



Rational design of biochar for carbon dioxide capture and catalytic conversion

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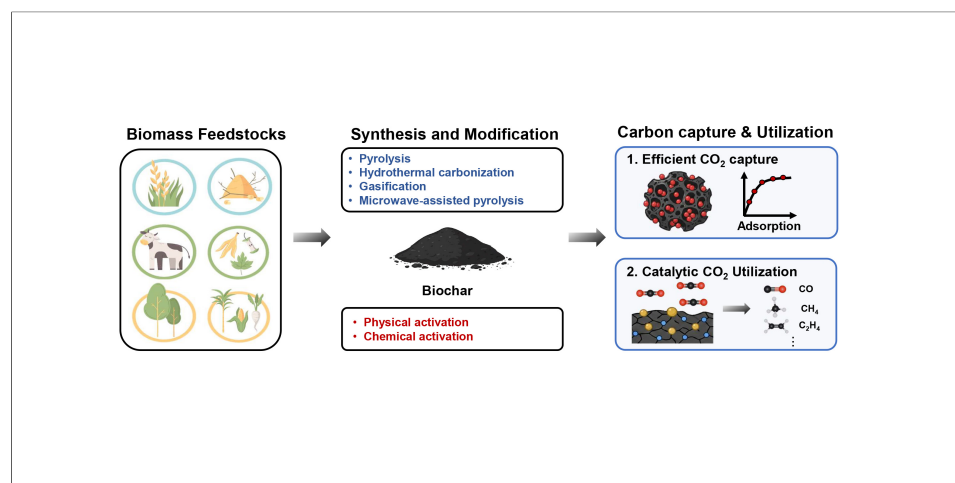
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Abstract

The continuous increase in carbon dioxide (CO₂) emissions has intensified the need for efficient carbon capture and utilization (CCU) technologies. Biochar has emerged as a promising, cost-effective, and sustainable platform for CCU. This review provides a comprehensive overview of the rational design of biochar for CO₂ capture and subsequent catalytic conversion. We first discuss various synthesis methods and activation strategies for tailoring the physicochemical properties of biochar. We then elucidate the mechanisms of CO₂ capture, highlighting the roles of pore modification and heteroatom functionalities in enhancing both physisorption and chemisorption. Furthermore, the roles of biochar in thermocatalytic, electrocatalytic, and photocatalytic CO₂ conversion are critically examined, with particular emphasis on its function as a multifunctional support for metal nanoparticles, molecular catalysts, single atoms, and nanoclusters. Finally, we outline key challenges and future directions for the rational development of next-generation biochar toward practical carbon-neutral technologies. Accordingly, this review establishes a rational design framework based on application demand, key performance parameters, and targeted synthesis strategies, thereby linking practical CCU requirements with the controlled engineering of biochar porosity, surface chemistry, conductivity, and catalytic functionality.

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INTRODUCTION

The intensifying environmental pollution caused by excessive fossil fuel consumption, together with the growing global energy demand, poses a critical challenge to modern society^[1]. Addressing these issues requires the urgent development of efficient and sustainable technologies to reduce carbon emissions and meet future energy demands. In this context, carbon capture and utilization (CCU) has gained significant attention as an integrated strategy that not only captures carbon dioxide (CO₂) from emission sources but also converts it into value-added chemicals and fuels, thereby contributing to climate change mitigation and resource circularity^[2–5].

However, the high cost associated with the CO₂ capture stage remains one of the major barriers to the practical implementation of CCU technologies^[6,7]. Therefore, the development of efficient and economically viable CO₂ sorbent materials is of critical importance. Over the past several decades, a variety of materials, including zeolites^[8,9], mesoporous carbons^[10], and activated carbons^[11], have been extensively explored as CO₂ adsorbents. Although these materials often exhibit promising adsorption capacities, many suffer from inherent drawbacks, such as high production costs, reliance on non-renewable precursors, and diminished performance under humid conditions or in the presence of competing gases^[12]. These limitations significantly restrict their large-scale application. Consequently, there is growing demand for alternative adsorbent materials that are cost-effective, sustainable, and compatible with circular resource utilization principles.

Biomass has emerged as an abundant and renewable carbon source originating from agricultural residues, forestry by-products, livestock waste, and municipal solid waste streams^[13–15]. Compared with conventional carbon precursors, biomass offers inherent sustainability, broad accessibility, economic feasibility, and a reduced environmental footprint^[16–19]. These characteristics make it an attractive feedstock for the preparation of next-generation sustainable carbon materials. Among various biomass-derived products, biochar is a carbon-rich solid material derived from abundant biomass resources and has recently attracted considerable attention as a viable alternative for CO₂ capture^[20,21]. Owing to its controllable pore structure, large surface area, and modifiable surface functionalities, biochar demonstrates considerable potential for CO₂ adsorption^[22,23]. Moreover, biochar can be synthesized from diverse biomass feedstocks and waste resources, making it a sustainable material from the perspectives of resource recovery and carbon emission mitigation^[24]. Its comparatively low manufacturing cost relative to conventional CO₂ adsorbents further strengthens its economic competitiveness and practical appeal.

Building on these advantages, recent studies have increasingly focused on tailoring the structural and chemical characteristics of biochar to extend its functionality beyond CO₂ adsorption toward catalytic conversion and electrochemical energy storage and conversion applications. A variety of high-value biochar-based carbon materials derived from diverse biomass sources have been reported, demonstrating their potential as multifunctional platforms capable of integrating CO₂ capture and conversion within CCU systems^[25–27]. Therefore, a comprehensive understanding of how precursor selection, preparation strategies, and structural characteristics govern the performance of biomass-derived biochar is essential for advancing its practical implementation in CCU technologies.

In this review, we first introduce the major synthesis approaches for biomass-derived biochar and examine how different processing conditions influence its structural and physicochemical properties. We then discuss recent advances in biochar-based CO₂ capture, with particular emphasis on physisorption and chemisorption mechanisms and the key parameters governing capture performance. Subsequently, biochar-enabled carbon-utilization pathways, including thermocatalytic conversion, electrochemical CO₂ reduction, and

Table 1. Comparison of representative biochar preparation methods

Method	Operating conditions	Product yield	Biochar characteristics	Advantages	Disadvantages	Ref.
Pyrolysis	300–1,200 °C under inert atmospheres	Relatively high, particularly under slow-pyrolysis conditions	High surface areas, aromatic carbon-rich	Simple preparation process, Tunable through temperature, heating rate, and residence time, low-cost	High energy consumption (fast pyrolysis)	[28]
Hydrothermal carbonization	180–250 °C	Moderate	Abundant oxygen-containing functional groups	Low energy consumption	High liquid byproducts	[31]
Gasification	500–1,400 °C	Low	Various porosity, High ash content	High gas yield, High efficiency	Low biochar yield, high ash content	[33]
Microwave-assisted Pyrolysis	Microwave powers of 300–3,000 W, under inert atmospheres	Moderate	Uniform structure, High porosity, High specific surface area	Fast preparation speed Uniform internal heating High energy efficiency	High equipment requirements	[34]

photocatalytic processes, are critically reviewed. Finally, the current state of the art, remaining challenges, and future research directions are discussed, with particular emphasis on AI-assisted materials discovery and Integrated Carbon Capture and Utilization (ICCU) systems.

To establish a comprehensive design approach, this review connects practical application needs with critical material performance targets and corresponding synthesis strategies. For CO₂ capture, practical demands such as high adsorption capacity, selectivity, rapid adsorption kinetics, moisture tolerance, and low regeneration energy are translated into key structural and chemical parameters, including microporosity, pore connectivity, surface basicity, hydrophobicity, and functional-group density. For catalytic CO₂ conversion, the principal design criteria include electrical conductivity, active-site accessibility, interfacial coupling, mass transport, and long-term stability. These performance requirements subsequently guide the selection of biomass precursors, pyrolysis conditions, activation methods, pore-engineering approaches, heteroatom-doping strategies, and catalyst-immobilization techniques. Through this systematic design strategy, biochar synthesis is regarded not merely as a material preparation process, but as a targeted engineering approach tailored to the requirements of specific CCU applications.

BIOCHAR SYNTHESIS METHODS

Biochar is a porous carbon-rich material obtained through the thermochemical conversion of biomass under oxygen-deficient environments. Biochar can be synthesized through various routes, including pyrolysis^[28–30], hydrothermal carbonization (HTC)^[31,32], gasification^[33], and microwave-assisted processes (MAP)^[34,35], frequently followed by activation steps to further tailor its structure and surface properties^[36–39]. The structural and physicochemical properties of biochar are highly dependent on the selected synthesis strategy, and the intrinsic composition of the biomass precursor. These factors collectively determine key properties such as specific surface area, pore architecture, surface functional groups, and electronic characteristics, which ultimately govern its performance in CCU applications. As summarized in Table 1, each preparation route exhibits distinct characteristics in terms of operating conditions, product yield, structural features, advantages, and limitations. Therefore, the selection of an appropriate synthesis route should be guided by the desired structural properties and performance requirements of the resulting biochar. In the following section, the principal synthesis approaches for biochar are outlined.

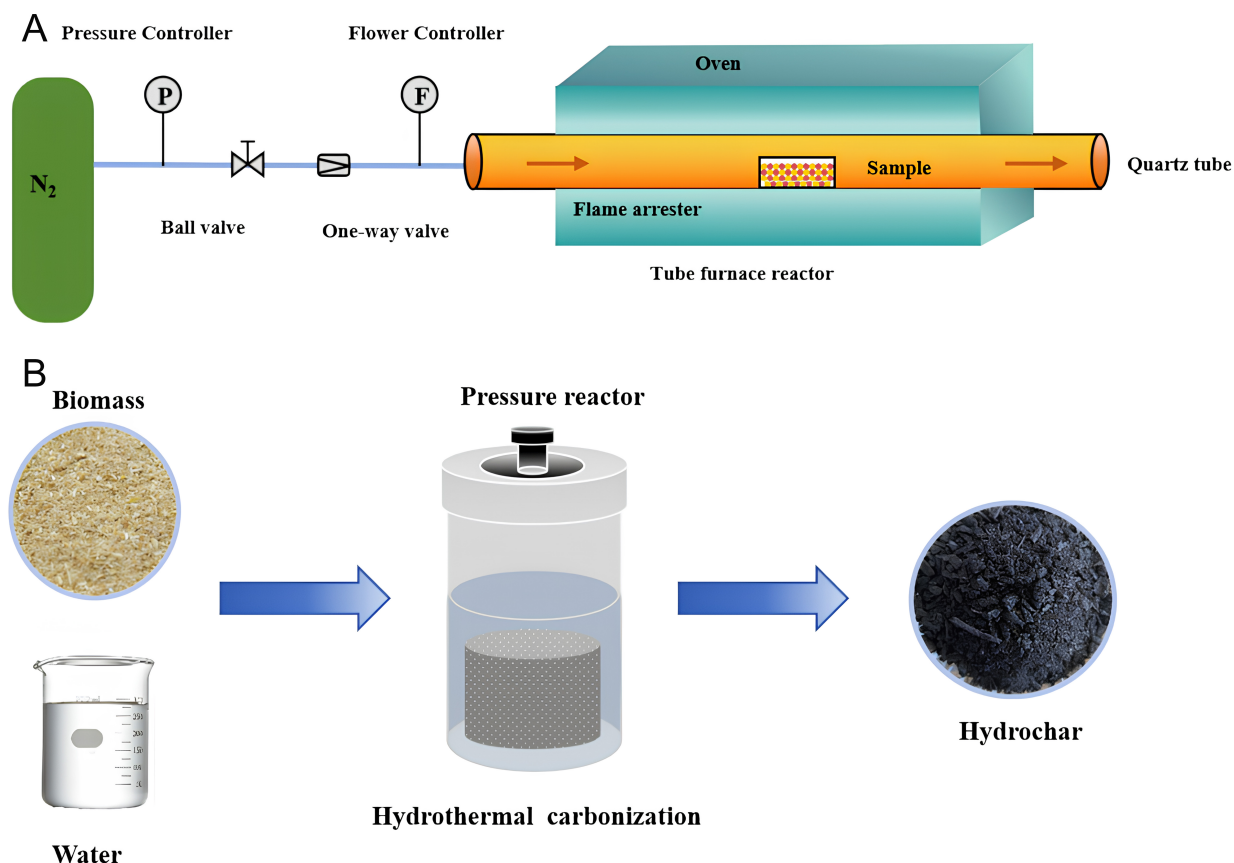


Figure 1. (A) Graphical illustration of the pyrolysis procedure. (B) Schematic representation of the hydrothermal carbonization process. This figure quoted with permission^[40]. Copyright 2026, Elsevier.

Pyrolysis

Pyrolysis is the most employed route for biochar production, involving the thermal decomposition of biomass in an oxygen-limited atmosphere at elevated temperatures, typically between 300 and 900 °C, and in some cases up to 1,200 °C [Figure 1A]^[40]. Depending on operational parameters such as heating rate and vapor residence time, pyrolysis can be categorized into slow, fast, and flash modes. Among these, slow pyrolysis is particularly favorable for biochar generation, as it enables efficient volatilization of organic compounds while maximizing solid carbon yield^[41]. For this reason, most biochar synthesis processes are conducted via slow pyrolysis under inert gas environments such as nitrogen (N₂) or argon^[42,43]. The resulting biochar yield and properties are highly sensitive to processing conditions. At relatively lower temperatures (300–500 °C), the produced biochar tends to retain abundant oxygen-containing functional groups, including hydroxyl and carboxyl functionalities. In contrast, increasing the temperature above 700 °C and prolonging the residence time promote aromatic condensation and partial graphitization, thereby enhancing electrical conductivity and pore development while reducing the heteroatom content^[44,45]. Moreover, heating rate and reaction duration significantly affect carbon microstructure and porosity evolution. Slow pyrolysis generally leads to higher carbon yields and more structurally ordered frameworks, whereas fast pyrolysis typically produces defect-rich and less ordered carbon structures^[46].

Hydrothermal carbonization

HTC has been widely explored as a complementary approach to conventional pyrolysis for converting biomass into biochar^[40]. This process is carried out in a closed reaction system where water functions simultaneously as solvent and reaction medium under self-generated pressure, typically at moderate temperatures between 180 and 250 °C [Figure 1B]. The solid product formed through HTC, commonly

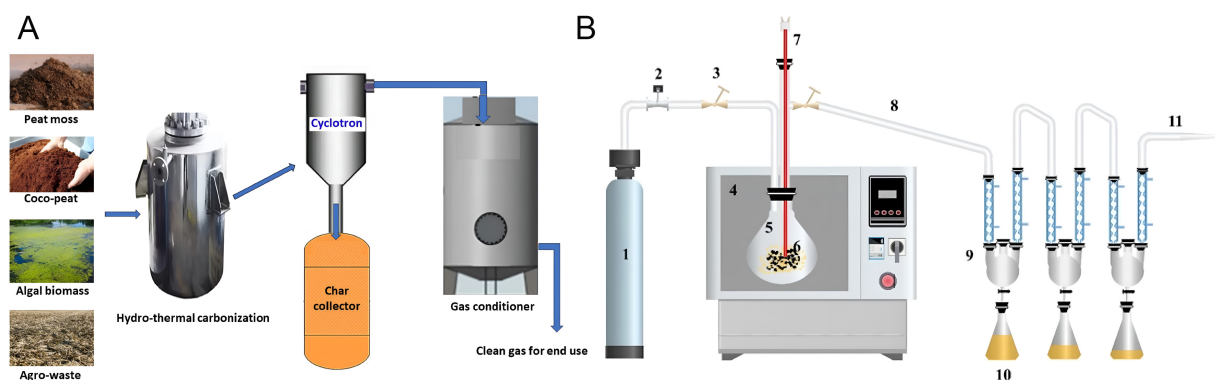


Figure 2. (A) Schematic representation of gasification. Reprinted with permission^[56]. Licensed under CC BY 4.0. (B) Overview schematic of microwave-assisted pyrolysis. Reprinted with permission^[62]. Copyright 2022, Elsevier.

termed hydrochar, exhibits enhanced carbonization compared with the original biomass precursor^[47].

A key advantage of HTC lies in its ability to process wet biomass directly, eliminating the need for pre-drying. This feature makes the technique particularly attractive for treating moisture-rich feedstocks such as food waste, agricultural by-products, and sewage sludge^[48–50]. Throughout the hydrothermal process, biomass undergoes a cascade of chemical transformations, including hydrolysis, dehydration, and decarboxylation, which collectively modify its molecular structure and carbon framework. Compared with high-temperature pyrolysis-derived biochar, hydrochar generally retains a higher proportion of oxygen-containing functionalities and exhibits a distinct surface chemistry^[51]. The final material characteristics can be systematically tuned by adjusting reaction temperature and duration. Lower temperatures tend to preserve surface functional groups, which are advantageous for chemical modification and adsorption-related applications^[52]. Conversely, increasing reaction severity promotes aromatic condensation and structural ordering, thereby enhancing electrical conductivity. Owing to this controllability, HTC-derived carbons are considered promising candidates for applications requiring abundant surface functionalities, such as CO₂ capture^[53,54] and catalyst-support engineering^[55].

Gasification

Gasification is a high-temperature thermochemical process that converts carbonaceous feedstocks into a mixture of gaseous products under limited oxygen conditions, typically at temperatures between approximately 700 and 1,400 °C [Figure 2A]^[56]. During this process, biomass undergoes a sequence of transformations including drying, thermal decomposition, partial oxidation, and reduction reactions. The main products are combustible gases such as hydrogen (H₂), carbon monoxide (CO), CO₂, and methane (CH₄), along with minor amounts of N₂ depending on the gasifying agent. In addition, condensable hydrocarbons and solid carbonaceous residue are formed^[57]. Unlike pyrolysis, which is primarily designed to maximize solid carbon yield, gasification aims to enhance syngas production for energy applications. This objective is achieved by introducing controlled amounts of oxidizing agents such as oxygen, air, or steam at elevated temperatures^[56,58]. As a result, only a limited fraction of carbon remains in the solid phase, leading to significantly lower biochar yields compared with pyrolysis^[59]. Furthermore, the residual char obtained from gasification generally exhibits less developed porosity, reduced specific surface area, and diminished surface functional group density relative to biochar produced via conventional pyrolysis^[60,61]. The combination of low solid yield, limited control over surface functionality, and difficulty in tailoring active-site distribution makes gasification less suitable as a dedicated route for high-performance biochar production.

Microwave-assisted pyrolysis

MAP represents a microwave-driven thermochemical approach for biomass conversion [Figure 2B]^[62]. Unlike conventional furnace heating, microwave irradiation delivers electromagnetic energy directly into the material, enabling volumetric heating throughout the biomass matrix. This mechanism allows for rapid temperature rise and more uniform internal heating, often resulting in improved energy utilization efficiency compared with traditional externally heated pyrolysis systems^[63]. The distinct heating characteristics of MAP can significantly influence the structure of the resulting biochar. Accelerated heating rates and efficient energy transfer may promote enhanced pore development and increased specific surface area. Moreover, localized high-temperature zones generated by microwave irradiation can intensify biomass decomposition and facilitate structural reorganization of carbon frameworks, potentially improving adsorption-related properties. Owing to these advantages, microwave-assisted pyrolysis is generally considered more energy-efficient than conventional electrically heated pyrolysis and has been widely explored for applications such as catalysis and soil remediation^[64,65]. However, the performance of MAP-derived biochar is highly dependent on operational parameters such as microwave power, irradiation time, and frequency. Excessive localized heating may lead to thermal runaway or superheating effects, which can cause pore collapse and structural degradation. Therefore, precise control of microwave input and careful optimization of process conditions are essential to ensure uniform heating and preserve the structural integrity of the produced biochar.

Activation strategies

Biochar produced solely through thermochemical conversion typically exhibits lower specific surface area and less-developed porosity compared with commercial activated carbons^[66]. To overcome these inherent limitations, additional activation treatments are commonly applied to tailor its structural and surface properties. Activation strategies are broadly categorized into two main types: physical activation and chemical activation^[67]. While physical activation relies on controlled gas-solid reactions at high temperatures to develop porosity, chemical activation involves the use of activating agents that promote simultaneous carbonization and pore formation^[68–70]. Through these activation processes, pore architecture can be significantly enhanced, surface functional groups can be introduced, and defect density can be precisely tuned^[71,72]. Such structural and chemical modifications are crucial for optimizing biochar performance in carbon capture and broader CCU applications.

Physical activations

Physical activation typically involves a two-step process^[67]. First, biomass is carbonized to form a primary biochar framework. The resulting material is then treated at elevated temperatures, usually above 700 °C, under a flow of activating gases such as CO₂ or steam^[73]. During this stage, controlled gas-solid reactions selectively remove reactive carbon atoms from the matrix, effectively etching the structure. This process opens blocked pores, enhances pore connectivity, and promotes the formation of predominantly microporous structures with increased specific surface area. The properties of physically activated biochar are governed by several parameters, including precursor type, activation temperature, activating atmosphere, and treatment duration^[74,75]. Higher temperatures and longer activation times generally enhance pore development. However, excessive burn-off may broaden pore size distribution, reduce structural integrity, and compromise adsorption selectivity^[76]. Therefore, careful optimization is required to achieve a balance between pore generation and structural stability.

Chemical activations

Chemical activation is widely employed to produce biochar with highly developed microporous structures, making it particularly attractive for gas adsorption and electrochemical applications^[77,78]. In this method, the carbon precursor is first impregnated with activating agents, typically acids, alkalis, or metal salts, followed by thermal treatment under an inert atmosphere, generally within 400–900 °C^[79]. Unlike physical activation,

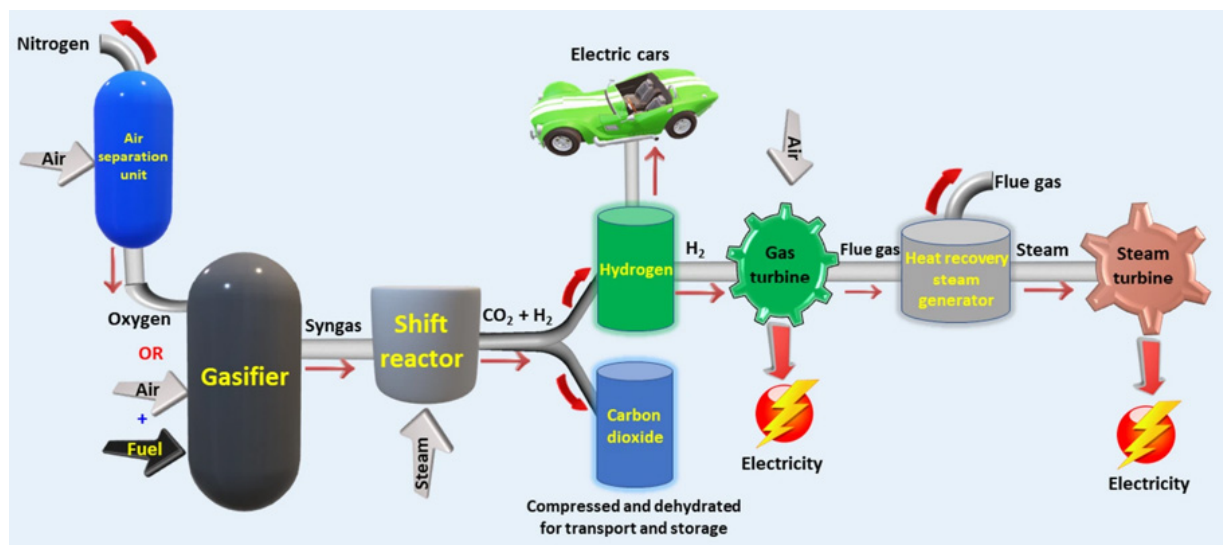


Figure 3. Schematic depiction of pre-combustion carbon capture process. Reprinted with permission^[87], licensed under CC BY 4.0.

carbonization and pore development occur simultaneously during this process. During heat treatment, the activating reagents promote dehydration, bond cleavage, and redox reactions, generating gaseous products such as H_2O , CO , and CO_2 ^[78,80]. The release of these species etches the carbon framework and facilitates the formation of new pore networks. The resulting textural properties and surface functionalities are governed by several parameters, including activation temperature, the type and concentration of activating agent, and the intrinsic composition of the biomass precursor^[81].

Common chemical activators include alkali compounds (e.g., KOH , K_2CO_3 , $NaOH$, Na_2CO_3)^[81,82], acids (e.g., H_3PO_4 , H_2SO_4)^[83], and metal salts (e.g., $ZnCl_2$, $AlCl_3$)^[84]. Among these, KOH is one of the most extensively utilized agents due to its strong ability to generate abundant microporosity and enhance structural ordering in carbon materials. Generally, KOH primarily induces micropore formation, $ZnCl_2$ tends to create widened micropores with limited mesoporosity, whereas H_3PO_4 favors the development of mesoporous and even macroporous structures^[85]. Compared with physical activation, chemical activation can achieve higher specific surface areas and more pronounced pore development at relatively lower temperatures and shorter processing times, often with improved carbon yields^[86]. However, this method typically requires extensive post-treatment washing to remove residual chemicals and may introduce practical concerns such as reagent recovery, equipment corrosion, and potential environmental impacts.

BIOCHAR FOR CO_2 CAPTURE

Pre-combustion & post-combustion CO_2 capture technologies

Pre-combustion CO_2 capture is primarily implemented in Integrated Gasification Combined Cycle (IGCC) systems. As shown in Figure 3, the process begins with the conversion of fossil fuel feedstocks such as coal, natural gas, or biomass into syngas, which mainly consists of CO and H_2 ^[87]. This conversion step is referred to as gasification when solid fuels are employed, whereas partial oxidation is used for gaseous or liquid feedstocks. Under high-temperature and high-pressure conditions, the feedstock reacts with controlled amounts of oxidants and steam to produce syngas. The resulting syngas subsequently undergoes catalytic conversion through the water-gas shift reaction, which converts CO into CO_2 while maximizing H_2 production. A key advantage of this pathway is its operation under elevated pressure, which significantly increases the partial pressure of CO_2 and thereby facilitates its separation and removal from the gas stream^[88]. After separation, CO_2 is compressed and dehydrated for transport and storage, while the purified H_2 can be utilized as a carbon-free fuel in gas turbines or fuel cells.

From a techno-economic perspective, pre-combustion carbon capture offers distinct advantages, including lower H₂O consumption compared to other capture methods and the co-production of valuable H₂ fuel^[89]. Despite the favorable thermodynamic conditions for CO₂ separation, the overall capital cost of IGCC plants remains high. Moreover, the complexity associated with integrating pre-combustion carbon capture into existing power plants limits its applicability to new installations, often accompanied by challenges related to reduced overall plant performance.

Post-combustion CO₂ capture involves the separation of CO₂ from flue gas generated after the complete combustion of carbon-based fuels^[90]. This approach represents the most mature and widely implemented capture strategy, largely due to its downstream configuration, which allows retrofitting into existing power plants without significant modification of the combustion process^[91]. However, prior to CO₂ separation, the flue gas typically requires pretreatment processes, such as desulphurization and denitrification, to eliminate impurities that can adversely affect capture performance^[92]. A variety of post-combustion capture technologies have been developed, including chemical absorption, physical adsorption, membrane separation, and cryogenic distillation^[93]. Among these, chemical absorption using amine-based solvents is the most commercially established technology^[94,95]. Despite its high capture efficiency, this approach suffers from several drawbacks, including substantial energy penalties associated with solvent regeneration, corrosion-related operational issues, and the formation of potentially harmful degradation products. Alternative approaches also face inherent limitations. Cryogenic distillation can produce high-purity liquid CO₂ suitable for direct transport, but its application is often restricted by the large energy demand required for refrigeration^[96]. Although membrane separation is attractive due to its chemical-free operation and simplicity, its efficacy is limited by the low CO₂ partial pressure in post-combustion flue streams as well as the susceptibility of membrane degradation from H₂O vapor.

Consequently, solid-based adsorption has emerged as a promising research direction due to its potential for improved energy efficiency and reversible operation via temperature or pressure swing cycles^[12,97]. A wide range of adsorbent materials such as zeolites, biochar, and metal-organic frameworks are actively being investigated. Nevertheless, the industrial scalability of adsorption-based capture remains constrained by trade-offs between adsorption capacity, selectivity, regeneration energy, and long-term stability under realistic flue gas conditions. Exposure to impurities like SO_x and NO_x can lead to adsorbent deactivation, posing significant challenges for sustained operation^[98,99]. Therefore, bridging the gap between laboratory-scale performance and industrial application remains a critical hurdle for adsorption technologies, especially with respect to durability and efficient gas-solid contact under practical operating conditions.

CO₂ capture strategies using biochar-based adsorbents

Biochar, a carbon-rich solid produced through the thermal decomposition of biomass under inert conditions, has emerged as a promising and sustainable precursor for carbon capture applications. One of the primary advantages of biochar is its economic viability. In contrast to commercial activated carbon, biochar production generally requires less energy-intensive activation processes, making it a cost-effective option for large-scale deployment^[100]. Despite these advantages, the direct utilization of pristine biochar is often constrained by its inherent material limitations. In its untreated form, biochar frequently exhibits a relatively low specific surface area and insufficient surface alkalinity, which hinders it from achieving the high adsorption capacities required for industrial implementation. As a result, improving the performance of biochar necessitates a fundamental understanding of the two primary adsorption mechanisms involved in carbon capture, namely physisorption and chemisorption.

Physisorption is predominantly governed by the textural properties of the material, including micropore volume and overall surface area, which facilitate the physical confinement of CO₂ molecules^[101]. In contrast, chemisorption relies on surface chemical interactions between acidic CO₂ molecules and basic active sites^[102].

These sites are primarily associated with functional groups, such as nitrogen-containing species, or with intrinsic inorganic components like alkaline earth metals.

To bridge the performance gap between pristine biochar and commercial adsorbents, recent studies have focused on various modification strategies that regulate both pore architecture and surface chemistry. Although physisorption and chemisorption are discussed separately for mechanistic clarity, they generally coexist in engineered biochars because activation and functionalization can simultaneously alter pore structure, defect density, surface polarity, and active-site accessibility. Their relative contributions therefore cannot be determined from adsorption capacity alone.

Complementary characterization methods are required for reliable mechanism assignment. Low-temperature CO₂ desorption, moderate adsorption heat, and reversible uptake generally support weak pore filling, whereas desorption extending to higher temperatures and the *in situ* Fourier transform infrared spectroscopy (FTIR) identification of carbonate, bicarbonate, carbamate, or other surface-bound species provide stronger evidence of chemical binding^[103]. Humidity-dependent measurements can reveal competitive H₂O adsorption within micropores and polar sites or, when supported by spectroscopic evidence, moisture-assisted chemical binding. Kinetic models are useful for describing adsorption rates but should not be regarded as independent proof of chemisorption. Accordingly, Sections “Enhancing CO₂ physisorption on biochar through structural optimization” and “Promoting CO₂ chemisorption on biochar via chemical modification” describe the dominant contributions of pore filling and surface interactions, respectively, while Section “Synergistic pore construction and heteroatom functionalization” discusses their synergistic integration for high-performance CO₂ capture.

Enhancing CO₂ physisorption on biochar through structural optimization

The effectiveness of CO₂ physisorption on biochar is primarily governed by the micropore filling mechanism^[104]. Because physical adsorption occurs through the confinement of gas molecules within the porous framework, the development of accessible microporous structures is the key determinant of adsorption capacity. Although increasing the specific surface area generally provides more adsorption sites, it is widely accepted that the availability of well-developed micropores is more critical for efficient CO₂ capture than the total surface area alone^[105].

Pore size distribution also plays a decisive role in determining CO₂ adsorption performance. Micropores in the range of approximately 0.3 to 0.8 nm are considered optimal, with ultra-micropores smaller than 0.5 nm exhibiting the strongest adsorption affinity. Previous studies have further demonstrated that equilibrium CO₂ uptake correlates more strongly with micropore volume than with the total Brunauer-Emmett-Teller surface area, indicating that accessible micropores are more critical than the overall surface area for effective CO₂ capture^[104]. Pores with dimensions comparable to the kinetic diameter of CO₂ (~0.33 nm) provide the most favorable adsorption environment, where overlapping adsorption potentials from opposing pore walls significantly enhance van der Waals interactions and CO₂ affinity^[106,107]. In contrast, mesopores and macropores contribute less directly to the equilibrium adsorption capacity but play indispensable roles in facilitating gas diffusion and improving adsorption kinetics by providing efficient transport pathways to the adsorption sites. Therefore, the rational design of biochar should maximize accessible ultramicropore volume while maintaining hierarchical pore connectivity to simultaneously achieve high equilibrium CO₂ uptake and efficient mass transport. Consequently, an effective biochar adsorbent integrates macropores for gas transport, mesopores for efficient diffusion, and micropores as the primary CO₂ adsorption domains^[108].

Table 2. Summary of biochar-based adsorbents for CO₂ capture

Primary modification strategies	Adsorbents	Specific surface area (m ² g ⁻¹)	CO ₂ adsorption capacity (mmol·g ⁻¹)	CO ₂ adsorption measurement conditions	CO ₂ /N ₂ selectivity (15 vol % CO ₂ in N ₂)	Ref.
Porous modification	ABC-ahp-6	3,380.4	6.60	Pure CO ₂ /30 °C/1 bar	-	[109]
	RHC-PC-2	1,343.8	1.55	Pure CO ₂ /30 °C/1 bar	37.80	[110]
	AF-700	1,371	3.34	Pure CO ₂ /0 °C/1 bar	72	[126]
Non-metallic heteroatom functionalization	ABC800	836.5	4.06	Pure CO ₂ /0 °C/1 bar	-	[127]
	OPPC ₃₁	1,445.71	4.31	Pure CO ₂ /25 °C/1 bar	17	[128]
	ASBC-800-0.5	2,890	2.95	Pure CO ₂ /30 °C/1 bar	44.03	[129]
	5 wt% Mg-loaded biochar	292	1.86	Pure CO ₂ /25 °C/1 bar	-	[134]
Introduction of alkali earth metals	MgO/biochar-1	1,453	6.65 3.72	Pure CO ₂ /0 °C/1 bar Pure CO ₂ /25 °C/1 bar	96.7	[135]
	BC(Ca)	445	2.42	Pure CO ₂ /25 °C/1 bar	36	[136]
Synergistic pore and surface modification	PAC 2	755	3.13 1.55	Pure CO ₂ /0 °C/1 bar Pure CO ₂ /50 °C/1 bar	37	[138]

Benchmark condition: Pure CO₂ at 25 °C and 1 bar under equilibrium adsorption. Values measured under other temperatures, pressures, gas compositions, or dynamic conditions should be interpreted within their respective experimental conditions and not directly compared.

To validate these structural design principles experimentally, recent studies have adopted synergistic activation strategies to simultaneously optimize micropore development and pore accessibility. Table 2 summarizes previous studies on biochar-based adsorbents for CO₂ capture. Wang *et al.*^[109] showed the integration of H₂O₂ pre-oxidation with KOH activation enables the fabrication of ultra-microporous biochar from pine sawdust. In this process, mild pre-oxidation introduced oxygen-containing functional groups into the precursor, which significantly enhanced the reactivity of the carbon matrix towards the subsequent chemical etching. As a result, an exceptionally well-developed microporous network was obtained, yielding a remarkable specific surface area of 3,380.4 m²·g⁻¹ and a microporosity ratio as high as 91.6%. Consistent with the micropore filling mechanism discussed above, this textural optimization led to high CO₂ adsorption capacity of 6.60 mmol·g⁻¹ at 30 °C, even in the absence of heteroatom doping. These findings confirmed that maximizing narrow microporosity while preserving pore accessibility remains a powerful strategy for CO₂ capture performance dominated by physisorption.

Beyond maximizing micropore volume through conventional chemical activation, recent studies have increasingly explored sustainable synthesis strategies that exploit the intrinsic mineral components of biomass to engineer hierarchical porosity. For example, Gan *et al.*^[110] developed a green synthesis strategy based on silicon-rich rice husk and potassium citrate. In this approach, naturally embedded silica nanoparticles within the biomass functioned as *in-situ* hard templates, while potassium citrate served as a low-corrosive activating agent. This dual role prevented structural collapse during carbonization, resulting in the formation of unique nanocapsule-like architectures featuring interconnected transport channels. Subsequent removal of the silica template, together with etching by *in-situ* generated activating species, created a refined pore network dominated by narrowly distributed ultra-micropores centered at 0.36 and 0.59 nm. As depicted in Figure 4A and B, this optimized biochar (RHC-PC-2) achieved a high CO₂ uptake of 1.55 mmol·g⁻¹ and a high CO₂/N₂ selectivity of 37.8, markedly outperforming samples prepared by conventional KOH activation. These results emphasized that leveraging natural structural templates offers a viable pathway to fabricate selective adsorbents with interconnected transport pathways, enabling a favorable balance between adsorption performance and environmental sustainability.

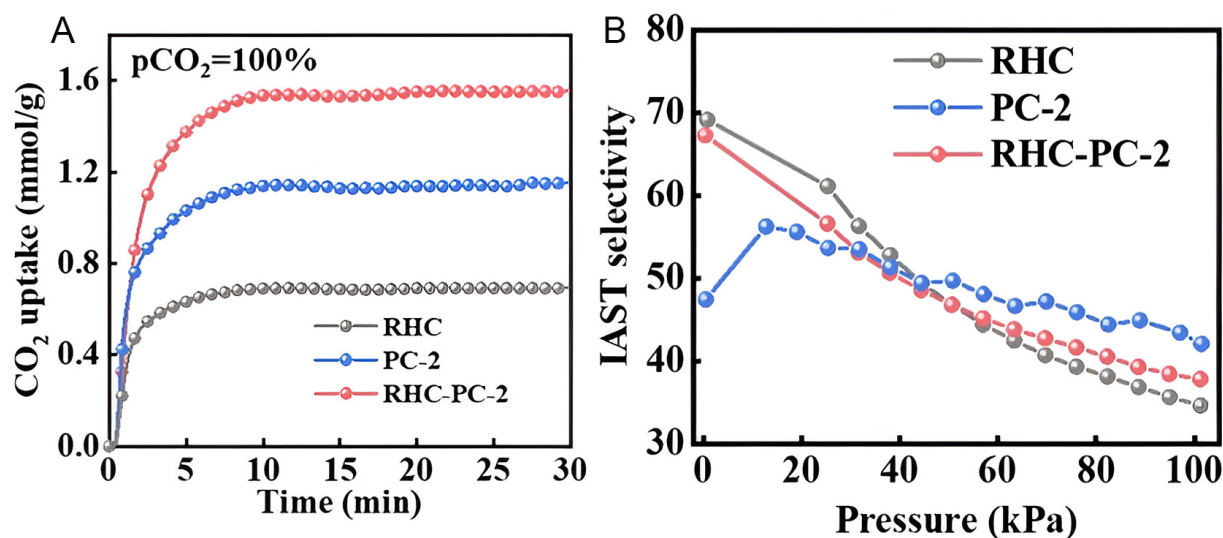


Figure 4. (A) Thermogravimetric analysis curves of the synthesized materials. (B) Comparison of CO₂/N₂ selectivity across the as-prepared samples. This figure quoted with permission^[110]. Copyright 2022, Elsevier.

Promoting CO₂ chemisorption on biochar via chemical modification

Beyond pore confinement, surface chemical properties provide complementary contributions to CO₂ adsorption by introducing basic and polar interaction sites. This mechanism is largely driven by Lewis acid-base interactions, in which acidic CO₂ molecules interact with basic active sites on the biochar surface^[111]. Consequently, enhancing surface basicity through the introduction of nitrogen or oxygen containing functional groups, or through the incorporation of alkaline earth metals, is considered an effective strategy for increasing CO₂ capture capacity. In addition to surface basicity, surface polarity also plays a crucial role in adsorption selectivity^[112]. Beyond heteroatom- and metal-derived sites, topological and edge defects within the carbon skeleton can also contribute to CO₂ capture. Non-hexagonal motifs, particularly five-membered rings, together with vacancies and exposed edge sites, disrupt the electronic symmetry of the sp² carbon lattice and induce localized charge redistribution. The resulting electron-rich carbon centers may act as weak Lewis-basic sites toward the electrophilic carbon atom of CO₂, thereby strengthening adsorption and promoting molecular polarization. Depending on the defect configuration and binding strength, this contribution may range from enhanced physisorption to weak chemisorption. Therefore, defect-derived adsorption should be distinguished from micropore confinement and heteroatom effects through complementary Raman, X-ray photoelectron spectroscopy (XPS), CO₂-temperature-programmed desorption (CO₂-TPD), and theoretical analyses rather than inferred from defect density alone^[113]. Moreover, a reduction in hydrophilicity increases surface hydrophobicity, which suppresses the competitive adsorption of H₂O molecules and thereby promotes preferential CO₂ uptake under humid conditions. Most adsorption capacities, however, are reported under dry conditions and may therefore overestimate performance in practical flue-gas streams. Under humid conditions, H₂O competes with CO₂ for polar surface sites and narrow micropores, reducing the accessible adsorption capacity. Although increasing surface hydrophobicity can mitigate this effect, excessive removal of polar functional groups may simultaneously weaken CO₂ affinity. Furthermore, co-adsorbed water increases the energy required for adsorbent regeneration^[114]. Therefore, humid working capacity and long-term cyclic stability under simulated flue-gas conditions should be considered together with dry equilibrium adsorption capacity.

To introduce chemically defined heteroatom- and metal-derived adsorption sites, pristine biochar typically requires chemical modification. Such treatments generally follow two main approaches. In pre-modification strategies, raw biomass is impregnated with chemical agents prior to pyrolysis^[115]. In contrast,

post-modification strategies involve chemical treatment and subsequent thermal activation of the biochar after carbonization^[116]. Both approaches aim to enrich the carbon framework with chemically active sites capable of forming strong intermolecular interactions with CO₂, including hydrogen bonding and dipole-related interactions.

Common chemical modifications include oxidation using basic solutions to introduce oxygen-containing functional groups such as carboxyl, phenolic and hydroxyl as well as high temperature amination to incorporate nitrogen-containing functionalities such as amine groups^[117–119]. Additionally, impregnation with metal oxide precursors is frequently utilized to anchor basic metal species onto the biochar matrix. Based on these considerations, the following subsections will systematically categorize and critically analyze chemisorption enhancement strategies focusing on non-metallic functional group modification and metal incorporation.

Non-metallic heteroatoms functionalities

Beyond porous structure engineering, the intrinsic surface chemistry of biochar fundamentally dictates its chemisorption behavior. While the incorporation of metal species creates localized basic sites, the introduction of non-metallic heteroatoms, particularly nitrogen, oxygen and sulfur, serves as a primary strategy for modulating the electronic structure and surface polarity of the carbon matrix^[120–122]. Among these heteroatoms, nitrogen doping has been extensively explored due to its ability to generate electron-rich Lewis basic sites, such as pyridinic, pyrrolic, and amine functionalities, directly within the carbon lattice^[123]. Among these nitrogen species, pyridinic N is generally regarded as the primary active site for CO₂ chemisorption because its lone-pair electrons readily interact with the electrophilic carbon atom of CO₂ through Lewis acid-base interactions. In contrast, pyrrolic N and amine functionalities mainly contribute by enhancing the local electron density and surface basicity of the carbon framework, thereby promoting CO₂ adsorption^[124,125]. Similarly, oxygen-containing ketone and carbonyl groups enhance the surface polarity and strengthen dipole-quadrupole interactions with CO₂, whereas sulfur containing functionalities primarily improve CO₂ affinity by redistributing the electron density and polarizability of adjacent carbon atoms. Collectively, the targeted incorporation of these non-metallic heteroatoms transforms the relatively inert carbon matrix into a chemically active CO₂ adsorption surface, indicating that the capture performance is governed not only by the overall heteroatom content but also by the chemical state and distribution of these surface functional groups.

Building upon these principles, nitrogen doping has been widely adopted as an effective strategy to introduce basic active sites into the carbon lattice, thereby markedly enhancing CO₂ affinity. For instance, Sun *et al.*^[126] reported the synthesis of nitrogen self-doped hierarchical porous biochar derived from carp fish scales via a KOH-mediated activation process. XPS analysis of the N 1s spectrum of the optimized sample (AF-700) revealed the successful substitution of carbon atoms with nitrogen, predominantly in the form of pyrrolic N (N-5) and pyridinic N (N-6) functionalities. These nitrogen configurations functioned as alkaline active sites that not only strengthened hydrogen bonding but also facilitated electron transfer with weakly acidic CO₂ molecules, creating a highly favorable environment for chemisorption. Benefiting from the synergistic combination of nitrogen-induced chemical interactions and a substantial specific surface area of 1,371 m²·g^{−1}, the AF-700 biochar achieved a CO₂ uptake capacity of 3.34 mmol·g^{−1} at 0 °C and 1 bar. These results provided compelling evidence that utilizing the intrinsic nitrogen of biomass for self-doping can maximize acid-base interactions, thereby driving highly efficient CO₂ capture beyond the limitations of purely physisorption-driven mechanisms.

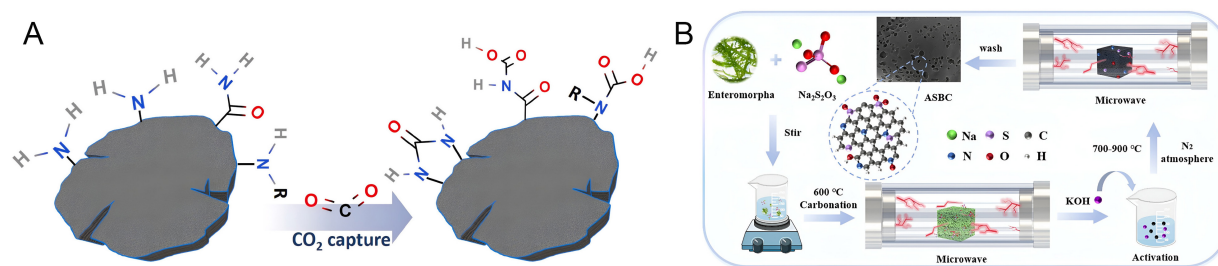


Figure 5. (A) Possible CO₂ capture mechanisms by chemisorption. Reprinted with permission^[127]. Copyright 2024, Springer. (B) Scheme of the synthesis process for N, S co-doped biochar. Reprinted with permission^[129]. Copyright 2025, Elsevier.

Active amination processes such as ammonialization represent a highly effective strategy to chemically graft strongly basic functional groups onto the carbon skeleton. For example, Hsu *et al.* demonstrated a single-step pyrolytic synthesis combining carbonization and ammonialization using *Leucaena leucocephala* biomass^[127]. During the high-temperature treatment, ammonia gas decomposed into reactive nitrogen radicals (NH[•] and NH₂[•]), which covalently bonded with the biochar matrix to form abundant amino (C-NH₂) and imine/pyrrolic (C-NH) functional groups [Figure 5A]. These introduced nitrogen species served as potent Lewis basic sites that chemically anchored the weakly acidic CO₂ molecules. The additional behavior was well described by the pseudo-second-order kinetic and Langmuir-Freundlich models, suggesting heterogeneous uptake involving both pore filling and interactions with nitrogen-containing sites. However, kinetic and isotherm fitting alone cannot conclusively establish chemisorption. The optimized ammonialized biochar (ABC800) exhibited a superior CO₂ capacity of 4.06 mmol·g⁻¹ at 0 °C, indicating that nitrogen functionalization enhanced CO₂ affinity in combination with its ultramicroporous structure.

In addition to nitrogen functionalities, the introduction of oxygen-containing functional groups offers another effective avenue to manipulate the surface polarity of biochar, thereby promoting CO₂ adsorption through strong electrostatic interactions. In a recent study, Wang *et al.*^[128] developed a green synthesis route based on a dual organic salt activation process to produce highly oxygenated porous biochar from orange peels. This approach enabled simultaneous control over porous architecture and surface chemistry, leading to a substantial enrichment of oxygen functionalities on the carbon surface. By integrating experimental characterizations with density functional theory (DFT) calculations, they elucidated the specific roles of distinct oxygen-containing groups in CO₂ adsorption. Notably, ketone functionalities, identified as the dominant oxygen species in the optimized sample, exhibited particularly strong electrostatic interactions with CO₂ molecules. DFT calculations demonstrated that the incorporation of ketone groups dramatically increased the CO₂ adsorption energy by 109.9% compared to a pristine carbon substrate, highlighting their critical contribution to adsorption affinity. Driven by the synergistic effects of a well-developed microporous framework and enhanced surface polarity, the resulting biochar delivered an outstanding CO₂ capture capacity of 4.31 mmol·g⁻¹ at 25 °C. This work suggested that rational oxygen functionalization can significantly amplify electrostatic interactions, offering an effective chemisorption pathway that complements physical confinement within micropores.

To further push the boundaries of chemisorption, recent advancements have focused on synergistic effects of multi-heteroatom co-doping, particularly combining nitrogen and sulfur. As depicted in Figure 5B, Chen *et al.*^[129] synthesized an N, S co-doped biochar via microwave pyrolysis, utilizing *Enteromorpha* as a natural nitrogen precursor and sodium thiosulfate as an external sulfur source. While physical microporosity initiated the capture via van der Waals forces, the remarkable enhancement in CO₂ uptake (reaching 2.95 mmol·g⁻¹) was primarily driven by the sophisticated surface chemistry. The integration of pyridinic and pyrrolic nitrogen provided direct Lewis basic sites, whereas the incorporation of oxidized sulfur groups

fundamentally modulated the electron density and polarizability of the surrounding carbon lattice. XPS and kinetic analyses demonstrated that the dual-doping strategy significantly enhanced acid-base interactions and facilitated rapid electron transfer between the active sites and CO₂ molecules. This synergistic interplay confirmed that strategically coupling distinct heteroatoms not only optimizes physical confinement but fundamentally establishes a highly reactive chemical environment for superior CO₂ chemisorption.

Incorporation of alkaline earth metals

Biomass exhibits an intrinsically heterogeneous elemental composition that depends on its feedstock origin. In addition to carbon, oxygen and nitrogen, biomass typically contains trace amounts of inorganic mineral species, including alkaline earth metals. The inherent presence or intentional enrichment of these metals, particularly calcium (Ca) and magnesium (Mg), plays a critical role in tuning the surface chemistry of biochar^[130–133]. By increasing surface alkalinity, these metal species enhance the affinity of the adsorbent toward acidic CO₂ molecules. This interaction promotes chemisorption mechanisms, enabling CO₂ fixation through the formation of stable carbonate and bicarbonate species. As a result, exploiting these unique chemical properties to improve adsorption capacity has become a major focus in recent biochar-based CO₂ capture research.

To enhance chemisorption performance, the incorporation of alkaline earth metals into biochar has been extensively investigated. Lahijani *et al.*^[134] studied metal-impregnated biochar derived from walnut shells, highlighting the pivotal role of metal selection in CO₂ adsorption behavior. As illustrated in Figure 6A, among various samples loaded with 5 wt% metals, Mg-modified biochar exhibited the highest CO₂ uptake compared to other counterparts. This superior performance was attributed to the formation of basic magnesium oxide (MgO) species on the carbon surface, which strongly interact with acidic CO₂ molecules. Metal loading was also found to critically influence adsorption capacity. As shown in Figure 6B, increasing Mg content initially enhanced CO₂ uptake due to the increased density of basic active sites. However, excessive metal loading resulted in a decline in performance, likely caused by metal agglomeration and partial blockage of micropores that restrict gas diffusion. These results highlighted the importance of optimizing metal content to balance chemical activity and pore accessibility. In addition to capacity, Mg-loaded biochar revealed high selectivity for CO₂ over N₂ and CH₄ [Figure 6C]. This selectivity arose from preferential acid-base interactions, confirming the potential of Mg impregnated biochar for post-combustion CO₂ capture.

To overcome the limitations of conventional metal impregnation and maximize the synergy between physisorption and chemisorption, Li *et al.*^[135] employed an *in situ* structural engineering approach, fabricating hierarchically porous MgO/biochar composites via a microwave-assisted hydrothermal method [Figure 6D]. Unlike conventional pyrolysis, this approach facilitated rapid and uniform nucleation of MgO nanocrystals within the carbon matrix. The resulting composite achieved a remarkable specific surface area of 1,453 m²·g^{−1} with abundant narrow micropores, providing a favorable architecture for CO₂ adsorption. CO₂-TPD analysis revealed broad desorption features extending toward higher temperatures, consistent with a distribution of MgO-derived basic sites and stronger CO₂ binding than that of pristine biochar [Figure 6E]. These results support a contribution from surface chemical interactions in addition to micropore filling. However, CO₂-TPD alone cannot identify magnesium carbonate or other specific adsorbed species, which requires direct spectroscopic evidence such as *in situ* FTIR. Consequently, the composite demonstrates how hierarchical porosity and MgO-derived basic sites can jointly contribute to CO₂ capture through improved transport and enhanced adsorption affinity.

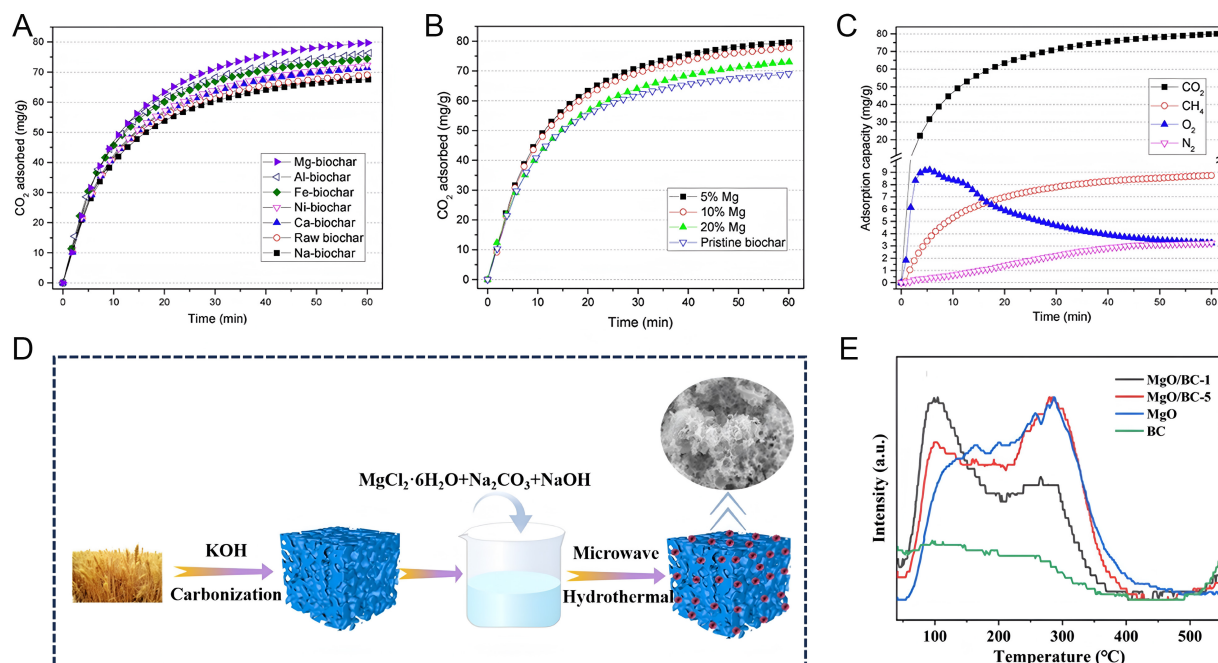


Figure 6. (A) CO₂ adsorption curves for biochars modified with 5 wt% of different metals. (B) CO₂ uptake profiles of biochars for varying Mg loadings. (C) Gas adsorption selectivity of Mg-loaded biochar for CO₂ over competing gases. (A–C) Reprinted with permission^[134]. Copyright 2018, Elsevier. (D) Illustration of the fabrication route for the hierarchically porous MgO/biochar composites. (E) CO₂-TPD profiles of the fabricated samples. (D and E) Reprinted with permission^[135]. Copyright 2024, Elsevier.

Expanding the range of alkaline earth metals, Ca has emerged as a cost-effective alternative for enhancing surface basicity in biochar-based adsorbents. Arjona-Jaime *et al.*^[136] displayed that Ca-modified biochar prepared through a rapid microwave-assisted irradiation method enabled uniform dispersion of Ca-based active sites within the carbon matrix while avoiding the prolonged processing times associated with conventional thermal treatments. The resulting adsorbent exhibited enhanced CO₂ uptake capacity along with high selectivity toward CO₂ over N₂, which is a key requirement for post-combustion capture applications. Crucially, the Ca-functionalized biochar effectively addressed a major limitation of many physical adsorbents, namely performance degradation under humid conditions. When evaluated under simulated flue gas environments containing H₂O vapor, the adsorbent maintained stable CO₂ uptake. This moisture tolerance suggests that Ca-derived basic sites preserved CO₂ affinity in the presence of H₂O and may have promoted the formation of carbonate and bicarbonate species. Nevertheless, humidity resistance alone cannot conclusively distinguish chemisorption from suppressed competitive H₂O adsorption, and direct spectroscopic identification of the adsorbed species is required. Taken together, these findings suggest that Ca incorporation can increase CO₂ adsorption through acid-base interactions while improving the potential applicability of biochar under humid industrial conditions.

Synergistic pore construction and heteroatom functionalization

High-performance biochar adsorbents generally rely on the coupled contributions of pore confinement and surface chemical interactions rather than on either factor alone. In particular, activation strategies such as KOH treatment can simultaneously develop accessible micropores and topological defects while altering retention, exposure, and accessibility of heteroatom-containing sites^[137]. The resulting non-hexagonal carbon rings and exposed edge sites can redistribute local electron density and provide additional weak Lewis-basic sites for CO₂ adsorption. Therefore, activation conditions affect not only pore architecture but also the electronic and chemical environment surrounding the adsorption sites.

Nandi *et al.*^[138] demonstrated this synergistic behavior using rice husk-derived biochar. By adjusting the KOH-to-biomass ratio, they synthesized PAC 2 with a moderate specific surface area of $755 \text{ m}^2\cdot\text{g}^{-1}$ and a well-developed micropore volume of $0.243 \text{ cm}^3\cdot\text{g}^{-1}$. Importantly, the optimized adsorbent retained approximately 2.27% of intrinsic nitrogen present in the biomass precursor, which effectively enhanced the isosteric heat of adsorption without additional heteroatom doping. The combination of micropore-driven CO_2 confinement and nitrogen-derived adsorption affinity enabled high CO_2 uptake and CO_2/N_2 selectivity at flue-gas-relevant temperatures.

This example illustrates that the simultaneous engineering of pore architecture and heteroatom functionalities is a central design principle for high-performance CO_2 capture. Accessible ultramicropores increase local CO_2 concentration, whereas N-, O-, S-containing sites enhance adsorption affinity and selectivity through basic or polar interactions. Nevertheless, these properties should be balanced because excessive activation may widen micropores or remove surface functionalities, whereas excessive heteroatom incorporation may block pores and restrict CO_2 transport. Rational biochar design should therefore optimize accessible microporosity and CO_2 -philic surface sites simultaneously rather than treating them as independent targets.

Overall, the available studies support several common design principles. Accessible micropores in the range of approximately 0.3–0.8 nm, particularly ultramicropores below 0.5 nm, are generally most strongly associated with low-pressure CO_2 uptake, whereas larger pores primarily facilitate mass transport. Appropriately distributed heteroatom sites enhance adsorption affinity and selectivity; however, no universal optimum doping ratio has been established because their effects depend more strongly on chemical state, spatial distribution, and accessibility than on total heteroatom content. Alkaline-earth-metal loading generally exhibits a non-monotonic relationship with adsorption performance, as moderate loading increases the density of basic sites, whereas excessive loading promotes particle agglomeration and pore blockage. Nevertheless, transferable quantitative relationships among these descriptors remain unresolved because pore structure, heteroatom speciation, and metal loading are commonly altered simultaneously. Their effects are further complicated by differences in adsorption temperature, pressure, gas composition, and measurement protocol. Future studies should therefore independently control these parameters and employ standardized equilibrium, breakthrough, humidity-dependent and cyclic adsorption measurements to establish reliable structure-performance correlations.

BIOCHAR FOR CO_2 CHEMICAL UTILIZATION

In addition to its role in CO_2 capture, biochar has increasingly been recognized as a multifunctional platform for carbon utilization, wherein captured CO_2 is converted into value-added chemicals and fuels. Benefiting from its tunable pore architecture, modifiable surface chemistry, and defect-rich carbon framework, biochar can function not only as a passive adsorbent but also as a catalyst support or, in some cases, an active catalytic medium. In most biochar-based CO_2 utilization systems, however, the primary catalytic centers are supported metals, metal oxides, molecular complexes, or atomically dispersed metal sites, while biochar primarily serves as a versatile support. Its key roles include enhancing CO_2 adsorption, stabilizing and dispersing active species, facilitating charge and mass transport, and modulating the local electronic environment through surface functionalities and metal-support interactions.

Compared with conventional carbon materials such as activated carbon, carbon nanotubes, and graphene, biochar offers notable advantages in terms of low cost, renewable feedstocks, and structural tunability^[106,139]. Activation and functionalization can further tailor its pore architecture, surface chemistry, and defect density, thereby improving active-site accessibility and promoting the uniform dispersion and stabilization of catalytic species. Nevertheless, biochar-based systems still face several challenges, including

feedstock-dependent variability, structural heterogeneity, and the need for additional post-treatment. Moreover, their catalytic performance is generally governed by the supported active species rather than the carbon framework itself. Therefore, the key competitive advantage of biochar-based systems lies not simply in providing higher intrinsic catalytic activity, but in combining competitive catalytic performance with sustainability, low material cost, and tunable physicochemical properties.

Depending on the energy input and reaction environment, CO₂ utilization pathways can be broadly classified into thermocatalytic, electrochemical, and photocatalytic processes. Although these approaches operate under distinct driving forces and reaction conditions, they share fundamental requirements, including efficient CO₂ adsorption, activation of the C=O bond, stabilization of reaction intermediates, and effective charge or heat transfer. The following sections provide a comprehensive overview of recent progress in biochar-based CO₂ conversion, covering thermocatalytic hydrogenation, electrochemical CO₂ reduction, and photocatalytic transformation processes.

Thermocatalytic CO₂ conversion

Thermocatalytic CO₂ conversion refers to the transformation of carbon dioxide into value-added chemicals and fuels through heat-driven catalytic reactions^[140]. Representative thermocatalytic pathways mainly involve CO₂ hydrogenation reactions, including the reverse water gas shift (RWGS) reaction for CO production, methanation to CH₄, and methanol (CH₃OH) synthesis^[141].

For instance, Pan *et al.*^[142] developed a Cu-Mo₂C cluster catalyst supported on nitrogen-doped biochar (NBC) derived from *Enteromorpha prolifera* (Cu-Mo₂C/EPBC) for the RWGS reaction. The algae-derived precursor enabled the formation of N-doped mesoporous carbon enriched with nitrogen functionalities, strengthening interactions with β-Mo₂C and promoting the generation of well-defined Cu-Mo₂C interfacial active sites. Compared with the activated carbon-supported counterpart (Cu-Mo₂C/AC), the EPBC-supported catalyst exhibited higher graphitization, larger surface area, and abundant pyridinic-N species capable of stabilizing Cu-Mo₂C clusters. Catalytic performance was evaluated using a fixed-bed reactor. The catalyst containing 20 wt% Mo₂C and 0.8 wt% Cu achieved optimal CO₂ conversion and CO selectivity. At 500 °C, Cu-Mo₂C/EPBC delivered a CO selectivity of 99.95% and nearly threefold higher CO₂ conversion than Cu-Mo₂C/AC. Control experiments confirmed that the enhanced performance originated from the synergistic effect between pyridinic-N anchoring and Cu-Mo₂C cluster interactions. The catalyst also maintained over 99% of its initial activity after 50 h, demonstrating excellent stability. In the case of CH₃OH synthesis, Xu *et al.*^[143] reported CuZn catalysts supported on coconut shell-derived mesoporous biochar (CuZn/MC). Reference catalysts were prepared via sequential impregnation, including Cu-Zn/MC, Zn-Cu/MC, and CuZn/SiO₂. The mesoporous carbon framework facilitated uniform dispersion of Cu-ZnO species and promoted the formation of low-valence Cu (Cu⁰/Cu⁺) sites essential for CH₃OH production. One-step incorporation of Cu and Zn strengthened metal-support interactions and increased the abundance of Cu⁺ species. As a result, CuZn/MC exhibited significantly higher CO₂ conversion and space-time yield (STY) than CuZn/SiO₂, while maintaining comparable CH₃OH selectivity [Figure 7A]. Notably, CuZn/MC reached a CH₃OH STY of 121.25 g_{MeOH}·kg_{cat}⁻¹·h⁻¹ at 260 °C, nearly three times that of CuZn/SiO₂, with stable performance over 50 h [Figure 7B and C]. Similarly, Vali *et al.*^[144] demonstrated that biochar derived from renewable waste can function as an effective support for Cu/ZnO nanoparticles in CO₂ hydrogenation to CH₃OH. The resulting catalyst delivered a CH₃OH STY of 496.5 mg_{MeOH}·g_{Cu}⁻¹·h⁻¹ with 71% selectivity and maintained stable operation for more than 45 h. Under identical reaction conditions, its performance markedly surpassed that of conventional Cu/ZnO/Al₂O₃, which exhibited lower productivity and more rapid deactivation. Structural characterization revealed that the enhanced activity and durability originated from enriched Cu-Zn interfacial sites, enabled by the uniform dispersion of ultrasmall nanoparticles and improved H₂ and CO₂ adsorption on the biochar support.

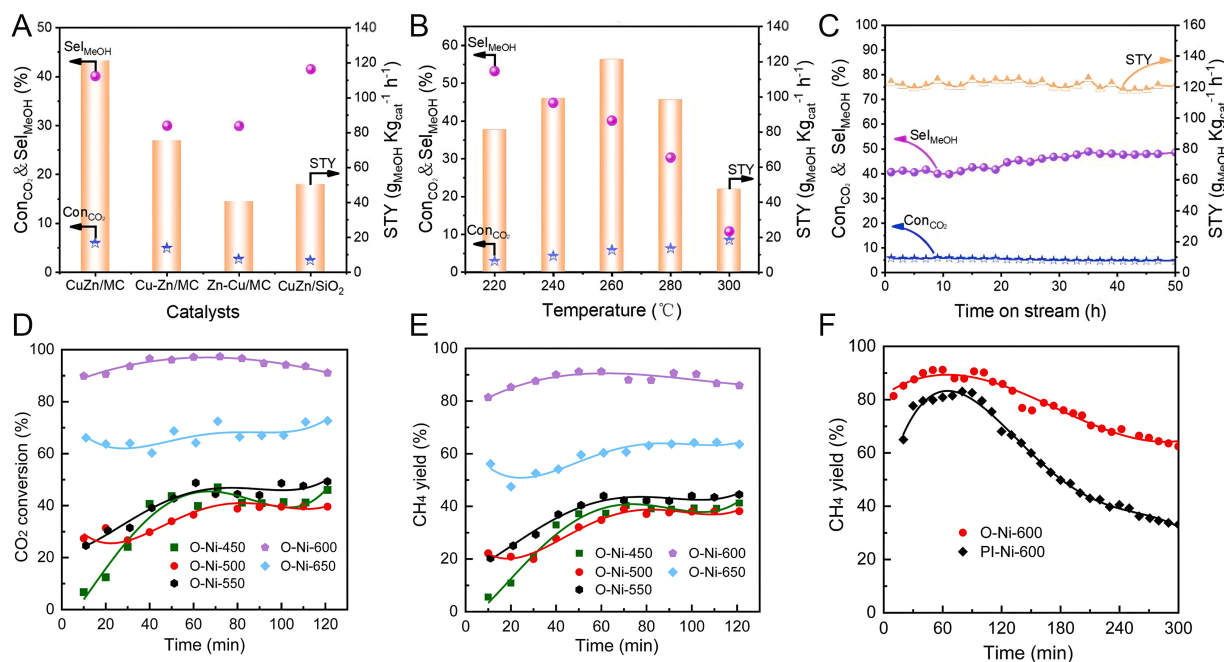


Figure 7. Performance of CO₂ hydrogenation to methanol over (A) series of Cu-Zn catalysts and (B) varying reaction temperatures. (C) Durability evaluation of the CuZn/MC catalyst. (A-C) Reprinted with permission^[143]. Copyright 2025, Elsevier. Influence of pyrolysis temperature on catalytic performance in CO₂ methanation at 400 °C: (D) CO₂ conversion, (E) CH₄ yield. (F) CH₄ yield in CO₂ methanation at 400 °C as a function of preparation method. (D-F) Reprinted with permission^[147]. Copyright 2026, Elsevier.

Beyond CH₃OH synthesis, CO₂ methanation to CH₄ has received considerable attention as an attractive pathway for synthetic natural gas production. Villardon *et al.*^[145] investigated olive stone-derived biochar as a sustainable support for Ni-based methanation catalysts. To tailor the structural and surface characteristics of the support, chemical activation was performed using KOH, ZnCl₂, or H₃PO₄. Among the resulting materials, the KOH-activated biochar exhibited the highest surface area, superior Ni dispersion, and a greater density of moderately strong basic sites favorable for CO₂ activation. Consequently, this catalyst achieved 72% CO₂ conversion with 95.5% CH₄ selectivity, outperforming the other activated counterparts. In contrast, H₃PO₄ activation led to partial encapsulation of Ni species, while ZnCl treatment promoted Ni-Zn alloy formation, both of which negatively affected methanation performance.

Furthermore, Wang *et al.*^[146] developed NBC from *Pinus sylvestris* through an *in-situ* pyrolysis process employing urea as a nitrogen precursor and NaHCO₃ as an activating agent. By adjusting the pyrolysis temperature, the distribution of nitrogen functionalities and surface basicity were systematically tuned. The catalytic performance showed a strong dependence on the proportion of pyridinic-N species. Notably, the Ru/N-ABC-600 catalyst, containing the highest pyridinic-N content (37.7%), delivered 93.8% CO₂ conversion and 99.7% CH₄ selectivity at 380 °C. The superior activity was attributed to enhanced electron density and surface basicity introduced by nitrogen incorporation, which facilitated RuO formation for H₂ dissociation and strengthened CO₂ adsorption, thereby promoting CH₄ formation. Recently, Yang *et al.*^[147] reported the fabrication of Ni catalysts supported on biochar via a one-pot strategy employing metal-impregnated pine sawdust. First, the effect of pyrolysis temperature on CO₂ methanation activity was systematically examined at 400 °C. Notably, among the prepared samples, the catalyst carbonized at 600 °C (denoted as O-Ni-600) exhibited the best performance, achieving CO₂ conversions of 90%-98% and CH₄ yields of 90%-95%, as shown in Figure 7D and E. Moreover, the effect of the preparation method on CH₄ yield was investigated by comparing the performance of O-Ni-600, prepared via a one-pot method, with that of a catalyst prepared by post-impregnation (PI-Ni-600). As a result, O-Ni-600 showed superior activity and stability compared to

PI-Ni-600. Under optimized reaction conditions, O-Ni-600 maintained outstanding catalytic performance over a 600 min methanation test, delivering CH₄ selectivity exceeding 91% [Figure 7F]. The superior activity of O-Ni-600 is attributed to the generation of finely dispersed Ni⁰ and NiO nanoparticles embedded within a porous carbon matrix during the one-pot process. The small particle size and intimate metal-support interaction promote efficient H₂ dissociation, while the high surface area and well-developed pore structure enhance CO₂ adsorption and activation.

Electrocatalytic CO₂ conversion

Electrochemical conversion of CO₂ has emerged as a promising strategy for decarbonizing chemical industries, particularly when driven by renewable electricity. The electrochemical CO₂ reduction reaction (CO₂RR) enables the generation of a wide range of value-added products, including CO, formate, CH₄, ethylene (C₂H₄), and ethanol (C₂H₅OH) [148–151]. By tailoring synthesis and activation processes, biochar with tunable porosity, surface functionalities, and defect density can be engineered, making it a versatile platform for electrocatalytic CO₂ reduction.

One effective strategy involves integrating biochar into gas diffusion electrode (GDE) architectures to improve mass transport and interfacial charge transfer. Tan *et al.* [152] reported biochar-modified GDEs based on coconut husk (CH)-derived biochar. In their configuration, a polytetrafluoroethylene membrane served as the gas diffusion layer, while Ag nanoparticles constituted the catalyst layer. An additional conductive biochar layer, obtained by pyrolyzing CH at 700–900 °C, was introduced to enhance electrical conductivity and facilitate interfacial charge transport [Figure 8A]. Among the prepared electrodes, Ag/CH-900 exhibited the highest conductivity and superior electrochemical performance. Although all electrodes reached current densities of 300 mA cm⁻², Ag/CH-900 required the least negative cathodic potential to achieve this value, indicating improved energy efficiency. Furthermore, it delivered CO faradaic efficiency (FE_{CO}) values of 94.4% at 50 mA cm⁻² and 86.5% at 100 mA·cm⁻², while maintaining stable operation for 8 h at 100 mA·cm⁻² [Figure 8B and C]. These results underscore the importance of conductive biochar layers in optimizing GDE configurations for high current density CO₂RR. Hu *et al.* [153] successfully developed a molecular electrocatalyst by anchoring nickel phthalocyanine (NiPc) onto N-doped ball-milled biochar (NiPc/N-BMBC). The ball-milling process reduced particle size and exposed the internal carbon framework, generating a more accessible and defect-rich surface. Subsequent nitrogen doping further increased defect density and introduced additional coordination sites for immobilizing NiPc molecules. The strong electronic coupling between NiPc and N-doped biochar support enabled uniform molecular dispersion, facilitated charge transfer, and accelerated reaction kinetics, thereby improving CO₂ reduction activity. Specifically, the NiPc/N-BMBC achieved a FE_{CO} of 86% at -0.80 V vs. reversible hydrogen electrode (RHE), and a CO partial current density (j_{CO}) of 96 mA·cm⁻² at -1.0 V vs. RHE, outperforming both pristine NiPc and the N-BMBC. Furthermore, it maintained stable catalytic performance over 24 h of continuous electrolysis, demonstrating excellent durability and catalytic robustness. Recently, Zhang *et al.* [154] synthesized N-doped biochar electrocatalysts derived from citrus peel, an abundant agricultural by-product rich in cellulose and oxygen-containing functional groups. The inherent porous structure and oxygen-rich composition of the precursor promoted *in situ* nitrogen incorporation and the formation of catalytically active sites during pyrolysis. FeCl₃ was introduced as a chemical activating agent to further enhance pore development and expose active sites, producing cost-effective N-doped biochar catalysts for CO₂ electroreduction. The optimized catalyst achieved an FE_{CO} of 89.8% at -0.62 V vs. RHE in an H-type cell [Figure 8D]. When implemented in a membrane electrode assembly (MEA) and operated at applied voltages between -2.5 and -3.25 V, it delivered a current density of -174 mA·cm⁻² with an FE_{CO} of 90.79% [Figure 8E and F]. These results highlight the strong potential of biomass-derived N-doped biochar for scalable and high-performance CO₂ electroreduction.

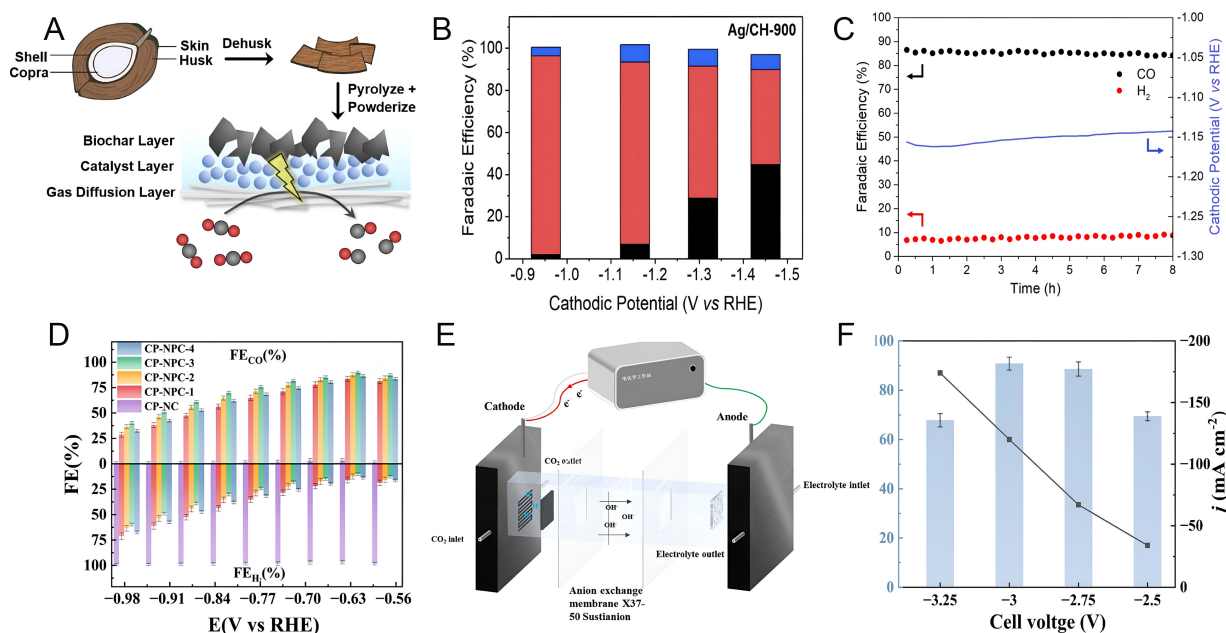


Figure 8. (A) Conceptual schematic of GDE using coconut husks-derived biochar. (B) FE_{CO} as a function of cathodic potential for Ag/CH-900. (C) Long-term stability test of Ag/CH-900. (A–C) Reprinted with permission^[152]. Copyright 2023, Elsevier. (D) FE_{CO} and FE_{H₂} for all prepared samples. (E) Schematic illustration of MEA cell. (F) FE_{CO} and corresponding current density of CP-NPC-3. (D–F) Reprinted with permission^[154]. Copyright 2025, Elsevier.

Additionally, porosity engineering has been demonstrated to play a crucial role in modulating catalytic performance. Zhang *et al.*^[155] reported the fabrication of biochar-derived Ni single-atom catalysts with precisely controlled pore architectures for efficient CO₂ electroreduction. By tailoring the activation process through different combinations of KHCO₃, KCl, and LiCl, microporous, mesoporous, and hierarchically porous carbon frameworks were constructed to anchor atomically dispersed Ni sites [Figure 9A]. In a typical synthesis, glossy privet biomass was first subjected to HTC, followed by high-temperature activation at 900 °C using distinct etching agents to generate porous biochar supports. Subsequent Ni ion adsorption and pyrolysis at 800 °C for 1 h yielded the corresponding Ni single-atom catalysts (hp-BioNC-Ni). Among the series, the hierarchically porous catalyst exhibited superior CO₂RR performance, achieving a maximum FE_{CO} of 97.4% at -1.2 V vs. RHE. Notably, it maintained FE_{CO} values above 85% over a broad potential window ranging from -0.7 to -1.7 V vs. RHE, significantly outperforming the counterparts [Figure 9B]. When compared with state-of-the-art carbon-based single-atom catalysts, this hierarchically porous system demonstrated one of the widest operational potential windows while retaining high CO selectivity [Figure 9C].

Moreover, Wang *et al.*^[156] synthesized biochar-supported Au nanoparticle (Au NP) composites using swine manure as a biomass precursor. Due to its intrinsic abundance of heteroatoms such as nitrogen and oxygen, swine manure provides a favorable source for producing functional carbon materials. Manure-derived biochar was first obtained via hydrothermal treatment, followed by KOH activation to construct a porous carbon framework. Pre-synthesized Au nanoparticles were then uniformly deposited onto the activated biochar through ultrasonic-assisted dispersion, yielding a series of composites with different Au loadings, designated as Au/BC-0.1, Au/BC-0.6, and Au/BC-1.2. The electrocatalytic performance was evaluated in 1 M KOH electrolyte. Among the prepared catalysts, Au/BC-1.2 exhibited the highest CO selectivity, achieving a FE_{CO} of 87.72% at -0.4 V vs. RHE, along with a *j*_{CO} of 41.3 mA·cm⁻². Notably, Au/BC-0.1 delivered a remarkable mass activity of 9,451 A·g·Au⁻¹, highlighting the possibility of reducing noble metal loading while maintaining high catalytic performance.

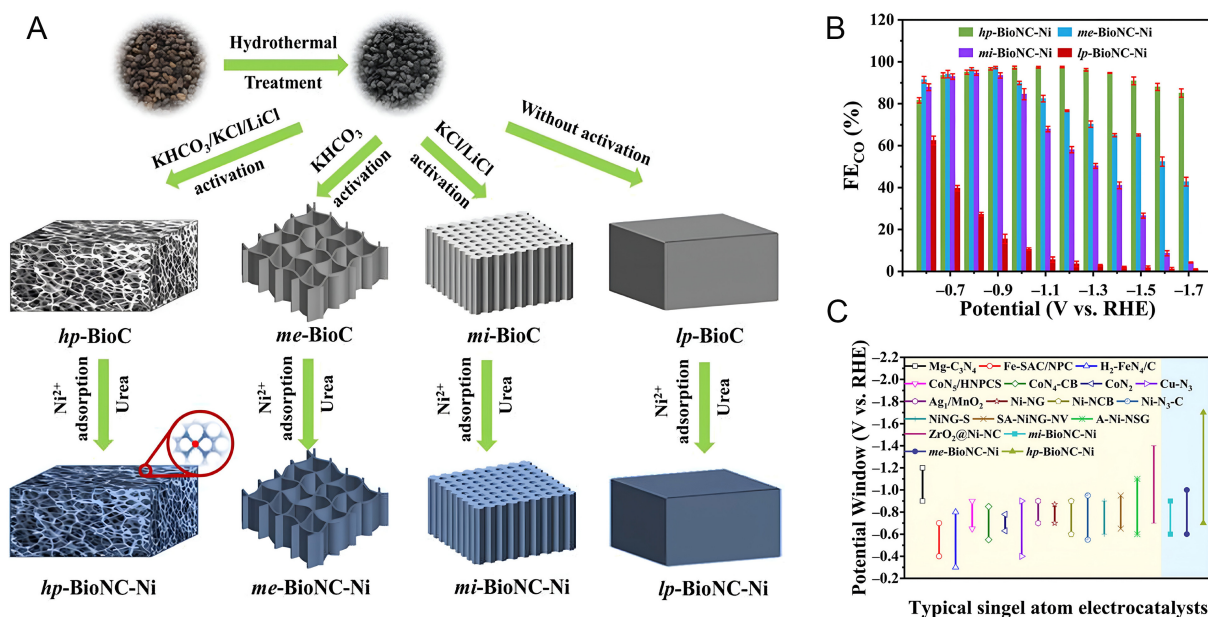


Figure 9. (A) Schematic representation of the preparation of biochar-derived single-atom Ni catalysts with tunable porosity. (B) FE_{CO} comparison of hp-BioNC-Ni, me-BioNC-Ni, mi-BioNC-Ni, and lp-BioNC-Ni. (C) Potential ranges of state-of-the-art carbon-based SACs. This figure quoted with permission^[155]. Copyright 2023, John Wiley and Sons.

Beyond selective CO production, biochar-based catalysts have been investigated for the generation of multicarbon (C_{2+}) products such as C_2H_4 and C_2H_5OH ^[157–161]. The tunable pore architecture and abundant surface functionalities of biochar can modulate intermediate adsorption and facilitate C-C coupling, a critical step in C_{2+} formation. For example, Yu *et al.*^[159] designed a Cu/CuO catalyst supported on phosphorus-enriched carbon obtained from *Ceratophyllum demersum* L. (denoted as Cu-CuO/P-CCDL) for the selective electrochemical reduction of CO_2 to C_2H_5OH . The biomass precursor inherently contains substantial amounts of carbon, oxygen, and phosphorus within its biological framework, enabling direct phosphorus incorporation into the carbon matrix during carbonization without the need for external dopants. Electrochemical measurements were conducted in an H-type cell using CO_2 -saturated 0.5 M NH_4Cl as the electrolyte. Under these conditions, the Cu-CuO/P-CCDL-600 catalyst achieved a C_2H_5OH selectivity of 38.9% at -1.5 V vs. RHE. Additionally, it exhibited a favorable faradaic efficiency distribution, with a higher proportion of C_{2+} products relative to competing C_1 species and hydrogen evolution. The enhanced CC coupling capability was attributed to the synergistic interaction between Cu/CuO active sites and the phosphorus-modified carbon framework.

Chen *et al.*^[160] employed locust leaves as a biomass precursor to fabricate high-performance Cu-based electrocatalysts for CO_2 reduction. The biomass-derived carbon was first activated with K_2CO_3 and pyrolyzed under an N_2 atmosphere to produce porous biochar. Subsequently, a series of $Cu_xO@C$ composites were prepared via a solvothermal method, in which the carbon content was systematically adjusted by varying the amount of introduced biochar. The electrocatalytic performance was evaluated in an H-type cell using 0.5 M $KHCO_3$ as the electrolyte. Among the series, $Cu_xO@C-2$, exhibited the highest $FE_{C_{2+}}$ of 41.3% at -1.08 V vs. RHE, approximately 1.7 times higher than that of the pristine Cu_xO catalyst. To further elucidate the interaction between the catalyst surface and reaction intermediates, single oxidative scans were conducted to probe OH^- adsorption behavior. $Cu_xO@C-2$ displayed the most negative OH^- adsorption potential (-0.71 V vs. RHE), followed by $Cu_xO@C-3$ (-0.66 V), $Cu_xO@C-1$ (-0.60 V), and pristine Cu_xO (-0.55 V). The more negative adsorption potential indicates stronger binding affinity toward OH^- species, suggesting more favorable intermediate stabilization in $Cu_xO@C-2$. Hu *et al.*^[161] developed Cu-based electrocatalysts for

selective C_{2+} production using pig manure-derived biochar as a carbon support prepared via a hydrothermal strategy. The optimized catalyst, denoted as Cu-NB-2000, achieved an $FE_{C_{2+}}$ of 47.35% with a $j_{C_{2+}}$ of $241.2 \text{ mA}\cdot\text{cm}^{-2}$ at -1.51 V vs. RHE. In addition to its high activity, the catalyst demonstrated good durability, maintaining stable current density and $FE_{C_{2+}}$ during 8 h of continuous electrolysis at -0.91 V vs. RHE.

Photocatalytic CO_2 conversion

Solar-driven CO_2 reduction into value-added fuels has attracted significant attention as a sustainable strategy to address energy shortages and climate change. Nevertheless, the practical efficiency and product selectivity of photocatalytic CO_2 conversion are often limited by the high thermodynamic barrier for C=O bond activation and the rapid recombination of photogenerated charge carriers. Therefore, the rational design of photocatalysts with optimized electronic structures and efficient charge-separation pathways is essential to improve CO_2 reduction performance. In this context, biochar has emerged as a promising component in photocatalytic systems. Owing to its intrinsic electrical conductivity and tunable surface chemistry, biochar can serve as an electron mediator or conductive scaffold in semiconductor-based composites, effectively suppressing charge recombination. This conductive network facilitates rapid electron transport, reduces interfacial charge-transfer resistance, and enhances overall photocatalytic activity.

For example, Lv *et al.*^[162] reported the hydrothermal synthesis of a CuS-loaded NBC composite derived from corncob powder. Electrostatic attraction between negatively charged NBC and positively charged CuS in aqueous solution enabled uniform immobilization of CuS nanoparticles on the biochar surface, forming well-defined heterointerfaces. Zeta potential measurements [Figure 10A] confirmed the opposite surface charges of the two components, supporting their spontaneous assembly. The resulting interfacial junctions generated localized electric fields that promoted directional charge transfer and improved the utilization of active sites. Consequently, the CuS/NBC composite achieved a CO production rate of $2.85 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ under 4 h of continuous illumination, significantly surpassing that of pristine CuS ($0.82 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) and NBC ($0.83 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) [Figure 10B]. Moreover, the optimized CuS/NBC sample exhibits significant performance stability during four cycles under light illumination, with a total test duration of 16 h [Figure 10C]. The enhanced performance was attributed to more efficient separation and migration of photogenerated charge carriers at the CuS/NBC interface, leading to improved CO_2 activation and reduction. Lin *et al.*^[163] developed amphiphilic CoO_x /biochar (CDB) photocatalysts using loofah sponge as a biomass-derived template for CO_2 photoreduction. The loofah precursor, characterized by its highly porous structure and strong ion-adsorption capability, was first impregnated with cobalt ions and subsequently calcined under an N_2 atmosphere to obtain CDB materials with different CoO_x loadings. Among the synthesized samples, the composite containing 3.0 wt% CoO_x (CDB-3) exhibited irregular micro-/nanostructures that imparted pronounced amphiphilic properties. Such surface characteristics enhanced CO_2 diffusion within the reaction medium and facilitated mass transport toward active sites. As a result, CDB-3 achieved a CO production rate of $48.3 \mu\text{mol}\cdot\text{h}^{-1}$ with a turnover frequency of 0.29 s^{-1} , highlighting the importance of amphiphilic surface design in improving photocatalytic CO_2 conversion. Furthermore, Yu *et al.*^[164] constructed a facile biochar-assisted S-scheme CeO_2 -based heterojunction photocatalyst, denoted as CN-BIO/ CeO_2 . In this system, strong interfacial coupling between CeO_2 and $g-C_3N_4$ generated an internal electric field characteristic of the S-scheme architecture, while conductive biochar served as an efficient electron-transport pathway. As a result, photogenerated electrons were rapidly extracted through the biochar framework rather than accumulating on the semiconductor surface, effectively suppressing charge recombination and enhancing redox capability during CO_2 photoreduction. The photocatalytic performance was evaluated under full-spectrum simulated solar irradiation in a gas-solid reaction system. Pristine $g-C_3N_4$ and CeO_2 exhibited low CO production rates of 5.98 and $5.21 \mu\text{mol}\cdot\text{g}^{-1}$, respectively. In comparison, the CN/ CeO_2 produced $22.2 \mu\text{mol}\cdot\text{g}^{-1}$ of CO, whereas CN-BIO/ CeO_2 achieved a significantly higher yield of $69.1 \mu\text{mol}\cdot\text{g}^{-1}$ with a CO

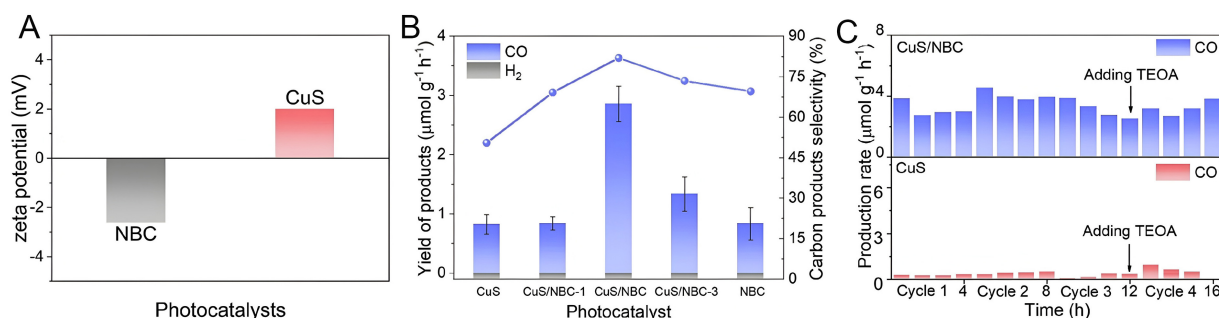


Figure 10. (A) Comparison of zeta potential between NBC and CuS. (B) Photocatalytic CO and H₂ production yields of the as-synthesized samples. (C) Catalyst recyclability of CuS/NBC compared with CuS. This figure quoted with permission^[162]. Copyright 2026, Elsevier.

selectivity of approximately 95%, the highest among the tested samples. Moreover, the catalyst maintained stable activity over four consecutive cycles, indicating good durability.

Yang *et al.*^[165] prepared a cherry blossom-derived biochar-modified Co-Al layered double hydroxide photocatalyst (Co-Al LDH-C) via an ultrasonic-assisted solvent treatment. Compared with pristine Co-Al LDH, the biochar-integrated composite demonstrated markedly enhanced CO₂ reduction performance. Under optimized conditions, Co-Al LDH-C achieved a CO production rate of 29.2 μmol·g⁻¹ approximately 15 times higher than that of the unmodified Co-Al LDH (2.1 μmol·g⁻¹). The enhanced activity was attributed to improved light absorption, accelerated charge separation, and reduced carrier transport resistance induced by biochar incorporation, which collectively increased the density of accessible active sites. Furthermore, only a slight decrease in CO evolution was observed after 30 h of continuous operation, confirming satisfactory long-term stability. Structural and spectroscopic analyses indicated that the synergistic interaction between biochar and Co-Al LDH was critical for promoting photocatalytic CO₂ conversion. Zhang *et al.*^[166] synthesized NiO nanoparticle-decorated activated pinecone-derived biochar (NiO/APC) composites via a two-step strategy. Pinecones were first carbonized and chemically activated with KOH to construct a tubular porous carbon framework, where gaseous species generated during activation created abundant pore structures. The surface functional groups formed during this process promoted the adsorption of Ni²⁺ ions, which were subsequently converted into NiO nanoparticles through heat treatment at 300 °C under oxygen-deficient conditions. Photoluminescence (PL) spectra revealed that the NiO/APC composites exhibited markedly lower emission intensities than pristine NiO, with NiO/APC-3 showing the weakest signal. The suppressed PL intensity indicates reduced charge recombination and improved separation of photogenerated carriers, attributed to efficient electron transfer across the conductive APC support. Consequently, NiO/APC-3 demonstrated markedly enhanced photocatalytic activity, achieving CH₄ and CO production yields of 81.06 and 15.00 μmol·g⁻¹, respectively, which are 66.4 and 1.9 times higher than those of pristine NiO, and 2.0 and 1.2 times higher than those of NiO/PC.

Table 3 highlights that product selectivity differs markedly among thermocatalytic, electrocatalytic, and photocatalytic CO₂ conversion pathways. While pore architecture influences local CO₂ enrichment, reactant transport, and active-site accessibility, product selectivity is ultimately governed by the interplay between the supported active centers and their interactions with key reaction intermediates. Therefore, rational engineering of biochar porosity and surface chemistry should be tailored to the specific reaction pathway rather than relying on a single structural parameter.

CONCLUSION AND FUTURE PROSPECTS

In summary, this review has systematically highlighted the immense potential of rationally designed biochar as a sustainable, cost-effective, and highly efficient platform for both CO₂ capture and subsequent catalytic

Table 3. Summary of biochar-based catalysts for CO₂ chemical utilization

	Catalysts	Main product	Selectivity	Ref.
Thermocatalytic	Cu-Mo ₂ C/EPBC	CO	99.95%	[142]
	CuZn/MC	CH ₃ OH	STY of 121.25 g _{MeOH} ·Kg _{cat} ⁻¹ ·h ⁻¹	[143]
	Cu/ZnO@BC		STY of 496.5 mg _{MeOH} ·g _{Cu} ⁻¹ ·h ⁻¹	[144]
	10Ni-KOH		95.4%	[145]
	Ru/N-ABC-600	CH ₄	99.7%	[146]
	O-Ni-600		90%-95%	[147]
	Ag/CH-900		94.4% @ 50 mA cm ⁻² and 86.5% @100 mA cm ⁻² (Flow cell)	[152]
	NiPc/N-BMBC		86% @ -0.80 V _{RHE} (H-cell)	[153]
Electrocatalytic	CP-NPC-3	CO	89.8% @ -0.62 V _{RHE} (H-cell)/90.79% (MEA)	[154]
	hp-BioNC-Ni		97.4% @ -1.2 V _{RHE} (H-cell)	[155]
	Au/BC-1.2		87.72% @ -0.4 V _{RHE} (Flow cell)	[156]
	Cu-CuO/P-CCDL	C ₂ H ₅ OH	38.9% @ -1.5 V _{RHE} (H-cell)	[159]
	Cu ₂ O@C-2	C ₂₊	41.3% @ -1.08 V _{RHE} (H-cell)	[160]
	Cu-NB-2000		47.35% @ -1.51 V _{RHE} (Flow cell)	[161]
	CuS/NBC		12 μmol·g ⁻¹	[162]
	CDB-3	CO	48.3 μmol·h ⁻¹	[163]
Photocatalytic	CN-BIO/CeO ₂		69.1 μmol·g ⁻¹	[164]
	Co-Al LDH		29.2 μmol·g ⁻¹	[165]
	NiO/APC	CH ₄	81.06 μmol·g ⁻¹	[166]

conversion. Driven by the urgent need to mitigate anthropogenic greenhouse gas emissions, biochar has transcended its traditional role as a passive carbon storage medium. Through the judicious selection of biomass precursors and advanced synthesis strategies such as tailored pyrolysis, hydrothermal method, and targeted activation, the physicochemical properties of biochar can be precisely engineered. We have discussed how hierarchical pore architectures govern physical adsorption, while the introduction of non-metallic heteroatoms via chemical modification substantially enhances surface basicity, thereby boosting chemisorption. Furthermore, this review comprehensively covered the catalytic utilization of biochar-based materials. By serving as an intrinsic catalyst or as a robust support for metal nanoparticles and single atoms, biochar significantly improves the efficiency, selectivity, and stability of CO₂ conversion across thermocatalytic, electrocatalytic, and photocatalytic pathways.

Despite these promising advancements, several critical challenges must be addressed to overcome the disparity between laboratory-scale research and industrial-scale deployment. First, the inherent heterogeneity of biomass sources often leads to batch-to-batch variations, complicating the reproducibility of biochar properties. Second, the fundamental understanding of the structure-property-performance relationships remains insufficiently explored, especially concerning the dynamic interactions between CO₂ molecules, reaction intermediates, and the active sites on the biochar surface during complex reaction conditions. Finally, the long-term stability and resistance to poisoning by impurities typically present in real-world flue gases such as moisture, SO_x and NO_x demand more rigorous evaluation.

To overcome these hurdles and advance the field, several future research directions are highly recommended. Foremost, the integration of advanced *in-situ* and operando characterization techniques combined with theoretical calculations is imperative. These tools will elucidate the dynamic evolution of active sites, clarify the exact mechanisms of CO₂ activation, and identify intermediate species in real time, thereby guiding the

molecular-level design of both superior biochar adsorbents and catalysts. Concurrently, to resolve the critical issues of competitive adsorption and the poisoning of both biochar-based adsorbents and catalysts, future studies should prioritize the advanced surface engineering of biochar. Strategies such as tuning surface hydrophobicity or introducing highly CO₂-selective functional groups are essential to repel moisture and resist SO_x and NO_x degradation. Additionally, rigorous long-term cyclic testing under simulated or actual industrial flue gas conditions rather than pure CO₂ streams should be established as a standard protocol to validate the commercial viability of these materials.

Moreover, the traditional trial-and-error approach to biochar synthesis is highly resource-intensive and time-consuming. Therefore, the implementation of machine learning (ML) and artificial intelligence algorithms is emerging as a critical necessity for future breakthroughs. ML models can efficiently manage and analyze vast datasets derived from diverse experimental studies, establishing complex correlations among biomass precursors, pyrolysis parameters, activation methods, and the resulting catalytic or adsorptive performance. By predicting the optimal synthesis conditions required to achieve specific pore structures or target heteroatom configurations, ML-guided materials design will drastically accelerate the discovery and optimization of high-performance biochar architecture.

Ultimately, the future of CO₂ mitigation technologies lies in the development of ICCU systems. Conventional CCU processes operate in tandem, requiring highly energy-intensive desorption, compression, and transportation steps between the capture and conversion stages. In this context, biochar can act as a uniquely promising platform for ICCU as a dual functional material. Thanks to its highly tunable nature, biochar can be engineered to possess both robust CO₂ adsorption sites and highly active catalytic centers. In an ICCU framework, the rationally designed biochar can directly capture CO₂ from dilute emission sources and immediately convert the trapped CO₂ into value-added chemicals upon switching to the requisite catalytic reaction conditions. This integrated approach can decrease the thermodynamic penalty of intermediate CO₂ desorption, significantly reducing the overall energy footprint and operational costs.

In conclusion, leveraging rationally designed biochar for CO₂ capture and conversion represents a highly promising, circular economy approach to global carbon management. By embracing predictive modeling through ML and advancing toward integrated ICCU technologies, the transition of biochar-based systems from laboratory-scale research to practical climate solutions can be successfully realized.

DECLARATIONS

Authors' contributions

Proposed the topic of this review: Kim, S. Y.

Prepared the manuscript: Ma, J.; Kim, J. H.

Data curation: Abdi-Jalebi, M.

Availability of data and materials

Not applicable.

AI and AI-assisted tools statement

During the preparation of this manuscript, the AI tool ChatGPT (OpenAI) (version GPT-5.6, released 2026 07-09) was used solely for language editing. The tool did not influence the study design, data collection, analysis, interpretation, or the scientific content of the work. The AI tool Nano Banana 2 (version Gemini 3.1 Flash Image, released 2026 02-26) was used only for the partial creation of the Graphical Abstract. Specifically, it was used to generate three graphical elements: (i) the porous biochar structure illustrating CO₂ adsorption, (ii) the biochar-supported catalytic structure, and (iii) the biochar powder illustration. The AI tools did not influence the study design, data collection, analysis, interpretation, or scientific content of the

work. All authors take full responsibility for the accuracy, integrity, and final content of the manuscript and Graphical Abstract.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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