

Optimizing biochar production: a review of recent progress in lignocellulosic biomass pyrolysis

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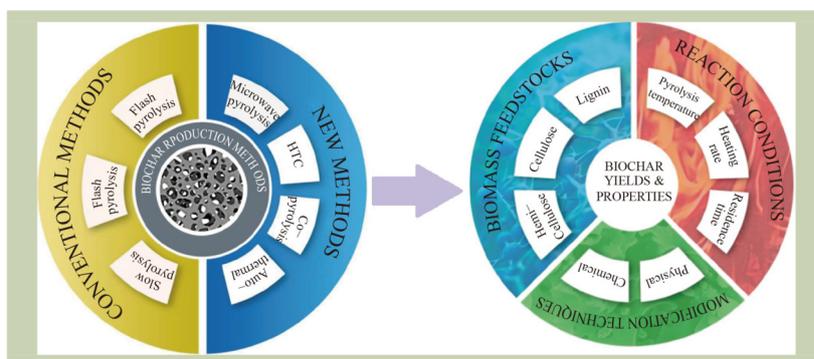
KEYWORDS

Biochar, lignocellulosic biomass, optimization, properties, pyrolysis, yield

HIGHLIGHTS

- The review provides an examination of recent advancements in optimizing biochar production from lignocellulosic biomass through pyrolysis, covering both conventional and new techniques.
- The study emphasizes the critical role of feedstock composition, pyrolysis conditions (temperature, heating rate, residence time), and modification methods in determining biochar yield and properties.
- Choosing renewable, readily available feedstocks is crucial for reducing dependence on finite resources and repurposing waste materials, thereby mitigating environmental impacts and enhancing sustainability.
- Key pyrolysis parameters, such as temperature and heating rate, must be carefully optimized to maximize biochar yield and quality while minimizing energy consumption and environmental footprint.
- Modification methods are essential for tailoring biochar properties to specific applications, overcoming limitations of pristine biochar, and improving its effectiveness, all while promoting resource efficiency and sustainability.

GRAPHICAL ABSTRACT



ABSTRACT

Biochar, a carbon-rich material produced by biomass pyrolysis, is valued for soil amendment, carbon sequestration and environmental remediation. Optimum biochar production depends on understanding key factors, including feedstock characteristics, pyrolysis conditions and modification methods. This review examines various pyrolysis techniques, ranging from well-established to new methods, assessing their mechanisms, strengths and limitations for large-scale production. It emphasizes the importance of feedstock selection, pyrolysis conditions and modification methods in affecting biochar yield and properties. By synthesizing current research findings, this review aims to provide insights into optimizing biochar production for sustainable utilization of lignocellulosic biomass resources.

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1 Introduction

Biochar is a stable, carbon-rich material produced from biomass through pyrolysis at 300–800 °C in an oxygen-limited environment^[1]. During this process, the biochar undergoes structural modifications where the original surface structure is reorganized. This can lead to the formation of larger cavities from smaller pores, resulting in a more accessible pore network predominantly composed of macropores^[2]. During pyrolysis, biomass decomposes in the absence of oxygen, releasing moisture and volatile compounds through dehydration, decarboxylation, evaporation and polymerization. Dehydration produces steam and hydrocarbons. Decarboxylation releases CO₂, yielding carbon-rich intermediates. Evaporation releases volatile organic compounds that can be used as syngas formation. Polymerization forms bio-oil. The solid residue left after pyrolysis is biochar^[3]. Generally, pyrolysis involves the release of moisture and volatile compounds from biomass through reactions, resulting in the production of syngas, bio-oil and biochar.

Biomass (feedstock) selection for pyrolysis depends on availability, composition and desired products. Lignocellulosic biomass is favored for its abundance and renewability, containing cellulose, hemicellulose and lignin components^[4]. Understanding the thermal degradation pathways of these components is crucial for biochar production. Hemicellulose, with simpler sugar units, decomposes at lower temperatures (220–315 °C), releasing volatile compounds^[5]. Cellulose degradation occurs at slightly higher temperatures (315–400 °C), while lignin, with its complex aromatic structure, decomposes at even higher temperatures (350–500 °C), contributing to biochar formation^[6]. The properties of biochar are closely tied to feedstock composition. Cellulose and hemicellulose-rich feedstocks produce biochar with lower fixed carbon and aromaticity but higher oxygen-containing functional groups, enhancing sorption and contaminant adsorption^[7–9]. Conversely, lignin-rich biomass, produces biochar with higher porosity, surface area, aromaticity, stability and fixed carbon content suitable for soil improvement and environmental remediation^[10,11].

Biochar production has progressed from laboratory, pilot to commercial scales. At the laboratory scale, research focuses on understanding fundamental processes and optimizing production parameters using small-scale reactors to evaluate the effects of various conditions on biochar properties^[1]. The pilot-scale bridges research with commercialization by expanding production to test economic feasibility and process efficiency, while addressing operational and environmental

challenges^[12]. At the commercial scale, biochar is produced industrially using large-scale reactors to meet market demands, with continuous operations and stringent adherence to quality and regulatory standards^[13]. Recent advancements in biomass pyrolysis include both well-established and new techniques. Established methods are classified into slow, fast and flash pyrolysis. Slow pyrolysis, with a low heating rate (< 20 °C·min⁻¹) and long retention time (> 1 h) at 300–700 °C, primarily produces biochar. Fast pyrolysis uses rapid heating (> 200 °C·min⁻¹) and short residence times (< 10 min) at 400–800 °C, focusing on bio-oil. Flash pyrolysis involves extremely rapid heating (> 1000 °C·s⁻¹) at 900–1300 °C, requiring smaller feedstock particles for efficient processing^[14].

New pyrolysis techniques enhance yield and quality by providing precise control over the process, addressing the limitations of established methods^[15]. Key approaches include microwave-assisted pyrolysis, co-pyrolysis, hydrothermal carbonization and autothermal pyrolysis, each offering unique benefits for optimizing the processing of various biomass feedstocks. In microwave-assisted pyrolysis, microwave energy is primarily absorbed by the water content within the biomass, leading to rapid and localized heating. This indirect heating of the biomass through its water content allows for more efficient and controlled pyrolysis compared to earlier methods^[16]. Unlike conventional heating, which heats from the surface inward, microwave-assisted pyrolysis directly converts electromagnetic energy into heat within the material, offering faster, more efficient heating and better control. This method improves reaction kinetics and product yields^[17]. For example, microwave heating of gumwood at 600–800 °C achieved 23% and 26% higher energy and exergy rates, respectively, and increased char yields by 46% compared to established methods^[18]. Hydrothermal carbonization (HTC) differs from pyrolysis by using water as the primary solvent and operating at lower temperatures. Unlike pyrolysis, which produces biochar, HTC forms hydrochar and has less flexibility in controlling reaction parameters due to its high-pressure, closed system^[19]. Another new technique, co-pyrolysis, involves the simultaneous thermal decomposition of multiple biomass feedstocks or biomass with other materials such as plastics or waste tires. By blending different feedstocks, co-pyrolysis can synergistically enhance product yields and properties while diversifying the range of potential applications for the resulting pyrolysis products. For example, Liu et al.^[20] found that co-pyrolysis of pinewood and polycarbonate at 900 °C in a fixed bed reactor increased H₂ by 33%, CO by 26% and total syngas yields by 19%, while improving overall energy efficiency from 42.9% to 48.6%. Autothermal pyrolysis, unlike current methods, use air for fluidization instead of nitrogen and generates thermal energy through the partial oxidation of

pyrolysis products. Polin et al.^[21] showed that autothermal pyrolysis with maize stover increased throughput from 7.8 to 21.9 kg·h⁻¹, though it reduced light biochar and bio-oil yields by 18.5% and 4.7%, respectively, while heavy bio-oil yields remained stable.

Although numerous reviews have addressed both established and new biochar production techniques, they frequently overlook a detailed analysis of their strengths and limitations for large-scale production. Additionally, these reviews often fail to discuss critical factors required to achieve optimal biochar yield and properties. This gap means that while theoretical aspects are well-covered, practical considerations and real-world challenges in scaling up production and optimizing biochar quality may not be fully addressed. This gap highlights the need for comprehensive research into all aspects of biochar production, including feedstock selection, pyrolysis conditions and modification methods. Addressing these factors will help researchers better understand and refine production strategies, improving efficiency and tailoring biochar for various applications.

2 Data collection and data processing

The Web of Science (Clarivate, Philadelphia, PA, USA) is a leading global citation database covering science, arts and humanities. For the period from 2014 to 2024, articles were

selected using the keyword “biochar production”. The search, spanning from January 2014 to August 2024, yielded 4671 relevant research papers and reviews after excluding non-research materials such as conference calls and book reviews. The data, exported as complete records with references, includes data for authors, affiliations, titles, sources, abstracts, keywords and references.

CiteSpace was used to analyze these 4671 papers, employing a one-year time slice and default settings to focus on keyword networks^[22]. The map (Fig. 1) shows keyword frequencies, with larger nodes indicating higher frequencies. The colors denote various keyword groups and larger circles represent stronger connections between keywords^[23]. “Biochar” emerges as the most frequently co-occurring keyword, underscoring its central role in the research. Other significant keywords include “bio-oil”, “microalgae” and “plastic waste”. The increase in publications on biochar pyrolysis since 2019, as shown in Fig. 1, highlights a marked rise in interest and advancements in the field, reflecting intensified research activity and ongoing improvements in biochar production processes.

3 Production of biochar

3.1 Lignocellulosic biomass feedstock

Biomass is a complex, biogenic organic-inorganic material from both natural and anthropogenic sources. It includes:

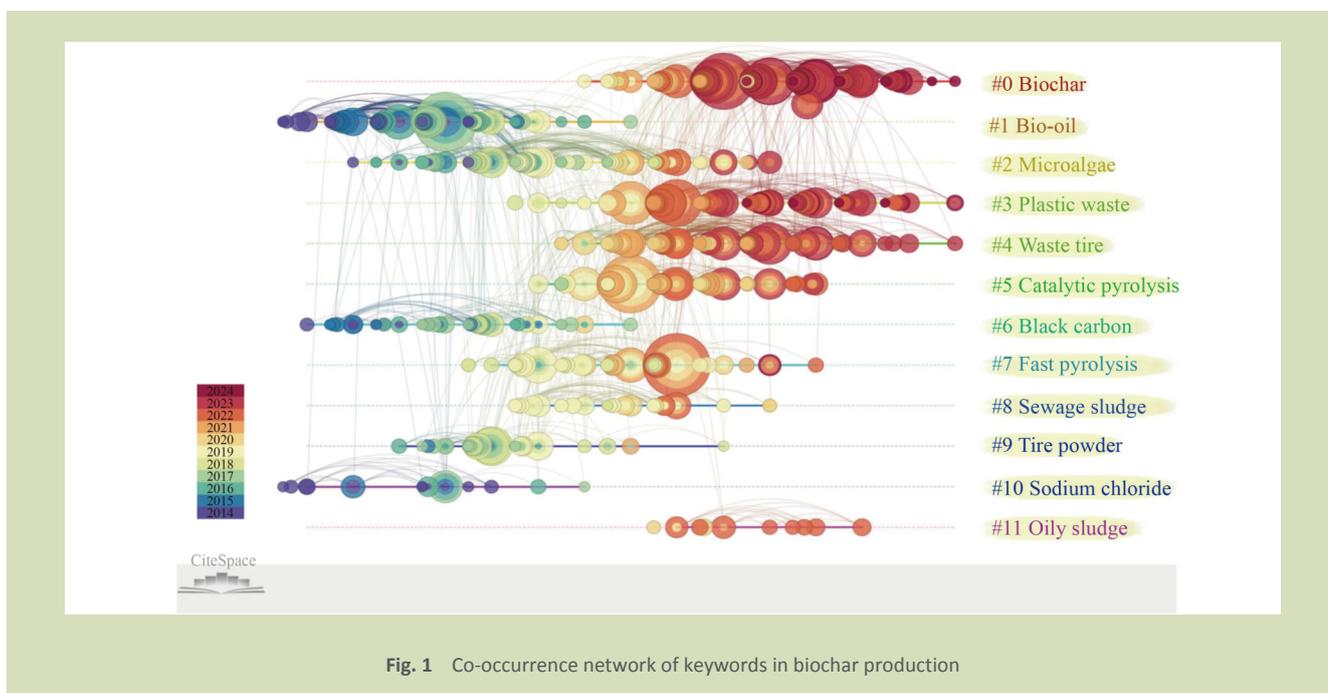


Fig. 1 Co-occurrence network of keywords in biochar production

(1) natural constituents from photosynthesis and food digestion, and (2) technogenic products from processing these natural materials. Biomass can be broadly classified based on biological diversity and source^[24] (Fig. 2).

Biomass can also be classified into two main types: (1) lignocellulosic biomass, which is widely used for biochar production, and (2) non-lignocellulosic biomass^[25,26]. Lignocellulosic biomass primarily composes cellulose, hemicellulose and lignin, as show in Fig. 3. Cellulose, hemicellulose and lignin are distributed in the cell wall as a skeleton, linking material and hard solids, respectively^[27]. Cellulose is a linear polysaccharide of d-glucose units joined by β -1,4-glycosidic bonds whereas hemicellulose is a group of

complex heteropolysaccharides comprised from various sugars (d-xylose, d-glucose, d-mannose, d-galactose, and l-arabinose) and sugar acids (d-glucuronic and d-galacturonic acids)^[28]. Lignin is an amorphous heteropolymer consisting of phenylpropane units (coniferyl alcohol, sinapyl alcohol and coumaryl alcohol) joined together by different types of linkages^[29]. Also, biomass usually contains a small amount of alkali and alkaline earth metals (i.e., K, Na, Ca and Mg) that can act as self-activators in pore formation of biochar during pyrolysis^[30].

The proportions of cellulose, hemicellulose, and lignin in lignocellulosic feedstocks can vary widely based on several factors such as plant species, tissue type, maturity and

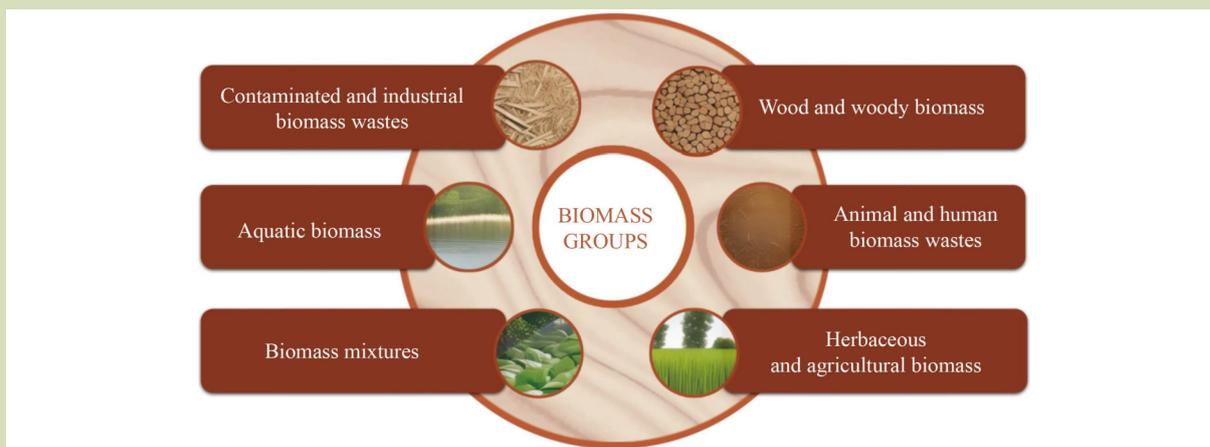


Fig. 2 General classification of biomass types based on biological diversity, source and origin.

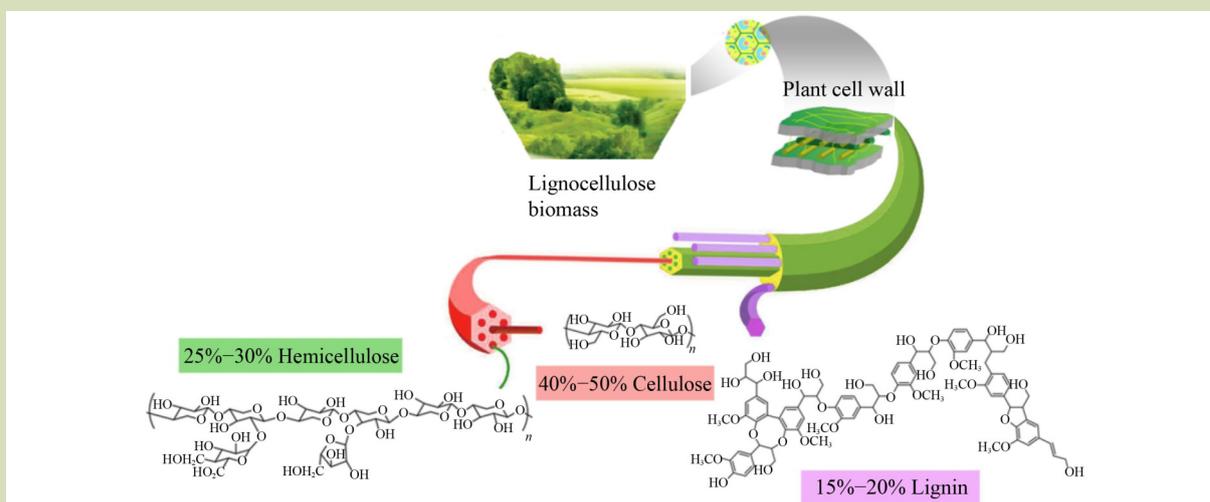


Fig. 3 The three components in lignocellulosic biomass.

environmental conditions^[31]. Figure 4 shows the proximate and ultimate compositions of various lignocellulosic feedstocks, which are critical for designing biochar production processes. Hardwoods generally have higher lignin content than softwoods, while grasses contain more hemicellulose. This difference in composition reflects the diverse structural characteristics of different plant species and their environmental adaptation^[4,32]. Also, agricultural residues such as wheat straw or maize cobs differ in composition from forestry residues such as wood chips or *Leucaena leucocephala* wood. Such differences in composition can arise from differences in plant anatomy, growth patterns and the specific conditions under which the biomass is produced and harvested^[4,32].

3.2 Pyrolysis mechanisms

The thermal degradation of lignocellulosic components (hemicellulose, cellulose and lignin) in biochar production varies due to differences in their composition and structure. Hemicellulose and cellulose, composed of simpler sugar units, exhibit susceptibility to thermal decomposition at relatively lower temperatures, typically ranging from 220 to 315 °C and 315 to 400 °C, respectively^[5]. Similar observations have been reported, indicating that hemicellulose has the lowest decomposition temperature and the widest decomposition range compared to cellulose and lignin^[35]. During pyrolysis, both components undergo depolymerization and degradation reactions, such as dehydration, decarboxylation and

fragmentation, resulting in the release of volatile compounds like water vapor, carbon dioxide, and organic acids^[36]. As a result, cellulose and hemicellulose are useful for generating volatile products.

In contrast, lignin, with its complex aromatic polymer structure, is the primary precursor for biochar formation during pyrolysis. It has superior thermal stability compared to cellulose and hemicellulose, typically decomposing at 350–500 °C^[6]. Given its cross-linked and aromatic nature, lignin does not fully decompose during pyrolysis. Instead, it partially decomposes and rearranges, forming carbonaceous residues that contribute to the solid fraction of biochar^[36]. For example, the biochar yield from woody biomass is about 19 wt% at 900 °C for 64 min^[37] whereas lignin can yield up to 45.7% biochar under similar conditions^[38].

Figure 5 illustrates the degradation pathways of lignocellulosic components and organic extractives during pyrolysis, highlighting the production of various products and byproducts. Each component of lignocellulosic biomass degrades at different temperatures, resulting in distinct outputs. In the 50–100 °C range, biomass undergoes nonreactive drying, removing moisture and reducing porosity while preserving chemical constituents. At 120–150 °C, lignin softens, forming cohesive structures essential for later decomposition. In the 150–200 °C range, known as the reactive drying range, significant thermal transformations occur. This phase marks the initiation of the breakdown of hydrogen and

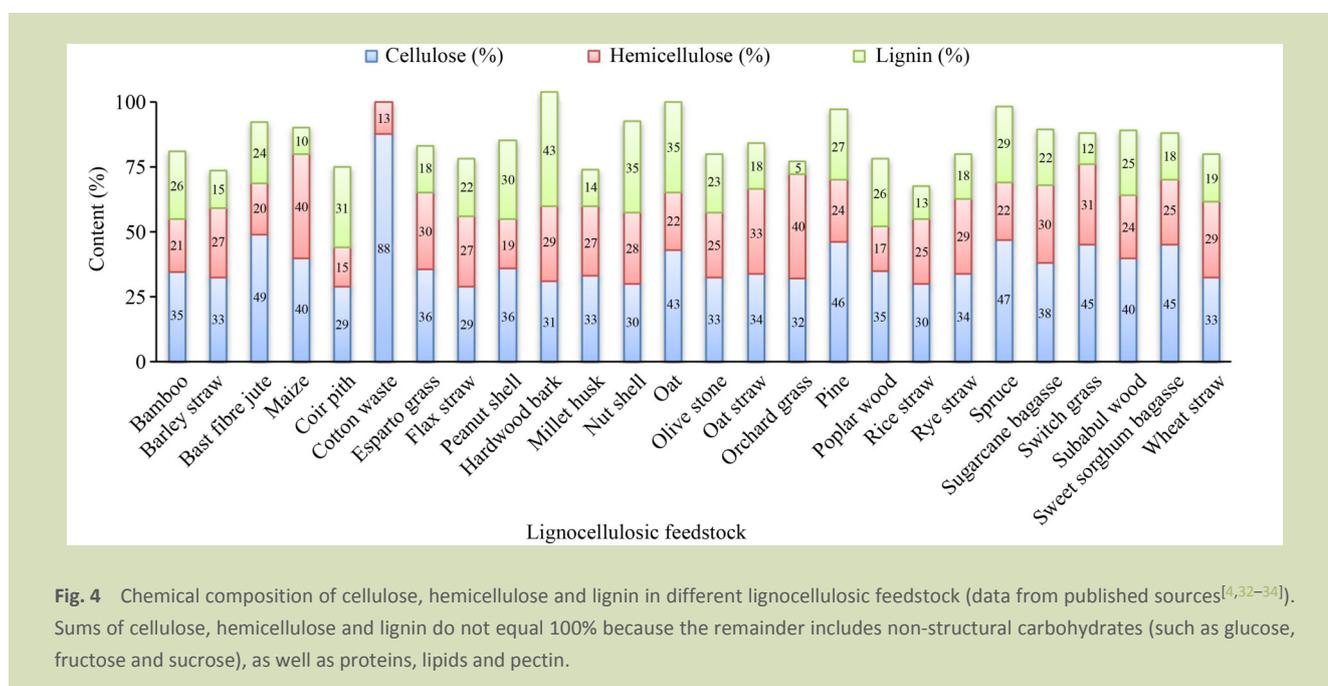


Fig. 4 Chemical composition of cellulose, hemicellulose and lignin in different lignocellulosic feedstock (data from published sources^[4,32–34]). Sums of cellulose, hemicellulose and lignin do not equal 100% because the remainder includes non-structural carbohydrates (such as glucose, fructose and sucrose), as well as proteins, lipids and pectin.

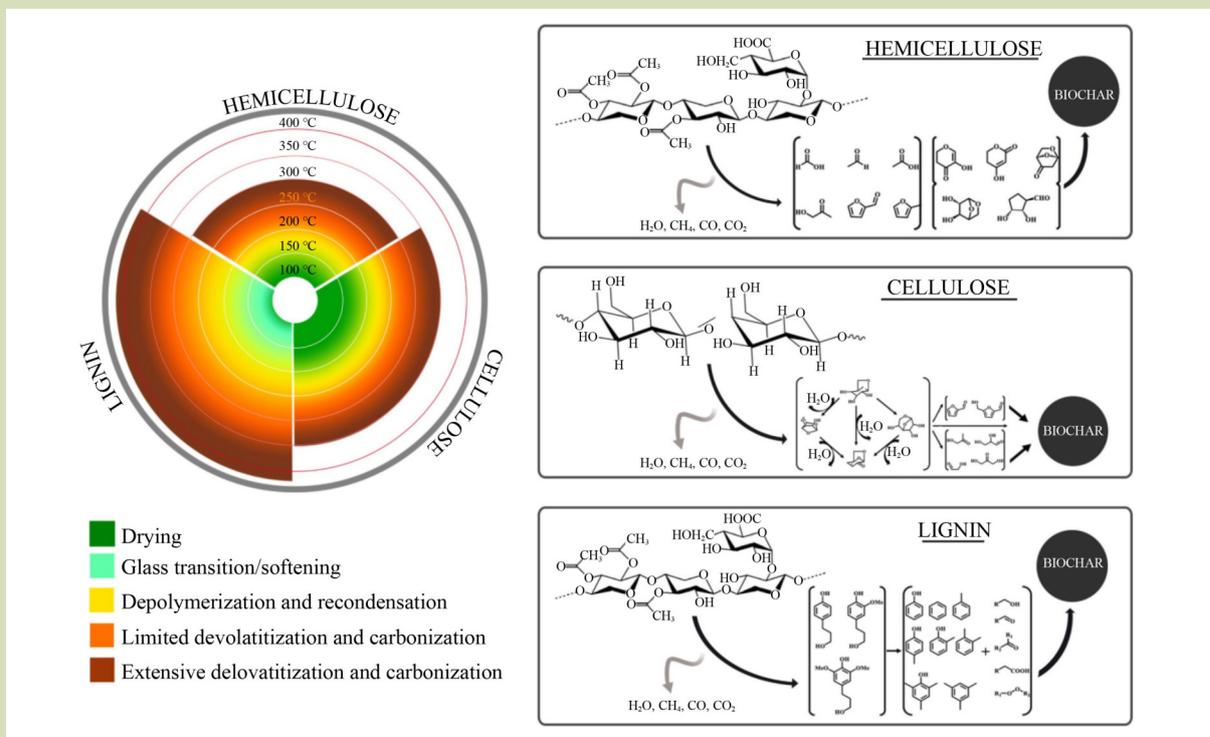


Fig. 5 Decomposition of hemicellulose, cellulose and lignin.

carbon bonds, releasing lipophilic extractives and volatile compounds, and causes the depolymerization of hemicellulose^[39]. As a consequence, hemicellulose molecules fragment and transform into shortened, condensed polymers with solid structures.

As the temperature exceed 200–300 °C, cellulose undergoes carbonization and devolatilization, whereas lignin starts to carbonize and devolatilize at 300–500 °C^[40]. These processes convert biomass into carbon-rich biochar and release volatile gases, resulting in a stable carbonaceous material.

3.3 Pyrolysis technologies

Pyrolysis is the process of heating lignocellulosic material at high temperatures without oxygen, serving as the initial stage for gasification and combustion^[41]. During pyrolysis, heat is externally generated and transferred to the biomass in a reactor via conduction, convection and thermal radiation^[42]. Pyrolysis produces biochar, a carbon-rich solid material, along with condensable and non-condensable volatile byproducts^[43].

Recent advancements in biomass pyrolysis can be broadly categorized into established and new techniques (Fig. 6). Established pyrolysis methods are typically divided into three

main types based on heating rate, residence time and heating mode: (1) slow pyrolysis, (2) fast pyrolysis, and (3) flash pyrolysis. Fast and flash pyrolysis, with high heating rates and short vapor residence times, favor liquid yields (bio-oil), whereas slow pyrolysis, with longer residence times, primarily produces solid yields (biochar)^[44,45]. Newer pyrolysis techniques, however, are designed to overcome the limitations

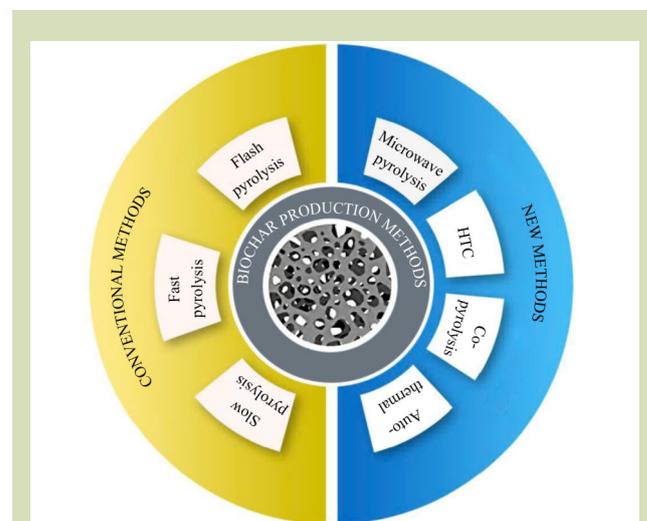


Fig. 6 Biomass pyrolysis methods.

of these current methods, with a focus on improving both the yield and quality of products and achieving more precise process control^[15]. These new techniques, such as microwave-assisted pyrolysis, co-pyrolysis, hydrothermal carbonization and autothermal pyrolysis, each offer distinct benefits for optimizing the pyrolysis process^[46]. Details on their scalability, efficiency, environmental impact and operating conditions are summarized in [Table 1](#).

Established pyrolysis methods

Slow pyrolysis of lignocellulosic biomass involves gradual

heating at 5–20 °C·min⁻¹ to 300–700 °C in an oxygen-limited environment with extended vapor residence times from minutes to days. This method enables precise control over biomass conversion into high-quality biochar with increased carbon content and stability, minimizing gas and bio-oil production. Compared to fast and flash pyrolysis, slow pyrolysis effectively reduces heat and mass transfer limitations, enhances biochar yield, and promotes the formation of stable carbon structures. One study showed that slow pyrolysis biochar typically has a higher carbon content (around 69.6% by weight) compared to fast pyrolysis biochar (about 49.3% by weight), improving stability and reducing microbial

Table 1 Established and new pyrolysis processes, along with their respective strengths and limitations

Pyrolysis method	Conditions & yield	Scalability, efficiency, environmental impact, limitations and barriers*	Reference
Slow pyrolysis	Temp: 300–700 °C; Heating rate: 1–10 °C·min ⁻¹ ; Residence time: > 1 h; Bio-oil: ~30%; Biochar: ~35%; Gases: ~35%	Adaptable to various scales; High biochar yield, efficient carbonization; Low emissions if designed properly, but high energy use, long processing times, feedstock quality variability; High costs, infrastructure investment, feedstock consistency	[47–54]
Fast pyrolysis	Temp: 400–800 °C; Heating rate: 20–200 °C·min ⁻¹ ; Residence time: < 10 min; Bio-oil: ~50%; Biochar: ~20%; Gases: ~30%	Scalable from small to large; High bio-oil yield, rapid decomposition; Sustainable but high energy consumption, advanced combustion required; Lower biochar yield, feedstock consistency, heat transfer challenges	[55–62]
Flash pyrolysis	Temp: 900–1300 °C; Heating rate: > 1000 °C·s ⁻¹ ; Residence time: < 10 s; Bio-oil: ~75%; Biochar: ~12%; Gases: ~13%	Suitable for various scales; Efficient conversion, minimal by-products; Reduces dependence on non-renewables, bio-oil needs refining; Expensive equipment, complex by-product separation, high capital cost	[63–71]
Microwave pyrolysis	Temp: 300–600 °C; Heating rate: 15–30 min; Bio-oil: ~15%; Biochar: ~50%; Gases: ~35%	Scalable from laboratory to industrial; Fast heating, efficient biochar production; Reduced energy consumption, higher product quality; Low yield, expensive equipment, scaling issues, uniform heating challenges	[72–83]
Co-pyrolysis	Temp: 300–1200 °C; Heating rate and residence time vary; Bio-oil: ~32%; Biochar: ~40%; Gases: ~28%	Adaptable scalability; Enhances biochar yield with mixed feedstocks; Reduces waste and emissions; Feedstock variability, complex equipment; Scaling challenges, quality control, by-product separation	[84–95]
Hydrothermal carbonization	Temp: 220–240 °C; Pressure: 2–10 MPa; Residence time: 1–72 h; Bio-oil: ~25%; Hydrochar: ~65%; Gases: ~10%	Mostly batch systems, pilot scale; High carbon conversion, low energy use; Reduces waste, mitigates GHG; Longer processing, feedstock variability; Scale-up challenges, reactor design issues	[96–102]
Autothermal pyrolysis	Pre-heat temp: ~450 °C, Heating rate: ~10 °C·min ⁻¹ , Residence time: ~10 min; Bio-oil: ~50%; Biochar: ~30%; Gases: ~20%	Flexible scalability; Self-sustained thermal process, energy-efficient; Lower carbon footprint, promotes circular economy; Complex reactor design, supplemental energy needs, energy balance and scaling challenges	[103–107]

Note: *A detailed analysis of scalability, efficiency, environmental impact, limitations, and barriers of each established and new pyrolysis processes is provided in the Table S1 of the Supplementary Materials.

degradation^[50]. In another study, slow pyrolysis yielded more biochar (41%–44% by weight) compared to fast pyrolysis. The latter, characterized by high heating rates and shorter processing times, results in lower biochar yields (21%–4% by weight)^[61]. Meanwhile, flash pyrolysis efficiently converts biomass into bio-oil with low water content and high conversion rates up to 70% by using very short residence times of less than 10 s^[63]. This rapid process requires finely ground biomass particles (105–250 μm) for effective heat transfer^[64]. Compared to slow and fast pyrolysis, flash pyrolysis faces challenges including cooling rates that can affect product quality, potential impurities in the bio-oil, high energy consumption and equipment degradation from corrosive feedstocks.

Numerous pyrolysis reactor types have been designed to convert biomass feedstocks into bio-oil, biochar and gas products. The yields of each product depend on the specific configuration and operational conditions of each reactor. Pyrolysis reactors can be operated in batch, semi-batch and continuous modes. Typically, reactors used for slow pyrolysis include cylindrical fixed-bed, batch, rotatory kiln and packed bed. The bubbling fluidized bed, circulating fluidized bed, transported bed, rotating cone, vortex, ablative and auger reactor are examples that are typical for either fast or flash pyrolysis^[69]. Regardless of the reactor type, the external heat is generated by either the burning biomass, electric heaters or gas burners and transferred directly or indirectly to the biomass within a furnace^[108].

New pyrolysis methods

Emerging pyrolysis techniques for biochar production involve new methods to enhance biochar yield, quality and properties. These techniques often incorporate modifications to traditional pyrolysis processes, including adjustments to temperature, heating rates, residence times and reactor configurations, and may use catalysts or additives. The overarching goal is to maximize the efficiency and sustainability of biochar production while minimizing environmental impact and resource consumption.

Co-pyrolysis uses two or more feedstocks to improve biomass pyrolysis through synergistic interactions among radicals, which influence processes like depolymerization, hydrogen transfer and isomerization. The success of co-pyrolysis depends on the interplay between feedstocks, affecting efficiency and product quality based on factors such as biomass type, blending ratio, reactor type, temperature and the presence of catalysts^[86,87]. Unlike established pyrolysis, co-pyrolysis does

not require equipment changes but does require careful material preparation. Different biomass components, such as cellulose, hemicellulose and lignin, affect pyrolysis outcomes, as illustrated by how blending these materials can alter yields of sugars and other compounds compared to native biomass^[109].

Also, the blending ratio of different biomasses can alter the overall yield and composition of the pyrolysis products (Fig. 7). Co-pyrolysis of palm kernel shell and palm oil sludge shows that increasing the latter from 0 to 100 wt%, there was a distinct decrease in bio-oil yield, approximately by 27%, whereas there was a significant increase in biochar yield, nearly by 1.5 times^[110]. This shift is primarily attributed to the presence of inorganic materials, specifically alkali and alkaline earth metals, present in the biomass blend. These materials exhibit catalytic properties that can potentially enhance the production of organic acids during the pyrolysis process^[111]. Adjusting raw material ratios can thus optimize co-pyrolysis to achieve desired biochar and bio-oil yields.

Microwave pyrolysis, or microwave-assisted pyrolysis, heats biomass using the electric field of microwaves, causing the electric dipoles in the biomass to flip and generate heat. This process occurs at 300–600 °C, pressures of 1–2 MPa, and a residence time of about 30 min^[112], converting biomass into biochar with 70%–80% fixed carbon and a yield of 40%–50%^[13]. The process involves four stages: (1) initial heating from dielectric recovery of water molecules; (2) stabilization of temperature based on feedstock properties; (3) rapid temperature rise and biomass reduction; and (4) reaching thermal equilibrium^[75]. Unlike established pyrolysis, which uses electric resistance heating, microwave pyrolysis achieves rapid and efficient volumetric heating without the need for external drying. However, it faces challenges like uneven temperature distribution due to the lack

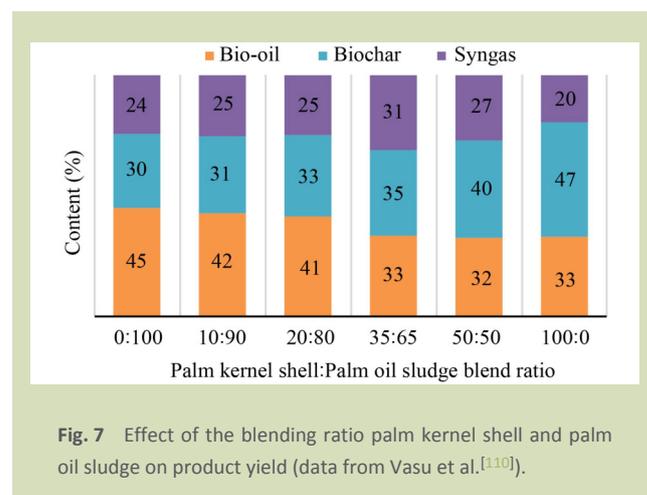


Fig. 7 Effect of the blending ratio palm kernel shell and palm oil sludge on product yield (data from Vasu et al.^[110]).

of agitation and difficulties in scaling up due to efficient microwave energy transfer^[77].

HTC is a thermochemical process for pretreatment high-moisture biomass using compressed water at temperatures of 220–240 °C, under considerable pressure, usually between 2 and 10 MPa^[97] within a reactor for several hours. This process, also known as wet torrefaction, converts organic components into hydrochar, a carbon-rich solid, along with minor fractions of aqueous and gaseous phases like CO₂, CO, CH₄ and H₂^[100]. HTC primarily involves decarboxylation, dehydration and polymerization, reducing the O:C ratio and increasing energy density. The yield of hydrochar (35% to 65% of dry feedstock) and its properties are influenced by temperature, residence time, water: biomass ratio, and the pH of the biomass-water-solution system^[113]. Generally, higher temperatures speed up biomass conversion but decrease hydrochar yield as more organic matter is converted into gaseous products such as methane, carbon dioxide and hydrogen^[114]. For example, increasing the temperature from 150 to 350 °C reduce hydrochar yield by 49% and increase bio-oil by 10%^[115]. Residence time also impacts the process, research has shown that extending the residence time in HTC led to a minor reduction in higher heating values ($16 \pm 0.3 \text{ MJ}\cdot\text{kg}^{-1}$) but improved several slagging and fouling indices of the hydrochar^[116].

In established pyrolysis, biomass is transformed into biochar, bio-oil, and synthesis gas using an external energy source due to its endothermic nature. This becomes challenging at larger scales because the energy needed (proportional to volume) often exceeds the energy supplied through heat transfer (proportional to surface area)^[21], leading to inefficiencies and variations in product quality^[85]. Autothermal pyrolysis, or oxidative pyrolysis, addresses this by balancing endothermic and exothermic reactions. It either recycles heat generated from the biomass itself or introduces controlled amount of oxygen to facilitate combustion, producing the necessary heat for the process. As an illustration, Mesa-Pérez et al.^[103] achieved 470 °C in a pilot-scale fluidized bed reactor using an equivalence ratio of 7:5 without external energy supply^[103], whereas Polin et al.^[21] demonstrated a threefold increase in pyrolysis intensity using an equivalence ratio of 1:10.

4 Key factors for biochar yield and properties

Determining the key factors for biochar yield and properties is crucial for optimizing biochar production efficiency. Figure 8 presents these key factors: feedstock selection, reaction

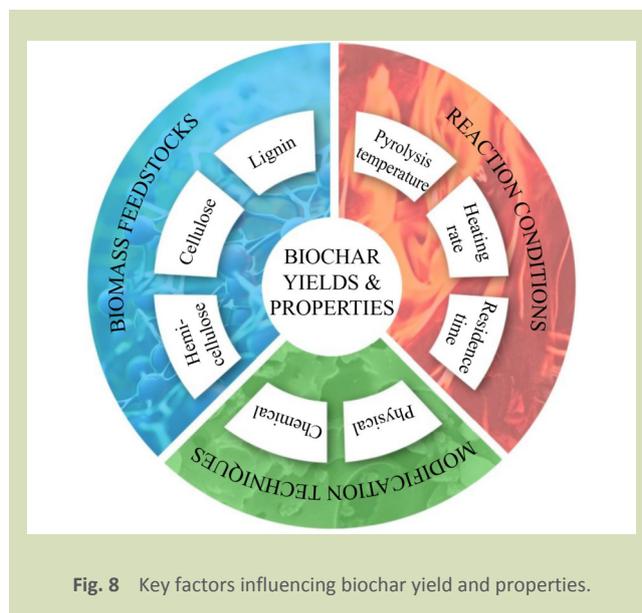


Fig. 8 Key factors influencing biochar yield and properties.

conditions and modification techniques.

4.1 Biomass feedstock

Biochar properties are heavily influenced by the type of biomass utilized in its production, affecting its chemical composition, structure and characteristics^[46]. Different biomass sources contain different levels of organic compounds, including lignin, cellulose, hemicellulose and other constituents. During pyrolysis, these compounds decompose and transform differently, resulting in biochars with unique chemical compositions. For example, feedstocks in high cellulose and hemicellulose, such as sugarcane bagasse, generally produce biochar with a lower fixed carbon content and aromaticity but higher levels of oxygen-containing functional groups ($-\text{COOH}$, $-\text{OH}$ and $-\text{CHO}$)^[7]. Oxygen-containing functional groups in biochar act as key binding sites for contaminants, increasing its adsorption properties^[8,9]. Lignin-rich biomass feedstocks, such as palm shell, produce biochar with a more porous structure, higher surface area, aromaticity, stability and fixed carbon content^[10]. Biochar with higher fixed carbon contents and aromaticity tends to be more recalcitrant, making it more effective for carbon sequestration in soils, improving soil quality and supporting plant growth^[117]. Figure 9 provides an overview of how lignin content in biomass influences biochar properties.

Lignin produces more biochar upon heating than hemicellulose or cellulose. This explains why wood biochar, such as that from mesquite wood, often yields more biochar compared to grasses such as *Miscanthus*. Mesquite wood has a lignin content of about $640 \text{ g}\cdot\text{kg}^{-1}$, whereas *Miscanthus*

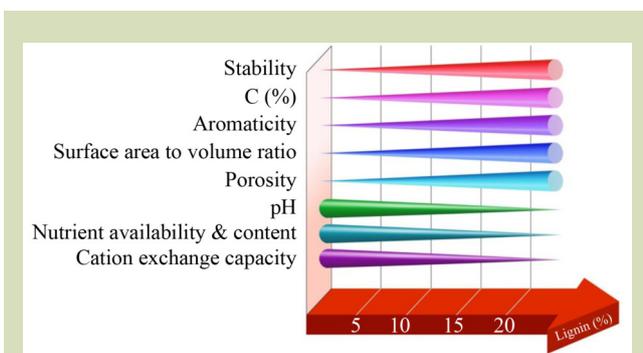


Fig. 9 Effect of lignin content in feedstock on biochar properties (data from published sources^[7-10,117,118]).

contains between 100 g·kg⁻¹ to 300 g·kg⁻¹ of lignin^[118]. Therefore, the higher lignin content in wood biomass results in greater production during pyrolysis, leading to higher biochar yields. The properties of biochar are greatly affected by the characteristics of the original plant tissue^[119]. Lignocellulosic biomass, which is the precursor of biochar, typically has low water content, minimal debris, low porosity, high density and high calorific value^[120]. Consequently, biochar from lignocellulosic biomass retains structural features from its source material, such as the xylem structure^[121]. Structural factors like particle size, density and porosity influence the physical and mechanical properties of biochar, including its surface area, pore volume and mechanical strength^[122]. Dense, compact woody biomass generally produces biochar with higher density and lower porosity, whereas more porous agricultural residues result in biochar with increased surface

area and water-holding capacity. For example, wood biochar has densities of 0.47–0.6 g·cm⁻³, compared to 0.25–0.3 g·cm⁻³ for grass biochar^[118]. Moisture content, ash content, and volatile matter also impact biochar properties. High moisture may require extra drying to avoid steam-induced reactions^[123], high ash content can increase mineral content and pH^[1], and high volatile matter can lead to more gas production and lower biochar yield^[124].

Figure 10 highlights the substantial variations in biochar properties resulting from the use of different feedstocks under identical pyrolysis temperatures (e.g., 500 °C), confirming that the selection of biomass feedstock greatly affects biochar characteristics.

4.2 Pyrolysis conditions

Pyrolysis conditions, including temperature, heating rate and residence time, directly affect biochar properties by influencing biomass decomposition, which impacts yield, chemical composition and physical characteristics of biochar. Table 2 provides a detailed summary of how various operational parameters influence the properties of biochar.

Pyrolysis temperature

In addition to the feedstock, pyrolysis temperature significantly affects the physicochemical properties of biochar. Increasing temperature increases the fixed carbon content, ash,

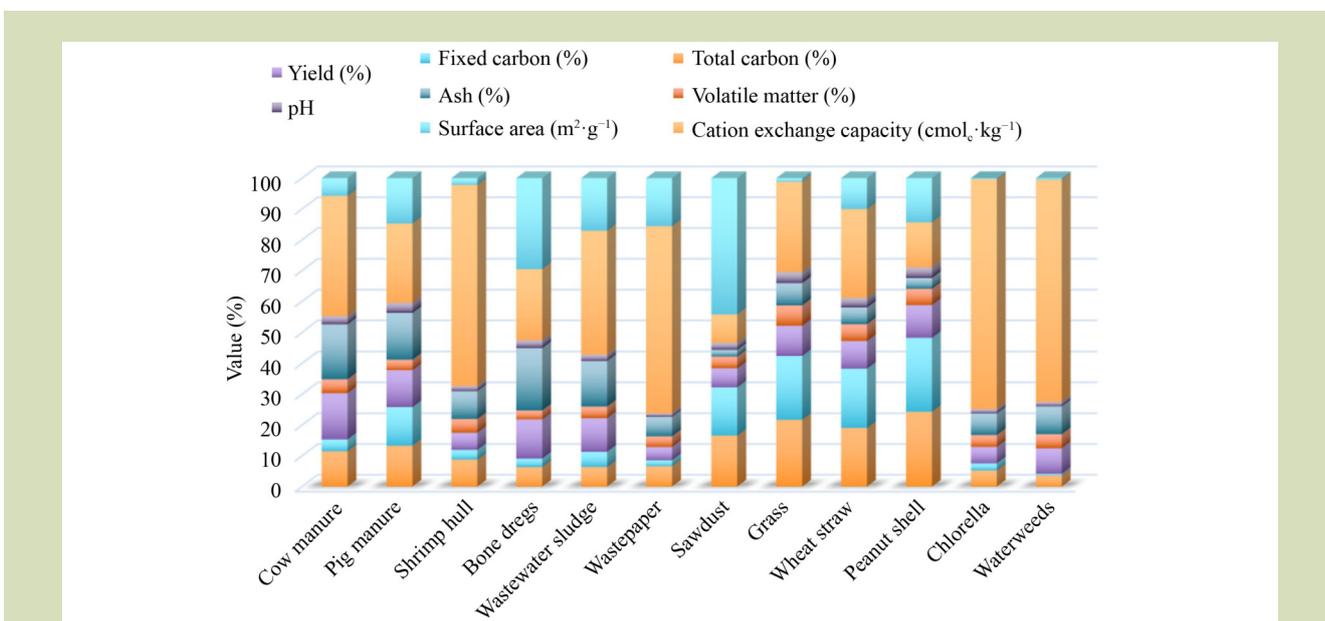


Fig. 10 Physical and chemical characteristics of biochar from different feedstocks produced at 500 °C (data from Zhao et al.^[125])

Table 2 Impact of operational parameters on biochar properties

Parameter	Biochar property	Observation	Reference
Pyrolysis temperature	Fixed carbon	Higher temperatures increase volatile decomposition, resulting in higher fixed carbon content in biochar	[126,127]
	Ash	Higher temperatures increase ash content by volatilizing minerals	[128,129]
	Aromaticity	Higher temperatures enhance aromaticity in biochar by forming more aromatic carbon structures	[10,130]
	Zeta potential	Higher temperatures usually increase zeta potential due to changes in surface chemistry and structure	[131,132]
	Hydrophobicity	Biochar becomes more hydrophobic with higher temperatures, but extreme temperatures may lower hydrophobicity	[122,133,134]
	Yield	Higher temperatures reduce biochar yield by increasing organic matter decomposition and volatilization	[129,135]
	Hydrogen and oxygen	Higher temperatures reduce hydrogen and oxygen content in biochar by breaking C–H and C–O bonds	[136,137]
	Polarity	Higher temperatures lower biochar polarity by removing polar groups and increasing aromatic structures	[138,139]
	Surface area	Surface area increase with temperature but can decline due to excessive degradation and ash accumulation	[30,129,140]
Residence time	pH and ash	Longer residence times increase the pH and ash content of biochar	[141,142]
	C, N, and H	Longer residence times lower the carbon, nitrogen, and hydrogen contents of biochar	[143,144]
	Surface area and pore volume	Increase up to a point, then decrease with extended residence time	[143,145]
	Iodine adsorption (slow pyrolysis)	Increasing residence time decreases iodine adsorption	[146–148]
	Iodine adsorption (fast pyrolysis)	Increasing residence time increases iodine adsorption	[146]
Heating rate	Surface area	Higher heating rates produce biochar with a larger surface area	[135,149]
		Increase up to a point, then decrease with higher heating rate	[5]
Heating rate and residence time	Vapor and yield	Higher heating rates and shorter residence times increase vapor production, decreasing biochar yield	[141,150]
Residence times, temperature and heating rate	Yield	Longer residence times at lower temperatures and heating rates maximize biochar yield	[135,151]

aromaticity, surface area and zeta potential, while decreasing yield, hydrogen, oxygen and polarity (Fig. 11).

Increasing temperature during pyrolysis impacts biochar characteristics in several ways. Higher temperature enhanced fixed carbon content due to thermal decomposition of biomass in the absence of oxygen. As temperature rises, biomass releases volatile components like water, gases and organic compounds, leaving behind more fixed carbon in the biochar^[126]. Higher temperatures enhance decomposition by breaking more chemical bonds, which increase the proportion of fixed carbon in the solid residue^[127]. Besides, higher temperature during pyrolysis increases the ash content of biochar by converting volatile minerals in the feedstock into ash residues. High temperatures break chemical bonds minerals, leading to their volatilization and incorporation into the biochar^[128]. Additionally, aromaticity, which indicates the presence of aromatic carbon structures, generally increases

with temperature during pyrolysis. Higher temperatures also promote the breakdown of complex organic compounds in biomass into simpler aromatic structures, resulting in a greater proportion of aromatic carbon structures in the biochar^[10]. Also, as temperature rises, the zeta potential of biochar particles typically increases, reflecting changes in their electrical charge^[131]. Higher temperatures alter surface chemistry by triggering reactions that modify functional groups and chemical species, impacting the distribution and density of charged sites. These changes, along with structural rearrangements and increased thermal energy, affect zeta potential and surface properties^[132]. Increasing pyrolysis temperature enhances hydrophobicity of biochar by removing polar groups^[133], forming less polar aromatic carbon structures and reducing surface oxygen^[122]. However, extremely high temperatures can cause excessive degradation and carbonization, potentially decreasing hydrophobicity^[134]. Mineral residues or ash can also negatively affect

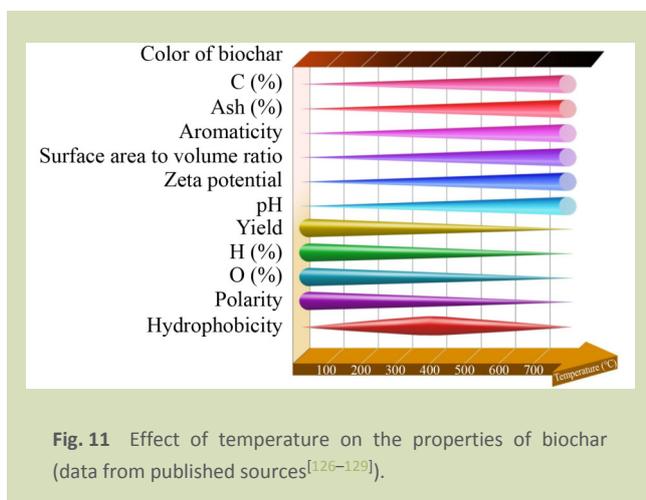


Fig. 11 Effect of temperature on the properties of biochar (data from published sources^[126–129]).

hydrophobicity. Increasing pyrolysis temperature generally decreases biochar yield^[135]. Higher temperatures enhance the decomposition of organic compounds into volatile components, enhancing their volatilization and leading to greater losses in the gas phase. This reduces the carbon content retained in the solid biochar. Also, during pyrolysis, higher temperatures increase thermal energy, promoting the breakdown of organic compounds and cleavage of C–H and C–O bonds^[136]. This process releases volatile gases, leading to a decrease in hydrogen and oxygen in the solid biochar residue. Consequently, biochar produced at higher temperatures typically has lower hydrogen and oxygen content compared to biochar produced at lower temperatures^[137]. Finally, as pyrolysis temperature increases, biochar surface area typically grows due to volatile removal, carbon re-structuring and pore formation^[129]. However, excessive thermal degradation and carbonization can collapse pores and reduce surface area^[30],

whereas ash residue can block pores^[140]. Therefore, although higher temperatures initially boost biochar surface area, this effect may plateau and decline with further increases due to detrimental effects on pore structure and carbonization.

The impact of biomass feedstock and pyrolysis temperature on biochar characteristics can be seen in Fig. 12. Higher pyrolysis temperatures led to a decrease in volatile content and an increase in ash content. Biochars derived from rice residues had higher ash content because of their greater mineral content, which supports plant growth, whereas biochars from woody materials contained more fixed carbon.

Residence time

Residence time is the total duration that components spend in the reactor, closely related to carrier gas flow rate^[153]. In pyrolysis, it includes both solid and gas phase residence time, with the latter typically being more significant^[154]. Depending on the pyrolysis method, residence time can last either seconds (fast pyrolysis) or hours (slow pyrolysis), impacting biomass carbonization and influencing biochar yield and properties. Generally, higher heating rate and shorter the residence time increase vapor production. Conversely, higher carbonization temperature and longer residence time produce more vapor and lower biochar yields. To maximize biochar yield, a longer residence time at slower temperature and slower heating rate is preferred^[141].

Prolonged residence time increases the pH and ash content of biochar but decreases its H, C and N contents^[143]. Surface area

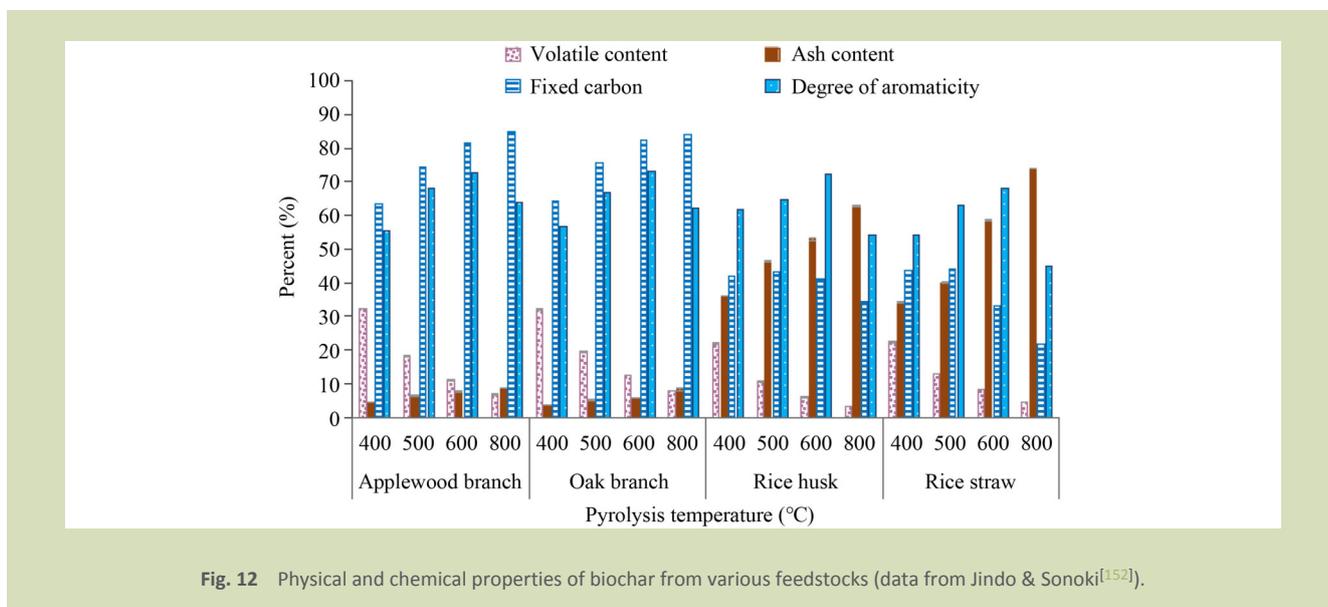


Fig. 12 Physical and chemical properties of biochar from various feedstocks (data from Jindo & Sonoki^[152]).

and pore volume rise with residence times up to 90 min but decline beyond 150 min^[143]. For residence times under 2 h, surface area and pore volume improve, whereas longer durations have the opposite effect^[145]. Additionally, residence time impacts iodine adsorption differently, it decreases with longer residence times in slow pyrolysis, but increases in fast pyrolysis^[146].

Heating rate

Residence time in the pyrolysis reactor affects biomass decomposition and biochar yield. Longer residence times generally ensure more complete conversion but may increase energy consumption and costs, whereas shorter residence times can result in incomplete pyrolysis and lower yields. For example, Parthasarathy et al.^[155] found that higher heating rates significantly increased biochar yield from camel manure, with yields of 5.25 (22.5%), 7.00 (28.3%) and 8.64 mg (31.5%) at heating rates of 10, 20 and 50 °C·min⁻¹, respectively. The impact of heating rate on biochar properties, particularly surface area, has been reported to vary (Fig. 13). Some studies indicate that higher heating rates increase the surface area of biochar. For example, biochar derived from walnut shells exhibited a gradual and consistent rise in specific surface area across different heating rates from 10 to 40 °C·min⁻¹, ranging from 19.3 to 127 m²·g⁻¹ ^[149]. Zhao et al.^[135] also observed a surface area increase from 296 to 384 m²·g⁻¹ with heating rate rising from 1 to 20 °C·min⁻¹, suggesting that faster heating promotes more extensive thermal decomposition and surface characteristics in the biochar.

Some studies indicate that there is an optimal heating rate for maximizing biochar surface area, with surface area initially increasing before decreasing beyond a certain threshold. For example, surface area rose from 210 to 245 m²·g⁻¹ as heating rate increased from 10 to 30 °C·min⁻¹ ^[163] but dropped to 385 m²·g⁻¹ at 50 °C·min⁻¹^[163]. Excessively high heating rates can negatively affect surface area by melting particles, smoothing surface, blockage of pore channels^[167] or causing micropore collapse^[30].

5 Biochar modification techniques

Biochar from biomass pyrolysis is often characterized by its low specific surface area, constrained porosity, and limited surface functional groups^[168], which can restrict its applications, especially if surface area is below 200 m²·g⁻¹ ^[126]. To overcome these limitations, biochar is modified using agents like alkalis, acids, metal oxides and oxidizing, which

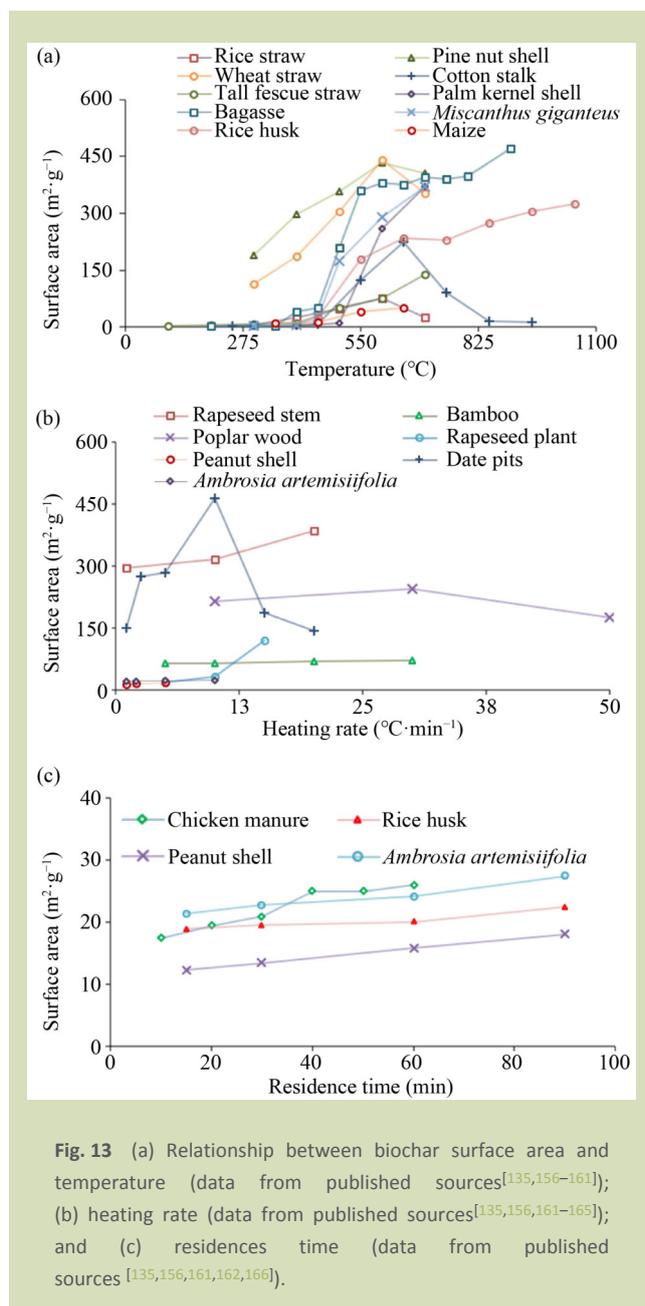


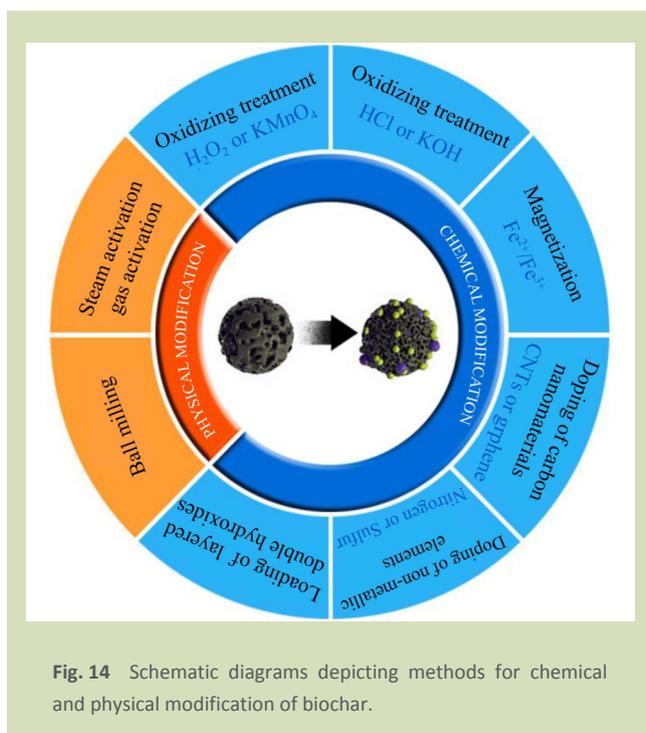
Fig. 13 (a) Relationship between biochar surface area and temperature (data from published sources^[135,156–161]); (b) heating rate (data from published sources^[135,156,161–165]); and (c) residences time (data from published sources ^[135,156,161,162,166]).

improve surface properties create new structures^[133]. These modifications are generally of two main types: chemical and physical (Fig. 14).

Chemical modification

Chemical modification techniques for biochar involve various treatments aimed at altering its chemical composition and surface properties. Key methods, as illustrated in the Fig. 14, are briefly as follows.

- Oxidizing treatment: oxidizing agents such as hydrogen



peroxide or potassium permanganate can be used to introduce oxygen-containing functional groups onto the biochar surface. This enhances the ability of biochar to complex with heavy metals, increasing its reactivity and adsorption capacity of biochar for these metals^[169].

- Acid/base soaking: acid modification introduces acidic functional groups, such as amine and carboxyl groups, to biochar, increasing its metal removal capacity through surface complexation and cation exchange^[170]. In contrast, alkaline modification increases the presence of oxygen-containing functional groups, such as ether, carbonyl, carboxyl and hydroxyl groups, while also enhancing the specific surface area of biochar^[171]. This process improves the ability of biochar to remove various environmental contaminants.
- Magnetization: incorporating magnetic nanoparticles to biochar, typically through methods like coprecipitation or impregnation, enables magnetic separation, enhancing the recovery and reusability of biochar in water treatment. This modification facilitates easy separation of biochar from water using magnetic fields, thereby simplifying the treatment process and allowing for the efficient recovery of biochar for repeated use, thus improving the sustainability of water treatment^[172].
- Doping of carbon nanomaterials: depositing carbon nanotubes onto biochar enhances pollutant removal efficiency

and promotes sustainable use in environmental remediation. Carbon nanotubes are effective due to their excellent physicochemical characteristics, including high surface area, exceptional thermal conductivity, superior electron mobility, and high mechanical strength^[173]. However, their high cost and engineering challenges limit their use. To overcome these limitations, biochar can serve as a mesoporous and microporous carrier for carbon nanotubes, facilitating the development of novel, recyclable, and effective sorbents for wastewater and polluted soil treatment. Combining them with biochar, which acts as a porous carrier, creates a cost-effective and recyclable composite that enhances sorption capabilities for wastewater and soil treatment^[170].

- Non-metallic elements: introducing non-metallic elements such as nitrogen, phosphorus or sulfur to biochar via chemical treatments or precursor materials can modify its electronic characteristics, therefore increasing its functionality, reactivity and adsorption capacity.
- Layered double hydroxides: Layered double hydroxides known for their easy synthesis, uniform layered structure, surface hydroxyl groups and compatibility with various molecules, and promising for composite applications^[174,175]. Their alkaline properties and positively charged surfaces enables electrostatic interactions with anionic pollutants, a feature absent in biochar^[176]. Nonetheless, their dense layered structure may limit pollutant adsorption when used alone^[177]. Therefore, integrating LDHs into biochar synergistically enhances their adsorptive capacity for a wide range of contaminants in water, leveraging the unique characteristics of both materials. This combining the strengths of both materials and improving water remediation efficiency and versatility^[178].

In general, these chemical modification techniques are designed to enhance the chemical properties of biochar, particularly surface area. Additionally, they impact the chemical characteristics of biochar, such as surface functional groups, elemental distribution, zeta potential, electron transfer capacity and cation exchange capacity^[170,179]. Such modifications are essential for enhancing the performance and adaptability of biochar across various applications. The preparation of porous biochar through chemical activation can be achieved via one- or two-step methods. The one-step method involves directly pyrolyzing a mixture of biomass and activator at elevated temperatures (700–900 °C)^[163], eliminating the need for separate pyrolysis and activation stages. Conversely, in the two-step approach, biochar is first produced from biomass pyrolysis at lower temperatures (400–600 °C). Activators are then introduced to the biochar,

which is further heated to higher temperatures (700–900 °C) to create the desired porous structure^[159]. For example, using KOH activation followed by pyrolysis can dramatically increase the surface area of biochar, achieving up to 3000 m²·g⁻¹^[180,181]. A recent study found that bamboo biochar pyrolyzed at 600 °C had a specific surface area of only 24.9 m²·g⁻¹. However, with KOH activation, the surface area improved to 457 m²·g⁻¹ at a KOH/bamboo ratio of 1:8 (with ~2 g bamboo mass), and further increased to 913 m²·g⁻¹ at a ratio of 1:1. This enhancement is due to KOH etching carbon fragments and reacting with the oxygen species in biomass to form large quantities of pores and release gaseous products^[163,182].

A thorough evaluation of activation processes and heating rates on biochar properties was reported^[149]. The study highlighted the significant influence of activation process and heating rates on biochar yield and surface area. KOH-activated biochar showed higher yields compared to steam-activated biochar and neutral walnut shell biochar, demonstrating the efficacy of KOH activation in enhancing production, see Fig. 15(a). Additionally, the surface area of KOH-activated biochar varied notably with heating rates, with a 26% varied observed between 10 and 20 °C·min⁻¹. Significant increases in surface area were recorded at higher heating rates, reaching about 89% and 104% at 30 and 40 °C·min⁻¹, respectively, highlighting the impact of both activation process and heating rates on biochar surface area, see Fig. 15(b).

Physical modification

Physical modification methods have proven effective in

enhancing the functionality of biochar. These techniques improve the performance of biochar by adjusting its hydrophobicity, polarity, and surface functional groups. Enhancing hydrophobicity can enhance the affinity of biochar for specific contaminants or improve its compatibility with aqueous environments. Similarly, modifying polarity and surface functional groups can impact the adsorption capacity and reactivity of biochar toward specific pollutants or target molecules^[183].

Physical activation methods, while effective in improving biochar properties, have some drawbacks. One notable limitation is the extended activation time, typically around 4 h, due to the gradual changes in the structure and surface characteristics of biochar. Additionally, these methods generally require more energy than chemical activation, with energy requirements ranging from 10.6 to 58.0 kcal^[184], due to prolonged heating or mechanical agitation. Despite these challenges, physical activation remains a valuable approach for enhancing biochar functionality, though its time and energy requirements need to be considered^[170]. Physical modification techniques commonly using oxidizing agents like gas and steam. Gas treatment exposes biochar to gases such as carbon dioxide or air, altering its surface chemistry and structure. Steam treatment involved high-temperature steam to enhance the porosity and surface area of biochar. During pyrolysis, steam treatment facilitates partial devolatilization and the formation of crystalline carbon, removing trapped byproducts of incomplete combustion and thereby increasing in surface area^[136]. CO₂ purging during pyrolysis can increase the surface area of biochar by forming additional micropores through CO₂

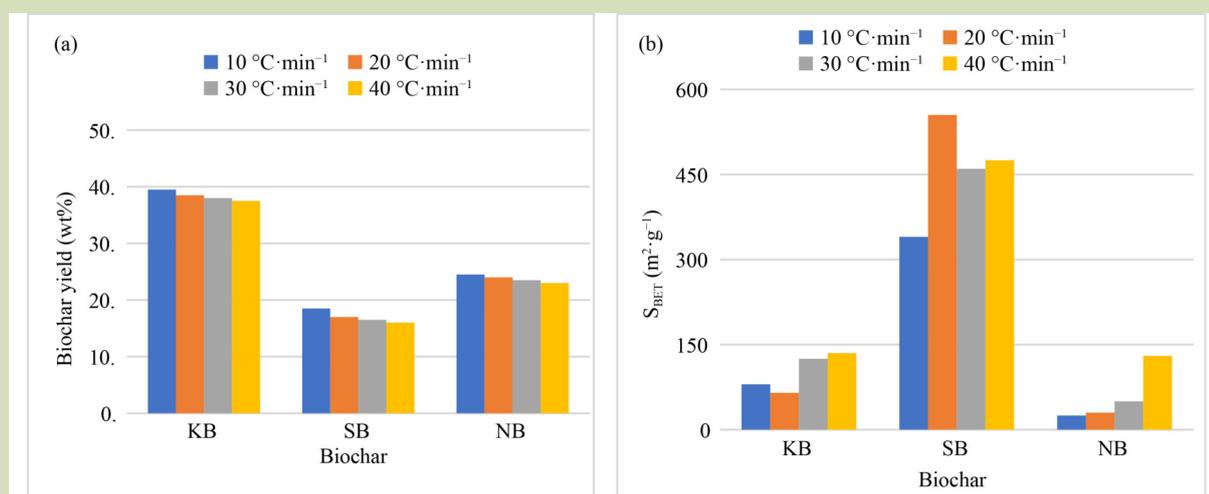


Fig. 15 Comparative heating rate effects on the yield and surface area of KOH-activated (KB), steam-activated (SB) and neutral biochar (NB) (data from Shagali et al.^[149]).

activation. CO₂ reacts with the surface carbon structure of the biochar, releasing CO and creating new pores^[185]. For example, the surface area of biochar derived from orange peel waste increased from 95.6 to 159 m²·g⁻¹ for CO₂ activation and up to 305 m²·g⁻¹ for steam activation^[186]. Similarly, research indicates that biochar produced from biomass feedstocks like barley straw, through CO₂ activation, has microporosity with a high surface area (e.g., 789 m²·g⁻¹), whereas steam activation results in pore enlargement and increased mesoporosity (e.g., 552 m²·g⁻¹)^[187]. Also, combining microwave heating with steam or CO₂ offers advantages such as lower temperature requirements, reduced flow rate and shorter processing times compared to established methods^[188].

In addition to steam and air activation, ball milling offers a cost-effective and ecofriendly technique for modifying biochar. This mechanical method uses grinding balls to break down biochar particles, which increases their surface area and enhances their reactivity. Ball milling improves key characteristics such as pore structure, specific surface area and the development of various surface functional groups compared to unmodified biochar^[189]. Xiang et al.^[190] studied the impact of ball milling on biochar, focusing on surface characteristics and adsorption capabilities, especially in capturing volatile organic compounds. Similarly, Yuan et al.^[191] examined the impact of wet and dry ball milling on sawdust-derived biochar, observing a significant increase in specific surface area to 360 m²·g⁻¹, compared to 154 m²·g⁻¹ for unmodified biochar, marking a notable enhancement by up to 200 times. This improved surface area boosts the effectiveness of biochar as an adsorbent. Also, incorporating Al/Mg layered double hydroxide into the biochar through ball milling created a composite material with enhanced adsorption properties, notably achieving a Cd²⁺ ions uptake capacity of 119 mg·g⁻¹^[192].

6 Conclusions

In conclusion, this review has aimed to provide an extensive overview of recent advancements in optimizing biochar production from lignocellulosic biomass through pyrolysis. It has examined various pyrolysis techniques, including both established and new methods, revealing crucial insights into the factors that affect biochar yield and properties. The study emphasizes the importance of understanding the intricate relationship between feedstock composition, pyrolysis conditions and modification methods in determining biochar characteristics and yields. Through careful selection of feedstock, optimization of pyrolysis parameters and using

appropriate modification techniques to tailor biochar properties for specific application.

In biochar production, achieving objectives like enhancing properties, ensuring cost-effectiveness, minimizing environmental impact, and maximizing coproduct generation necessitates a comprehensive approach that includes careful feedstock selection, optimized pyrolysis conditions, and effective modification methods. The selection of feedstock is critical for achieving the desired final characteristics and performance of biochar. Choosing renewable and readily available feedstocks reduces dependence on finite resources and repurposes waste materials, thereby mitigating environmental impacts. Key pyrolysis conditions, such as temperature, heating rate and residence time, are vital for maximizing biochar yield and quality while reducing energy consumption and environmental impact. Employing renewable energy sources, efficient heat recovery systems and effective management of byproducts and emissions further enhances sustainability. Also, modification techniques are essential for improving biochar properties to meet specific applications, overcoming the limitations of standard biochar, and enhancing its effectiveness. Sustainable modification approaches can minimize waste, reduce environmental impacts and promote resource efficiency throughout the production process.

Based on the findings presented in this review, several recommendations can be made to further optimize biochar production efficiency and effectiveness:

- Integration of new pyrolysis techniques: promote the use of new pyrolysis techniques, including microwave-assisted pyrolysis, co-pyrolysis, and autothermal pyrolysis, for their benefits in efficiency, scalability, and reduced environmental impact.
- Optimization of feedstock selection: prioritize the selection of feedstocks with optimal lignocellulosic compositions to maximize biochar yield and tailor its properties to specific application requirements.
- Optimization of pyrolysis conditions: adjust pyrolysis parameters, including temperature, heating rate and residence time, to balance biochar yield, properties and process efficiency.
- Exploration of modification methods: investigate both physical and chemical modification to further enhance biochar properties and functionality for targeted applications.

• Integration of sustainable practices: implement sustainable practices, such as renewable energy sources and optimizing feedstock sourcing, to minimize environmental impact and improve the overall sustainability of biochar production.

Implementing these recommendations enables researchers and practitioners to advance biochar production, and fully realize its potential for the sustainable utilization of lignocellulosic biomass resources.

Supplementary materials

The online version of this article at <https://doi.org/10.15302/J-FASE-2024597> contains supplementary material (Tables S1).

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Compliance with ethics guidelines

Nguyen Xuan Loc and Do Thi My Phuong declare that they have no conflicts of interest or financial conflicts to disclose. This article does not contain any studies with human or animal subjects performed by any of the authors.

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