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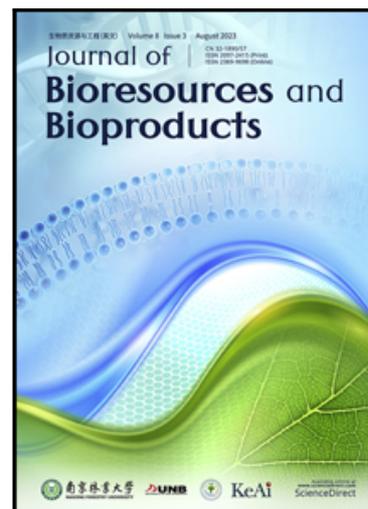
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Emerging Engineered Biochar for Environmental and Energy Applications

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1. Introduction

The continuous increase in the consumption of conventional fossil fuels has raised severe concerns towards global energy security and environmental sustainability. Thus, developing alternative resources of energy is extremely urgent. Biomass, as an abundant and renewable resource on Earth, currently contributes approximately 10% of the global primary energy supply (Popp et al., 2021). Recently, the upcycling of biomass, with thermochemical processes and/or biological conversions, into advanced carbon materials has emerged as a promising alternative (Fig. 1). Owing to its cost-effectiveness, low energy requirements and mild operational conditions, anaerobic digestion (AD) is a promising technology. However, its broader application is constrained by the need for extended residence times and high-quality feedstock (Shen and Chen, 2023). In contrast, thermochemical conversion technologies, including pyrolysis, hydrothermal carbonisation (HTC), and gasification, utilise diverse feedstocks such as lignocellulosic waste, municipal waste, sludge, and algal biomass, to produce biochar and value-added products, offering advantages in terms of operational simplicity, high yield, and cost-effectiveness (Kumar et al., 2021). For instance, pyrolysis, a typical thermochemical process conducted in oxygen-limited or oxygen-absent conditions at temperatures

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between 300 and 600 °C, represents a promising approach for converting biomass waste into biochar materials, thereby contributing to the development of a low-carbon, circular economy and advancing efforts towards carbon peak and carbon neutralisation (Zhang et al., 2023). Herein, temperature plays a critical role, as the release of volatile compounds into the gaseous phase intensifies with increasing thermal conditions (heating rate and residence time). Subsequently, gas-phase reactions such as cracking and polymerisation take place, resulting in the formation of the final products: biochar, bio-oil, and pyrolytic gases. A portion of the volatiles present in the gaseous phase may condense into the liquid phase, forming bio-oil. Besides, the pyrolytic gases also consist of non-condensable species, including CO, CO₂, CH₄ and H₂ (Wang et al., 2024). The HTC, often referred to as wet torrefaction, presents an alternative to conventional pyrolysis, operating in a water-based medium under elevated pressures (2–10 MPa) and temperatures (180–250 °C). In this process, water serves as a critical reaction medium, facilitating key reactions such as hydrolysis, dehydration, decarboxylation, polymerization, and coalification. The products of HTC include gases (primarily CO₂), an aqueous phase containing inorganic salts, sugars, and organic acids, and a solid hydrochar. The distribution of these products is influenced by various reaction parameters, including temperature, pressure, residence time, and the water-to-biomass ratio (Yu et al., 2024). Gasification is an advanced technique performed within a controlled oxidising environment, utilising oxygen, air, or steam at elevated temperatures exceeding 700 °C. This process yields syngas, a gaseous mixture primarily composed of hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), and methane (CH₄) (Erdem et al., 2024). It is important to note that the composition of syngas, biochar and other by-products may vary significantly based on several factors, including the choice of oxidising agent, particle size, residence time, reaction temperature, type of feedstock, and the ratio of oxidizing agent to feedstock. On account of its easy availability, inherent porous structure and stable property, biochar has contributed to a pivotal role in environmental remediation (e.g., soil amendment, water purification, CO₂ adsorption) (Obey et al., 2022; Ding et al., 2024; Mishra et al., 2024) and energy storage and conversion (e.g., supercapacitor, battery, H₂O splitting, CO₂ reduction) (Kim et al., 2019; Liu et al., 2024; Lv et al., 2024).

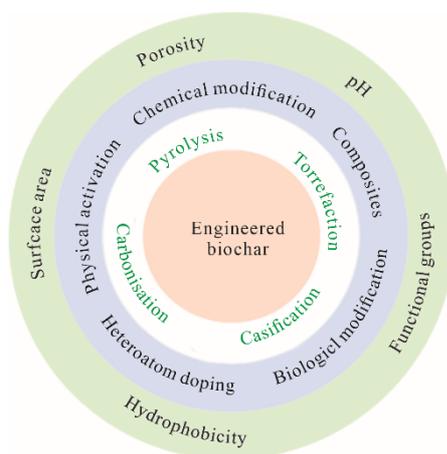


Fig. 1 An overview of synthesis and modification of biochar

2. Modification Strategies

In comparison to the performance of conventional carbon-based materials, for example carbon nanotubes and graphene, rational engineering of biochar is prerequisite for modulating its structural and morphological characteristics (Mohanty et al., 2024). Till now, a wide range of application-specific modification strategies have been meticulously developed (Tian et al., 2020). For instance, biochar materials with high specific surface area and controllable pore configuration are highly anticipated for applications in environmental remediation and electrochemical energy storage. To this end, various chemical (using familiar reagents of KOH, K_2CO_3 or $ZnCl_2$) and physical (using media of CO_2 or steam) activation techniques have been developed. The selected activation pathways and the use of various reagents can significantly influence the tuning of pore structures and biochar yield. Additionally, the inherent inertness of the pristine carbon framework is also challenging for its application in catalysis. To address this issue, heteroatom doping is commonly adopted to improve the intrinsic properties of biochar. By introducing non-metallic elements with distinct electronegativity (e.g., O, N, S, P and B) into the carbon matrix, the electron structures and interfacial features could be regulated, leading to the generation of sufficient active centres (e.g., C sites adjacent to these dopants), as well as boosting the electron transfer (Sun et al., 2013; Zhang et al., 2022). For instance, corncobs-derived biochar demonstrated a direct correlation between the quantity of nitrogen functionalities and its capacity for CO_2 adsorption (Li et al., 2023). Although some special categories of biomass feedstocks already contain desirable dopants, external precursors containing preferred elements are often supplemented during synthesis procedures. In addition to these modification strategies, integrating biochar with other functional materials, such as metallic compounds, could enhance its physicochemical properties. Herein, biochar not only serves as an ideal support for improving the dispersion of loaded materials but also contributes to the formation of crucial load-support interactions, synergistically improving the performance.

3. Challenges and Future Perspectives

Despite the attractive merits of biochar materials, several challenges still need to be addressed for reliable applications in future technologies. Biomass generally possesses complicated compositions and diverse structures, presenting significant challenges to the standardisation of well-established preparation and modification protocols. In other words, it is difficult to acquire specific biochar properties with different biomass feedstocks. Therefore, there is an urgent need to establish a well-classified database to thoroughly understand the correlations between biomass feedstock, the preparation processes employed, and the performance of the resulting biochar materials. Machine learning (ML), a subset of artificial intelligence, offers a powerful approach for rapidly screening large datasets, providing accurate predictions of material properties and revealing fundamental correlations between material characteristics and their applications (Chinenye Divine et al., 2024). However, the need for open database with standardised format is limiting its application in the field of advanced materials.

Moreover, to meet ever-growing demands for biochar materials, development of reliable and environmentally friendly techniques and pathways are highly anticipated for large-scale biochar production. Nevertheless, most of the state-of-the-art biochar materials were produced at a lab scale with tedious procedures. Scaling up production while maintaining reproducible biochar properties is indispensable in practice. Besides, additional post-treatment processes are often required to enhance the performance of biochar materials, which, in turn, increases manufacturing costs. Therefore, future research should be prioritised achieving a balance between these aspects especially for the application-oriented biochar design. Overall, a comprehensive evaluation of economic feasibilities between total costs incurred in the preparation, usage and waste disposal, and potential economic benefit is highly recommended to guide the sustainable development for biochar application. Additionally, it is essential to consider the potential environmental risks posed by biochar materials, as this represents a crucial yet often overlooked factor in their implementation (Tan and Yu, 2024). For example, micro-sized biochar samples are inhalable, posing a risk to human health once improperly released into atmosphere. Besides, due to the ageing and potential self-degradation, engineered biochar (especially pre-treated with diverse chemicals or loaded with functional materials) would definitely lead to the secondary pollution into the environment. Consequently, an objective oriented assessment of long-term environment impacts of biochar materials is essential. Finally, apart from unremitting efforts from the research community, the successful industrial applications of biochar materials require continuous supports and collaborations from national governments, international organisations (e.g., International Biochar Initiative), biochar producers and final-end users. Through formulating and providing preferential policies, establishing widely accepted standards, updating the technology and equipment, and

offering first-hand feedback, a booming development and broad application of biochar materials would be anticipated in near future.

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Declaration of Competing Interest

The authors declare no competing financial interest.

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