pathway to meet the rapidly growing demand for aromatics. The distinct conversion performance of various metal-doped (Cu, Ni, or Fe)-activated biochar catalysts was observed based on their different activity trends and BTX yields (Maneechakr and Karnjanakom, 2021). The Ni/activated carbon with 15% Ni loading exhibited the best performance of 72% in the fast pyrolysis (heating rate of 1000 °C/min) of waste palm kernel cake to hydrocarbons at 550 °C.

Acid-functionalized biochars and metal-free catalysts with porous structures, acidic active sites, and unique surface properties have been developed for ideal pyrolysis systems. In particular, biomass pretreated with H_3PO_4 demonstrated apparent advantages in the selective production of phenol-rich bio-oils, furfural, HMF, and levoglucosenone from biomass and other specific feedstocks. An activated carbon catalyst with P-containing functional groups was prepared by microwave-assisted pyrolysis of H_3PO_4 pretreated corn stover, which exhibited high selectivity (99%) for phenol production (Zhang et al., 2018). Various phosphoric groups (e.g., $-P-O$, $-P{=}O$, and $-C-O-P$) can be successfully incorporated into activated carbon to enhance its acidity, hydrogen supply capacity, and dehydration ability, as validated by FTIR spectroscopy (Ye et al., 2017). In the case of levoglucosenone production, two types of functional groups ($-C-O-PO_3$ and $-C-PO_3$) enabled the highest yields of 7.8 wt% and 14.7 wt% from pine wood and cellulose, with selectivities of 43.0% and 76.3%, respectively. Another green strategy for the selective production of phenolic products has been achieved using an N-doped biochar catalyst that can be easily produced by fast pyrolysis of bamboo at 600 °C with NH_3. It possesses multiple catalytically active sites (N- and O-containing groups) that synergistically promote phenol production (Chen et al., 2020c). Typically, pyridinic N with Lewis basicity in the catalyst can serve as an H-acceptor, promoting the dehydration of intermediates. O-containing groups (e.g., OH and COOH groups) serving as acid sites can prompt the decomposition of biomass precursors and subsequent conversion of aromatic intermediates to phenols (82% selectivity). Compared to biochar derived from raw biomass, the nanocellulose-derived biochar catalyst produced by microwave-assisted pyrolysis is likely to exhibit high thermal stability with an opportunity for its facilitated reuse. Interestingly, a high acidity of nanocellulose-derived biochar, similar to that of steam-activated biochar, was proven because of the high stability of the inherent oxygenated groups over the biochar surface. These properties are favorable in terms of producing a high concentration of phenolic monomers (53.77 mg/mL) from Douglas fir and retaining stable selectivity (65%) despite 15 cycles of reuse (Wang et al., 2021b). Hence, the appropriate feedstock choice is critical for controlling the surface properties and thermal stability of biochar-based catalysts.

4. Applications of biochar-based catalysts in environmental remediation

4.1. Mitigation of atmospheric pollutants

The thermochemical-based industry and transportation sectors commonly release different pollutants, including volatile organic compounds (VOCs), toxic metals (e.g., Hg, Pb, and Cr), nitrogen oxides (Nox), acidic gases (H_2S and SO_2), dioxins, and furans. These pollutants pose substantial environmental threats and health risks for human beings once emitted into the atmosphere. Therefore, concerted efforts should be made to reduce emissions.

In addition to adsorption, biochar-based catalytic treatment is considered a promising and effective route for mitigating gaseous contaminants. For example, Chen et al. (2021a) synthesized biochar-based N-rich hierarchical porous carbon with carbon nitride via a one-step strategy, exhibiting a high H_2S removal capacity of 426 mg/g at room temperature with high reusability and low cost. Wu et al. (2022) prepared N-doped activated carbon derived from biomass using supramolecular melamine cyanurate via a one-step pyrolysis route, displaying a sulfur capacity of 1872 mg/g for the catalytic oxidation of H_2S at room temperature; their work suggests that a microchannel structure with a mesopore structure can enhance mass transfer and emigrate elemental sulfur products to form multilayer sulfur. Lee et al. (2018) synthesized a biochar-based catalyst from an empty fruit bunch for selective catalytic Nox reduction by purging NH_3; they found that the Cu-loaded biochar composite exhibited excellent Nox removal efficiency, which was attributed to the O functional groups. Bhandari et al. (2014a) prepared three biochar-based catalysts for simultaneously removing tar, NH_3, and H_2S from syngas, demonstrating that the biochar-based catalysts successfully removed tar (up to 97% removal efficiency), H_2S (breakthrough time of 80–110 min), and NH_3 (breakthrough time of 90–150 min), simultaneously. Nargesi et al. (2021) developed a promising and inexpensive catalyst for engine emission mitigation. Their Cu-loaded biochar reduced all the measured contaminants (e.g., CO, CO_2, Nox, etc.) to below the standard level. This is beneficial for simultaneously mitigating engine gas emissions and increasing the engine life span.

Biochar-based catalysts commonly have well-developed pore structures, which are beneficial for adsorbing atmospheric pollutants. This suggests that a catalytic process can occur with adsorption in practical applications. Compared to adsorption, biochar-based catalytic processes can directly convert contaminants into a less toxic and/or non-harmful phase or even into high-value-added products via catalytic degradation (e.g., catalytic oxidation), which is beneficial for achieving a ‘waste-to-source’ strategy. However, the application of biochar-based catalysts to mitigate atmospheric pollutants is still in its infancy, suggesting that more efforts are needed to develop biochar-based catalytic applications for mitigating atmospheric pollutants.

4.2. Degradation of organic contaminants in wastewater

Owing to rapid urbanization and unchecked industrialization, environmental and scientific communities have focused extensively on water contamination (Li et al., 2021c; Nidheesh et al., 2021). They have recognized the urgency of finding a practical and sustainable solution to eliminate pollutants from water with the long-term view of mitigating the waste that causes water pollution. Among the potential candidates, biochar-based technology is still considered one of the most promising methods of environmental remediation owing to its high efficiency, facile procedure, cost-effectiveness, and well-developed pore structure (Huang et al., 2019; Li et al., 2021c).

4.2.1. Photocatalytic degradation

Numerous excellent biochar-based catalysts (i.e., composited with CdS, TiO_2, ZnO, and Fe_3O_4, amongst others) have been synthesized for photocatalytically degrading organic contaminants (Huang et al., 2019). These catalysts have several advantages. 1) Biochar expands the light absorption range because abundant functionalities on the biochar surface support various light-active components; 2) it facilitates the photodegradation process owing to its excellent adsorption capacity; 3) it improves the separation of photogenerated electron-hole pairs; and 4) the regulable particle size of biochar is beneficial for enhancing catalyst reusability (Minh et al., 2020; Wang et al., 2019b). Zhang and Lu (2018) synthesized a TiO_2/biochar composite for innovatively decolorizing Reactive Brilliant Blue KN-R, a typical anthraquinone used in dyeing treatments. The optimal decolorization efficiencies were achieved at 99.71% at $pH = 1$ and 96.99 at $pH = 11$ within 1 h, respectively. The TiO_2/biochar composite exhibited excellent reusability and durability for KN-R degradation, mainly owing to TiO_2-supported photocatalytic degradation and the adsorption property of biochar. This suggests that TiO_2/biochar-based catalysts could be considered valuable and effective materials for anthraquinone dyeing wastewater treatment.

Biochar-based catalysts, which have abundant functional groups, are considered promising materials for photocatalytically degrading organic pollutants in aqueous solutions. This implies that further research using industrial wastewater case studies is needed. This will help us gain insights into the novel design of biochar-based catalysts. Moreover, owing to their well-developed pore structure and effective functional groups, other competitive reactions (e.g., adsorption) can coexist with photocatalyst degradation for specific contaminants. Therefore, a more detailed mechanism for biochar-based photocatalytic degradation of industrial wastewater should be further explored to accelerate its commercialization.

4.2.2. Advanced oxidation processes (AOPs)

The persulfate-based AOP is a promising approach for the degradation of emerging pollutants by the activation of peroxydisulfate, peroxymonosulfate (PMS), or persulfate into active sulfate radicals (Huang et al., 2018; Zhao et al., 2021). The activation efficiency of the catalysts and the oxidant yield are key factors in the effectiveness of the persulfate-based AOP, suggesting the desirability of synthesizing cost-effective and highly efficient activators with excellent cyclic stability and the catalytic ability for persulfate decomposition. Furthermore, due to their abundant and renewable characteristics, biomass and waste are considered promising and sustainable candidates for preparing carbon (metal-free)-based catalysts (Huang et al., 2018; Liu et al., 2015a). Moreover, transition metal or heteroatom treatment could significantly enhance their catalytic performance, such as metal ion leaching, which could be reduced by doping transition metals into biochar. In contrast, good catalytic performance can be maintained (Xu et al., 2020). Furthermore, electronic properties can be effectively regulated, and catalytic capacity can be significantly improved by doping heteroatoms into biochar (Sun et al., 2017b).

The biochar-based catalytic mechanisms in persulfate-based AOPs are displayed in Fig. 7 (He et al., 2021; Zhao et al., 2021). The catalytic mechanism can generally be categorized into two pathways: free radical and non-radical. In the free radical pathway, reactive oxygen species (ROS; including $\bullet OH$, $SO_4^{\bullet -}$, and $\bullet O_2^-$) play a dominant role in degrading emerging pollutants, owing to the O−O bond from persulfate breaking into ROS for the degradation of pollutants. In the non-radical pathway, the generation of singlet oxygen ($^1O_2$) and surface electron transfer are effectively achieved by a biochar-based catalyst; through surface electron transfer, biochar-based catalysts transfer electrons to persulfate from the adsorbed pollutants. In addition, $^1O_2$ can be produced by self-decomposition of PS. The non-radical pathway can readily oxidize pollutants at an early stage owing to its weak oxidative potential, and free radicals further mineralize the organic substrates into H_2O and CO_2, implying that the mineralization of organic pollutants can be enhanced by the collaboration between radical and non-radical pathways (Zhao et al., 2021).

Biochar-based catalysts can be prepared from different biomasses in a cost-effective manner, and heteroatom- and/or metal-doping treatments could further enhance the catalytic activities facilitating the efficient development of persulfate activators. However, some points for practical application should be carefully addressed on biochar-based catalysts in AOPs. 1) To develop an effective and efficient biochar-based catalyst, the precise regulation of the desired properties of biochar-based catalysts is one of the critical gaps (Fig. 7a). To address this critical gap, ML could play a significant role in the performance prediction and inverse design of novel materials (Palansooriya et al., 2022; Yuan et al., 2021b). 2) The mechanism of persulfate activation by biochar-based catalysts should be further explored to synthesize the desired characteristics of biochar-based catalysts for degrading organic contaminants through radical or non-radical routes, which is also beneficial for mitigating the catalyst deactivation or poisoning caused by intermediates during AOPs; 3) Most biochar-based catalysts are successfully used for degrading organic contaminants in aqueous solutions; however, practical applications such, as in industrial wastewater and sewage sludge, have received insufficient attention owing to the competitive sorption of contaminants present in real wastewater and other regions. This suggests that more research is needed to develop practical and effective technologies for solving real issues. 4) In addition to lab-scale investigations, pilot-scale research is needed to gain insights into biochar-based catalytic applications using practical reactors.

4.3. Remediation of emerging pollutants in soil

4.3.1. Catalytic reduction

Biochar and biochar-based carbon materials are potential redox mediators in earth subsurface systems. Therefore, enhanced soil and underground water remediation approaches could be developed by introducing biochar cooperating with sulfide or microbial reduction systems. Two main underlying mechanisms for the reduction process are generally recognized. First, the surface oxygen-containing groups can either receive or donate electrons between reductants and target pollutants, namely the "electron-shuttling mechanism." Biochar prepared at low temperatures is rich in quinone and phenol groups (Rhim et al., 2010). Considerable efforts have been undertaken to identify the electron exchange capacity (EEC) of pyrogenic carbons, including Boehm titration and spectroscopy (Uchimiya et al., 2018). Kluepfel et al. (2014) developed a new electrochemical method to quantify the surface EEC, and the sum of the electron donor and acceptor capacities reached the mmol/g level (Prevoteau et al., 2016). Some studies have observed that the reduction performance of biochar-based materials is proportional to the content of surface oxygen-containing functional groups (Wu et al., 2017; Yu et al., 2015).

Second, the graphene-like aromatic structure can promote reductive transformation via direct electron conduction, namely the "electron-conducting mechanism." This mechanism could be enhanced by applying a representative graphene or carbon nanotube as a catalyst in specific reduction systems. For a deeper understanding, the edge sites of

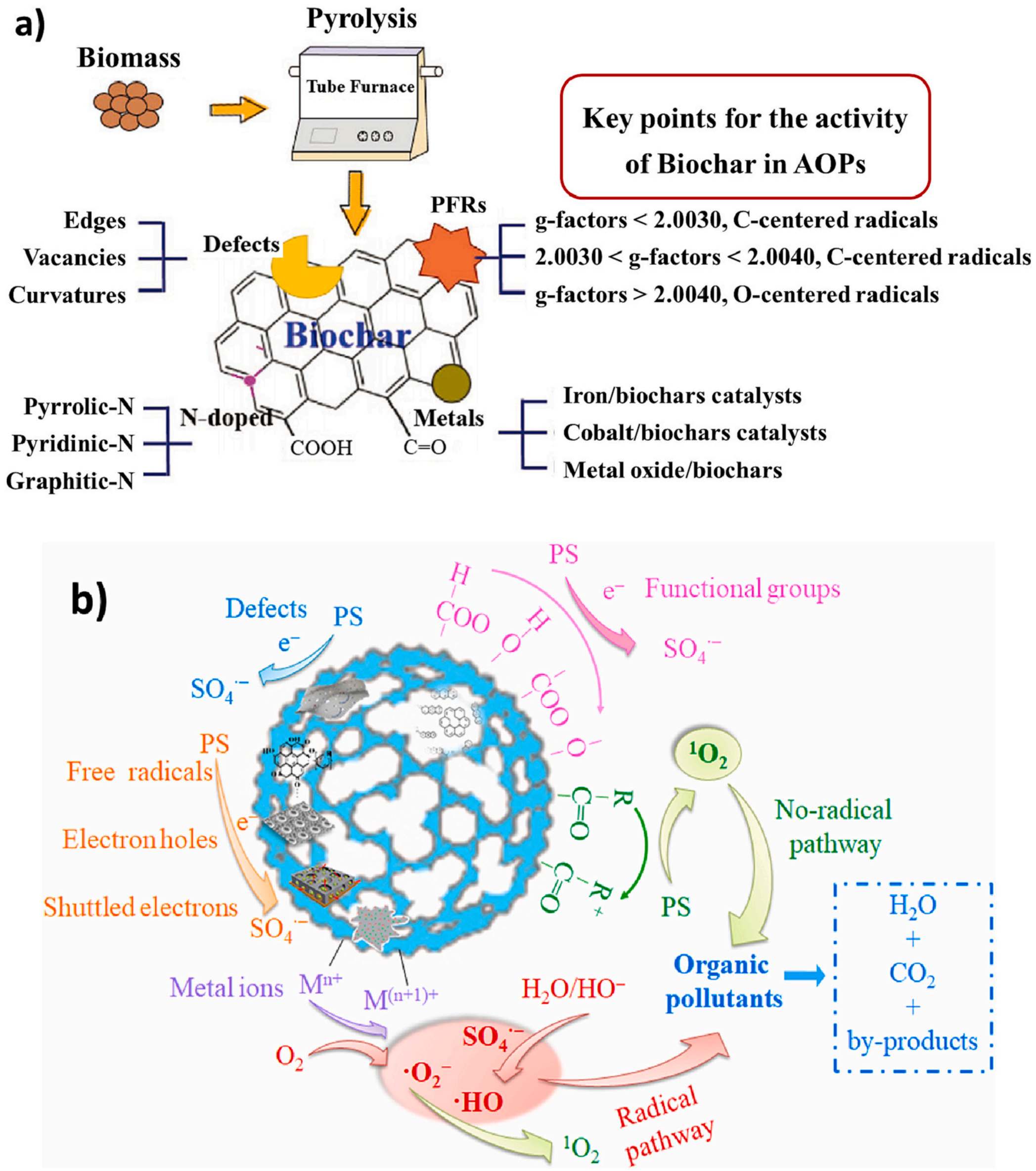


Fig. 7. a) Key points of biochar-based catalysts in advanced oxidation processes (AOPs); b) potential mechanisms involved in biochar-based catalytic persulfate-based AOP, referred from the publications by He et al. (2021) and Zhao et al. (2021).

a graphene or carbon nanotube could show four orders of magnitude higher specific capacity, resulting in a faster electron transfer rate and stronger electrocatalytic activity than the graphene basal plane (Banks et al., 2005; Yuan et al., 2013), especially at the edge zig-zag sites (Ritter and Lyding, 2009). Therefore, the catalytic activity of pyrogenic carbon is typically related to its number of defects (Fu and Zhu, 2013; Gao et al., 2011). Pyrogenic temperature is the most critical factor for controlling the surface properties of biochar. Sun et al. (2017a) investigated the surface charging/discharging properties of biochar using the cyclic voltammetry (CV) method, resulting in the biochars that were prepared at temperatures <550 °C exhibiting significant reversible redox CV peaks from the surface oxygen-containing groups. Those prepared at temperatures >700 °C exhibited higher electron conductivity from the carbon matrix, while those prepared at temperatures in between 550 °C and 700 °C possessed both functions.

However, carbon-mediated reduction mechanisms are more complicated than the recognized electron shuttling or conducting mechanisms. In carbon sulfide systems, the formation of surface bonding (poly)sulfides (e.g., C—S—S—H) is necessary as a reactive intermediate (Xu et al., 2015; Zhao et al., 2019). The pyrogenic carbon-rich N content is more redox-active because N is relatively electron-rich (Wu et al., 2017). Therefore, N-doping in carbonaceous materials is usually proposed as a promising approach to enhance catalytic performance. In addition, the size effect of biochar-based materials cannot be ignored because the smaller particle size (μm level) of biochars could provide more oxygen functional groups or serve higher available surface areas (Jin et al., 2022). Although there is still a lack of a unified perspective on carbon-mediated reduction mechanisms for a wide range of carbon materials and contaminants (Ding and Xu, 2016; Xu et al., 2015), using biochar or biochar-based materials for the reductive remediation of soil pollutants is promising.

4.3.2. Catalytic oxidation

The surface redox-active moieties on biochar, including phenolic-OH, semiquinone-type persistent free radicals, and quinoid C—O, can also promote oxidation processes by producing highly reactive oxygen species (ROS) (Zhong et al., 2019b). Such oxidation processes usually occur in mild soil conditions (e.g., paddy fields) when the field moisture fluctuates and could be responsible for the oxidation of soil contaminants. Oxygen is the primary driving force. The graphite matrix in biochar is also involved in the direct transfer of electrons. For example, in the oxic carbon-sulfide system, the graphite crystallites are responsible for the electron transfer from sulfide to the chemisorbed oxygen at carbon defect sites and the generation of ·OH and H_2O_2, thereby oxidizing As(III) and sulfanilamide (Wang et al., 2021a). In the biochar/$KMnO_4$ system, graphite crystallites can extract one electron from organic contaminants (e.g., sulfamethoxazole) to $KMnO_4$ (Peng et al., 2021), which can further activate $KMnO_4$ to produce highly oxidative intermediate manganese species (Tian et al., 2019).

Biochar and biochar-based materials can also efficiently activate H_2O_2 and persulfate to generate abundant ROS and/or sulfate radicals (Fang et al., 2014; Fang et al., 2015). In these cases, persistent free radicals (PFRs) are mainly responsible for single-electron transfer processes. Multiple factors, including the pyrolysis temperature, pyrolysis time, metal loading, heteroatom-doping, and subsequent pre-treatment (e.g., acid treatment and washing with organic solvent), could significantly affect the level and types of PFRs. Generally, an increase in the pyrolysis temperature and low metal loading is favorable for maintaining high PFR concentrations. In contrast, excessive temperature and metal loading inactivate the PFRs (Zhou et al., 2021b). The inherent PFRs can also interact with substances (e.g., antibiotic-resistant genes) via direct contact (Lian et al., 2020).

The water-dissolved black carbon sourced from biochar is photochemically active. This could be attributed to the specific properties of its relatively low molecular weight, high aromaticity, and rich oxygen-containing groups, which can induce a higher quantum yield of ROS compared to some well-studied dissolved organic matter (Wang et al., 2020d; Zhou et al., 2018). As an inherent biochar constituent, the influence of dissolved black carbon on the phototransformation of organic and inorganic pollutants should be considered, even in field soil systems (Li et al., 2020a; Zhang et al., 2020).

5. Machine learning-aided catalytic applications of biochar

5.1. Machine learning methodology

ML, a branch of artificial intelligence, has been widely applied in the research community due to the rapid development of computer science and computational power. The emergence of python programming and ML libraries, such as Sikit-learn, Keras, and TensorFlow, have made it easy for many researchers or experimentalists to write codes and train their own ML models. Typically, there are three types of ML, namely, supervised learning, unsupervised learning, and reinforcement learning (Li et al., 2022b,d). Supervised learning is the development of ML models based on data that are well labeled by conducting experiments or characterization. Unsupervised learning exists mainly to perform clustering analysis and dimension reduction for unlabeled data, with the aim of finding hidden data groupings without human intervention. Reinforcement learning involves setting goals for a computer program to learn certain rules using trial-and-error iterations by maximizing numerical reward signals.

In biochar-related fields, supervised learning is the best choice as all biochar-related data is collected from experimental research, which actually labels the data. Supervised learning includes two typical problems, i.e., regression and classification. The regression problem is the handling of continuous output variables, and classification the development of ML models to model the categorical variables for identifying some categories as targets. Furthermore, almost all biochar-related ML works are regression problems because most biochar properties can be quantified to obtain continuous values. Thus far, different kinds of ML algorithms, including linear regression and decision tree-based ensemble methods, such as random forest (RF), gradient boosting regression (GBR), supporting vector regression (SVR), and neural networks (NN), have been widely applied to aid the characterization and application of biochar. ML methods also exhibit great potential for the guidance of functional biochar synthesis as a catalyst.

5.2. Machine learning-aided biochar characterization

Characterization of biochar is the prerequisite to understanding biochar for determining its application and explaining its specific performance. Recently, many studies on the application of ML to predict the composition and typical properties of biochar have been reported. Li et al. (2022b) used ML methods to assist in proximate and ultimate analyses to predict the basic composition (contents of carbon, hydrogen, oxygen, nitrogen, fixed carbon, volatile matter, and ash) of biochar. They found that an NN model had high predictive accuracy with an R^2 of 0.85–0.96, which was better than the fuzzy inference system and RF model. To evaluate the potential application of biochar in soils, Chen et al. (2023) developed a data-enhanced ML model to predict the contents of P, N, and ash as well as the pH of hydrothermal biochar. It was found that the prediction performance improved by 5.8–15.8% compared to traditional SVR, NN, and RF. Furthermore, sensitivity analysis indicated that the reaction temperature, pressure, and specific element of feedstock were critical factors influencing biochar properties. To understand the fuel properties of biochar, Li et al. (2020c) applied SVR and RF algorithms to train ML models for the prediction of the higher heating value, energy recovery efficiency, and energy densification of biochar. The results suggest that SVR had better accuracy with an average testing R^2 of 0.90 and 0.94 for hydrothermal biochar and pyrolysis biochar, respectively.

Previous literature reviews indicate that ML methods have been well applied for the evaluation of biochar properties for specific applications. In the terms of the catalytic applications of biochar, other properties, such as the surface area, surface functional groups, pore structure, and modified metal elements, are more important. Hai et al. (2023) developed ML models to predict the SSA of biochar and found that RF was the best when compared with SVR, Decision Tree, and K-Nearest Neighbor models. Leng et al. (2022) employed ML methods to understand the SSA and N-containing functional groups of biochar from biomass pyrolysis by developing predictive models for the prediction of the SSA and N content of biochar. They found that the GBR model outperformed the RF model for both single-target and multi-target prediction, with testing R^2 ranging from 0.81 to 0.95. Furthermore, it was found that the N and ash contents in biomass exceeded the N content in biochar; ash and pyrolysis temperature had significant impacts on the SSA of biochar. Although the N content of biochar can be an index for the N-containing functional group of biochar, other specific data from FTIR, XPS, and XRD may be more suitable for identifying the functional groups and modified metals of biochar. However, works using these characterization data for ML modeling are rare, which could be a future direction for ML-aided biochar characterization.

5.3. Machine learning-aided biochar application

Biochar is a multi-functional material that can be used in many domains, such as soil amendment, organic pollutant removal from contaminated water, and the acceleration of biomass and organic waste valorization as catalysts. Regarding the role of ML in biochar applications, the biochar performance could be predicted and interpreted by ML modeling based on high-dimensional data with the consideration of different kinds of factors. Zhu et al. (2022a) explored the performance of biochar in the removal of pharmaceuticals and personal care products. They indicated that the RF model could predict the biochar performance for the adsorption of pharmaceuticals and personal care products, and the functional groups on biochar had an importance order of C−O bond > C=O bond > non-polar carbon for adsorption capacity. Furthermore, the authors employed ML to explore the role of Fe in Cr (VI) removal by Fe-modified biochar and found that impregnation of Fe could improve the surface oxygen-containing functional groups for enhancing Cr (VI) removal. More specifically, they found that C−O was more important than C=O for Cr(VI) removal by Fe-modified biochar (Zhu et al., 2022b). In addition, Palansooriya et al. (2022) applied ML methods to explore complicated biochar-amended soils for the immobilization of heavy metals with consideration of the properties of the soil, biochar, and heavy metals. They found that the RF model could predict the immobilization efficiency of heavy metals in soils, with testing R^2 of 0.92. A model-based interpretation implied that biochar nitrogen and biochar rates in soils were the two most critical factors affecting HM immobilization. In general, ML methods have been widely used for the performance evaluation of biochar applications, especially the use of biochar as adsorbents and soil conditioners.

In terms of the application of biochar as a catalyst, ML methods can contribute to catalytic performance predictions and interpretation. For example, Liu et al. (2022b) prepared digestate-derived biochar as a catalyst to activate peroxymonosulfate for the degradation of diclofenac. They found that the diclofenac (initial concentration of 20 mg/L) was degraded efficiently by the biochar, with a removal efficiency of 93% under a biochar dosage of 0.3 g/L and PMS concentration of 1.0 mM. Furthermore, the ML method (i.e., SVR) was applied to simulate and predict the removal efficiency with high training and testing R^2 of 0.95 and 0.94, respectively. In addition, the interactions among multiple factors were well interpreted using the ML model-based partial dependence analysis, which indicated that the reaction time, peroxymonosulfate concentration, and digestate-derived biochar dosage had higher importance than the initial pH and reaction temperature in diclofenac degradation. It should be addressed that most ML-related works have focused on biochar applications for contaminant removal, while not too many have reported on the ML-aided catalytic applications in biomass waste biorefineries, the mitigation of atmospheric pollutants, photocatalytic degradation for organic pollutant removal from wastewater, and catalytic reduction and oxidation for the remediation of emerging pollutants in soils.

5.4. Machine learning-aided biochar synthesis

To promote the catalytic application of biochar, it is essential to synthesize biochar with high catalytic performance for a specific application. ML models are flexible tools with high modularity ability and can be combined with optimization algorithms to perform optimization, inverse design, and material screening processes (Li et al., 2022b). For instance, Li et al. (2021b) employed NN algorithms to model supercritical water gasification with the consideration of feedstock composition, process conditions, and catalyst information to enhance H_2-rich syngas production. The developed NN models were further integrated with multi-objective optimization methods to achieve catalyst screening and process optimization with the objectives of maximizing H_2 yield and minimizing CO_2 yield. This integrated model suggested that Fe-based catalysts have greater potential to promote the conversion of wet wastes to H_2-rich syngas corresponding to optimal operational conditions. Li et al. also developed an ML-based optimization model design for hydrothermal liquefication (Li et al., 2021f) and anaerobic digestion (Li et al., 2022e) to promote the generation of high-quality bio-oil with a low N content and biogas rich in CH_4. Furthermore, the authors conducted experimental validation based on the optimization results from ML-based optimization, which indicated that the calculation errors between the models and experimental results were less than 23%. Previous works indicated that ML methods exhibit great potential for process design and optimization.

Using the same process design and optimization, biochar synthesis can also be tailored based on specific purposes. Li et al. (2023) developed GBR and RF models for the prediction of SSA and TPV for engineering biochar. They found that biomass ash, volatile matter, and pyrolysis temperature were the top three factors influencing the SSA and TPV. Moreover, their developed ML model was further applied to design the pyrolysis process based on six kinds of biomass with the aim of maximizing both the SSA and TPV. Surprisingly, they achieved a significant improvement in the two biochar properties, with an SSA and TPV of 608 m^2/g and 0.82 cm^3/g, respectively. For ML-aided synthesis of biochar as a catalyst, Wang et al. (2023) enhanced the performance of nonradical persulfate activation of biochar using ML technologies. The ML algorithms were first used to bridge the inputs (preparation parameters, textural properties, and elemental composition of biochar) and output (nonradical contribution efficiency). Then, the importance and correlation of the inputs were determined using ML model explainers to aid the design of biochar with a high SSA and O content by choosing specific feedstocks and controlling the pyrolysis temperature. Finally, two nonradical-enhanced biochar with different active sites were synthesized, and they exhibited an outstanding performance for the degradation of sulfathiazole. Although a few works have reported on ML-guided biochar synthesis (Wang et al., 2023; Yuan et al., 2021b), this domain is still in its infancy since many other biochar catalysts have not been designed by ML for other applications, such as the catalytic conversion of biomass, mitigation of atmospheric pollutants, photocatalytic degradation of organic pollutants in wastewater, and reduction and oxidation of emerging pollutants in soils.

6. Challenges and prospects

Biochar-based catalysts have been recognized as promising and practical candidates for biorefinery and environmental protection. The widespread use of high-quality biochar-based catalysts will reduce carbon emissions and contribute to solutions for the challenge of achieving carbon neutrality. More specifically, on the topic of “carbon-neutral” utilization of biomass, using renewable biomass feedstocks to fabricate biochar-based catalysts can considerably reduce the carbon footprint through a self-contained system and improve the economic viability and sustainability of biorefineries. However, a concerted effort should be made to address the following challenges.

First, guidelines for the preparation of biochar-based catalysts remain unclear. As discussed in *Section 2*, carbonization, activation, and functional-group-doping are commonly used to develop high-performance biochar-based catalysts. Conventional synthesis methods have been widely used, including a) intuition-based, b) one factor at a time, and c) designing experiments via response surface methodology, which is time-consuming and inefficient. ML (Fig. 8) has been successfully used to accelerate material synthesis and discovery and elaborate on the underlying relationship between material design and practical applications. Moreover, inverse design ML has revolutionized the on-demand design of structures and devices, suggesting that biochar-based catalysts could be inversely designed using ML approaches and experimental evaluations according to specific applications (Ren et al., 2020). Therefore, to synthesize a biochar-based catalyst with high performance for a particular application, inverse design ML could be considered a promising and feasible approach. Therefore, future efforts should be directed toward providing reasonable guidelines for synthesizing BC-based catalysts.

Second, the stability of biochar-based catalysts is a crucial issue in liquid-phase reactions, as the solvent can dramatically influence catalyst characteristics and performance. For example, water at elevated temperatures is very reactive. It can hydrolyze the loaded metal species and induce the leaching of active sites, thereby resulting in the loss of catalyst activity and/or selectivity with time on stream. Biochar supports are typically stable against hydrolytic attacks. In addition, the sintering and restructuring of metal particles and poisoning of active sites owing to strongly chemisorbed species significantly influence the microstructures of the catalyst and its surface properties. Among the different deactivation modes, metal leaching dominates in liquid media. In addition to the loss of active sites, it poses a significant challenge, as it might incur downstream separation, resulting in environmental pollution. The current understanding of efficient catalysts has primarily focused on overcoming the selective production of targets from complex biomass. Because catalyst deactivation is inevitable, understanding the catalyst deactivation mechanisms may provide new insights into designing more stable catalysts. *In-situ* characterization, such as XPS, FTIR, NMR, and mass spectroscopy, may allow the exploration of reaction mechanisms to better understand their deactivation modes in different catalytic reactions to decelerate catalyst deactivation by optimizing the process conditions. Several fabrication strategies have been proposed to enhance the structural stability of biochar catalysts, such as the optimization of hydrophilic/hydrophobic surfaces, introduction of surface defects by heteroatom-doping, encapsulation of active sites in well-defined structures, construction of bimetallic nanoparticles immobilized by porous structures, and design of larger, accessible SSAs for highly dispersed active sites that can strongly interact with biochar supports.

In addition to metal-loaded biochar catalysts, modified biochars with various N-, O-, and P-containing functionalities have been developed as a new class of metal-free catalysts. For example, sulfonated biochar, an "ideal replacement catalyst" for homogeneous acids, shows great potential for commercial applications of acidic solid catalysts, but it is also subjected to deactivation under different operating conditions (e.g., temperature, pH, and solvent). The activity loss of biochar catalysts is mainly associated with active site leaching and pore blockage caused by the strong chemisorption of impurities. For biochar-based metal-free catalysts, three main factors—the characteristics of the biomass precursor, synthesis route, and activation procedure—are strongly linked to their textural and surface properties, which influence their catalytic activity, selectivity, and stability. Ordered mesoporous carbons from liquefiable biomass precursors using soft/hard templates have recently garnered particular attention because they can easily realize structural design, uniform doping, and functionalization at the molecular level (He et al., 2022; Wang et al., 2021d). In addition, these materials exhibit desirable properties, such as tailorable porosity, distributed active sites, a controllable particle size distribution, and high thermal stability, enabling the catalyst to work continuously. Overall, thermally stable and porous biochar fabrication could be a promising structuration strategy to diminish catalyst deactivation caused by leaching.

Third, coking and sintering are prevalent in high-temperature gas-phase reactions. Both issues are closely intertwined in catalyst deactivation because carbon deposition and growth preferentially occur on larger particles. As previously described, carbon deposition can cover the particle surfaces and block the pores of the catalyst, which causes a continuous decrease in catalyst activity or quick deactivation. Several transition metals such as Ni and Fe and the acidic nature of biochar catalysts are prone to coke deposition; this tendency can be inhibited or eliminated by introducing surface-active oxygen species or by subsequent regeneration with oxygen under mild conditions. However, metal sintering results in a limited number of active sites and inaccessible active sites, thereby leading to irreversible deactivation of the catalyst.

In many cases, structural changes in unstable support materials can lead to the sintering of metal particles. Alternatively, using stable thermal biochar as support might avoid sintering to some extent. Additionally, atoms from the bulk become mobile at high reaction temperatures. Therefore, the strong interaction of metals with biochar support and high dispersion of the active site could simultaneously prevent sintering and reduce carbon deposition. Several approaches have been applied to stabilize the metal species on multifunctional biochars to achieve a stable catalyst against sintering and coking. For example, the one-pot pyrolysis of metal salts and liquefiable biomass is an efficient and simple route for obtaining metal-doped or heteroatom-doped biochar catalysts. In particular, the appropriate choice of biomass feedstock (e.g., raw biomass, nanocellulose, starch, and lignin) for biochar production is critical for controlling the surface properties and thermal stability of the catalyst. Overall, biochar-based catalysts have the industrial potential for the scale-up of biorefinery because of their desirable textural properties and low production costs, facilitating the achievement of the ambitious carbon neutrality target. Although catalyst deactivation poses a significant challenge for efficient biomass conversion, the rational design of stable catalysts with an understanding of deactivation modes could advance the development of high-performance biochar-based catalysts.

Fourth, environmental benefits and economic feasibility should be comprehensively assessed for the practical application of biochar-based catalysts, which could provide essential knowledge to industries and policymakers for commercial-scale technology deployment (Fig. 8). Liu et al. (2018) reported that slow pyrolysis for the production of high-quality biochar could achieve a positive net present value of $12.07

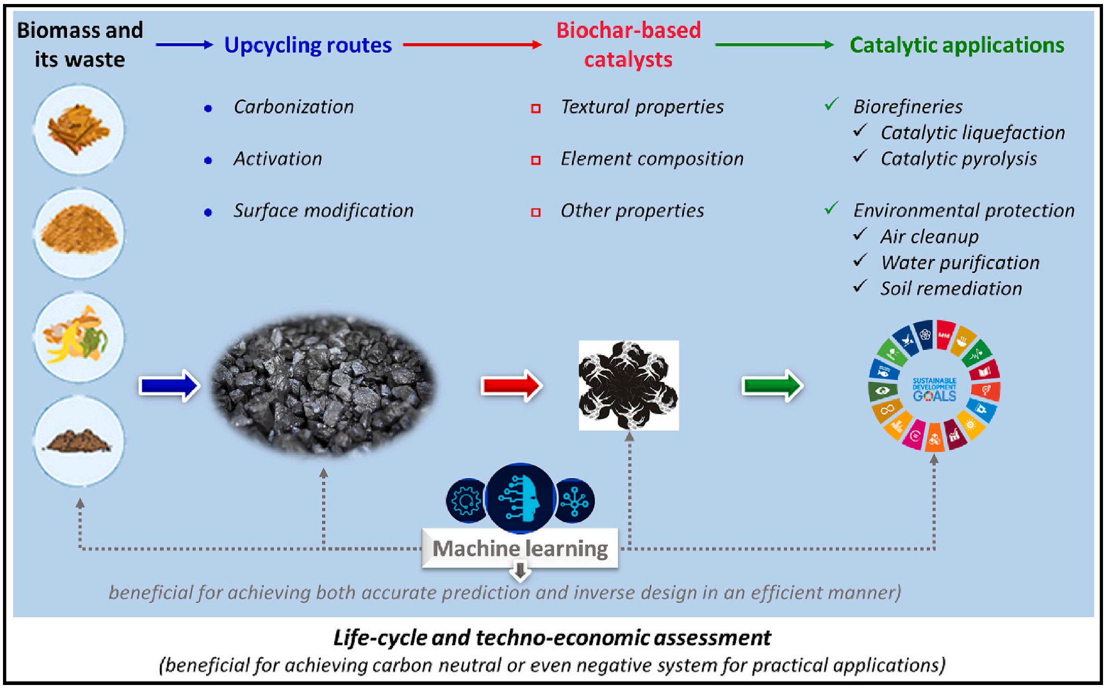


Fig. 8. Sustainable biochar-based catalytic applications, contributing to a circular economy.

× 10^6 after a 25-year operation. Frank et al. (2020) analyzed the financial viability of two pyrolysis pathways for the production of fuels and biochar to assess whether slow-pyrolysis pathways are more attractive than fast-pyrolysis pathways at realistic carbon prices. The results showed that fast pyrolysis achieved the lowest baseline minimum carbon prices of \$61.38/t. Lee et al. (2020) categorized biochar production facilities and biodiesel conversion for a techno-economic analysis of biodiesel production using biochar catalysts. The production cost of biochar-based biodiesel was \$1.8/kg per unit of biochar catalysts, suggesting that this technology, after further improvement and optimization, could be economically feasible (commercial diesel price: \$0.97–1.88/kg). Wang et al. (2020c) doped both Ni and Ce on biochar catalysts to synthesize CH_4 from CO_2, which could be regarded as an alternative to fossil fuels. Liao et al. (2022) conducted an economic analysis of the preparation of biochar and its application in heavy metal adsorption, showing that biochar prepared at 500 °C has the highest economic value (292.73 mg/\$ for Pb^{2+}, 84.29 mg/\$ for Cu^{2+}). Briefly, biochar-based catalysts should be economically feasible for energy production and environmental protection. In addition, spent biochar-based catalysts can be recycled/regenerated or applied in second-stage applications that have certain economic benefits, which necessitate further research to improve the economic performance of biochar in the entire life cycle.

From a life-cycle perspective, Wang et al. (2020b) concluded that biochar-based catalysts exhibited lower environmental impacts than metal oxide catalysts, which is incredibly beneficial for achieving efficient CO_2 utilization that is environmentally friendly. Loy et al. (2021) valorized wheat straw to produce biochar-based catalysts; the life cycle assessment results showed that it offers almost similar catalytic performance to other metal-based catalysts but with a lower environmental impact. Yuan et al. (2022a) upcycled plastic waste into novel porous materials for CO_2 capture, which helps towards mitigating climate change and achieving sustainable plastic management. The life cycle and techno-economic assessments were investigated thoroughly based on a simulated industrial-scale CO_2 capture plant. Based on the environmental benefits and economic feasibility results from life cycle and techno-economic assessments, Yuan et al. (2022a) concluded that plastic waste-derived novel porous materials for CO_2 capture could provide viable alternatives to conventional CO_2 absorption and plastic waste management technologies. Therefore, the synthesis of biochar-based catalysts with end-of-life management should be considered for practical applications, demonstrating a potential alternative to existing catalysts.

7. Conclusions

Understanding the beneficial properties of biochar and consistently producing high-quality biochar for practical applications are the primary goals of current studies investigating the multifunctional applications of biochar-based catalysts. The conversion of biomass into valuable chemicals and functional biochar can be considered a carbon-neutral circular framework that contributes to a sustainable circular economy. The low production costs, unique physicochemical properties, and stable chemical structure of engineered biochars enable their large-scale utilization across broad applications. Biochar-based catalysts in biorefineries can contribute to achieving carbon neutrality via the production of low-carbon-footprint chemicals and fuels. Biochar-based catalysts can be easily operationalized to obtain distributed active sites, adjustable porosity, a large SSA, and abundant functionalities using various modification approaches (i.e., chemical activation, heteroatom-doping, and transition-metal doping) to improve their catalytic activity and thermal stability. Catalyst deactivation owing to leaching and coking is crucial for scaling-up to industrial-level applications. Understanding the catalytic performance and deactivation mechanisms of different catalytic systems may provide new insights into developing efficient and practical biochar-based catalysts for biorefinery and environmental protection. In particular, ML inverse design could substantially accelerate biochar-based catalysts for a specific application, owing to the latest innovation wherein the underlying mechanisms and relationships can be elaborated using ML prediction. Environmental benefits and economic feasibility should be comprehensively assessed and standardized to provide science-based guidelines for industries and policymakers. Upcycling biomass waste into high-performance catalysts for biorefinery and environmental protection can, with concerted effort, achieve several UN SDGs and ESG.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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